

Characterisation of the Mechanical Properties and Microstructure of Three Pressable All-Ceramic Dental Materials

By

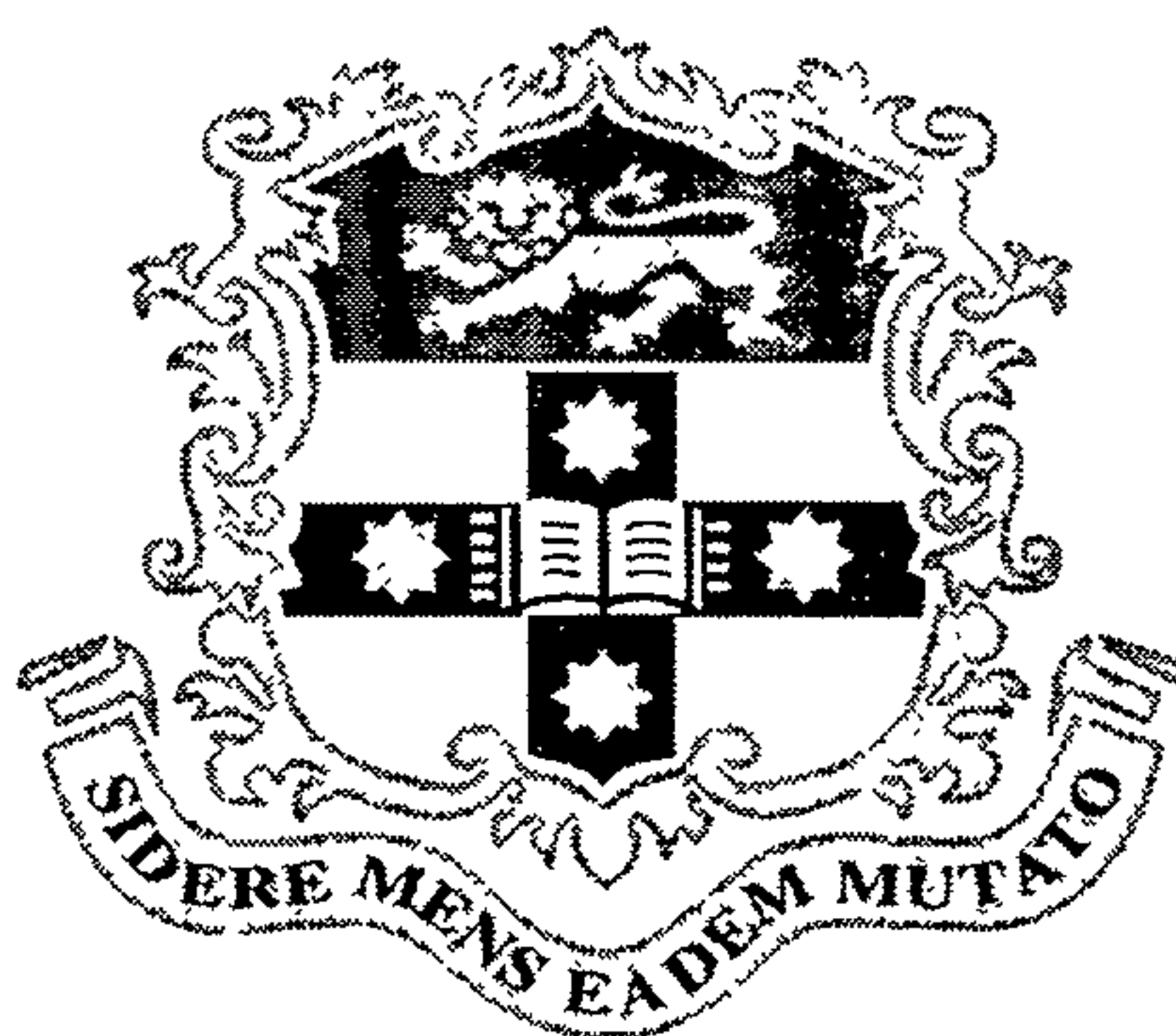
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To my beloved country, Kingdom of Saudi Arabia.

Abstract

The well-known pressable all-ceramic dental materials Empress 1 and Empress 2 are used widely in prosthetic dentistry. These materials have generated considerable interest because of their ease of fabrication and excellent aesthetic features. The first material, leucite-reinforced glass-ceramic, was released in the early 1990s, and was recommended for the fabrication of single units, such as crowns, inlays, onlays and veneers. The flexural strength of this material ranges from 95 to 180 MPa, and its fracture toughness is $1.3 \text{ MPa} \cdot \text{m}^{1/2}$. Empress 2 was released in 1998, by the same manufacturer (Ivoclar-Vivadent, Schaan, Liechtenstein), and was recommended for the fabrication of 3-unit fixed partial dentures up to the second premolar. The improved mechanical properties of this material, flexural strength of 300-400 MPa and fracture toughness of $2.5\text{-}3.5 \text{ MPa} \cdot \text{m}^{1/2}$, have been attributed to the unique chemical composition of this material, which is composed of approximately 60% of fine lithium disilicate crystals dispersed in a glass matrix. A new pressable all-ceramic dental core material (referred to in this study as experimental pressable ceramic material) is about to be released by the same manufacturer. It is claimed by the manufacturer that this material possesses improved mechanical and optical properties over those offered by the previous pressable systems, Empress 1 and Empress 2.

The literature review identified the flexural strength, fracture toughness, Young's modulus and Poisson's ratio as important mechanical properties that delineate the behaviour of brittle dental ceramics submitted to load. Strength is the maximum tensile stress that a material withstands before fracture onset. This mechanical property is very sensitive to flaws and defects that develop either

inherently or during fabrication. Fracture toughness is thought to be more consistent as it is independent from flaws or defects. It delineates the ability of a material to resist rapid crack propagation. Elastic modulus is an indication of the amount of reversible deformation that will occur in a structure when a load is applied to it. Within the elastic range the ratio of the lateral to the axial strain is called Poisson's ratio. The reliability or probability of fracture of brittle materials can be characterised by means of a Weibull statistical treatment, which provides a means for assessing the influence on strength of stress gradients and size of the specimen.

The purpose of this study was to appraise the intrinsic mechanical properties of Empress 1, Empress 2 and an experimental pressable all-ceramic material and, in the case of Empress 1 and Empress 2, to assess the effect of different processing and fabrication procedures on their intrinsic mechanical properties. Microstructure characterisations and crystalline phases of each system were also appraised. A mechanical comparative study with some peer all-ceramic dental materials has also been carried out. The all-ceramic dental materials compared with the pressable materials were as follows: In-Ceram Alumina (slip and dry-pressed), In-Ceram Zirconia (slip and dry-pressed), DC-Zircon and an experimental zirconia material.

This study found that Empress 2 and the experimental pressable material have improved mechanical properties over that of the Empress 1 material. The improvements in mechanical properties of these systems were attributed to the chemical composition of the two materials. X-ray diffraction and scanning electron microscopic imaging confirmed that Empress 2 and the experimental ceramic are composed of the same crystalline content, lithium disilicate. However, smaller lithium disilicate crystals in the experimental ceramic than those of Empress 2 were observed. It was anticipated that this might enhance the mechanical properties of the

experimental ceramic. However, this study found no significant difference in the flexural strength of the two ceramics. Both materials demonstrated similar fracture toughness and elastic modulus. Finally, the three pressable materials exhibited almost the same Poisson's ratio.

The second part of this study appraised the effect of different fabrication processing on the flexural strength of Empress 1 and Empress 2, namely polishing, grinding, sandblasting, heat treatment and repressing. Grinding and sandblasting decreased the flexural strength of these materials, but not significantly from a statistical point of view. Polishing significantly increased the flexural strength of both materials. Repressing showed no significant effect on the flexural strength or fracture toughness of the two materials.

The mechanical properties comparison of a selected all-ceramic dental materials showed that the highest flexural strength and fracture toughness were recorded by DC-Zircon, 840 MPa and $7.4 \text{ MPa} \cdot \text{m}^{1/2}$ respectively. Despite the similarities found between this material and the experimental zirconia material, the latter demonstrated significantly lower fracture toughness and flexural strength. Such difference was found to be due to different toughening mechanisms operating in the two materials brought about by the presence of other phases, such as glass or alumina particles, and to the metastability of the tetragonal to monoclinic transformation process. There was no statistical difference in the flexural strength between the experimental zirconia material, In-Ceram Zirconia slip and In-Ceram Alumina slip. However, the experimental zirconia exhibited higher fracture toughness than these three materials.

The improvement of the flexural strength of In-Ceram Alumina slip over that of the dry pressed is due to its microstructure. Many elongated alumina crystals are

present within the microstructure, and may be oriented during slip preparation. This alignment of crystals is thought to play a major role in the mechanical properties of this material. On the other hand, the addition of 33% 12 mol-% CeO₂ partially stabilised zirconia (ZrO₂) to In-Ceram Alumina (resulted in the two systems of In-Ceram Zirconia, slip and dry pressed) to enhance the fracture toughness did not result in a significant improvement in the fracture toughness of this material. Apart from the different amount of porosity found between the two In-Ceram Zirconia materials, being greater in the dry-pressed material, the two materials had very similar microstructure, toughening mechanisms and consequently fracture toughness. Their strength difference might be related to the amount of porosity. In-Ceram Alumina dry pressed had a higher, but not significantly different, flexural strength and fracture toughness than those of the two lithium disilicate systems (Empress 2 and the experimental ceramic). Finally, Empress 1 exhibited the lowest flexural strength and fracture toughness.

The comparative investigation has shown that the nine dental ceramics demonstrate a wide range of values in strength and fracture toughness, and point to the affiliation offered between microstructure, toughening mechanisms, processing and mechanical properties. It was noticed that an increase of the crystalline content corresponds to an improvement of the mechanical properties. However, in materials with similar crystalline content, other factors such as porosity, the crystals' size, shape and orientation and the effectiveness of each toughening mechanism are important in determining the mechanical properties.

Declaration

Candidate's Certificate

I hereby certify that the work presented in this thesis was carried out by the candidate in the Discipline of Biomaterials Science, Faculty of Dentistry, the University of Sydney, and has not been submitted to any other university or institution for a higher degree.

Mohammad Albakry, December 2003

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Table of Contents

Abstract.....	III
Declaration.....	VII
Acknowledgments.....	VIII
Table of Contents.....	IX
List of Tables.....	XIX
List of Figures.....	XXI
Publication and Scientific Meetings.....	XXXIII

CHAPTER 1: Introduction	1
1.1 Historical Review.....	2
1.2 All-Ceramic Dental Restorations.....	3
1.3 Purpose.....	5
1.4 Thesis Structure.....	8
1.5 References.....	10
 CHAPTER 2: Literature Review	 13
2.1 Fracture Mechanics.....	14
2.1.1 Criteria of crack growth.....	15
2.1.2 Fracture theory (Griffith's principle).....	15
2.1.3 Linear elastic fracture mechanics (LEFM).....	17
2.1.4 Non-linear fracture mechanics (NLFM)	19
2.1.5 The work of fracture.....	19
2.1.6 Crack resistance curve (R-curve behaviour).....	20

2.2	Introduction.....	22
2.3	Glass Ceramics.....	23
2.3.1	Definition.....	23
2.3.2	Crystallisation.....	23
2.3.2.1	Mechanisms of crystallisation.....	24
2.3.3	Properties.....	25
2.3.4	Applications.....	26
2.4	Dental Ceramics.....	26
2.4.1	Definition.....	26
2.4.2	Composition.....	26
2.4.3	Classification.....	27
2.4.4	Properties.....	27
2.4.5	Shortcomings.....	28
2.4.6	Methods of strengthening.....	29
2.4.6.1	Residual compressive stresses.....	30
2.4.6.1.1	Ion exchange.....	30
2.4.6.1.2	Thermal tempering.....	31
2.4.6.1.3	Glazing.....	31
2.4.6.1.4	Crystalline reinforcement.....	31
2.4.7	Design.....	32
2.4.8	Toughening Mechanisms.....	33
2.5	All-Ceramic Restorations.....	34
2.5.1	Castable glass ceramics.....	35
2.5.1.1	Dicor castable glass ceramic.....	35
2.5.2	Leucite-reinforced systems.....	36

2.5.2.1	Leucite.....	37
2.5.2.1.1	Twining of leucite crystals..	37
2.5.2.2	Optec HSP (leucite-reinforced porcelain)....	37
2.5.2.3	Other leucite-based glass systems.....	38
2.5.3	Magnesia-based ceramic.....	39
2.5.4	Aluminous core ceramic.....	39
2.5.4.1	Hi Ceram.....	39
2.5.5	Glass-Infiltrated system.....	40
2.5.5.1	In-Ceram Alumina.....	40
2.5.5.2	In-Ceram Zirconia.....	41
2.5.5.3	In-Ceram Spinell.....	42
2.5.6	High purity alumina.....	43
2.5.6.1	Procera.....	43
2.5.7	High purity zirconia materials.....	44
2.5.7.1	DC-Zircon.....	44
2.5.7.2	Experimental partially stabilised zirconia material	45
2.5.8	Pressable ceramics.....	45
2.5.8.1	Advantage.....	46
2.5.8.2	Empress 1.....	47
2.5.8.2.1	Fabrication method and techniques	48
2.5.8.2.2	Mechanical properties.....	49
2.5.8.2.3	Clinical performance.....	50
2.5.8.3	Empress 2.....	51
2.5.8.3.1	Fabrication methods.....	52
2.5.8.3.2	Mechanical properties.....	53

	2.5.8.3.3	Clinical performance.....	55
2.6		Conclusion.....	55
2.7		References.....	56
CHAPTER 3: Materials and Methods			71
3.1		Materials.....	71
3.2		Specimen Preparation.....	72
	3.2.1	Number and dimension of specimens.....	72
	3.2.2	Spruing and investing.....	72
	3.2.3	Preheating and heat-pressing.....	73
	3.2.4	Divesting and cutting.....	74
	3.2.5	Grinding and polishing.....	76
3.3		Use of Specimens.....	77
	3.3.1	Disc specimens.....	77
	3.3.2	Bar specimens.....	77
	3.3.3	Plate specimen.....	78
3.4		Microstructural Investigations.....	78
	3.4.1	Preparation and etching.....	78
	3.4.2	Scanning electron microscope (SEM).....	78
	3.4.3	Field emission SEM (High resolution).....	80
3.5		X-ray diffraction.....	80
3.6		Statistics.....	81
CHAPTER 4: X-ray Diffraction, Microstructure and Porosity			82
4.1		Crystal Structure.....	83

4.1.1	Introduction.....	83
4.1.2	Non-crystalline materials.....	83
4.1.3	Crystalline materials.....	84
4.1.3.1	Unit cells and lattice.....	84
4.1.4	Crystal systems.....	86
4.1.4.1	Crystallographic directions.....	89
4.1.4.2	Crystallographic planes.....	90
4.2	X-ray Diffraction.....	90
4.2.1	Introduction.....	90
4.2.2	Definition and use.....	91
4.2.3	Purpose.....	95
4.2.4	Specimen preparation.....	95
4.2.5	Results.....	96
4.2.5.1	Empress 1.....	96
4.2.5.2	Empress 2.....	99
4.2.5.3	Experimental ceramic.....	102
4.2.6	Discussion.....	102
4.2.7	Conclusion.....	103
4.3	Microstructural Investigations.....	105
4.3.1	Introduction.....	105
4.3.2	Macroscopic investigation.....	105
4.3.3	Microscopic investigation.....	105
4.3.4	Scanning electron microscope.....	106
4.3.5	Purpose.....	106
4.3.6	Specimen preparation.....	106

4.3.7	Results.....	107
4.3.7.1	Empress 1.....	107
4.3.7.2	Empress 2.....	113
4.3.7.3	Experimental ceramic.....	118
4.3.8	Discussion.....	118
4.3.9	Conclusion.....	123
4.4	Porosity.....	125
4.4.1	Introduction.....	125
4.4.2	Purpose.....	125
4.4.3	Specimen preparation.....	126
4.4.4	Results.....	126
4.4.4.1	Empress 1.....	126
4.4.4.2	Empress 2.....	127
4.4.5	Discussion.....	129
4.4.6	Conclusion.....	130
4.5	References.....	131

CHAPTER 5: Elastic Modulus, Poisson's Ratio and Hardness 134

5.1	Stress and Strain.....	135
5.2	Elastic Modulus.....	136
5.2.1	Importance.....	137
5.2.2	Measurements of elastic modulus.....	138
5.3	Poisson's Ratio.....	138
5.4	Purpose.....	139
5.5	Testing Method.....	139

5.5.1	Test specimen.....	140
5.5.2	Apparatus.....	140
5.5.3	Procedure.....	141
5.5.3.1	The flexural resonant frequency.....	141
5.5.3.2	The torsional resonant frequency.....	142
5.6	Results.....	144
5.7	Discussion.....	145
5.8	Conclusion.....	146
5.9	Hardness.....	148
5.9.1	Definition.....	148
5.9.2	Importance.....	148
5.9.3	Measurements of hardness.....	148
5.9.3.1	Brinell hardness test.....	149
5.9.3.2	Knoop hardness test.....	150
5.9.3.3	Vickers hardness test.....	151
5.10	Purpose.....	152
5.11	Preparation of Specimens.....	152
5.12	Results.....	154
5.13	Discussion.....	155
5.14	Conclusion.....	156
5.15	References.....	157

CHAPTER 6: Fracture Toughness 160

6.1	Introduction.....	161

6.2	Definition.....	161
6.3	Importance.....	161
6.4	Measurements of Fracture Toughness.....	162
6.5	Purpose.....	164
6.6	Test Methods.....	165
6.6.1	Indentation fracture (IF).....	165
6.6.2	Indentation strength (IS).....	166
6.7	X-ray Diffraction.....	167
6.8	Results.....	168
6.9	Discussion.....	173
6.8.1	Fracture toughness results.....	173
6.8.2	Toughening mechanisms of the current ceramics.....	179
6.10	Conclusion.....	183
6.11	Effect of heat pressing on the fracture toughness of Empress 1 and Empress 2.....	184
6.11.1	Introduction.....	184
6.11.2	Indentation fracture technique.....	185
6.11.3	Results.....	186
6.11.4	Discussion.....	189
6.11.5	Conclusion.....	193
6.12	References.....	194

CHAPTER 7: Flexural Strength 199

7.1	Introduction.....	200
7.2	Definition.....	200
7.3	Methods of Measurements.....	201

7.3.1	3-point bending flexural test.....	201
7.3.2	Biaxial flexural strength.....	202
7.4	Weibull modulus.....	203
7.5	Purpose.....	205
7.6	Tests adopted in the present study.....	206
7.6.1	Uniaxial flexural strength (3-point bending test).....	206
7.6.2	Biaxial flexural strength (Piston on three ball method)	207
7.6.3	Weibull Modulus.....	208
7.7	Result.....	209
7.7.1	Biaxial flexural test.....	209
7.7.2	3-point bending test.....	212
7.8	Discussion.....	212
7.9	Conclusion.....	215
7.10	Effect of different fabricating procedures on the flexural strength of Empress 1 and Empress 2.....	216
7.10.1	Introduction.....	216
7.10.2	Purpose.....	217
7.11	Materials and Methods.....	218
7.11.1	Samples preparations and treatments.....	218
7.11.2	Biaxial flexural strength.....	220
7.11.3	Scanning electron microscopy observations.....	220
7.12	Results.....	220
7.13	Discussion.....	222
7.14	Conclusion.....	233
7.15	References.....	235

CHAPTER 8: Mechanical Properties and Microstructure of Several All-Ceramic

Dental Materials	242
8.1 Introduction.....	243
8.2 Aim.....	243
8.3 Materials and Methods.....	244
8.3.1 Preparation of specimens.....	244
8.3.2 X-ray diffraction.....	245
8.3.3 Microscopic observations.....	246
8.3.4 Volume fraction and porosity.....	246
8.4 Results.....	247
8.4.1 X-ray diffraction.....	247
8.4.2 Microstructure.....	253
8.4.2.1 In-Ceram Alumina materials.....	253
8.4.2.2 In-Ceram Zirconia materials.....	257
8.4.2.3 DC-Zircon and the experimental zirconia materials	260
8.4.3 Mechanical properties.....	262
8.5 Discussion.....	266
8.6 Conclusion.....	271
8.7 Future Directions.....	274
8.8 References.....	276

List of Tables

Table 2.1	The chemical composition of Empress 1.	49
Table 2.2	Firing temperature for staining and glazing of Empress 1.	49
Table 2.3	Chemical composition of Empress 2.	54
Table 2.4	Firing temperature schedule of veneering of Empress 2.	54
Table 5.1	Elastic modulus and Poisson's ratio of the three investigated materials.	144
Table 5.2	Hardness results (GPa) of the three investigated materials; load range was from 10 to 80 N.	154
Table 6.1	Fracture toughness ($\text{MPa} \cdot \text{m}^{1/2}$) results of the three pressable materials.	169
Table 6.2	Fracture toughness ($\text{MPa} \cdot \text{m}^{1/2}$) of the two materials, Empress 1 and Empress 2.	189
Table 7.1	Biaxial flexural strength (MPa) of the three materials.	210
Table 7.2	Uniaxial flexural strength (MPa) of the three materials.	212
Table 7.3	Biaxial strength (SD), Roughness (SD), and Weibull modulus for Empress 1 and Empress 2 following different surface treatments.	221
Table 8.1	Averages of flexural strength and fracture toughness of all materials. The superscript number indicates (for materials with the same number) groups with no significant statistical difference.	264

Table 8.2 Volume fractions of each phase of all materials, and porosity. 265

List of Figures

- Figure 2.1** Schematic illustration of the three main modes of fracture: (Mode I) opening mode; (Mode II) shearing mode; (Mode III) tearing mode. 15
- Figure 2.2** Illustration of a through-cracked plate. 16
- Figure 2.3** Illustration for the effect of tensile stresses on crack propagation in a ceramic material (brittle) and a metallic material (ductile). 29
- Figure 2.4** Schematic illustration of the possible strengthening and toughening mechanisms involved in the macrostructure of some dental ceramic materials. 34
- Figure 2.5** Schematic illustration for the pressing system. 47
- Figure 3.1** Spruing and investing of disc specimens. 73
- Figure 3.2** Furnace used for preheating of the refractory moulds with the ingots, and the Alumina plunger. 74
- Figure 3.3** The pressing machine used in the current study (Programat EP 500, Ivoclar-Vivadent). 75
- Figure 3.4** Ingots were inserted into the moulds and the preheated plunger placed on top and pressing started. 75
- Figure 3.5** Metallographic machine used for grinding and polishing samples. 76
- Figure 3.6** Ingots and specimens (discs, bars, plates and buttons) of Empress 1 and Empress 2. 77
- Figure 3.7** The scanning electron microscope used for microstructural investigations. 79

Figure 3.8	Optical microscope in a UMIS machine used for crack length measurements.	79
Figure 3.9	The field emission Scanning Electron Microscope used to show further details such as crystal size, crack and crystal interactions and crack paths.	80
Figure 3.10	The diffractometer used to identify crystalline phases (D5000; Siemens, Munich, Germany).	81
Figure 4.1	The possible unit cell of a two dimensional pattern includes: (a) a square, (b) a rectangle or (c) a parallelogram.	85
Figure 4.2	A unit cell with x , y and z co-ordinate axes, showing axial lengths (a , b and c), and interaxial angles (α , β and γ).	86
Figure 4.3	lattice parameter relationships and figures showing unit cell geometries for the cubic, tetragonal, monoclinic and orthorhombic crystal systems.	88
Figure 4.4	The $[100]$, $[110]$ and $[111]$ directions within a unit cell.	89
Figure 4.5	Series of crystallographic planes, (a) (001) , (b) (110) and (c) (111) .	90
Figure 4.6	Wave interferences: (a) the general case, (b) constructive interference and (c) destructive interference.	92
Figure 4.7	The geometry of X-rays reflected from parallel atomic planes. The angle of incidence is θ , the wavelength of the x rays is λ , and the spacing between parallel planes of atoms is d .	94
Figure 4.8	X-ray diffraction pattern of Empress 1 before heat-pressing, showing leucite peaks (arrowed) at 2θ values of 25.89, 27.22, 30.41, and 31.36 degrees.	97

- Figure 4.9** X-ray diffraction pattern of Empress 1 after heat-pressing, showing a similar diffraction pattern to the pattern achieved before pressing. 97
- Figure 4.10** X-ray diffraction pattern of Empress 1 after further heat treatments, showing a similar X-ray diffraction pattern to those patterns achieved before and after heat-pressing. 98
- Figure 4.11** X-ray diffraction pattern of Empress 1 after repressing, showing a similar result to those achieved before and after pressing, and after further heat treatment. 98
- Figure 4.12** X-ray diffraction pattern of Empress 2 before heat-pressing, where arrows indicate the highest three peaks (at 23.9, 24.45 and 25 degrees) of the lithium disilicate. 100
- Figure 4.13** X-ray diffraction pattern of Empress 2 after heat-pressing, showing different lithium disilicate peak positions and intensities. 101
- Figure 4.14** X-ray diffraction pattern of Empress 2 after further heat treatments, showing a further background intensity decrease. 101
- Figure 4.15** X-ray diffraction pattern of Empress 2 after repressing, showing an identical pattern to that observed after first pressing. 102
- Figure 4.16** X-ray diffraction pattern of the new experimental ceramic, showing a similar pattern to Empress 2. 103
- Figure 4.17** Small leucite crystals are embedded in a glass matrix of a specimen before pressing, where some crystals appeared cracked and others are twinned. 108
- Figure 4.18** Clusters of leucite crystals in Empress 1 and vacant sites of glass matrix before pressing (magnification x 2, 200). 108

Figure 4.19	Clusters and cracking of leucite crystals before pressing.	109
Figure 4.20	Better distribution of leucite crystals than that observed before pressing (magnification 2200 x).	109
Figure 4.21	Extensive twinning of leucite crystals after pressing.	110
Figure 4.22	Microfracturing within the glass matrix and surrounding the leucite crystals was observed in some images.	110
Figure 4.23	Areas of accumulated cracks resulted from scratching damage during polishing or grinding after pressing.	111
Figure 4.24	Microstructural features of Empress 1 after repressing were similar to those after pressing, where glassy areas, leucite crystals and twinning can be seen.	111
Figure 4.25	Homogenous distribution of leucite crystals in a glass matrix after pressing.	112
Figure 4.26	Similar homogenous crystal distribution was also observed after repressing.	112
Figure 4.27	Area of extensive glass microcracking after grinding and polishing after repressed sample of Empress 1.	113
Figure 4.28	Microstructure of Empress 2 before pressing, showing homogenous distribution of many elongated lithium disilicate crystals (magnification 3700 x).	114
Figure 4.29	Microstructure of Empress 2 after pressing, observed at the same magnification (3700 x), showing larger lithium disilicate crystals than those found before pressing, and the crystals' alignment in a bar-shaped specimen.	115

- Figure 4.30** Alignment of lithium disilicate crystals in a sprue, where most crystals oriented with their long axis parallel to the pressing direction. 115
- Figure 4.31** Lithium disilicate crystals in a disc-shaped specimen, showing crystals with slightly different directions (Magnification 1900x). 116
- Figure 4.32** Microstructure of Empress 2 after repressing, showing clusters of lithium disilicate crystals that are oriented in slightly different directions in disc shaped specimen (Magnification 3300x). 116
- Figure 4.33** Lithium disilicate crystals in a bar-shaped specimen after repressing, where most crystals are aligned in the Y-axis direction, which is parallel to the pressing direction. 117
- Figure 4.34** Lithium disilicate crystals after repressing appeared larger than those found after pressing, where clusters of crystals can also be seen. 117
- Figure 4.35** Lithium disilicate crystals of the new experimental ceramic material, showing an interlocking pattern of crystals. 118
- Figure 4.36** Illustration of a statistical plot of the size of lithium disilicate crystals (μm) before pressing, after pressing and repressing. Pressing took place at 920°C . 122
- Figure 4.37** Illustration of the effect of pressing time (minutes) at 920°C on the size of the lithium disilicate crystals (μm). 123
- Figure 4.38** Different sizes of many spherical pores are distributed in a finely polished surface of Empress 1 before pressing. 126
- Figure 4.39** A finely polished surface of Empress 1 after pressing, showing fewer spherical pores than those found before pressing. 127

Figure 4.40	A finely polished surface of Empress 1 after repressing, showing few spherical pores.	127
Figure 4.41	Various small spherical pores distributed throughout a polished surface of Empress 2 before heat pressing.	128
Figure 4.42	A finely polished surface of Empress 2 after pressing, showing very few small spherical pores.	128
Figure 4.43	Many images showed no pores after heat pressing.	129
Figure 4.44	Repressed material of Empress 2 showing no pores.	129
Figure 5.1	Diagram of a typical test apparatus (ASTM, C 1259-94).	140
Figure 5.2	Specimen oriented for flexural vibration.	142
Figure 5.3	Specimen oriented on the support for torsional vibration.	144
Figure 5.4	Schematic illustration of Brinell hardness test. A is the indentation in a soft material and B is the indentation in a harder material.	150
Figure 5.5	Schematic illustration of Vickers indenter: (A) is the side view of the indenter, and (B) is a top view.	151
Figure 5.6	Schematic illustration of resultant residual impression following indentation: d1 and d2 are horizontal and vertical diagonals.	152
Figure 5.7	SEM photomicrograph of a residual impression of Empress 2 after indentation, used for hardness measurements.	154
Figure 5.8	SEM photomicrograph of a residual impression of the new experimental glass ceramic after indentation.	155

- Figure 5.9** SEM photomicrograph of a residual impression of Empress 1 following indentation, used for hardness measurements. 155
- Figure 6.1** Schematic representation of Vickers-produced indentation fracture system, where a is half diagonal and C is radial crack measured from the middle of indentation. 163
- Figure 6.2** Schematic illustration of specimen shapes that were used to collect X-ray diffraction. A represents the sprue where the beam reflected from the tip of lithium disilicate crystals; B is the cross section of the sprue, showing the way in which most lithium disilicate crystals are aligned; C is the fracture surface of a bar; D is the fracture surface of a disc; E is a disc, showing the way in which the lithium disilicate crystals are aligned; F is a block prior to pressing. 168
- Figure 6.3** Fracture toughness ($\text{MPa} \cdot \text{m}^{1/2}$) of the three materials versus different testing techniques. 170
- Figure 6.4** SEM photomicrograph of orthogonal cracks emanating from the corners of an indentation of Empress 2 with different crack lengths along the X- and Y-axis. 170
- Figure 6.5** SEM photomicrograph of orthogonal cracks emanating from the corners of an indentation of the experimental ceramic material with different crack lengths along the X- and Y-axis. 171
- Figure 6.6** SEM photomicrograph of an indentation of Empress 1, showing similar cracks emanating from the corners of the indentation. 171
- Figure 6.7** X-ray diffraction patterns of Empress 2: (A) before pressing (block), (B) fractured surfaces of discs, (C) the end of cut sprues, (D) fractured surfaces of bars. (111) and (002) are the two crystallographic planes with the dominant peaks diffracted from the fractured surfaces of the bars and the sprues. 172

- Figure 6.8** The influence of pressing of bars and discs on the orientation of the lithium disilicate crystals in Empress 2 and Experimental materials, plus the different distribution of stresses in the biaxial and 3-point bending test and the crack interaction with the lithium disilicate crystals. 178
- Figure 6.9** Crack is assumed to propagate across the preferred orientation of the grains, which results in a shorter crack path, and consequently greater fracture toughness. 180
- Figure 6.10** Crack is deflected by the needle-shaped crystals of lithium disilicate, giving a mixture of transgranular and intergranular crack patterns (arrows indicate the crack path). 180
- Figure 6.11** Microcracks and twinning of leucite crystals in the glassy matrix of Empress 1. 182
- Figure 6.12** The crack propagates through both the crystals and the glassy matrix after indentation of Empress 1 (crack-microstructure interaction). 182
- Figure 6.13** Cracks of similar length emanating from the corners of Vickers indentation of Empress 2 material before pressing. 187
- Figure 6.14** Cracks of different length emanating from corners of Vickers indentation of Empress 2 material in a bar after repressing; long axis of the bar is parallel to X-axis (tips of cracks are arrowed). 187
- Figure 6.15** Cracks of different length emanating from corners of Vickers indentation of Empress 2 material in a disc after repressing (tip of cracks are arrowed). 188
- Figure 6.16** Cracks of different length emanating from corners of Vickers indentation of Empress 2 material in a sprue after repressing (tips of cracks are arrowed). 188

Figure 6.17	SEM of Vickers indentation of Empress 1 showing similar crack length of an indentation.	191
Figure 6.18	Multi-cracking pattern surrounding an indentation of Empress 1.	192
Figure 7.1	Diagrammatic representation of the 3-point bending flexural test.	202
Figure 7.2	Biaxial flexural test diagram, showing a disc-shaped specimen loaded by a piston and supported by three ball bearings.	203
Figure 7.3	Illustration of Weibull plot of Empress 1.	210
Figure 7.4	Illustration of Weibull plot of Empress 2.	211
Figure 7.5	Illustration of Weibull plot of the experimental ceramic material.	211
Figure 7.6	SEM photomicrograph of a fractured surface of Empress 1 after grinding, showing spherical porosity site and the fracture origin, which is arrowed.	226
Figure 7.7	SEM photomicrograph of Empress 1, showing the fine polished surface with the associated spherical and irregular shaped pores.	228
Figure 7.8	SEM photomicrograph of Empress 2 fine polished surface showing very few small spherical pores.	228
Figure 7.9	Fractured surface of Empress 1, showing some spherical pores.	229
Figure 7.10	SEM photomicrograph of a fractured surface of Empress 2, showing no pores and appeared very rough.	229
Figure 7.11	SEM photomicrograph of Empress 2, after surface grinding, showing scratches in different directions and associated surface removal.	230

Figure 7.12	SEM photomicrograph of Empress 1 ground surface, showing rough surface with some pores.	230
Figure 7.13	SEM photomicrograph of Empress 1 sandblasted surface, showing rough surface generated. Surface roughness measurements indicated that this surface had deeper pits than other treated surfaces.	231
Figure 7.14	SEM photomicrograph of Empress 2 sandblasted surface, showing uniform shallow surface damage and superficial pits.	232
Figure 8.1	X-ray diffraction pattern of In-Ceram Alumina slip.	247
Figure 8.2	X-ray diffraction pattern of In-Ceram Alumina dry-pressed.	248
Figure 8.3	X-ray diffraction pattern of the as-sintered In-Ceram Zirconia slip.	249
Figure 8.4	X-ray diffraction pattern of the as-sintered In-Ceram Zirconia dry-pressed.	249
Figure 8.5	X-ray diffraction pattern of the as-sintered DC-Zircon.	250
Figure 8.6	X-ray diffraction pattern of the as-sintered experimental zirconia.	250
Figure 8.7	X-ray diffraction pattern of a fractured surface of DC-Zircon.	251
Figure 8.8	X-ray diffraction pattern of a fractured surface of the experimental zirconia.	252
Figure 8.9	X-ray diffraction pattern of a fractured surface of In-Ceram zirconia dry-pressed.	252
Figure 8.10	X-ray diffraction pattern of a fractured surface of In-Ceram zirconia slip.	253

- Figure 8.11** SEM of the microstructure of In-Ceram Alumina dry-pressed, showing equi-axed alumina particles (faceted and spherical). 254
- Figure 8.12** SEM of In-Ceram Alumina dry-pressed, showing the crack propagation through the microstructure, where the crack is deflected by the faceted and spherical particles of alumina (intergranular crack pattern). 254
- Figure 8.13** SEM of In-Ceram Alumina dry-pressed at higher magnification, where toughening mechanisms such as bridging (A) and contact shielding (B), and crack deflection, can be seen. The arrow indicates chipping of one of the two crystals and also friction between crystals. 255
- Figure 8.14** SEM of In-Ceram Alumina slip microstructure, showing the three different types of alumina crystals: elongated, faceted and spherical. 256
- Figure 8.15** SEM of a residual impression of In-Ceram Alumina slip after indentation, showing non-symmetrical cracks. Shorter cracks were observed propagating perpendicular to the elongated grains, whereas the longer ones are propagating parallel to the length of the elongated crystals. 256
- Figure 8.16** SEM of In-Ceram Alumina slip showing 3 different toughening mechanisms: pull-out of crystals (A), bridging (B), and crack deflection (C). Arrows indicate crack propagation direction after indentation. 257
- Figure 8.17** SEM of In-Ceram Zirconia dry-pressed, showing the white crystals (zirconia crystals) are agglomerated, and black crystals (alumina crystals) are embedded in a glass matrix. The atomic number of the different phases highlights them in the back-scattered mode of the SEM. 258

- Figure 8.18** SEM of the microstructure of In-Ceram Zirconia slip, showing a very similar microstructure to that of In-Ceram Zirconia dry-pressed. 259
- Figure 8.19** SEM of In-Ceram Zirconia dry-pressed at higher magnification, showing a transgranular crack pattern for zirconia crystal (B). The arrows indicate location of microcracks in the glass matrix and at the boundary between particles and glass. 259
- Figure 8.20** SEM of In-Ceram Zirconia slip. The crack propagates through zirconia crystals, transgranular crack pattern (A and B) and around alumina crystals, resulting in an intergranular crack pattern. (C) 260
- Figure 8.21** SEM of DC-Zircon, showing dense and very fine crystals of zirconia. 261
- Figure 8.22** SEM of the experimental zirconia, showing very fine crystals of zirconia and an intergranular crack pattern. 261
- Figure 8.23** SEM of DC-Zircon, showing crack propagation through the particles of zirconia as well as interboundary regions. 262
- Figure 8.24** Relative amount of monoclinic of all materials after sintering and after fracture. 273

Publications and Scientific Meetings

Journal Publications

1. **Albakry M**, Guazzato M, Swain MV. Biaxial Flexural Strength, Elastic Moduli, and X-ray Diffraction Characterization of Three Pressable All-Ceramic Materials. *Journal of Prosthetic Dentistry* 2003;89:374-380.
2. **Albakry M**, Guazzato M, Swain MV. Fracture Toughness and Hardness Evaluation of Three Pressable All-ceramic Dental Materials. *Journal of Dentistry* 2003;31:181-188.
3. **Albakry M**, Guazzato M, Swain MV. "Fracture Toughness, Microstructure and Toughening Mechanism of Leucite and Lithium Disilicate Glass Ceramics". *Key Engineering Materials Vols 240-242*; 2003: 955-958.
4. **Albakry M**, Guazzato M, Swain MV. Effect of Sandblasting, Grinding, Polishing and Glazing on the Flexural Strength of Two Pressable All-ceramic Dental Materials. *Journal of Dentistry* 2003;in press.
5. **Albakry M**, Guazzato M, Swain MV. Biaxial Flexural Strength and Microstructure Changes of Two Recycled Pressable Glass Ceramics. *Journal of Prosthodontics* 2003;submitted.
6. **Albakry M**, Guazzato M, Swain MV. Influence of Hot Pressing on the Microstructure and Fracture Toughness of Two Pressable Dental Glass-ceramics. *Journal of Biomedical Materials Research (Applied Biomaterials)* 2003;submitted.
7. Guazzato M, **Albakry M**, Swain MV. Mechanical Properties of In-Ceram Alumina and In-Ceram Zirconia. *International Journal of Prosthodontics* 2002;15:339-346.

8. Guazzato M, **Albakry M**, Swain MV, Ringer SP. Microstructure of Alumina- and Alumina/Zirconia Glass-Infiltrated Dental Ceramics. Key Engineering Materials Vols 240-242; 2003: 879-882.
9. Guazzato M, **Albakry M**, Swain MV. Strength, Fracture Toughness and Microstructure of a Selection of All-ceramic Materials. Part I: Pressable and Alumina glass-infiltrated Ceramics. Dental Materials 2003;in press.
10. Guazzato M, **Albakry M**, Swain MV. Strength, Fracture toughness and Microstructure of a Selection of All-ceramic Materials. Part II: Zirconia-based Dental Ceramics. Dental Materials 2003;in press.
11. Guazzato M, **Albakry M**, Swain MV. Influence of Surface and Heat Treatments on the Flexural Strength of a Glass-Infiltrated Alumina/Zirconia-Reinforced Dental Ceramic. Dental materials 2003;in press.
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13. Guazzato M, **Albakry M**, Quach L, Swain MV. Influence of Surface and Heat Treatments on the Flexural Strength of Y-TZP Dental Ceramic. Submitted to the Journal of Dentistry.

Scientific Meetings

International Meetings

1. **Albakry M**, Guazzato M, Swain MV. The Mechanical Properties of Three Pressable All-ceramic Dental Materials. IADR 80th General Session and Exhibition, March 6-9, 2002, San Diego, California, USA.

2. **Albakry M**, Guazzato M, Swain MV. Fracture Toughness, Microstructure and Toughening Mechanism of Leucite and Lithium Disilicate Glass Ceramics. **Bioceramics - 15**, Proceedings of the 15th International Symposium on Ceramics in Medicine, The Annual Meeting of the International Society for Ceramics in Medicine, December 4-8, 2002, Sydney, NSW, Australia.
3. **Albakry M**, Guazzato M, Swain MV. Effects of Sandblasting, Grinding and Polishing on the Flexural Strength of Two Pressable All-ceramic Dental Materials. **IADR 81st** General Session, June 25-28, 2003, Göteborg, Sweden.
4. Guazzato M, **Albakry M**, Swain MV. Mechanical Properties of In-Ceram Alumina and In-Ceram Zirconia. **IADR 79th** General Session and Exhibition, June 27-30, 2001, Chiba, Japan.
5. Guazzato M, **Albakry M**, Swain MV. Influence of Sandblasting, Grinding, Polishing and Heat Treatment on the Flexural Strength of an Alumina-reinforced Glass-infiltrated Dental Ceramic. **IADR 81st** General Session, June 25-28, 2003, Göteborg, Sweden.
6. Swain MV, **Albakry M** Guazzato M. Microstructure of Alumina-and Alumina/Zirconia-glass Infiltrated Dental Ceramics. **Bioceramics - 15**, Proceedings of the 15th International Symposium on Ceramics in Medicine, The Annual Meeting of the International Society for Ceramics in Medicine, December 4-8, 2002, Sydney, NSW, Australia.

National Meetings

1. **Albakry M**, Guazzato M, Swain MV. The effect of heat pressing on the fracture toughness of two pressable all-ceramic dental materials. **IADR**, Australian and New Zealand Division 42nd Annual Meeting, September 29th – October 2nd 2002, Sydney, NSW, Australia.

2. Guazzato M, Albakry M, Simon R, Swain MV. Strength, fracture toughness and microstructure of Zirconia-based dental ceramics. **IADR** Australian and New Zealand Division, 42nd Annual Meeting, September 29th – October 2nd 2002, Sydney, NSW, Australia.

CHAPTER 1

INTRODUCTION

This introductory chapter will focus on three main issues of the current study. Firstly, a historical review of the use of ceramics in dental prostheses will be provided. The development of different dental prostheses such as porcelain jacket crowns and metal ceramic systems will be introduced in the second part, along with their advantages and disadvantages. This will be followed by a brief introduction to the more recently introduced dental ceramic restorations, the metal-free prostheses, the use of all-ceramic dental materials and their increasing acceptance in the last decade. The purpose and the structure of the current study will be presented in the third and fourth parts respectively of the chapter.

1.1 Historical Review

Since ancient times, humankind has always been afflicted by the problem of tooth loss. There are variable reasons for tooth loss; which include: 1) gum diseases, 2) decay and 3) trauma. The search for an effective means of replacing missing teeth has continued, and different materials and approaches have been used. Even in ancient Egyptian times, evidences have been found of examples of tooth replacement prostheses made from gold wire, ox bone or wood [1]. The Chinese are credited with the development of porcelain in 1000 AD [2], which, although it was not developed for tooth replacement, has been used for this purpose since then. European craftsmen attempted unsuccessfully to unravel the Chinese ceramic technology secrets [3]. Ceramics have gained the attention of man for many centuries. They were one of the most highly developed materials of the Stone Age and have preserved their significance in human life to the present day [4]. Furthermore, ceramics are probably the best existing materials for matching the aesthetics of an intricate human tooth. In the late 1700s, dental ceramics based upon porcelain were first used by Alexis Duchâteau to fabricate complete dentures [5, 6].

Porcelain jacket crowns were developed in 1900 by Land [7], and consisted of feldspathic or aluminous porcelain baked on a thin platinum foil [5]. Because of the lack of sufficient strength and possibly the difficulty in obtaining a reproducible and precise marginal fit, these crowns often failed, and hence their application was limited to anterior segments [5]. Following numerous modifications of the essential feldspar-quartz-kaolin constitution and many years of assessment and tribulations, the metal ceramic technology appeared to mature in the 1950s [3]. This development of metal ceramic restorations allowed the more reliable use of porcelain as a dental prosthesis.

This type of restoration is fabricated by fusing porcelain directly to a metal coping, which virtually fits the prepared tooth. However, initially there was inevitably a mismatch in the co-efficient of thermal expansion between the framework (metal substrate) and the veneering porcelain, which often led to porcelain fracture or cracking upon cooling [5]. This motivated the development of leucite (high thermal expansion mineral) containing feldspathic porcelain. Mixing a controlled amount of leucite with the feldspar glass at the manufacturing stage allowed for a better adjustment of the thermal expansion mismatch between the metal substructure and veneering porcelain [5]. This also allowed tailoring of the expansion coefficient such that it placed the veneering porcelain in compression, which favorably imparted increased resistance to shattering or fracture. The successful performance and reliability of such restorations has led to substantial improvements in alloy substrates and veneering porcelains and consequently to a widespread acceptance of these restorations [8].

1.2 All-ceramic Dental Restorations

Although metal-ceramic fixed partial denture restorations have been the standard for single and multiple tooth replacement [9], several factors have been cited as potential drawbacks of these restorations. Poor aesthetics, manifesting as a difficulty in producing similar translucency to that of a tooth, metal margin visibility especially in the anterior segments and poor biocompatibility were the major disadvantages of these restorations [10-12]. For example, in order to cover the metal substructure, which produces an opaque appearance, and porcelain veneer components, immense efforts from both dentists and dental technicians were required [9], and in some situations this did not meet the satisfaction of aesthetic conscious patients. Also, debonding of the porcelain veneer from the underlying metal substructure may be considered one of the

difficulties that many clinicians face when the metal porcelain treatment is chosen, and can be a source of failure.

The foremost aim of restorative dentistry is to replace the diseased or lost tooth structure with an appropriate substitute. "A material that is designed to be implanted in human body to replace or repair a damaged part is called a biomaterial, and must be biocompatible" [13]. Biocompatibility includes the cytotoxicity and tissue irritation. It is defined as "the ability of a material to elicit an appropriate biological response in a given application" [14]. Base metal alloys, which are commonly used as metal substrates, may exhibit corrosion and/or may cause an allergic reaction [15], and some constituents may even instigate a variety of acute and chronic health hazards to both dentists and laboratory technicians [16]. Biocompatibility is therefore a crucial aspect when metal-ceramic restoration treatment is chosen, particularly for people with known sensitivity to base metals.

The above-mentioned drawbacks of metal ceramic restorations, coupled with the desirability of a more conservative approach to tooth preparation, has led to the recent improvements in ceramic formulations and various techniques. The past decade has seen a tremendous development in ceramic products with improved fracture resistance and excellent aesthetic capability, which in turn led to increased interest in the use of all-ceramic restorations. The advent of these metal-free ceramic restorations has inundated the aesthetic-conscious patients with promises of excellent colour match, abrasion resistance, low thermal conductivity and biocompatibility. Moreover, these restorations benefit from the recent advances in adhesive techniques by bonding to an etched tooth, which is thought to improve the overall fracture resistance [16, 17], due to the ability of resin to reduce the consequences of possible ceramic defects, together with

the better distribution of the occlusal load to the supporting tooth structure [18]. Despite these developments, the brittle nature of ceramics, along with the presence of pores or voids and the inherent growth of microscopic flaws or defects, either during processing or mastication, have limited their wider use and success rate, especially in the posterior segments. The application of high-technology processes allowed for the development of various dental all-ceramic techniques and systems, which are currently available in the market. These systems can be classified according to the laboratory processing procedures (pressable, slip-casting, milling, and sintering) [19], and the chemical composition (feldspar: high leucite and low leucite; glass ceramic: lithium disilicate and mica; core reinforced: alumina, magnesia and zirconia) [13, 20]. Materials for all-ceramic restorations utilise these crystalline phases as reinforcing components. However, the nature, amount, size and distribution of these reinforcing phases significantly determine their mechanical, physical and optical properties [21]. Typically, the increase of crystalline content results in greater opacity of a ceramic material. It has therefore been a challenge for most researchers and manufacturers to fabricate a ceramic material that combines sufficient strength with the degree of translucency required in dentistry [22].

1.3 Purpose

As stated above, the past decade has seen a tremendous growth in the use of all-ceramic dental restorations. Because of the diversity of these systems, the appropriate selection in different clinical situations may become difficult. Furthermore, these materials are in fact brittle, and submitted to destructive parafunctional forces during functioning (mastication). While their long-term clinical performance and success depend on a number of factors, the mechanical properties are of significant interest, as they delineate

the behaviour of these materials under load. For example, relevant in vitro studies should be carried out before clinical trials can be contemplated.

A wide range of materials and systems are currently available for the construction of all-ceramic restorations. One class among these systems requires hot pressing by means of a special furnace to produce the required shape (pressable materials). Pressable materials Empress 1 (leucite-reinforced glass-ceramic) and Empress 2 (lithium disilicate-reinforced glass-ceramic) (Ivoclar-Vivadent, Schaan, Liechtenstein) are characterised by their optical properties and easy fabricating processes, utilising the traditional simple lost waxing technique.

The incentive for undertaking this study originated with the increased use and interest for single units, such as crowns, veneers, onlays and inlays made out of the high translucent pressable all-ceramic system Empress 1. The intrinsic properties of this system have been investigated thoroughly in the literature. The present study will use this material as a benchmark for the recently introduced material Empress 2, and selected peer all-ceramic dental materials. Furthermore, the effect of the processing procedure on the mechanical properties of this system will also be assessed.

This study was also encouraged by the introduction of the new pressable glass ceramic Empress 2, which brought with its release a promise of the fabrication of a 3-unit fixed partial denture up to the second premolar, utilising the same simple lost wax technique, and maintaining good aesthetic features. In addition, even following up to two years of clinical usage, there have been very few in vitro and in vivo studies for the Empress 2 system.

In 2000, the same manufacturer was about to release another pressable all-ceramic dental material, claiming that it possesses even better mechanical and optical properties than those offered by Empress 2. Samples were prepared by the manufacturer and sent for mechanical property evaluation and comparison with Empress 1 and Empress 2. Therefore, this study aimed at providing the following:

- 1) A comprehensive description of the microstructural features for Empress 1 and Empress 2, and the effect of heat pressing on these microstructures.
- 2) A description of the major and minor crystalline phases of which these materials are comprised, and the effect of different processing procedures on these phases.
- 3) A critical independent assessment of the mechanical properties of these materials, namely, flexural strength, fracture toughness, hardness, elastic modulus and Poisson's ratio, and strength reliability by calculating the Weibull modulus.
- 3) The effect of different laboratory fabricating procedures, and possible clinical adjustment methods on their flexural strength and reliability.
- 4) An assessment of the mechanical properties of recycled specimens of Empress 1 and Empress 2.
- 5) A collaborative assessment, with Dr M. Guazzato, of the mechanical properties of glass-infiltrated systems: In-Ceram Alumina, In-Ceram Zirconia, and several other advanced all-ceramic new systems. However, the main focus of this thesis will remain on the pressable glass ceramics Empress 1 and Empress 2.
- 6) A comparison of the mechanical properties of Empress 1 and Empress 2 with some peer advanced all-ceramic materials, such as In-Ceram Alumina, In-Ceram Zirconia, experimental zirconia material and DC-Zircon will also be provided.

1.4 Thesis Structure

The thesis has the following structure. An historical review of dental ceramics, along with the vast use of metal ceramic restorations, and finally the emergence of all-ceramic restorations are all presented in an introduction comprising the first part of Chapter 1. Included also in Chapter 1 are the purpose and structure of this thesis. Chapter 2 will present a brief review of fracture mechanics principles, followed by the definition, properties, method of forming and application of general glass ceramics.

The third section of Chapter 2 will review the composition, properties, classification, shortcomings, method of strengthening and toughening of dental ceramics. The fourth section will review the chemical composition, mechanical properties, microstructure and, wherever possible, the clinical performance of a number of all-ceramic dental materials.

The first section of Chapter 3 will introduce the dental materials that were prepared for the current investigations. The second section will provide a description of the procedures that were utilised to prepare samples for mechanical testing and microstructural observation.

The main body of this thesis starts with Chapter 4, where the crystalline phases and microstructure of Empress 1 and Empress 2 are presented. Mechanical properties are significantly determined by the microstructural features and crystalline phases; Chapter 5 will present the first evaluated three mechanical properties, namely, elastic modulus, Poisson's ratio and hardness. Chapter 6 will present the fracture toughness assessment, using two different techniques, indentation fracture (IF) and indentation strength (IS), using the biaxial strength and 3-point bending methods. The same chapter

will also present an evaluation of the effect of heat pressing on the fracture toughness of the two materials, Empress 1 and Empress 2. The final evaluated mechanical property in this thesis, flexural strength, will be presented in Chapter 7, which will also give an evaluation of the effect of different fabrication procedures on the flexural strength of the two materials. Chapter 8 provides a comparison of the mechanical properties of the pressable material Empress 1 and Empress 2 with several advanced peer all-ceramic materials such as In-Ceram Alumina, In-Ceram Zirconia, and DC Zircon. Future directions for research are also presented in Chapter 8.

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CHAPTER 2

REVIEW OF THE LITERATURE

This literature review chapter consists of four main parts. The first part presents a brief review of the fracture mechanics principles. Definition, properties, method of forming and application of general glass ceramics are given in the second part. The third part reviews the composition, properties, classification and shortcomings of dental ceramics. Methods of strengthening and toughening dental ceramics are also reviewed in this part. The last part reviews the chemical composition, mechanical properties and, wherever possible, the clinical performance of several types of all-ceramic dental materials.

2.1 Fracture Mechanics

The behaviour of a solid object to stress with the presence of a crack is defined by fracture mechanics [1]. The purpose of studying fracture mechanics is to impart a valid explanation and prediction of behaviour for certain problems related to cracks in structures [2]. It shows a relationship of fracture or failure, which is dependent upon the critical crack size, to crack growth and propagation and also the mechanisms for resisting crack growth [2-5]. This branch of materials technology has led to the safe design of a very wide range of engineering structures as diverse as pressure vessels, aircraft and most applicable engineering materials.

The fundamental loading mechanisms on a pre-existing crack are classified into three modes (Figure 2.1) [1, 3, 6]. The most commonly established pattern into which most brittle materials fail is the simple crack opening mode (mode I). In this mode, the displacement is normal to the crack surface. The second pattern is the shearing mode (mode II) where the displacement near the crack tip is in the plane of the crack surface and normal to the crack front. The third pattern is the tearing mode (mode III), where the displacement is in the plane of the crack surface but parallel to the crack front. Whichever mode of stress is pertinent, the study of failure or fracture mechanism can be studied on the basis of two approaches: Griffith's fracture theory and (1920) and a linear elastic fracture mechanics approach.

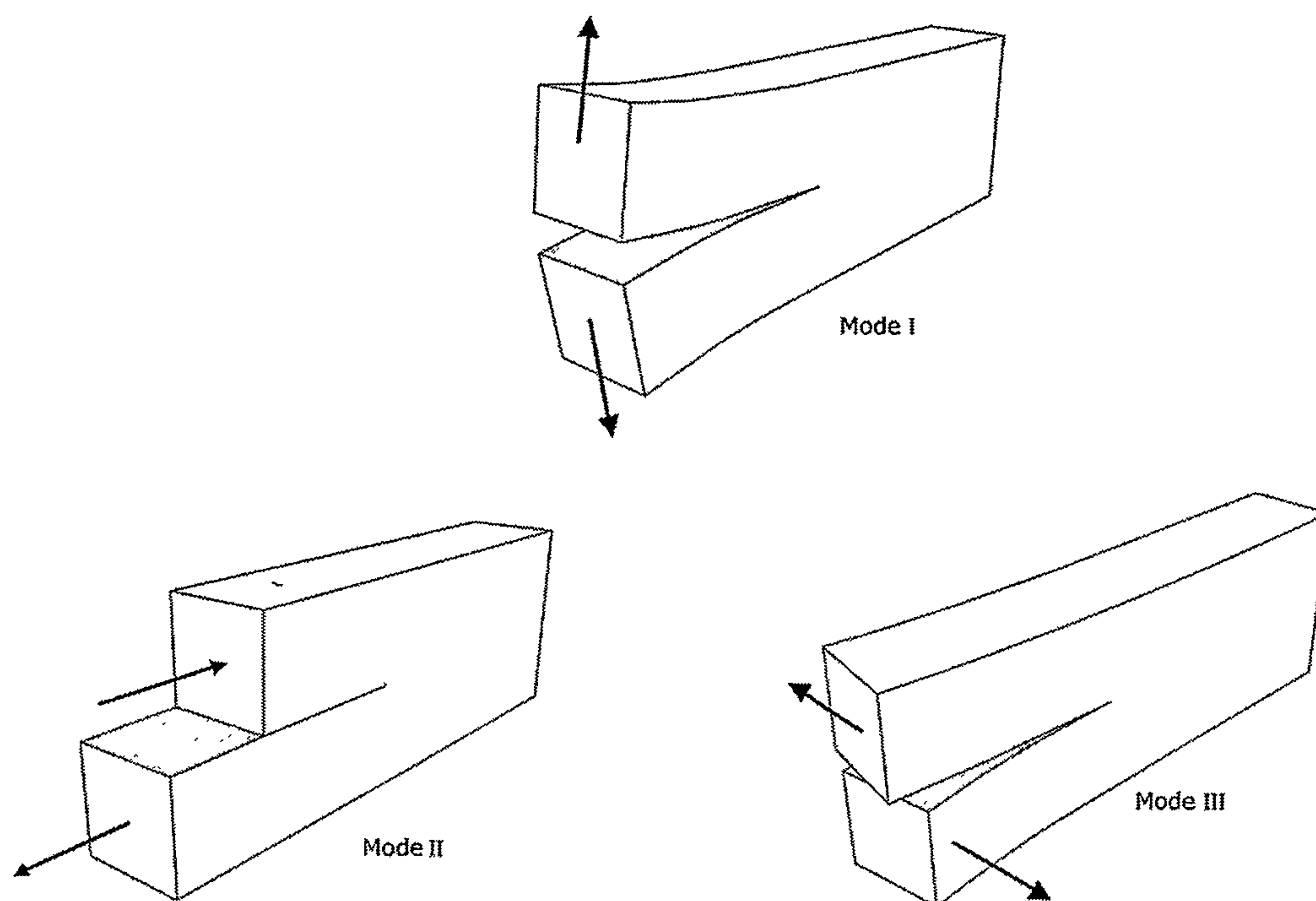


Figure 2.1 Schematic illustration of the three main modes of fracture: (Mode I) opening mode; (Mode II) shearing mode; (Mode III) tearing mode [1].

2.1.1 Criteria of crack growth

Linear fracture mechanics adopt two equivalent criteria for fracture, proposed by Irwin and Griffith. Irwin's criterion considers the stresses surrounding a crack tip, whereas Griffith's utilises the energy balance approach [1].

2.1.2 Fracture theory (Griffith's principle)

In 1920, British physicist A. A. Griffith proposed critical conditions for brittle fracture [7]. These conditions are based on the fundamental energy theorems of normal mechanics and thermodynamics [2, 4]. During static conditions or equilibrium, with a crack (a) in an ideal elastic-brittle phase (Fig. 2.2), the total energy of the whole system (U) can be described as the energy summation of the uncracked

plate (U_0). The energy changes when the crack extends (U_a), the surface energy changes (U_f), and the external force works (F).

$$U = U_0 + U_a + U_f - F \quad (1)$$

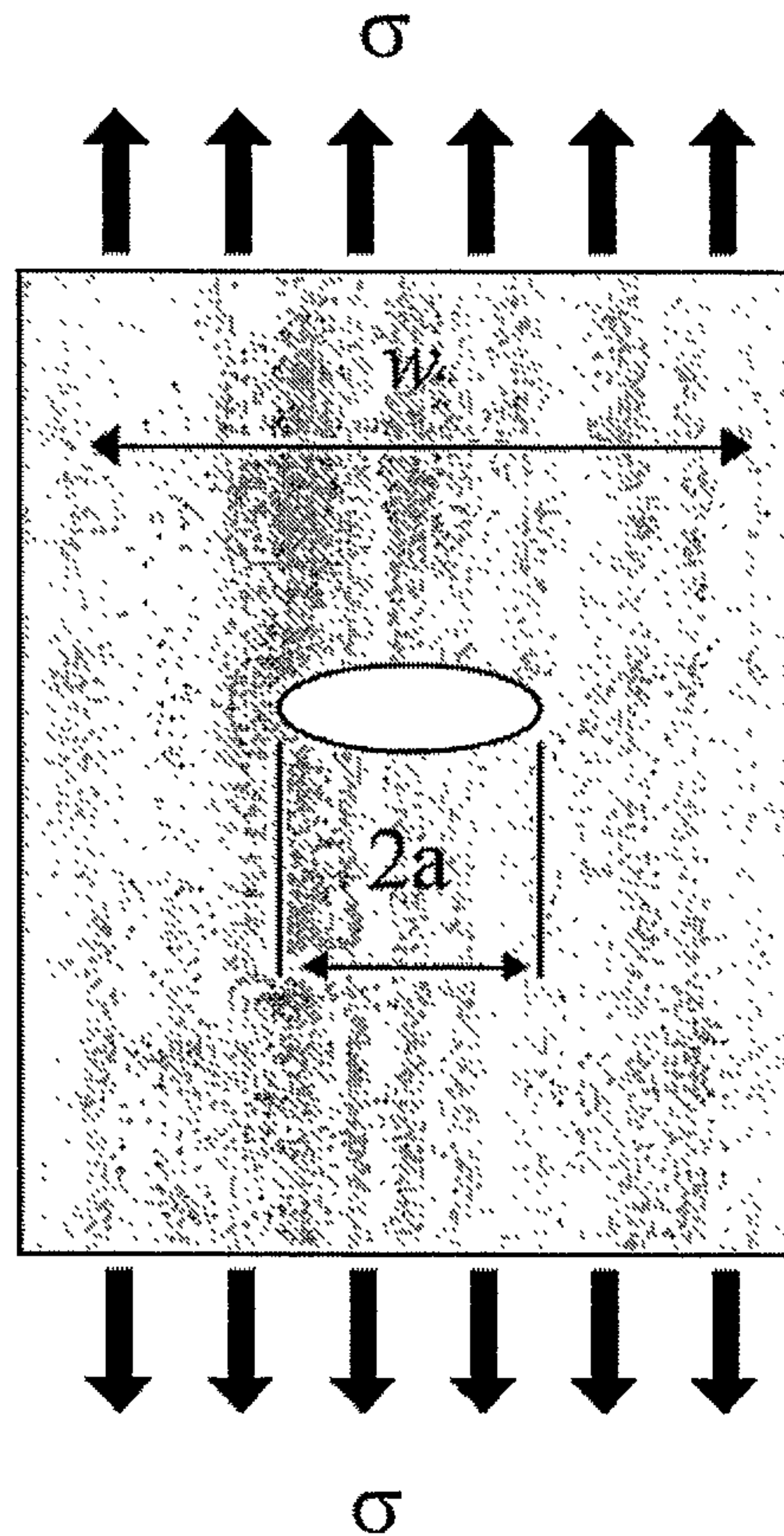


Figure 2.2: Illustration of a through-cracked plate [2].

The condition for crack growth is:

$$G_1 = \Delta U_a / \Delta a$$

where G_1 , the critical strain energy release rate, is the release rate of potential energy or crack extension force. Inglis (1913) proposed the relationship between fracture stress and G_1 as:

$$G_1 = \sigma^2 \pi a / E^* \quad \text{or} \quad \sigma = \sqrt{\frac{E^* G_1}{\pi a}} \quad (2)$$

A normal tensile stress is represented by σ and elastic modulus by E^* . For plane stress, $E^* = E$, the elastic modulus, and for plane strain, $E^* = E / (1 - \nu^2)$, where ν is Poisson's ratio. The state of stress produced within a structural element can be defined by plane stress or plain strain. If γ_s is the specific surface energy, the necessary work to produce a unit area of fracture is $2 \gamma_s B$. B is the cross-sectional area of the plate. The formula can be derived as follows:

$$\sigma = \sqrt{\frac{2 \gamma_s E^*}{\pi a}} \quad (3)$$

Some materials require more strain energy to initiate fracture than surface energy. This is considered to be the result of the non-elastic zone located at the crack tip that dissipates and absorbs the energy. This region can be defined as the fracture plastic zone. Irwin (1948) stated that Griffith's theory could be modified and applied to both brittle and ductile materials by involving the plastic strain work, γ_p into the relationship as follows:

$$\gamma = \gamma_s + \gamma_p \quad (4)$$

2.1.3 Linear elastic fracture mechanics (LEFM)

For brittle materials, linear fracture mechanics is appropriate. This is based on the hypothesis that a structure exhibits elastic behaviour obeying Hooke's law up to fracture, and all possible plastic deformations are limited to a localised area surrounding the crack tip [8].

Irwin (1957, 1958) and Williams (1957) introduced new stress approaches to analysis fracture. They found that the stresses near the tip of a crack are inversely proportional to the square root of the distance from the crack tip. They also defined the concept of stress intensity factor, which for a planar flaw of radius a in an infinite body is given by:

$$K = \sigma \sqrt{\pi a} \quad (5)$$

where K is the stress intensity factor having units of $\text{MPa} \cdot \text{m}^{1/2}$, applied stress (σ), and the crack length (a). For other geometries the stress intensity factor can be written as:

$$K = \sigma_N \phi \sqrt{\pi a} \quad (6)$$

where σ_N is the nominal stress at the crack and ϕ is a geometric factor that depends upon the geometry of the specimen. Regularly, the geometric factor (ϕ) is of the order of the unity but may increase or decrease with crack extension. The use of the stress approach is valuable as the superposition principle can be utilised, enabling the stress intensity factor to be divided into its classical modes (modes I, II and III). The conditions for propagation of a crack are that $K \geq K_C$ where K_C is the critical stress intensity factor for the material in question.

For an elastic-brittle material, both K_C and G_C are identical, specifically:

$$K_C^2 = E^* G_C \quad (7)$$

For plane stress, $E^*=E$, the Elastic modulus, and for plane strain,

$$E^*=E/(1-\nu^2) \quad (8)$$

where ν is Poisson's ratio. This is due to the fact that an ideal elastic-brittle material has a small fracture plastic zone in comparison with crack size and other dimensions of the specimen and the crack shape [1].

2.1.4 Non-linear fracture mechanics (NLFM)

Originally, non-linear fracture mechanics were developed for crack growth under essential elastic conditions. These conditions are only achieved for plane strain fracture of very strong ductile materials (metallic) or for fracture of materials that are inherently brittle, such as glass or ceramic materials. Non-linear fracture mechanics were designed to deal with materials that have relatively medium or low strength as a result of plastic yielding, where the plastic zone is exceedingly large to be controlled by the K-stress field [2-4]. In such circumstances, it is speculated that there is an internal fracture plastic zone contained by the plastic zone where a critical work of fracture must be overcome. Therefore, non-linear fracture mechanics separate the elemental work of fracture, which is as regarded as a material property, from the larger plastic work, which depends on the size and geometry of the specimen [3, 4].

2.1.5 The work of fracture

Fracture energy concepts have been widely used to define the fracture property of quasi-brittle materials due to their non-linear features, which limit the application of the linear elastic fracture mechanics. The work of fracture is the energy absorbed by a slowly propagating crack. It is typically determined from the entire area beneath the load-displacement curve divided by double the residual ligament area. However, for the evaluation of ductile materials, the essential work of fracture proposed by Broberg [9] has been utilised because of the high energy consumed by various in-elastic deformation. For the essential work of fracture principles, the total work of fracture (W_f) comprised both the essential work of fracture (W_e , the energy required to fracture the ductile material in its process zone) and the non-essential work of fracture (W_p , energy used by numerous deformation mechanisms in the plastic zone):

$$W_f = W_e + W_p \quad (9)$$

In fact, it is very difficult to separate the work of fracture energy in the case of brittle materials such as ceramics, and this is also regarded as unnecessary.

2.1.6 Crack resistance curve (R-curve behaviour)

When the apparent fracture toughness of a specific material increases with increasing crack extension, the material exhibits crack growth resistance behaviour, also called R-curve behaviour [10, 11]. This crack growth resistance is considered a true phenomenon for small crack extension [12]. Because of the additional energy required for a crack to propagate until fracture occurs, R-curve behaviour is a desirable mechanical effect, particularly in the field of dental materials [10]. The importance of such a mechanical property in dental restorative materials is due to the high and non-uniform stresses occurring during the mastication process [10]. R-curve behaviour mainly occurs as a result of microstructural effects [10, 11]; some of these are: 1) friction at the boundary of the crack tip (called also crack bridging), 2) energy-consuming effect due to, for example, crack branching, 3) phase transformation, characteristics of zirconia based-materials. R-curve behaviour results in many benefits for materials including, 1) improved fracture toughness and flexural strength, less scatter-in-strength results, less sub-critical crack growth and consequently better long-term strength behaviour [10].

Various procedures have been developed for the assessment of R-curve characteristics of ceramic materials. Indentation strength technique (IS) (Chapter 6, 6.4) has been widely used by many investigators [11, 13, 14]. Fisher et al., (2002)

adopted this technique to evaluate the R-curve behaviour for several dental ceramic materials [10]. Results showed that all materials exhibited R-curve, but it was more pronounced in materials with higher crystalline content, such as Empress 2 and In-Ceram Alumina.

2.2 Introduction

Different types of restorative materials are currently used in dental treatments. Some of them are: amalgam, composite resins, glass ionomers, dental alloys and ceramics. Each of these materials has unique properties that make it suitable for certain restorations. Glasses and ceramics are widely used in dentistry. Because of their chemical inertness in many media, good aesthetic qualities and abrasion resistance, they are an ideal group of materials to use in tooth replacement. However, their inherent brittleness and extreme sensitivity to microcrack-like defects have hampered their wider use and limited their application to relatively low stress-bearing areas, or metal substructures (metal-ceramic restoration) have traditionally been used to improve their performance and longevity. The mechanical properties of these materials are crucial and must be considered when these materials are chosen for restorative treatment.

In fact, many dental all-ceramic materials have recently become available for the construction of crowns, inlays, onlays, and also fixed partial dentures. The aesthetics and biocompatibility offered by these materials are duly recognised as superior when compared to the traditional metal-ceramic restorations. The majority of these restorations are constructed from a relatively strong core material covered by translucent veneering porcelain built up in layers. The core portion is made of high-performance pure ceramic or glass-ceramics.

2.3 Glass ceramics

2.3.1 Definition

Glass was first discovered thousands of years ago in ancient Egyptian times [15]. McMillan (1979) described it as a transparent, hard, rigid and brittle material [16]. A widely accepted definition of glass that includes various glasses is: an amorphous solid, usually inorganic substance, that exhibits only short-range order in the atomic arrangement, not greater than 10 nm [15, 16].

Glass is formed by heating a mixture of raw materials such as quartz, feldspar and dolomite at an adequately high temperature to allow the reaction of these materials together and to permit the escape of gas bubbles from the formed melt [15]. The mixture is then cooled from the melting point rapidly enough to avoid nucleation and growth of crystalline phases. Silica (SiO_2) is the most important constituent of all commercial glasses since it is the main glass-former (network former) [1]. Other oxides such as B_2O_3 and P_2O_5 also form glasses when adequately heated and cooled.

Glass ceramics are partially polycrystalline materials that are formed from the melt as a glass and converted by an appropriate heat treatment into fine-grained ceramics [15, 17, 18]. These materials may possess certain characteristics found in both glasses and ceramics.

2.3.2 Crystallisation

Stookey developed the first glass ceramic in the late 1950s, using controlled crystallisation of special glasses [19]. Crystallisation, also called devitrification, is a procedure in which the conventional crystal lattice is generated from a less well-

ordered liquid structure [16]. Crystallisation takes place by adding a nucleating agent such as TiO_2 , ZrO_2 , or P_2O_5 to the glass mixture during heat treatment. The amount of crystallite may be more than 50% in some cases and the size of crystals may be less than $10\text{ }\mu\text{m}$ [18]. The crystals grow on the particles of the nucleating agents, which have been added to the melt [16]. This results in a strong, hard, and chemically more stable material than the parent glass [20, 21].

2.3.2.1 Mechanisms of crystallisation

Crystallisation of a liquid can occur by two main mechanisms: homogenous and heterogeneous nucleation [15]. In the homogenous nucleation, the crystals which grow upon the tiny nuclei have the same structure as the nuclei. In the heterogeneous nucleation, the deposited crystals can be different from the nuclei [16]. The majority of nucleation occurs heterogeneously, however, homogenous nucleation is more open to analysis and better understood than heterogeneous nucleation [15].

Various glass ceramics have been developed according to the principle of Stookey (controlled volume crystallisation). In the volume crystallisation, crystals of almost the same size are uniformly dispersed in the base glass. Glass ceramics can be conveniently classified by their bulk chemical composition or by the composition of the developed crystalline phases. According to chemical composition they are: 1) silicate glass ceramics, 2) phosphate glass ceramics, or 3) oxide glass ceramics [18]. Examples of important glass ceramic systems are: $\text{SiO}_2\text{-LiO}_2$ and $\text{SiO}_2\text{-MgO-K}_2\text{O}$ [15]. Glasses that are based on the leucite system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ are very common glass ceramics. These materials are not converted by the well-known volume crystallisation mechanism. Another mechanism, controlled surface crystallisation, is

used to convert these glasses [22]. Oxides such as K_2O 12 wt % and CaO 1 wt % are added to the base glass [23], melted and submitted to further heat treatment to initiate nucleation and primary crystallisation, and then they are ground. Stabilisers, additives and fluorescent agents and pigments are added, and the mixture is heat treated to a relatively high temperature. The primary nucleation and crystallisation process is initiated at the grain boundary of the ground glass. The crystals grow directly inward from the interface of the glass particles, due to the reactive glass surface and the application of glass powder [22].

2.3.3 Properties of glass ceramics

Glass-ceramics exhibit a number of advantages over glasses and crystalline materials, which instigate a significant growth in their applications. These properties include [15]:

1) Ease of processing.

The presence of the viscous phase (glass) allows easier and faster sintering.

2) High deformation temperature

The glass ceramics possess a higher deformation temperature than the corresponding glasses with the same chemical composition. Accordingly, glass ceramics can retain their mechanical integrity and rigidity to a high temperature, approximately double that of glass.

3) Improved mechanical properties

Mechanical properties of glass-ceramics are usually higher than those of glass. This is thought to be due to the ability of crystals to limit the size of flaws or defects.

4) Adjustable coefficient of thermal expansion

The thermal expansion coefficient can be controlled by adjusting the composition.

2.3.4 Applications of glass ceramics

The unique combination of properties that glass ceramics possess renders these materials suitable for many applications. They have been used successfully in science, technology and medicine. For example, because of their high mechanical strength, good dimensional stability and abrasion resistance, they are broadly used in mechanical, electrical, nuclear and aerospace engineering. In the biomedical field, their use has been encouraged by both their chemical inertness and good mechanical properties [16]. In dentistry, they can be used to fabricate artificial teeth, frit dental materials (dental porcelain) suitable for metal ceramic applications. High-strength cores for all-ceramic restorations can also be developed from dental glass ceramics.

2.4 Dental Ceramics

2.4.1 Definition

Porcelain is defined as a white, translucent ceramic, which is fabricated by firing at a relatively high temperature to a glazed state [24]. Mclean (1979) defined it as a noncrystalline glass, and often referred to it as a ceramic, because its major constituent is feldspar, which forms a glass matrix to which other ingredients are added, making it distinct from the material in ceramic pottery [25]. A more acceptable terminology for dental porcelain is dental ceramics, however, some references use both terms interchangeably.

2.4.2 Composition

Dental porcelain is a vitreous ceramic based on silica (SiO_2) and potash feldspar ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) or soda feldspar ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) or both [26]. Glasses, opacifiers and pigments are appended to control fusion, sintering temperatures,

coefficient of thermal expansion and solubility [26]. The exact proportion varies with the particular type of porcelain (high-fusing 1,288°C to 1,371°C, medium-fusing 1,093°C to 1,260°C and low-fusing 660°C to 1066°C) [24]. Dental porcelains are different not only in their chemical composition but also in their use. The medium- and high-fusing are utilised to make denture teeth, and the low-fusing is used to fuse on metallic alloys for the metal ceramic restorations.

2.4.3 Classification

Dental ceramics can be classified according to type, use and method of fabrication. By type they can be divided into the following groups: 1) feldspathic porcelain, 2) leucite-reinforced porcelain, 3) aluminous porcelain, 4) lithium disilicate glass ceramic, 5) high pure alumina, 6) high pure zirconia, 7) glass-infiltrated ceramics (Alumina, Zirconia and Magnesia). They can be used as denture teeth, metal-ceramic restoration, veneers, crowns, anterior and posterior bridges [26]. Fabrication methods involve condensation and sintering, casting and ceramming, hot pressing, slip-casting, computer-aided or copy-aided milling followed by glass infiltration, and sintering [24, 27].

2.4.4 Properties

Dental ceramics exhibit many desirable properties. These properties include: 1) biocompatibility, 2) the ability to match colour and shading of natural tooth (aesthetics), 3) diminished plaque accumulation, due to their ability to exhibit highly glazed surfaces, 4) low thermal conductivity and 5) abrasion resistance [26].

2.4.5 Shortcomings

Dental ceramics, like all brittle materials, are unable to absorb appreciable amounts of elastic strain energy before fracture. This brittle behaviour and the low tensile strength of these materials compared to most metals can be understood by considering the stress concentration surrounding flaws or defects. While ductile materials, such as metals, can withstand high stress by plastic deformation (ductility), ceramics have very low plastic deformation capability before fracture. The tensile stresses surrounding a crack tip can not be minimised in a brittle material (Fig. 2.3). Therefore, cracks may propagate causing ultimate fracture at low-average tensile stresses.

Brittle materials fail to exhibit the strength predicted from the intrinsic bonding between atoms, and hence may fail at stresses far below their theoretical strength. This can be explained on the basis that most ceramics contain at least two populations of flaws: fabrication defects or scratches and surface cracks [19]. The tip of a defect may be similar in size to the space between atoms in a material. In fact, the stress concentration at the tip of these flaws causes the stress localisation to rise to the hypothetical strength of a material at a relatively low stress level. Therefore, the crack forms when the hypothetical strength is exceeded at the tip of the flaw and the bond breaks, which results in crack propagation through the material, unless the crack is arrested or deflected by a hindrance, which normally dissipates some energy.

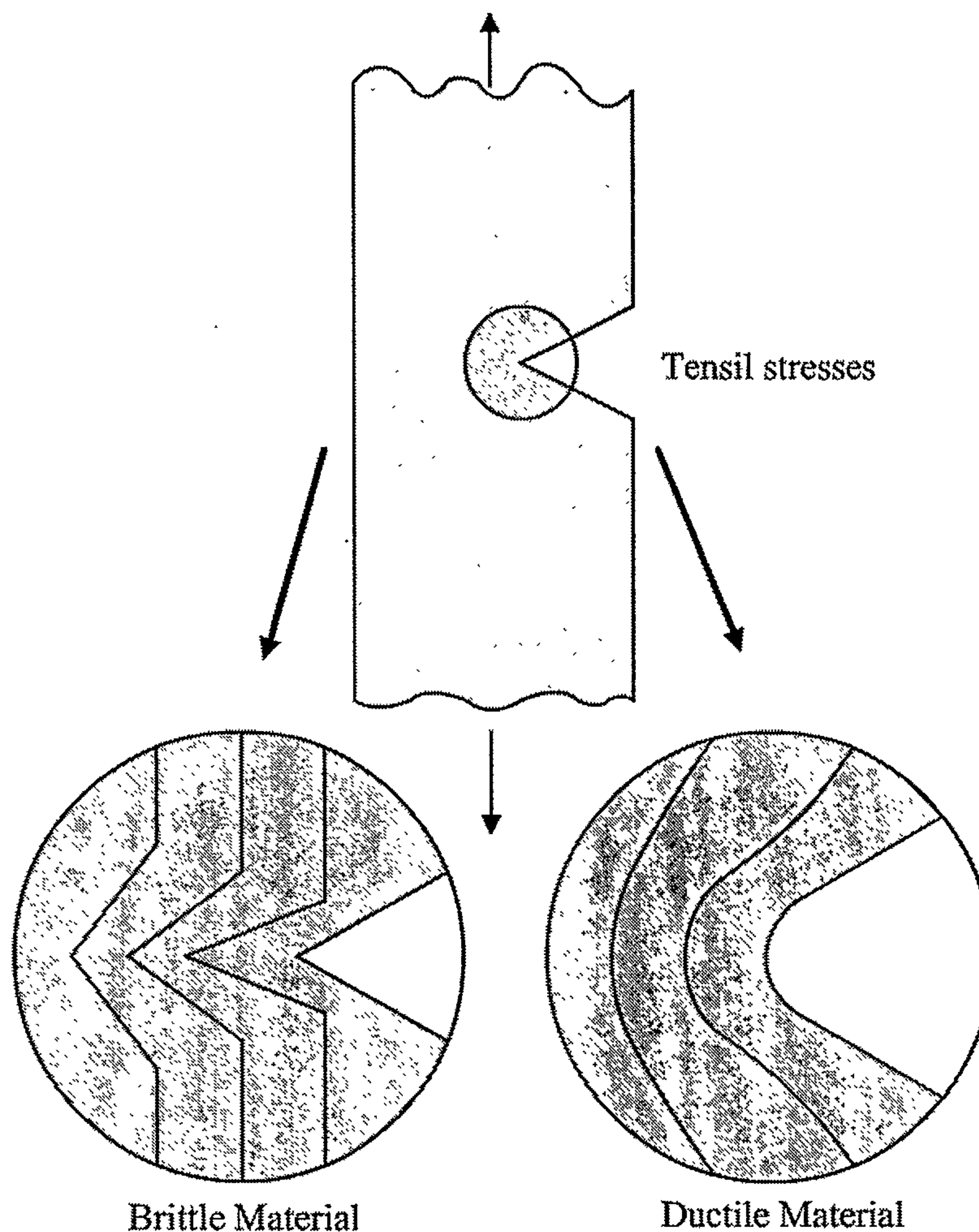


Figure 2.3 Illustration for the effect of tensile stresses on crack propagation in a ceramic material (brittle) and a metallic material (ductile) [24].

2.4.6 Methods of strengthening

Dental ceramics possess many desirable properties that make efforts to overcome their major shortcomings, such as brittleness and low fracture toughness, worthwhile. Methods used to overcome these disadvantages are divided into two groups: 1) methods that strengthen brittle materials and 2) methods that design components of the restoration to reduce the stress concentration and the effect of tensile stresses. The approaches that normally utilised to strengthen brittle ceramic are as follows [26]:

2.4.6.1 Residual compressive stresses

In the oral cavity, complex forces are generated during mastication. This involves bending forces, which are responsible for creation of the maximum tensile stresses. The tensile stresses are normally developed in the outer surface of a restoration where many potentially harmful surface defects or flaws may present. Because of these tensile stresses, surface defects can grow, causing catastrophic failure. Interior defects or bulk flaws can also cause the fracture initiation in some circumstances. In fact, strengthening glasses and ceramics, via the introduction of residual compressive stresses, which were found to occur on a wide range of ceramic materials following different treatment processes, is a widely used method. The strengthening takes place because the compressive stresses have to be negated before tensile stresses can develop. Several techniques can be used to introduce compressive stresses; some of these are briefly explained below.

2.4.6.1.1 Ion Exchange

This method, occasionally called chemical tempering, involves the swap of potassium ions with sodium ions. The potassium ion is larger than the sodium ion by approximately 35%. Compressing the potassium ion into a place occupied by the sodium ion creates a large amount of residual compressive stresses (700 MPa approximately) in the surface of a ceramic submitted to such treatment. This process is recommended for the internal surface of a restoration, as this surface can be protected from acids and grinding which may eliminate the effect of such an exercise. In fact, many researchers adopted this method to improve the reliability of dental ceramics [28-30].

2.4.6.1.2 Thermal Tempering

This method creates residual compressive stresses by rapidly cooling the surface of a ceramic material while glass is in the softening state. This rapid cooling creates a solid glass skin in the outer surface of the glass surrounding the molten core. When the molten core starts to solidify it shrinks, while the outer surface (solid skin) remains solid. Hence, the force developed by the outer solid surface, which resists contraction, causes the generation of tensile stresses in the core and compensating compressive stresses in the solid's outer surface [31, 32].

2.4.6.1.3 Glazing

This is virtually similar to the mechanism that enhances the surface compressive stresses during thermal tempering. It is achieved by applying a low-fusing glass material (glazing layer) that possesses lower thermal expansion than the adjacent ceramic (the core material). Upon cooling, the core material tends to shrink more than the glazing layer, which places this surface into a compressive state [32]. It may also reduce the depth and width of surface flaws, which can strengthen the ceramic material significantly [19]. Auto-glazing, which is based on firing for a certain time held at the maximum temperature, can also be used for strengthening. However, some studies showed that auto-glazing did not significantly increase the strength of feldspathic dental porcelain [32-34].

2.4.6.1.4 Crystalline reinforcement

This is known as dispersion strengthening, which involves the introduction of a high proportion of crystalline components. It is a fundamental method for improving strength and fracture resistance. The microstructure of many glass-ceramic materials

consists of a glass matrix surrounding a second phase of certain crystals. In a true glass ceramic, the material is initially an homogenous glass. Subsequent heat treatments nucleate and grow crystals. The interaction of the crystals and glass matrix, as well as the size and amount of crystals significantly determine the mechanical properties. The strengthening effect of crystals is thought to be due to the disruption of crack propagation. In addition to the dissipation of a crack's energy, crystals act as a roadblock to crack propagation and may stop it entirely. Common reinforcing crystalline phases are: 1) leucite, 2) lithium disilicate, 3) aluminum oxide, 4) zirconium oxide. Some dental materials may contain more than one crystalline phase. Important characteristics of crystalline phases include the coefficient of thermal expansion, toughness and elastic modulus, which significantly dictate the mechanical and optical properties of dental materials.

2.4.7 Design

Dental restorations made from ceramics should be designed to overcome their drawbacks. The design should allow a minimal amount of tensile stresses to develop upon exposure to occlusal forces. Stress concentration caused by a restoration's sharp angles or due to significant thickness variations are crucial aspects that should be considered during designing. Occlusion should also be adjusted properly to enhance surface contact and avoid contact points. Contact points can greatly increase the localised stresses in a ceramic surface as well as within the internal surface of a restoration.

2.4.8 Toughening mechanisms

Various toughening mechanisms within the microstructure of ceramic materials have been explained by several investigators [35-37], which significantly contribute to the toughening and strengthening of dental ceramics. These mechanisms include: 1) crack-tip interaction, 2) crack-tip shielding, and 3) crack bridging (Fig. 2.4). All these mechanisms aim at different approaches to increase the energy required for crack propagation. The crack-tip interaction mechanism takes place when a hindrance within a microstructure obstructs crack propagation, which leads to the reorientation of the crack motion and consequently requires more energy for the crack extension. The crack-tip shielding mechanism is involved when the stresses at the crack tip region are minimised by either a) microcrack toughening or by b) transformation toughening. Microcrack toughening occurs in multiphase materials and particularly when microstructure is associated with residual stresses. These residual stresses can occur in a region with thermal expansion anisotropy in polycrystalline materials with elongated grains and/or thermal expansion or elastic mismatch in polyphase materials and/or in transforming materials. The localised created compressive forces about the crack tip are responsible for counteracting the tensile forces, which drive the cracks forward. Transformation toughening, which occurs in tetragonal zirconia-based materials, is inherent with 4% volume expansion and consequently compressive stresses surrounding the crack tip. Crack bridging mechanisms occur when a second phase acts like a ligament to prevent the crack faces opening. This mechanism appears in fibre-reinforced or rod-like crystals containing materials.

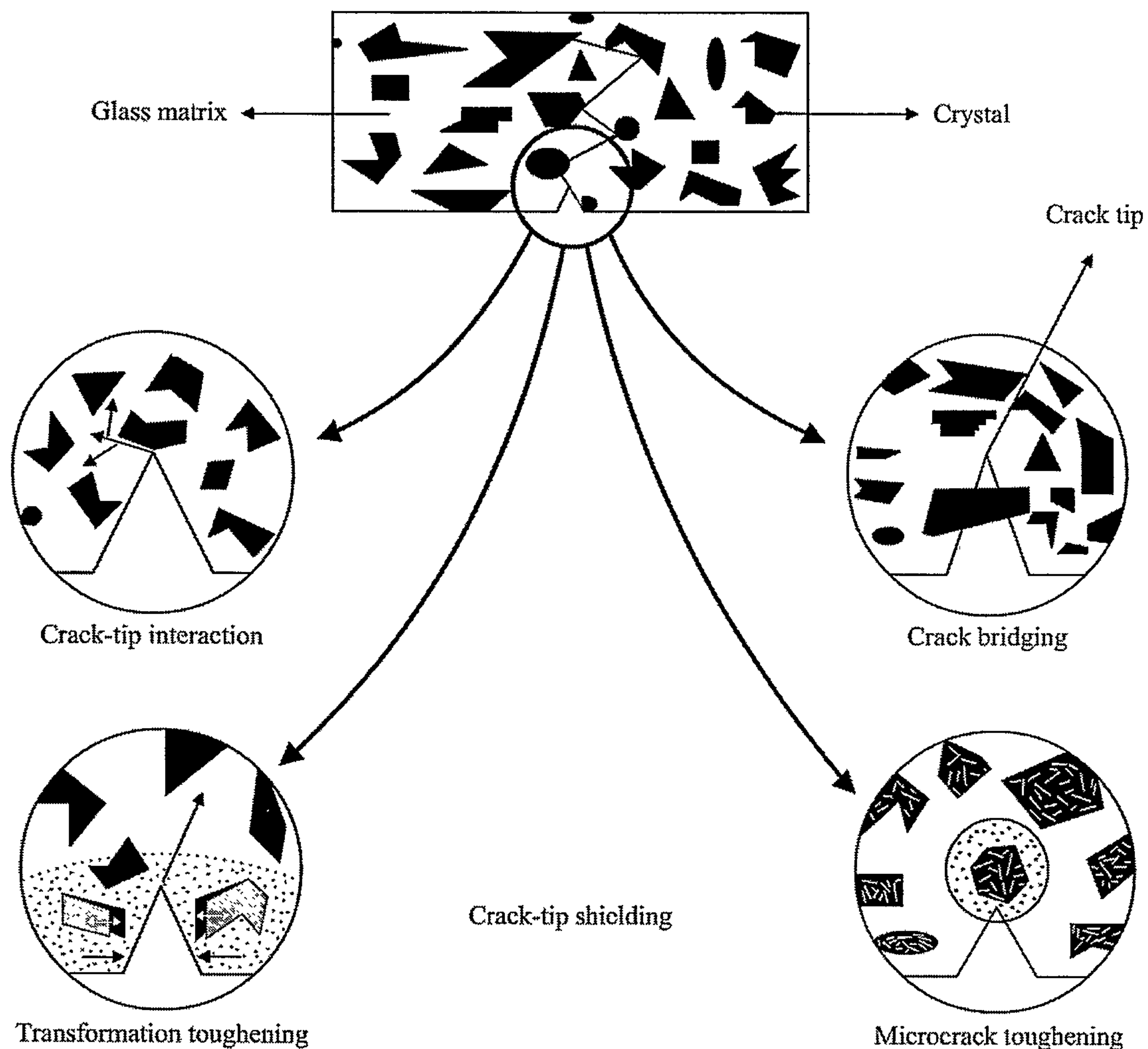


Figure 2.4 Schematic illustration of the possible strengthening and toughening mechanisms involved in the macrostructure of some dental ceramic materials [37].

2.5 All-Ceramic Restorations

For decades, the combination of metal substructure and ceramic veneering materials has been very successful in restorative dentistry. There have also been many attempts to develop ceramic systems that enable the fabrication of crown and fixed partial dentures without ancillary metal reinforcement. However, all-ceramic restorations have had limited life expectancy compared to metal ceramic restorations. This was thought to be a result of low strength and fracture resistance of these restorations. In the last 10 years, advances in dental materials fabrication and processing have

succeeded in developing a wide range of all-ceramic materials, which offer the potential for much broader use of more reliable all-ceramic restorations in both anterior and posterior segments. Some of the all-ceramic dental systems are briefly reviewed below.

2.5.1 Castable glass ceramic

2.5.1.1 Dicor castable glass ceramic

Dicor ceramic material (Dentsply Inc., York, PA) was the first commercially available castable ceramic for inlays, veneers and crowns. It was introduced in the 1980s as a micaceous glass ceramic processed by a combination of the traditional lost wax technique and glass casting [19, 38]. After casting, the Dicor glass is converted into glass ceramic by means of a single-step heat treatment, at 1070°C. The crystallisation procedure takes several hours and the heat treatment is called “ceramming” [24]. This treatment assists controlled nucleation and growth of tetrasilicic fluormica crystals as the major crystalline phase [19]. Mica crystals are classified as layer-type silicates that readily cleave along the planar layers of the structure [19]. Cleavage planes that develop along these crystals are considered beneficial for mechanical properties of this material. Crack extension is hindered by the mica crystals and may be reoriented along the cleavage planes of these layered silicates [39]. Mica crystals are elongated in shape and exhibit an interlocking pattern within the glass matrix [40]. This interlocking pattern makes crack propagation difficult in many directions and hence improves the fracture resistance of this material. This material demonstrates flexural strength and fracture toughness of 120 MPa and $1.4 \text{ MPa} \cdot \text{m}^{1/2}$ respectively [41] [27]. A new type of mica glass ceramic has been prepared by heat-pressing in an attempt to produce oriented mica crystals [42]. The resultant mica glass ceramic demonstrated

significantly higher flexural strength and fracture toughness, 380 MPa and 2.8 MPa·m^{1/2}. The improvement in the mechanical properties of this material after heat-pressing is due to the alignment of mica crystals normal to the pressing direction. The viscous flow of the residual glass phase and the rotation of mica crystals are considered the main reasons for the crystal alignment [42]. Another investigation assessed the effect of alumina and zirconia on the mechanical properties of the Dicor glass ceramic. It was reported that the addition of alumina successfully increased the bending strength, whereas zirconia had no effect [43].

Clinical studies showed a higher failure rate of Dicor crowns in the posterior regions, 35% and 64%, as a consequence of excessive microcracking damage [41, 44, 45]. Dicor restorations are very translucent and hence can be used in the anterior segment [41]. However, if they are used for posterior teeth, resin cement has been suggested to improve their fracture resistance [27].

2.5.2 Leucite-reinforced systems

2.5.2.1 Leucite

Leucite (4SiO₂-Al₂O₃-K₂O) is a rock-forming mineral of the feldspathoid group and is well known as one of the typical examples of pseudomorph [46]. It is formed by the melting of feldspar (6SiO₂-Al₂O₃-K₂O) [47], and often found as “porphyroblasts with euhaedral, pseudo-cubic symmetry” [48]. It has a high coefficient of thermal expansion and a polymorphic transformation accompanied by a large volume change [47].

2.5.2.1.1 Twinning of leucite crystals

X-ray diffraction studies by Wayert (1940) showed that leucite exhibits a tetragonal structure at room temperature [48]. At high temperatures, leucite becomes cubic. Leucite crystals are occasionally seen to consist of repeated lamellar twins [48]. Because of twinning, which develops always in tetragonal leucite during the transformation from the high temperature cubic phase, it was difficult to obtain a suitable single crystal of the tetragonal phase [49]. Twinning is a mechanism whereby plastic deformation occurs in crystals “when one part of a crystal reorients itself so that it becomes, crystallographically, the mirror image of the remainder of the crystal” [50].

The majority of frit dental materials (porcelain) used for metal ceramic restorations are composed of leucite crystals embedded in a brittle glassy matrix [51]. Originally, leucite was used to raise the inherently low thermal expansion of feldspathic porcelain to a level where it is compatible with the alloy for metal ceramic restorations [52]. Recently, it has been used as a reinforcing material for all-ceramic restorations [47].

2.5.2.2 Optec HSP (leucite-reinforced porcelain)

Optec HSP material (Jeneric/Pentron, Inc) is a leucite-reinforced feldspathic porcelain recommended for the construction of single units such as inlays, onlays and crowns [27]. As with the conventional feldspathic porcelain, it is processed in the dental laboratory by condensation and sintering [27, 38]. It contains more than 45% tetragonal leucite crystal, which is appreciably greater than many other leucite-reinforced systems or frit dental porcelains for metal ceramic restorations [19, 27, 38].

For this reason, this material possesses a higher modulus of rupture and compressive strength compared to the conventional feldspathic porcelain. Upon cooling, tangential compressive stresses developed surrounding the leucite crystal as a result of the significant difference in the coefficient of the thermal expansion between the leucite crystals and the glassy matrix [19]. These stresses can act as crack deflectors and hence improve the fracture resistance. Another crystalline phase that has been reported to develop in this system after heat treatment is sanidine (KAlSi_3O_8) [19]. The crystallisation of sanidine occurred at a temperature of 705 to 980°C [53]. This crystallisation is associated with alteration of optical properties, whereby the material may become more opaque [19]. The fracture toughness value of this system is very comparable to many other glass ceramics such as Empress 1 and Dicor castable ceramic, $1.3 \text{ MPa} \cdot \text{m}^{1/2}$. For an average period of 8 months a clinical performance study of 205 Optec inlays showed no failure, but slightly rough surfaces of the inlays have been reported [38]. It has been suggested that the use of this material should be limited to areas of low stress or resin cement should be used to improve the fracture resistance [27].

2.5.2.3 Other leucite-based systems

A wide range of leucite reinforced all-ceramic systems are currently used in daily dental restorative treatments. These include optimal and OPC pressable ceramics (Jeneric/Pentron, Wallingford), Cerpress (Dillon Co., Cranston), Finess (Dentsply Ceramco, Midford), Vitapress Omega 900 (Vident, Brea, CA), Empress 1 (Ivoclar, Schaan, Liechtenstein). The compositions of these materials are very similar, and hence the mechanical properties of these systems are very comparable. Their flexural

strength and fracture toughness respectively ranged from 110-150 MPa, and 1.1 to 1.4 MPa·m^{1/2} [21, 27, 54-57].

2.5.3 Magnesia-based Ceramic

In 1985 a Magnesia core ceramic was developed as an experimental glass ceramic [58]. This ceramic material is formed by reacting magnesia with silica glass at a relatively high temperature (1150°C), which results in forsterite crystals (Mg₂SiO₄) as a major reinforcing component. An advantage of such a ceramic was its coefficient of thermal expansion (14.5 x 10⁻⁶ °C). This value matches the coefficient of thermal expansion of the dental porcelain (14.5 x 10⁻⁶ °C) used for metal ceramic restoration [19]. However, the flexural strength of this system (130 MPa) didn't surpass the strength of most other leucite-reinforced systems [59].

2.5.4 Aluminous core ceramic

2.5.4.1 Hi Ceram

This all-ceramic material is one of the earliest alumina-reinforced glass-ceramic developed by Vita (Vita Zahnfabrik, Bad Säckingen, Germany). Alumina particles dispersed in a glass matrix represent the main crystalline-reinforcing phase. The core portion is directly fired on a designed refractory die at a high temperature. The resultant opaque ceramic substructure is then veneered with a thermally compatible leucite-free ceramic, Vitadur[®] N or Vitadur[®] Alpha (Vita Zahnfabrik, Bad Säckingen, Germany) [60]. During heat treatment or long firing cycles, the core was found to fuse on the refractory, which indicates that excessive flow has taken place leading to very close adaptation to the refractory die. This material demonstrates a mean

flexural strength of 140 MPa, which is very comparable to many leucite-reinforced systems [61].

2.5.5 Glass-infiltrated systems

2.5.5.1 In-Ceram Alumina

McLean and Hughes introduced the first alumina-reinforced dental porcelain in 1965 which contained 40 to 50% of alumina particles [62-64]. Because strength was found to improve by increasing the alumina weight, there has since been interest in dental ceramics that have a high alumina content [64]. In France (1988), Sadoun [65, 66] introduced In-Ceram Alumina (Vita Zahnfabrik, Bad Säckingen, Germany) with a glass-infiltrated core containing 70% of alumina particles. It is a well-known all-ceramic dental material and has been used for crowns and anterior three-unit fixed partial dentures [67]. This system is processed by partial sintering of a porous alumina structure at a high temperature (1100°C), and infiltrated with a molten borosilicate lanthanum glass at the same temperature [68]. The porous alumina structure is prepared by an alumina powder dispersed in water, which is painted onto a special plaster die to form the framework (slip casting technique), or by milling a partially sintered porous alumina block into the shape of the core with a computer-aided machining system (CAD/CAM), or by the copy milling technique [69-71].

In-Ceram Alumina obtains its strength by means of very dense stacked alumina particles, which leads to the dispersion strengthening of the material. The difference in the coefficient of thermal expansion between the glass and alumina particles further improves strength and fracture toughness because of compressive stresses, developed upon cooling, that limit the crack propagation effect. A range of

strength results are available in the literature for In-Ceram Alumina, which may vary according to testing methodology or polishing techniques. Values from 400 to 600 MPa have been reported [37, 64, 72-76], which are three to four times greater than strength values of many other glass ceramics. The fracture toughness of In-Ceram Alumina is also greater than the traditional feldspathic and glass ceramics, ranging from 2.7 to 4.49 MPa·m^{1/2} [72, 73, 77, 78]. An attempt to further improve the mechanical properties of In-Ceram Alumina by the addition of silicon carbide whiskers was conducted by Tan et al., (2001) [79]. Results showed no significant improvement in the mechanical properties. It was speculated that CO gas was formed during the oxidation of SiC, became entrapped in the glass matrix and hindered the total densification of the alumina particles by glass infiltration [79].

Clinical studies showed that the longevity and fracture resistance of In-Ceram Alumina crowns are similar to metal-porcelain crowns [67, 80-86]. Another clinical performance report indicates that this material can be reliably utilised for short-span anterior fixed partial dentures, provided a suitable design of the connectors can be applied [87, 88].

2.5.5.2 In-Ceram Zirconia

Because In-Ceram Alumina is indicated mainly for restoring crowns and interior fixed partial dentures, an attempt was made to improve its mechanical properties by adding zirconium oxide [76, 89]. This was done to enable the fabrication of 3-unit posterior fixed partial dentures. The same manufacturer, Vita (Vita Zahnfabrik, Bad Säckingen, Germany) developed In-Ceram Zirconia by adding 33% 12 mol-% CeO₂ partially stabilised zirconia to In-Ceram Alumina, in an attempt to combine the

toughening mechanism due to the phase transformation of zirconia to the versatility and ease of use of the partially sintered glass-infiltrated alumina. Like In-Ceram Alumina, In-Ceram Zirconia is available as either slip or dry-pressed materials.

The few mechanical studies suggested that this modification doubled the original fracture toughness and increased the flexural strength up to a value of 750 MPa [57]. Apholt et al. (2000) compared the three-point bending flexural strength of In-Ceram Alumina to In-Ceram Zirconia. The authors reported strength values of 530 MPa for In-Ceram Alumina (slip-casting technique), 511 MPa for In-Ceram Alumina (machined from blocks), 630 MPa for In-Ceram Alumina (wire-cut from blocks) and 624 MPa for In-Ceram Zirconia (machined from blocks). Recently, Chong et al. (2002) adopted a three-point bending technique to compare the flexural strength of In-Ceram Zirconia and In-Ceram Alumina with and without porcelain lamination. In-Ceram Zirconia was stronger than In-Ceram Alumina in both cases. The mean flexural strength of the cores of the two materials were 513 and 362 MPa respectively [76].

No clinical trials or performance of In-Ceram Zirconia are available in the literature. However, Giordano (2000) mentioned in a review of a selection of all-ceramic dental materials that this material has been clinically investigated by the manufacturer over seven years and recorded a high success rate, 98% [57].

2.5.5.3 In-Ceram Spinell

As a result of the opacity imparted by the alumina and zirconia particles in a glass matrix, which arises because of the refractive index difference between the glass and

alumina or zirconia, the optical qualities offered by In-Ceram Alumina and In-Ceram Zirconia may not be as pleasing in some treatment cases, where translucency is required. In-Ceram Spinell (MgAl_2O_4) is another glass-infiltrated material developed by the same manufacturer, Vita (Zahnfabrik, Bad Säckingen, Germany). A mixture of magnesia and alumina particles upon reaction resulted in a fairly translucent core material [66, 74]. In-Ceram Spinell enhanced the aesthetic features more than In-Ceram Alumina and In-Ceram Zirconia because of the lower mismatch index of refraction of the magnesium aluminate particles and the glass matrix. Nevertheless, this resulted in a decreased fracture resistance. Its flexural strength was shown to range from 280 to 380 MPa [37, 38, 57, 74]. Because of its relatively low strength, compared to other infiltrated systems, and high translucency, it has been recommended for anterior segments and in cases of very translucent teeth.

2.5.6 High-purity alumina

2.5.6.1 Procera

Procera (Procera AllCeram, Procera Sandvik AB, Stockholm, Sweden) is an all-ceramic dental material composed of densely sintered high-purity aluminum oxide particles, 99.9%, [90] and was first described in 1993 [91]. This system uses a scanner to digitise a traditional die at a dental laboratory. The image is sent to a computer-controlled milling machine (CAD-CAM) to fabricate a refractory die [92]. High-purity alumina is dry-pressed against the refractory die and fully sintered. This high alumina content imparts greater flexural strength and fracture toughness than most other all-ceramic materials. However, these condensed alumina particles may render the core material more opaque. The flexural strength of Procera ranges from 600 to 700 MPa, depending on the testing methodology adopted [64, 92, 93].

Previous reports found in the literature showed that the fracture toughness of Procera ($4.5 \text{ MPa} \cdot \text{m}^{1/2}$) was very similar to that of In-Ceram Alumina. However, the flexural strength of Procera was found in most cases to be higher than that of In-Ceram Alumina [73, 93, 94]. Five-year clinical trial of 97 crowns of Procera showed a 3% failure rate [95]. One drawback of the Procera system is the inability of the laboratory-scanning device to precisely identify internal line angles, curvature or depression in the die, which may result in poor fitting of the restoration [96].

2.5.7 High purity zirconia materials

2.5.7.1 DC-Zircon

DC-Zirkon (DCS Dental AG, Allschwil, Switzerland) is a new generation of the advanced all-ceramic dental materials that contain a high purity of zirconia particles. This material is developed by isostatical hot-pressing, and full sintering of 5 wt-% Y_2O_3 TZP at a relatively high temperature, which results in a density of many micron-like zirconia particles [97]. A specially designed milling CAD/CAM system, DCS Precident milling system (DCS Dental AG, Allschwil, Switzerland) is used to mill a substructure (core) of a dental restoration from a dry-pressed block of this material. The resultant core is subsequently layered with a thermally compatible feldspathic porcelain in order to achieve the final shape and the required translucency.

No mechanical studies or clinical performance investigations have been found in the literature for this material. The present study will assess both fracture toughness and flexural strength of this material and compare them to other all-ceramic dental materials. Microstructural features and crystalline phases will also be investigated (Chapter 8).

2.5.7.2 Experimental partially stabilised zirconia material

Another new all-ceramic dental material that is based on high percentage of zirconia particles, 3 mol-% Y_2O_3 TZP (corresponding to 6 wt-% Y_2O_3 TZP), and is referred to as an experimental zirconia material in this study. This system has been recently developed in-house from commercially available powders. A restoration is made from this material by milling a block of partially sintered ceramic, which is then sintered to full density at approximately 1400° C. The framework so obtained is then veneered with a conventional porcelain. Owing to the advantages brought about by the well-known transformation toughening mechanism of zirconia, DC-Zirkon and the experimental zirconia material, are expected to possess greater strength and fracture toughness than most of the other all-ceramic dental materials.

2.5.8 Pressable materials

Heat-pressing, also called high-temperature injection molding, is carried out by applying external pressure at high temperatures using a special porcelain furnace, with a pneumatic ram, to sinter and shape a dental restoration under vacuum (Fig. 2.5) [20, 21]. The first patented heat-pressing technique was described in 1936 by Seefeldter for the fabrication of complete dentures [98]. In 1969, Dröge described a two-part flasks heat-pressing technique, which was at a later stage modified by McPhee to produce full metal-ceramic coverage [99]. During the last ten years, heat-pressing has become a prevalent technique in dentistry for the fabrication of all-ceramic prostheses [100]. Compared to some other techniques such as sintering, heat-pressing is a simple technique and also provides several advantages, summarised below.

2.5.8.1 Advantages

1) Less shrinkage during dental laboratory procedure

Major ceramic shrinkage occurs during sintering or the ceramming procedure (controlled crystallisation) that is used during processing of some dental restorative systems, such as Dicor castable glass ceramic. Heat-pressing minimises such effects, due to the considerable shrinkage that occurs during the fabrication of the material at the factory [101] [102].

2) Better crystal distribution within a glass matrix

Heat-pressing also promotes better crystal distribution within a glass matrix. This is explained on the basis that the agglomerated crystals within the glass matrix before pressing are separated during the forcing of the softened material (ingot) through a small-diameter sprue [99, 103]. Dong et al. (1992) and Oh et al. (2000) reported that the better distribution of the crystals in the glass matrix of Empress 1 and Empress 2 materials respectively has a positive influence on their flexural strength [99, 103]. This is because better crystal dispersion within the glass matrix minimises the susceptibility of the brittle glass matrix phase to fracture, and enhances a degree of residual stress isotropy within the microstructure, to which this increment in strength and Weibull modulus might be related [21].

3) Net-shape forming, and resultant decreased porosity

Although this advantage was frequently mentioned in the literature [21, 56], no experiments were conducted to clarify how such an effect is produced.

4) Occlusal accuracy and better marginal integrity

Pressable restorations benefit from the occlusal accuracy and more precise marginal adaptation is associated with the wax pattern technique [56].

5) Furnace with different uses

Another advantage of the pressing technique is that the pressing furnace can be used as a conventional porcelain furnace [21].

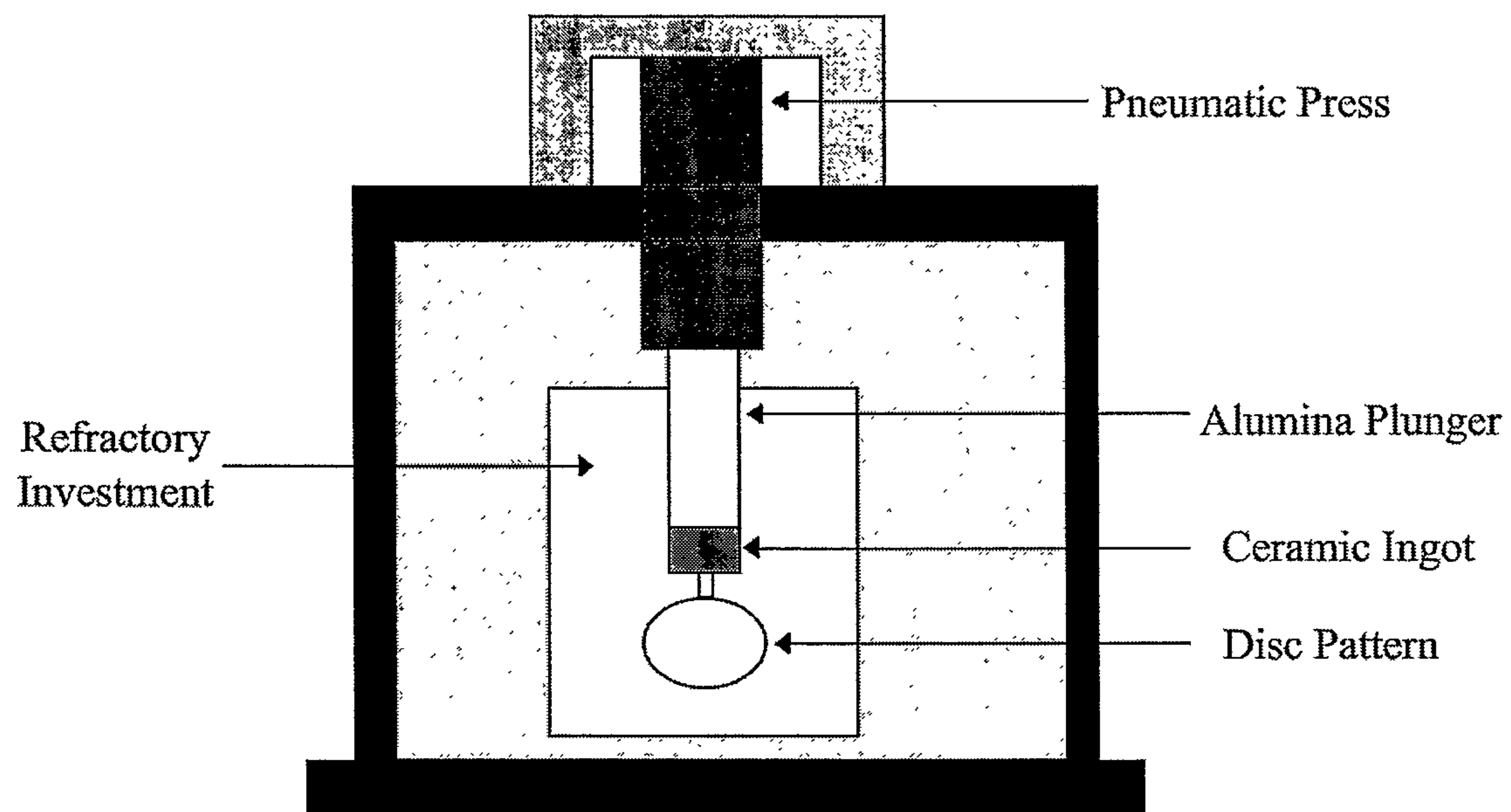


Figure 2.5 Schematic illustration for the pressing system.

2.5.8.2 Empress 1

Empress 1 (Ivoclar-Vivadent, Schaan, Liechtenstein) is a leucite-reinforced feldspathic glass ceramic released into the market in the early 1990s [41]. It was designed for the fabrication of single dental restorations such as inlays, onlays, veneers and crowns. This system is developed by the controlled surface crystallisation method, which results in small, fine leucite crystals ($4\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$) distributed in a glass matrix,

measuring approximately from 1 to 5 μm [22]. The chemical composition given in wt.% is presented in table 2.1.

2.5.8.2.1 Fabrication methods and techniques

To produce a restoration of Empress 1 in a dental laboratory, an accurate wax pattern of a specific object (inlay, onlay or crown) is sprued and invested in a refractory mould, which is burnt out (conventional lost wax technique) to allow a preheated ingot to be pressed into it by an alumina plunger under pressure from a pneumatic press furnace (Fig. 2.5). After cooling, the investment is removed from the pressed object by sandblasting using glass beads. Empress 1 ingots are pressed at 1175 °C under a pressure of 0.3 to 0.4 MPa. Two different techniques are used to fabricate Empress 1, a staining technique and a layering technique, using two different materials [47, 104]. For the staining technique, a wax pattern of full-contour core is prepared and pressed from a colourless ceramic ingot. A pigment surface colour is applied until the desired shade is obtained. This surface is also covered with a glaze material and fired; the staining and glazing procedures are outlined in table 2.2. For the layering technique, a wax pattern of a coping is prepared and pressed. Onto this coping, porcelain is added to achieve the definitive shape, and fired.

SiO₂	59 – 63
Al₂O₃	16 – 23
K₂O	10 – 14
Na₂O	3.5 - 6.5
B₂O₃	0 – 1
CeO₂	0 – 1
CaO	0.5 – 3
BaO	0 - 1.5
TiO₂	0 - 0.5

Table 2.1 The chemical composition of Empress 1.

Temperature	Stain firing	Glaze firing
Standby temperature (°C)	400	400
Drying time (°C)	2	2
Preheat treatment (min)	2	2
Temperature rise (°C/min)	60	60
Firing temperature (°C)	850	870
Vacuum release (°C)	849	865
Holding time (min)	2	2

Table 2.2 Firing temperature for staining and glazing of Empress 1.

2.5.8.2.2 Mechanical properties

Empress 1 obtains its strength by means of finely dispersed leucite crystals in a glass matrix. In fact, many previous studies [21, 37, 54-56, 64, 99, 105-109] reported the flexural strength of Empress 1, which ranged from 97 to 182 MPa. Dong et al. (1992) [99] reported that the flexural strength of this system was improved not only by the heat pressing but also by the subsequent heat treatments that are encountered during

laboratory fabrication processing, such as veneer firing. The improvement in the strength after additional heat treatments was due to further development of residual stresses within the glass matrix produced by different thermal expansion of leucite crystals and the glass matrix. This improvement in strength is interesting from a materials science point of view. Mackert et al. (1996) [47] subsequently studied different processing procedures of this material that can increase its leucite content. They found that first and second colorant firing caused a definitive increase in the definitive leucite content. X-ray diffraction was utilised by Gorman et al. (2000) [21] to identify the crystalline phases present and to evaluate the effect of heat pressing on the crystalline phases. Leucite was the main crystalline phase, which showed no volume fraction change after heat pressing.

While some previous mechanical studies [21, 27, 108, 110] reported similar fracture toughness results for Empress 1, $1.3 \text{ MPa} \cdot \text{m}^{1/2}$, some reports [73, 106, 111, 112] indicated higher values: 1.4, 1.42, 1.49, 1.58, $1.74 \text{ MPa} \cdot \text{m}^{1/2}$. Such differences might be attributed to: 1) shortcomings associated to techniques used to measure fracture toughness such as the inaccurate crack length measurement occurred using the indentation fracture technique, 2) the surface condition of samples used to measure fracture toughness, for example, annealed or unannealed surface [11]. The hardness and elastic modulus of Empress 1 are also documented in the literature, 6.6 GPa [27, 110] and 65 GPa [107] respectively.

2.5.8.2.3 Clinical performance

There is scarce knowledge of a valid link between the mechanical properties studies and clinical performance results of all-ceramic dental materials. Even so, the

reliability of Empress 1 as an all-ceramic material suitable for the fabrication of single units, such as inlays, onlays and crowns, has been recommended by many clinical investigations [102, 113-124].

2.5.8.3 Empress 2

The first lithium disilicate glass-ceramic was developed in 1950. However, the main disadvantage was its poor chemical resistance [125]. In 1975 Borom and Turkalo [17] investigated the strength and microstructure of a lithium disilicate glass-ceramics. Results showed that the parent glass (as cast) is an amorphous single-phase glass. However, crystallisation occurred after heat treatment and reached approximately 50%. The crystalline phases detected were lithium disilicate and/or lithium metasilicate, which varied according to the heat treatment adopted. Lithium orthophosphate (Li_3PO_4) was also found when phosphates were added as a fluxing aid, but only as a minor portion. The rod-like lithium disilicate crystals were found to significantly increase the strength of the material. Lithium metasilicate showed less coherence with the parent glass and consequently had less stress to fracture than the lithium disilicate crystals.

The lithia-based ceramic materials are developed by controlled volume crystallisation [126]. P_2O_5 is a very effective nucleating agent for many silica-based (SiO_2) glass ceramic [127]. It is added to the glass mixture in order to promote heterogeneous nucleation and produce a fine-grained interlocking morphology after heat treatment [127]. However, other nucleating agents may be added that can affect the size or volume fraction of the resultant crystalline phases of a glass ceramic, and consequently influence the mechanical properties [126]. Anusavice et al. (1994)

investigated the effect of colorants such as AgNO_3 and FeCl_3 as co-nucleating agents with P_2O_5 for a Lithia-based glass ceramic. AgNO_3 was very effective as a nucleating agent for the lithia-based glass-ceramic [126].

Empress 1 has been a successful restorative material for single units, but it can't be used to fabricate three-unit fixed partial dentures. Consequently, there has been an ongoing search for a dental restorative material that would be ideal for short-span fixed partial dentures. In 1999 Ivoclar released Empress 2 as a new all-ceramic dental material suitable for restoring three-unit fixed partial dentures up to the second premolar [125, 128]. Although this new system shares the same trade name and uses the same hot-press technique of Empress 1, it doesn't bear any resemblance to its chemical composition. It is a lithium disilicate glass ceramic, and the chemical basis of this system is $\text{SiO}_2 - \text{LiO}_2$.

Lithium disilicate crystals distributed in a glass matrix represent the main crystalline phase $\text{Li}_2\text{Si}_2\text{O}_5$, and lithium orthophosphate Li_3PO_4 occurs as the secondary phase. The chemical composition given in wt.%, and laboratory firing procedures of Empress 2 are given in Tables 2.3 and 2.4 [125, 129].

2.5.8.3.1 Fabrication method

Empress 2 is processed in the dental laboratory using the layering technique, in which the resultant core is laminated with a special Empress veneering porcelain (consisting of fluoroapatite crystals). The pressing temperature is 920°C , whereas lower temperatures are used for the veneering layers and glazing (Table 2.4).

SiO₂	57 – 80
Al₂O₃	0 – 5
K₂O	0 - 13
La₂O₃	0.1 – 6
MgO	0 – 5
ZnO	0 – 8
K₂O	0 - 13
Li₂O	11 - 19
P₂O₅	0 - 11

Table 2.3 Chemical composition of Empress 2.

Firing programme	Wash firing	Dentine firing	Glaze firing
Firing temperature (°C)	800	800	770
Temperature rise (°C/min)	60	60	60
Standby temperature (°C)	403	403	403
Entry time (min)	6	6	6
Holding time at high temperature (min)	1	2	2
Vacuum (hPa)	55	55	55
Vacuum on (°C)	420	450	450
Vacuum off (°C)	799	799	769

Table 2.4 Firing temperature schedule of veneering of Empress 2.

2.5.8.3.2 Mechanical properties

The few mechanical property reports [103, 108, 125, 129] on the Empress 2 material indicate that its flexural strength ranges from 300 to 400 MPa, and its fracture toughness from 2.5 to 3.5 MP·m^{1/2}. Like Empress 1, the flexural strength of Empress

2 was found to increase upon heat-pressing, but no further increase was noticed after further heat treatment [103]. The improved mechanical properties of this material, compared to most other pressable ceramics, is attributed to its chemical composition, which is composed of dense multi-elongated lithium disilicate crystals (60 wt.%) within a glass matrix [107]. A recent study even reported a higher crystalline content, reaching 90% [129]. It is well known that a higher crystalline content enhances the mechanical properties of ceramic materials [37]. Fischer et al. (2001) attributed the improved elastic modulus of Empress 2 (96 GPa) to the interlocking structure of the elongated lithium disilicate crystals [107]. The increase of fracture resistance with the crack extension (R-curve behaviour) for several dental all-ceramic materials has been investigated recently by Fischer et al. (2002) [10]. Most materials exhibited R-curve behaviour, however, this was more pronounced in the Empress 2 material [10].

Empress 2 has been designed for three-unit fixed partial dentures up to the second premolar. Manufacturers as well as researchers have critically emphasised the occluso-gingival dimension, which should not be less than 5.0 mm in posterior and 4.0 mm in anterior segments.

Tinschert et al. (2001), in an in vitro study, compared the fracture resistance of three-unit fixed partial dentures made out of lithium disilicate, Alumina and Zirconia-based materials. These researchers reported that the highest failure load was for DC-Zircon (partially stabilised zirconia ceramic) followed by In-Ceram Zirconia and then lithium disilicate, which demonstrated an intermediate value along with In-Ceram Zirconia. They also reported that the veneering material further increases the fracture resistance of these materials [130]. Fischer et al. (2003), in a recent study, reported

the lifetime prediction of all-ceramic fixed partial dentures of some advanced all-ceramic materials using a computational method [131]. Empress 2 was found to be very reliable as a material suitable for three-unit fixed partial dentures.

2.5.8.3.3 Clinical performance

Very few studies evaluated the clinical performance of Empress 2. Sorensen et al. (1999), in an in vivo study, reported that for sixty lithium disilicate fixed partial dentures there was a failure rate of 7% within a period of 6 to 12 months [132]. Giordano also reported in a review study that the success rate for this material ranges from 92 to 99% over a year [57].

2.6 Conclusion

This literature review shows that very few mechanical properties and clinical studies were conducted for Empress 2 and also for other advanced all-ceramics materials such as In-Ceram Zirconia, In-Ceram Alumina (dry-pressed) and DC-Zircon. The present study evaluates the mechanical properties of the pressable materials Empress 1, Empress 2 and an experimental pressable glass ceramic material, and also compares these properties with other peer materials such as In-Ceram Zirconia, In-Ceram Alumina, DC-Zircon and an experimental partially stabilised zirconia material.

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CHAPTER 3

MATERIALS AND METHODS

The materials and methods chapter comprises six parts. The first part introduces the dental materials that were prepared for the current investigations. The second part is a description of the procedures (specimen preparation) that were utilised to prepare samples for the following mechanical properties:

1. Biaxial flexural strength
2. Uniaxial flexural strength (3-point bending flexural strength)
3. Fracture toughness (indentation fracture and indentation strength techniques)
4. Hardness (indentation fracture technique)
5. Elastic modulus and Poisson's ratio.

The third part provides an outline of the use of prepared specimens. The fourth part presents a description of the processes that were used to study the microstructural features. The fifth part provides a description of how X-ray diffraction experiments were carried out. Finally, the statistical method adopted is outlined throughout the entire study in part six.

3.1 Materials

The current investigations include the following all-ceramic dental materials:

- 1) **Empress 1** (Ivoclar-Vivadent, Schaan, Liechtenstein), staining technique (Chapter 2, 2.5.8.2).

2) **Empress 2** (Ivoclar-Vivadent, Schaan, Liechtenstein), layering technique (Chapter 2, 2.5.8.3).

3) **Experimental pressable material**

This material was provided by the manufacturer (Ivoclar-Vivadent, Schaan, Liechtenstein) for mechanical property comparison with Empress 1 and Empress 2. It was recommended to be used as a core material for fixed partial dentures (layering technique).

3.2 Specimen Preparation

3.2.1 Number and dimension of specimens

A perspex material was used to reproduce the desired dimensions and shapes. It was machined in an engineering workshop to produce the following specimens:

- 1) 215 disc specimens measuring 14 mm (diameter) $\times$ 1.1 mm (thickness).
- 2) 55 bar specimens measuring 20 mm (length) $\times$ 1.2 mm (thickness) $\times$ 4 mm (width).
- 3) 6 plate specimens measuring 30 mm (length) $\times$ 12.75 (width) mm $\times$ 1.1 mm (thickness).

3.2.2 Spruing and investing

All samples were sprued and attached to muffle bases with surrounding paper cylinders (Figure 3.1). The samples were then invested using a total of 200 g investment powder and 52 ml of liquid, 40 ml special investment liquid and 12 ml of distilled water. Mixing was carried out for 60 seconds manually and 60 seconds under vacuum, then the mixtures were poured into a cylinder under vibration to

prevent the formation of air bubbles. The cylinders were allowed to set for 30 minutes.

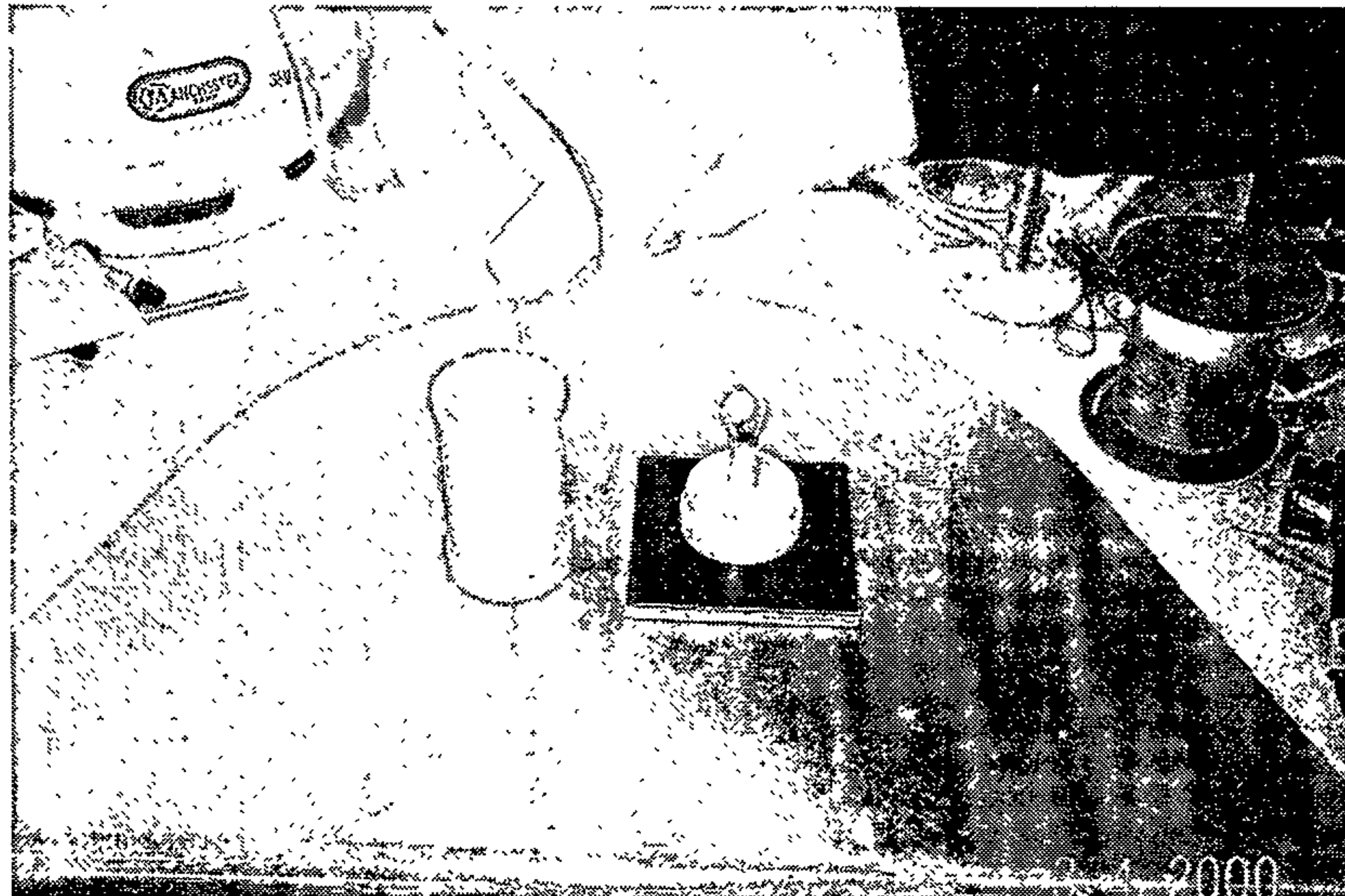


Figure 3.1 Spruing and investing of disc specimens.

3.2.3 Preheating and heat-pressing

The refractory moulds with the Empress 1 ingots, and the Alumina plunger were heated at a rate of 9°C/m from room temperature to 850°C in a preheating furnace (Kavo EWL, Type 2322; Kavo, Biberach, Germany) (Figure 3.2); this temperature was held for 90 minutes. When the preheating cycle was complete, the ingots were inserted into the moulds and the preheated plunger placed on top and then transformed to the pressing furnace (Programat EP 500, Ivoclar-Vivadent) and the pressing cycle started (Figures. 3.3 and 3.4). The pressing was performed at a temperature of 1175°C and a pressure of 5 bars, with a 20 minutes hold and 40 minutes' pressing. After pressing, the investment moulds were removed from the furnace and allowed to air cool.

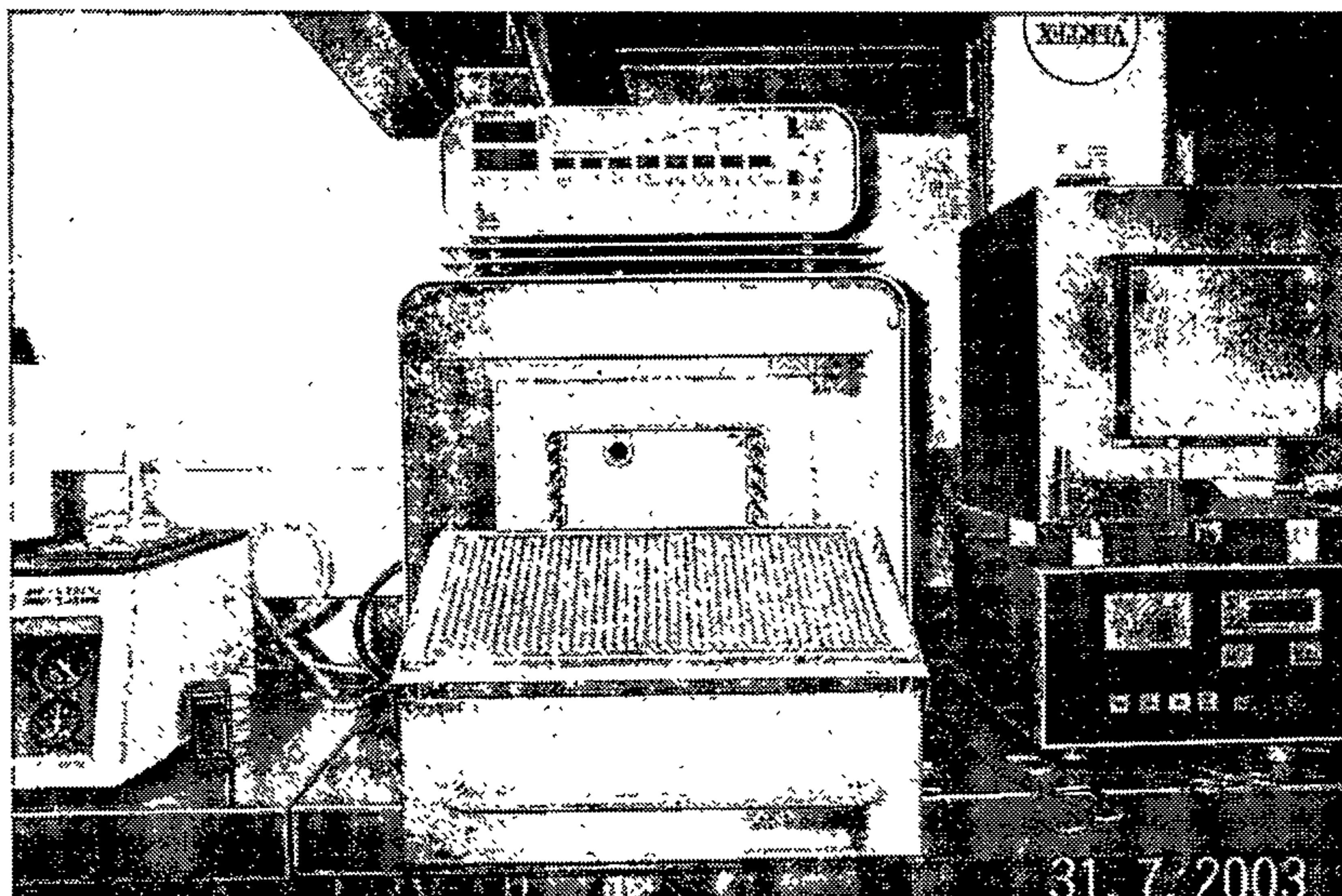


Figure 3.2 Furnace used for preheating of the refractory moulds with the ingots, and the Alumina plunger.

The same preparation procedure was also carried out for the Empress 2 material. However, the ingots (unpressed blocks) were not preheated along with the moulds (according to the manufacturer's recommendations), but inserted at room temperature into the preheated refractory mould. The pressing cycle was started at 920° C and a pressure of 5 bars with a 20 minutes hold and 30 minutes' pressing.

3.2.4 Divesting and cutting

The specimens were then carefully divested using an air abrasion unit (Kavo EWL, Type 5423; Kavo, Biberach, Germany) with 50µm glass beads at a pressure of 3 bars. The sprues were separated from the discs using a diamond-cutting wheel saw (Isomet, Buehler Ltd., Lake Bluff, Illinois, USA). In order to remove the reaction layer of the Empress 2 specimens, they were immersed in invex liquid (invex liquid, Ivoclar-Vivadent) in an ultrasonic unit (Ultrasonic cleaner; Unisonics, Manly Vale, New South Wales, Australia) for 10 minutes and then rinsed and dried; this was followed by Aluminum oxide sandblasting 50µm at 1 bar pressure.

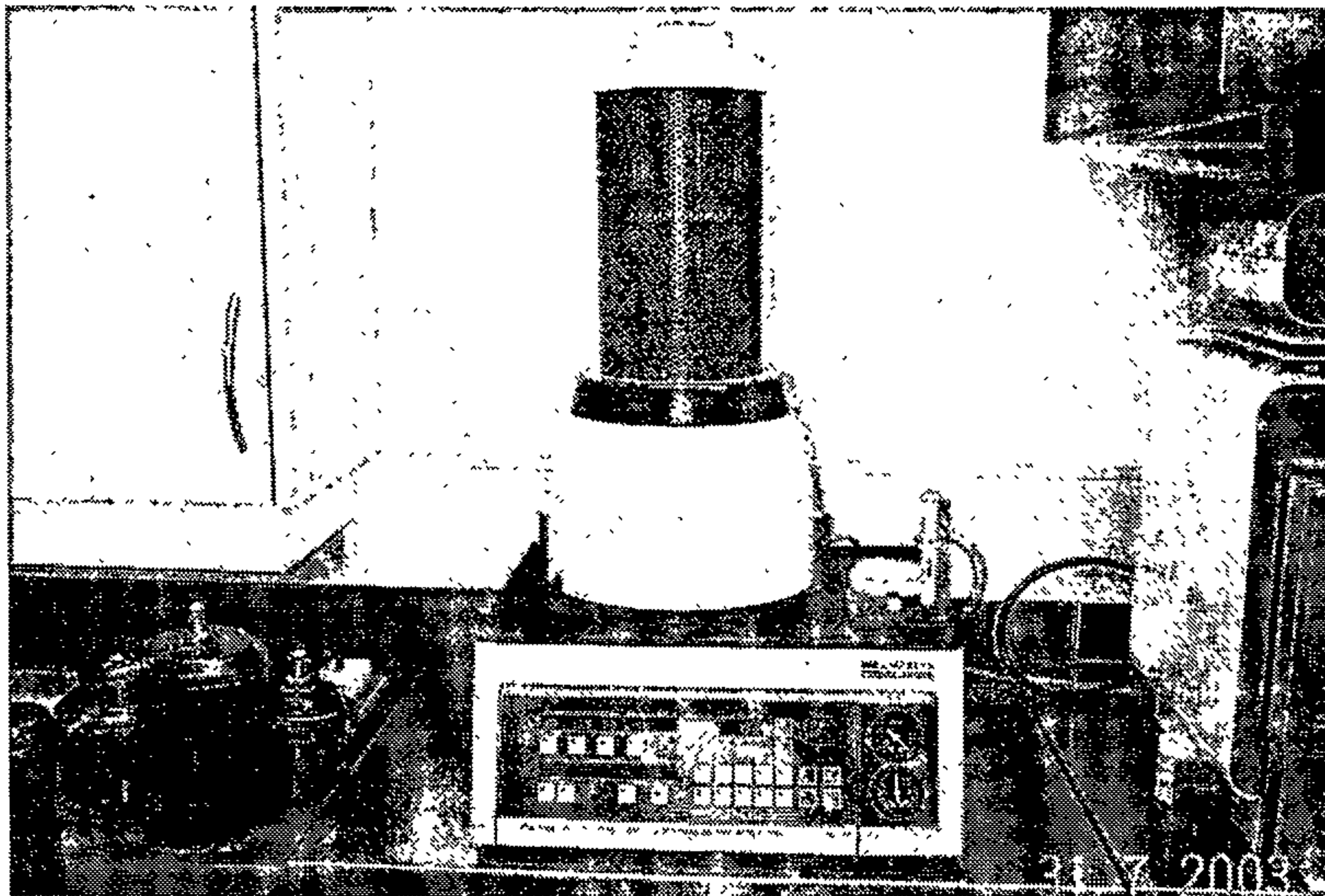


Figure 3.3 The pressing machine used in the current study (Programat EP 500, Ivoclar-Vivadent).

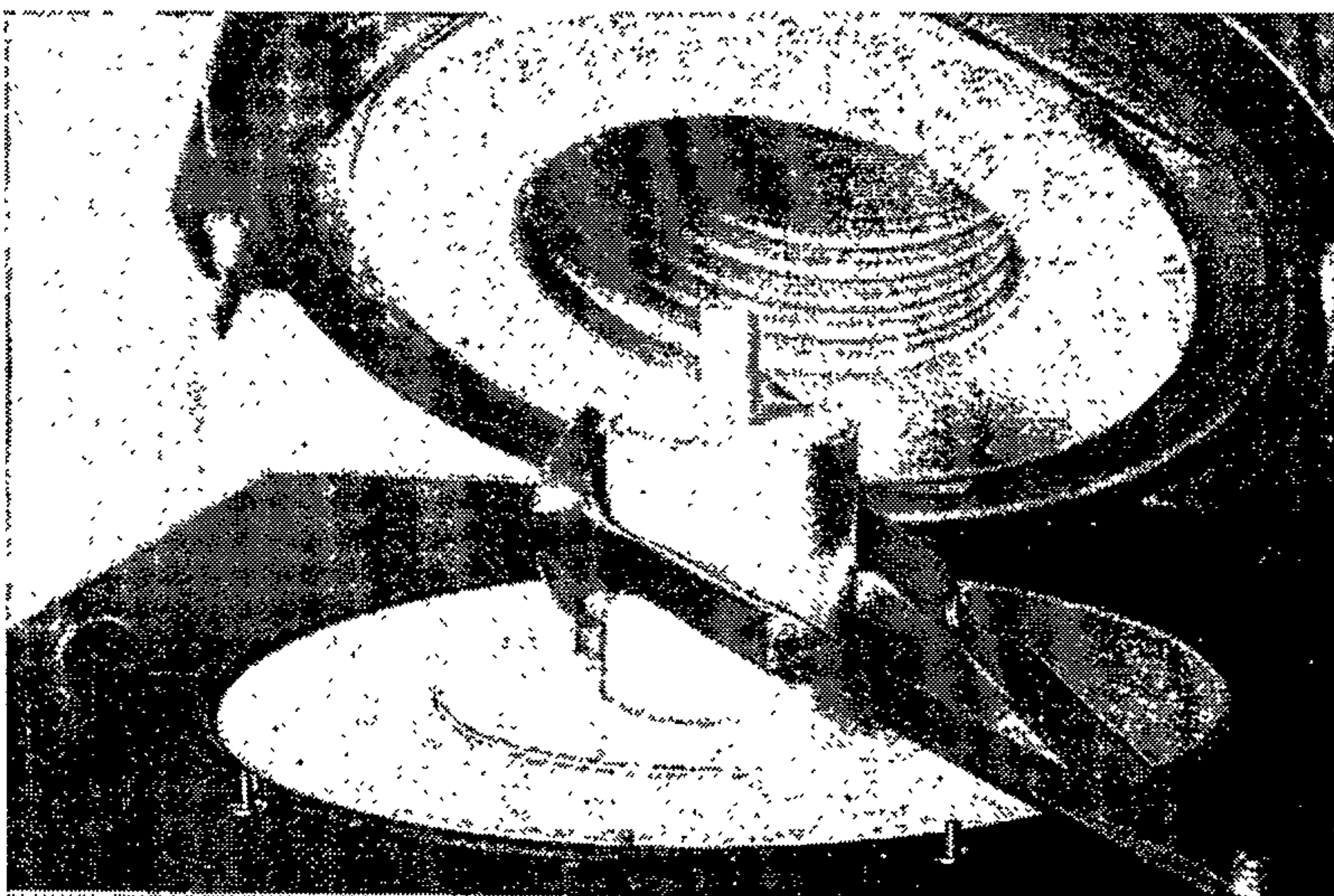


Figure 3.4 Ingots were inserted into the moulds and the preheated plunger placed on top and pressing started.

3.2.5 Grinding and polishing

All specimens were serially wet ground with 220, 320, 500, 600 grade silicon carbide paper mounted on a metallographic lapping machine (RotoPol-22, Struers A/S, Rodovre, Denmark) (Figure 3.5). All specimens were cleaned using an ultrasonic bath for 15 minutes at 90° C, followed by washing in detergent and boiling water. All specimens were fired in a porcelain furnace (Programat P100; Ivoclar-Vivadent) according to the manufacturer's recommended firing cycles to simulate laboratory procedures and release all stresses associated with grinding and polishing procedures.

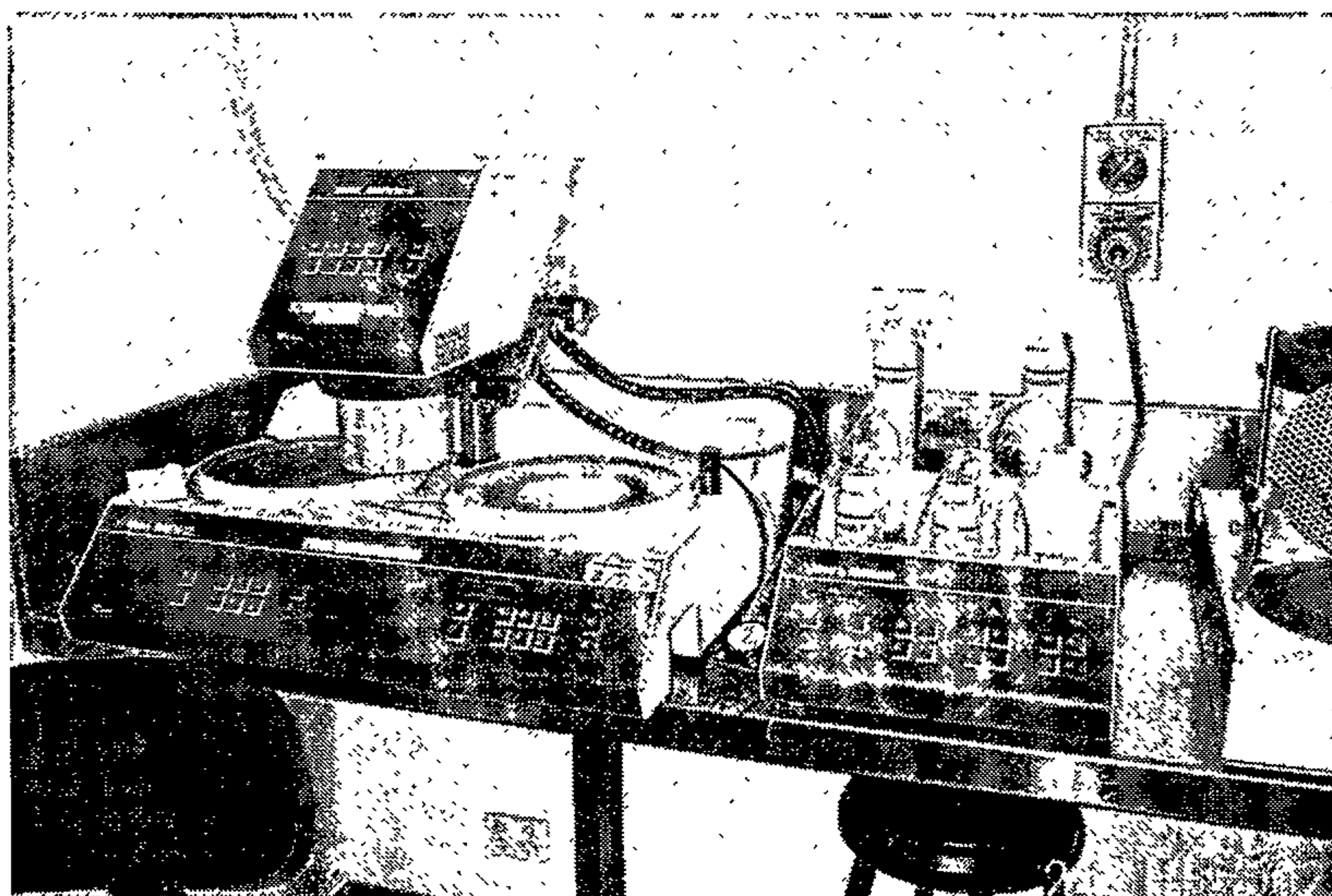


Figure 3.5 Metallographic machine used for grinding and polishing samples.

Specimens for the fracture toughness measurements were additionally polished with 6 μ and 1 μ diamond paste until a mirror-like surface was achieved.

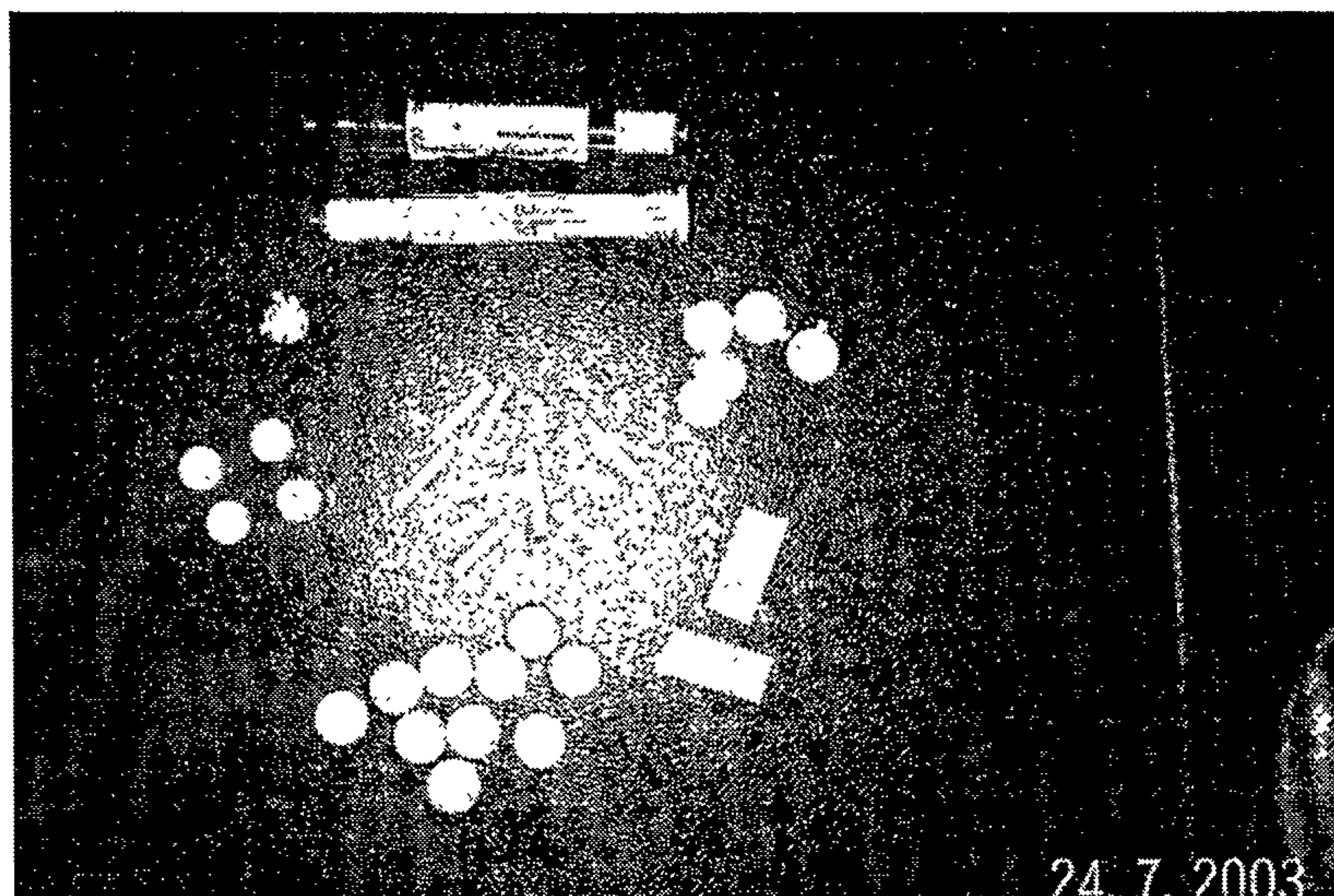


Figure 3.6 Ingots and specimens (discs, bars, plates and buttons) of Empress 1 and Empress 2.

3.3 Use of Specimens

3.3.1 Disc specimens

The disc specimens were used to assess:

- 1) The intrinsic biaxial flexural strength (Chapter 7, 7.6.2).
- 2) The effect of different processing fabricating procedures on the biaxial flexural strength (Chapter 7, 7.11.2).
- 3) The fracture toughness (indentation strength in biaxial flexural technique, Chapter 6, paragraph 6.6.2).
- 4) The fracture toughness (indentation fracture technique) (Chapter 6, 6.6.1). This was done after further polishing, until the mirror-like surface was achieved.

3.3.2 Bar specimens

The bar specimens were used to measure:

- 1) Uniaxial flexural strength (3-point bending flexural test) (Chapter 7, 7.6.1).

2) Fracture toughness (indentation strength in 3-point bending technique) (Chapter 6, 6.6.2).

3.3.3 Plate specimens

The plate specimens were used to measure Elastic modulus and Poisson's ratio (Chapter 5).

3.4 Microstructural Investigations

3.4.1 Preparation and etching

After fine polishing, several specimens were cleaned with ethanol and etched with HF acid. The etching procedure for microstructural observations was different according to the material investigated. Empress 1 was etched with 0.2 vol% of HF acid for 1 minute; Empress 2 and the experimental ceramic were etched with 10 vol% HF acid (a range of time from 2 to 20 minutes).

3.4.2 Scanning electron microscope (SEM)

After etching the samples were carbon-coated 20 nm. A scanning electron microscope (SEM) (XL 30, Philips, Eindhoven, Holland) (Figure 3.7) was then used to disclose microstructural features and measure the radial crack after indentation.

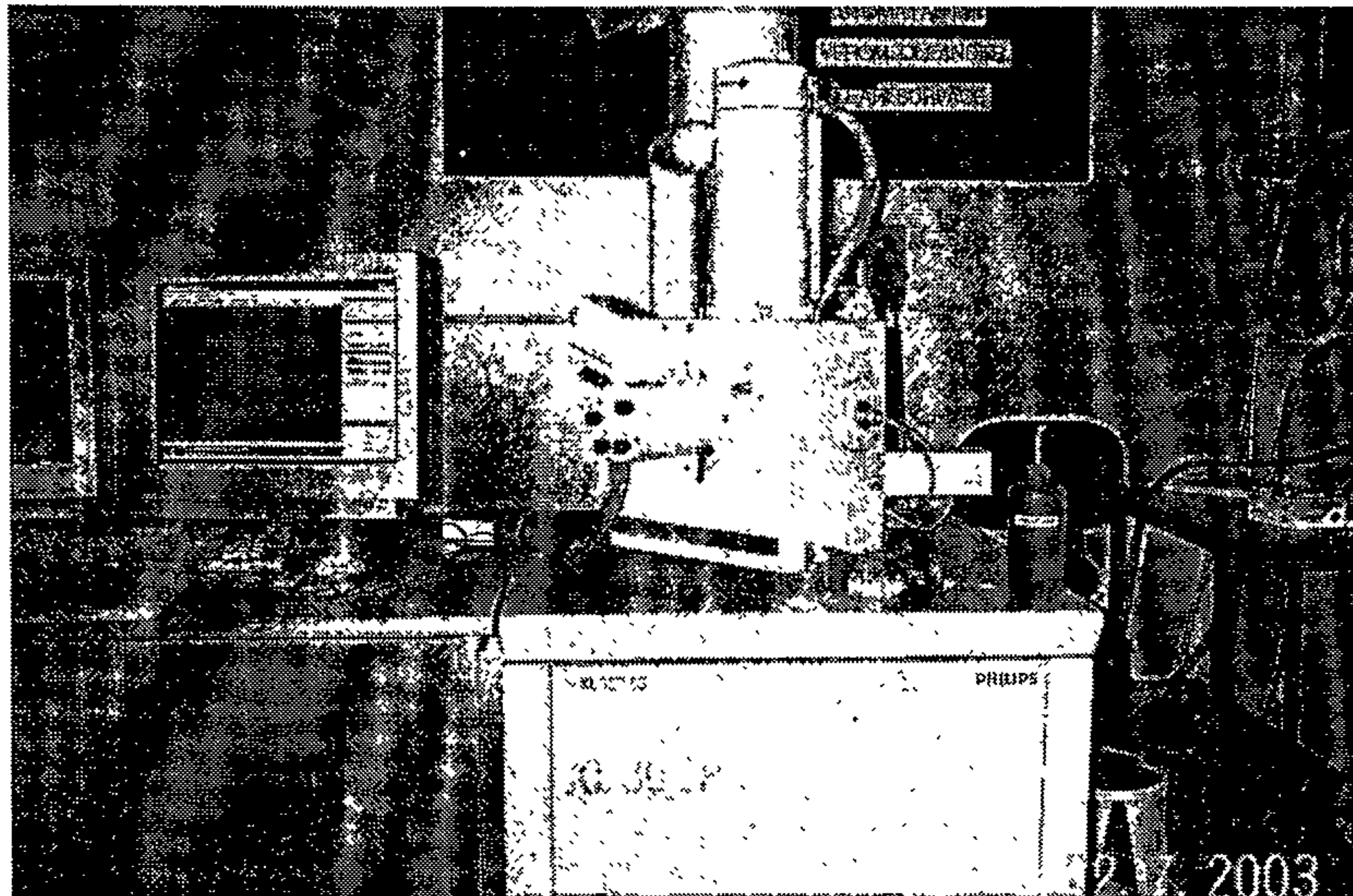


Figure 3.7 The scanning electron microscope used for microstructural investigations

Another device was also used to measure the radial cracks for the fracture toughness measurements, an optical microscope on an ultra micro-indentation system machine (UMIS 2000, CSIRO, Australia) (Figure 3.8).

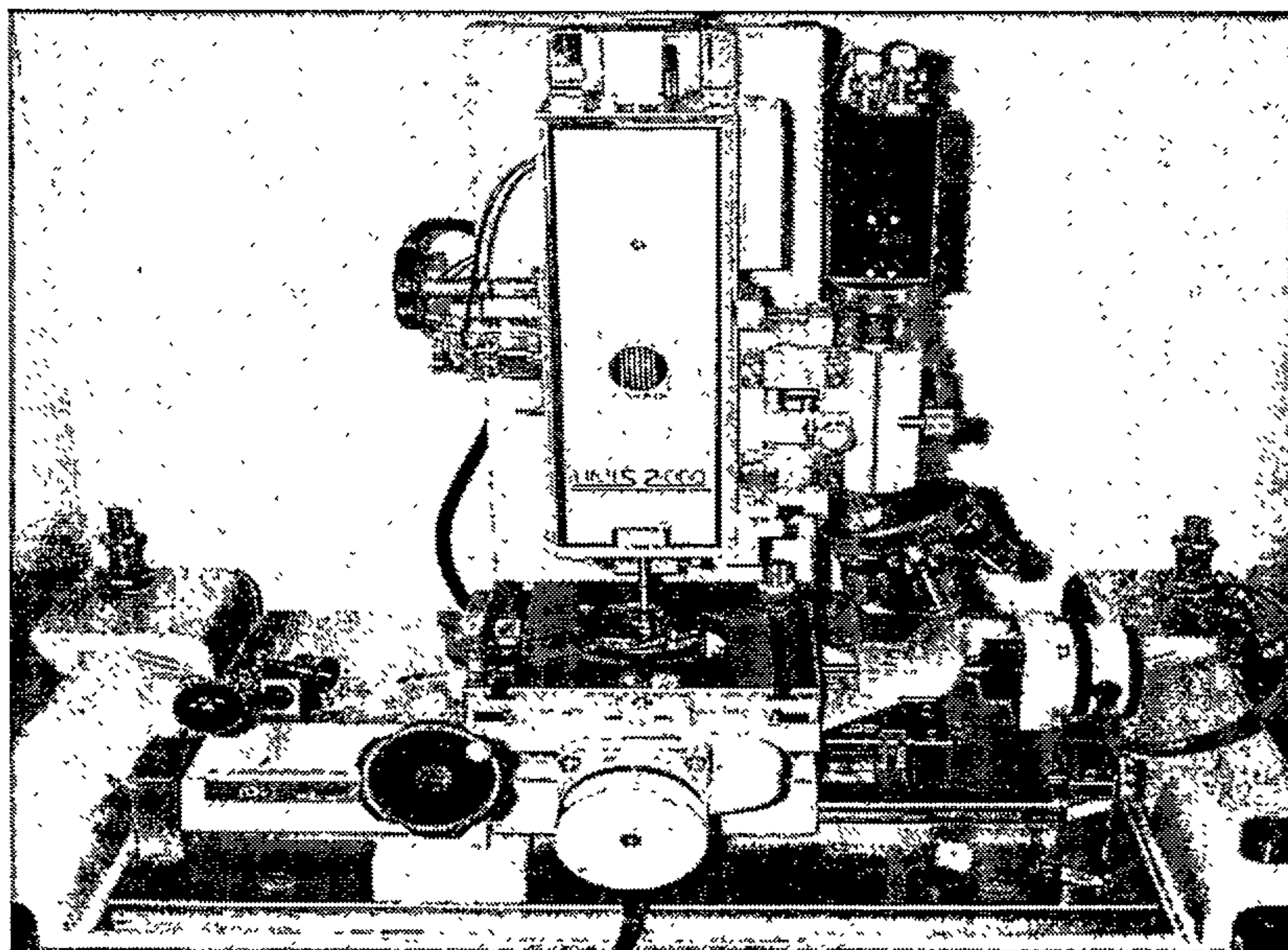


Figure 3.8 Optical microscope in a UMIS machine used for crack length measurements.

3.4.3 Field emission SEM (High resolution)

Some samples were platinum-coated 20 nm, and the microstructural features were observed using a field emission scanning electron microscope (JSM 6000 FSEM, Jeol, Tokyo, Japan) (Figure 3.9)

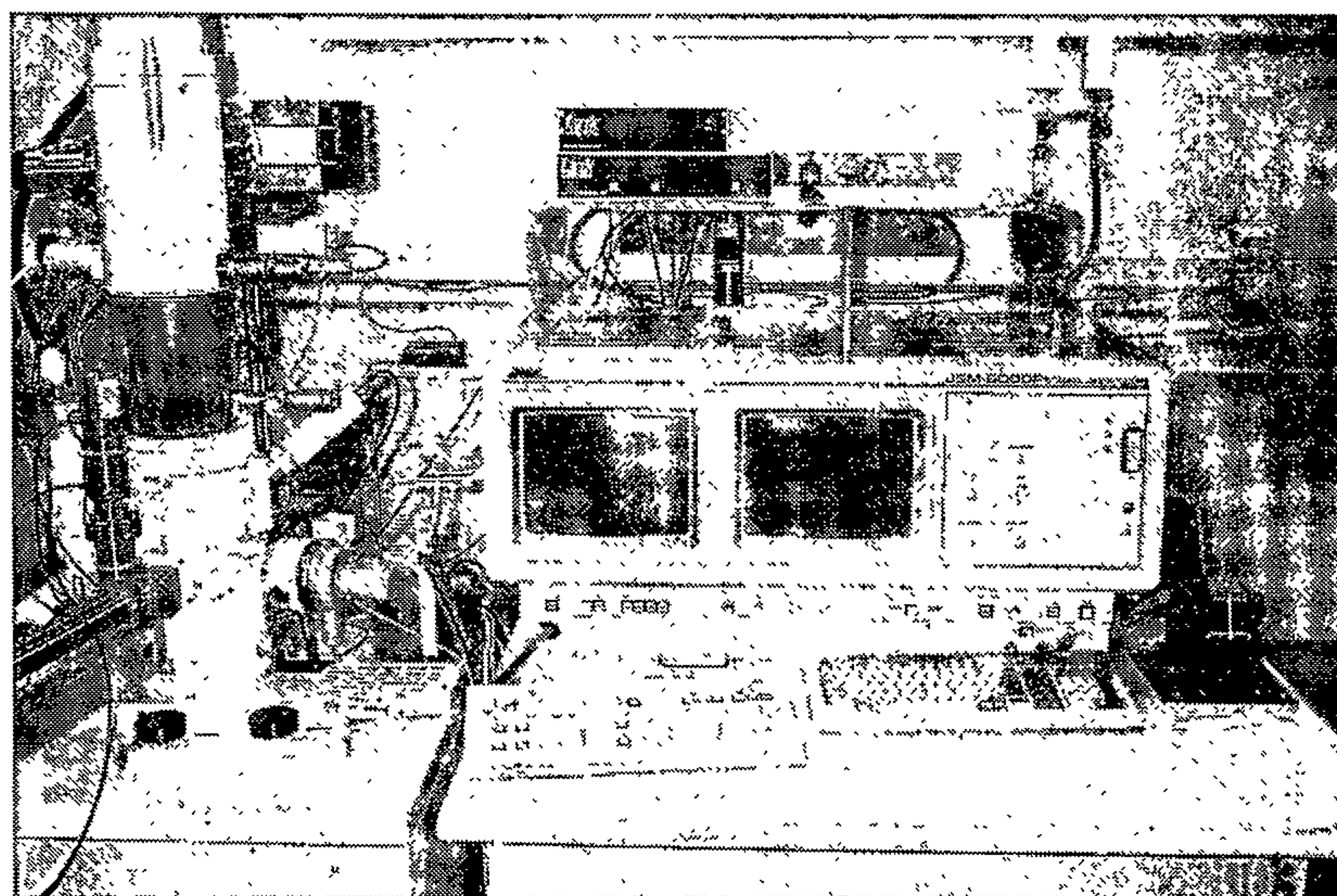


Figure 3.9 The field emission scanning electron microscope used to show further details such as crystal size, crack and crystal interactions and crack paths.

3.5 X-ray diffraction

X-ray diffraction (Diffractometer D5000; Siemens, Munich, Germany) was carried out to investigate and determine the crystalline phases in the materials studied. Further details are provided in Chapter 4.

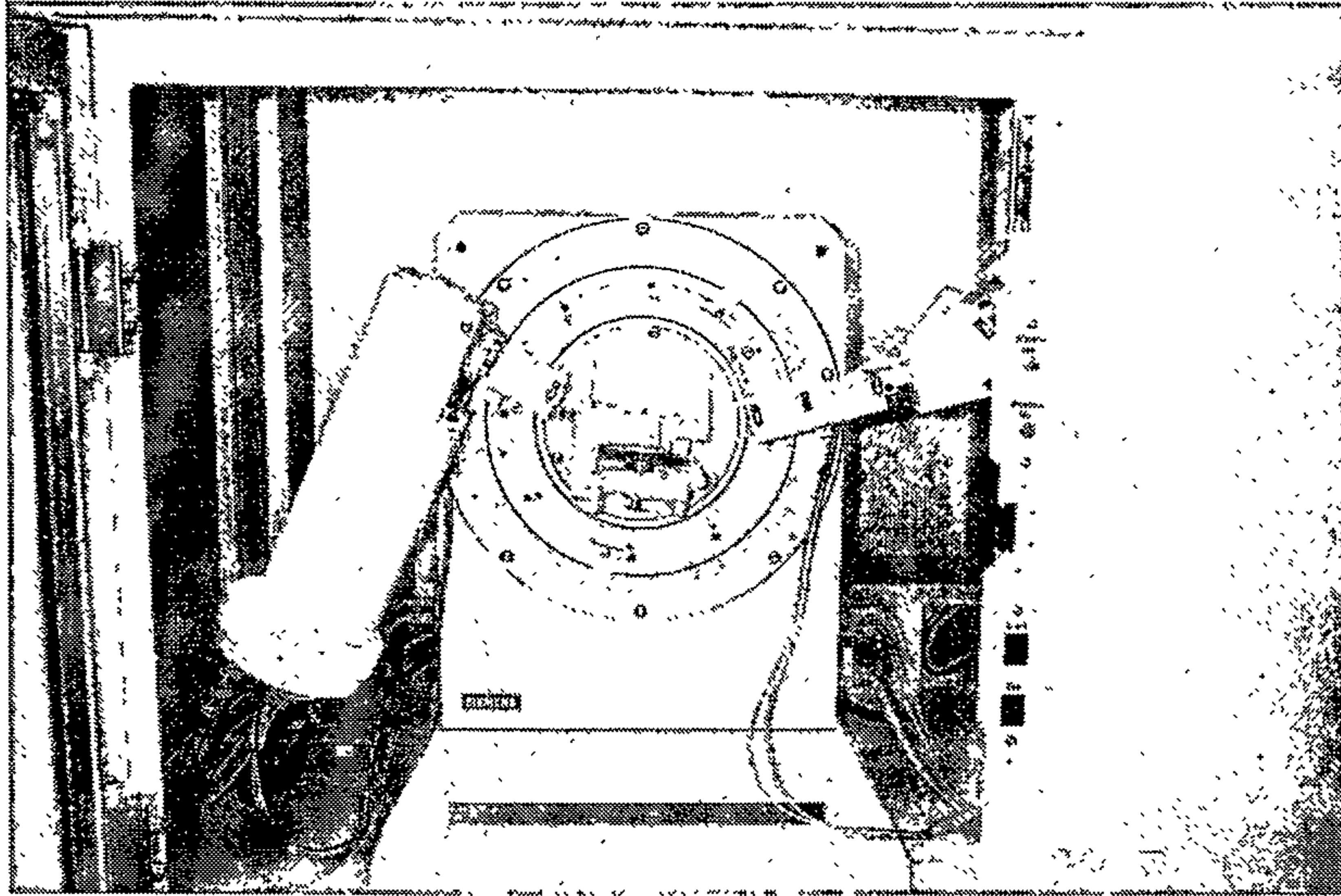


Figure 3.10 The diffractometer used to identify crystalline phases (D5000; Siemens, Munich, Germany).

3.6 Statistics

The statistics of the present study were analysed using the following techniques: 1) pairwise t-test was used when two groups were compared, followed by one-way ANOVA at overall significance level $P=0.05$ with respect to Bonferroni adjustment, 2) One-way ANOVA with Tukey's multiple comparison tests was used when more than two groups are compared.

CHAPTER 4

X-RAY DIFFRACTION, MICROSTRUCTURE AND POROSITY

This chapter will address two main issues of the current study, X-ray diffraction and microstructural features of the three investigated glass ceramic materials: Empress 1, Empress 2 and experimental ceramic. A description of porosity (size and shape) of Empress 1 and Empress 2 will also be provided. Porosity of the experimental ceramic was not investigated due to the unavailability of samples before pressing, and because of extreme similarities found between this material and Empress 2.

In the X-ray diffraction part, a review of crystal structure, crystalline and noncrystalline materials, lattice, unit cell, crystal systems will be presented firstly. This will be followed by a description of the concept and basis of X-ray diffraction; its definition, importance and purpose in the present study. Current investigations, results and conclusion will also be provided.

This chapter will also present a brief review of microstructure importance, and the aim in the current study. The investigations that were carried out in this study, the microstructure of the same materials, discussion and conclusion will also be provided.

The third part will focus on porosity and the effect of heat pressing on the pore size and shape in Empress 1 and Empress 2.

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4.1 Crystal structures

4.1.1 Introduction

Matter is composed of atoms [1]. The types of atoms, bonding between them and the way that these atoms are packed together significantly determine the properties of many materials [1]. The atoms can be arranged in long- or short-range order [2, 3]. Materials that exhibit an order of atoms greater than the bond length between these atoms are said to have long-range order [1]. In the case of gases, for example, the long-range interaction between atoms is negligible as atoms are free to move and the kinetic energy is large enough to overcome the short-range attractive forces between atomic particles [4]. Gases, consequently, show neither short- nor long-range order. However, this is not applicable in the case of condensed phases [1]. In a liquid, the atomic particles are closer together, and the nearest neighbours are at a well-defined distance. Therefore, short-range order is exhibited [1]. The kinetic energy of the atomic particles is lower than that of gases since particles are closer together and collision frequently occurs [4]. The atomic particles in solids are packed more closely together than those in either gases or liquids. Solids may exhibit short- or long-range atomic order. Those that exhibit only short-range order are termed non-crystalline solids [2].

4.1.2 Noncrystalline materials

These materials lack a systematic and regular atomic arrangements over a comparatively large number of atomic spaces [2]. They may be termed amorphous, which literally means “without form” and is the state of liquids [4]. Theoretically, any materials can form an amorphous solid if the melt is cooled rapidly enough to

suppress crystal growth [1]. Examples of noncrystalline materials are most thermoplastics, transparent polymers, rubbers, and oxide and metallic glasses.

4.1.3 Crystalline materials

A crystal can be defined as an homogeneous solid composed of atoms arranged in a regular three-dimensional lattice [4, 5]. The crystalline state is the lowest achievable energy level that a material may reach and hence noncrystalline materials are often unstable and can revert to crystalline form under certain treatments or circumstances [4]. Crystalline materials exhibit both the short- and the long-range atomic order in all three dimensions. The majority of engineering materials, for example, most metals, many ceramics, most minerals and some plastics, are crystalline [4]. Many of the physical properties of solids are affected by the crystal structure of the material, the way that atoms, ions or molecules are spatially arranged [2].

4.1.3.1 Unit cells and Lattice

Lattice is a term used in the perspective of crystal structure. It can be defined as an indefinitely extended arrangement of points that are surrounded by the same collection of neighbouring points (Figure 4.1) [1].

An example of a two-dimensional lattice is a wallpaper. The smallest part that describes this model is termed the unit cell. The only possible shapes for the two-dimensional unit cells are a square, a rectangle or a parallelogram [1]. This is because the unit cell must possess a form which allows it to be arranged in a manner that ultimately fills space. The length of the unit cell edges is termed the lattice parameter.

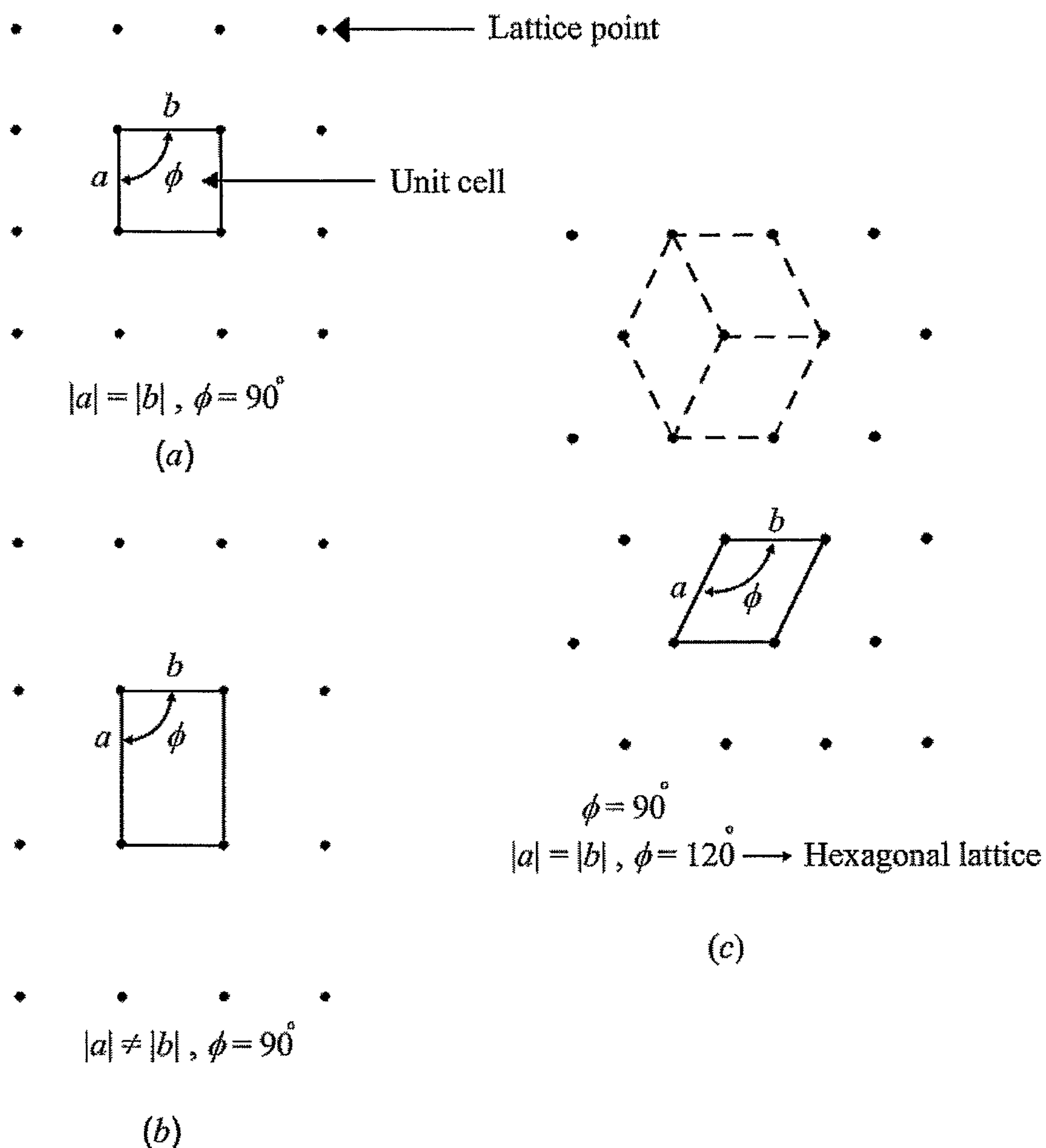


Figure 4.1 The possible unit cell of a two-dimensional pattern includes: (a) a square, (b) a rectangle or (c) a parallelogram.

The identification of a lattice is not merely enough to uniquely define a pattern. An exact description of what is located at each lattice point is indispensable. A group of things that are located on a lattice point is called the basis. For a two-dimensional pattern the basis is one or more illustrations while for a three-

dimensional crystal the basis is one or more atoms [1]. This can be formalised by the following relationship:

$$\text{Lattice} + \text{Basis} = \text{Crystal structure} \quad (1)$$

4.1.4 Crystal systems

Atoms may be arranged in many possible crystal structures. These can be divided into groups according to the unit cell configurations and/or atomic arrangements. The unit cell geometry is entirely described according to six parameters: the three edge lengths (a , b , c), and three interaxial angles (α , β , γ). These are termed the lattice parameters of a crystal structure [2] (Figure 4.2).

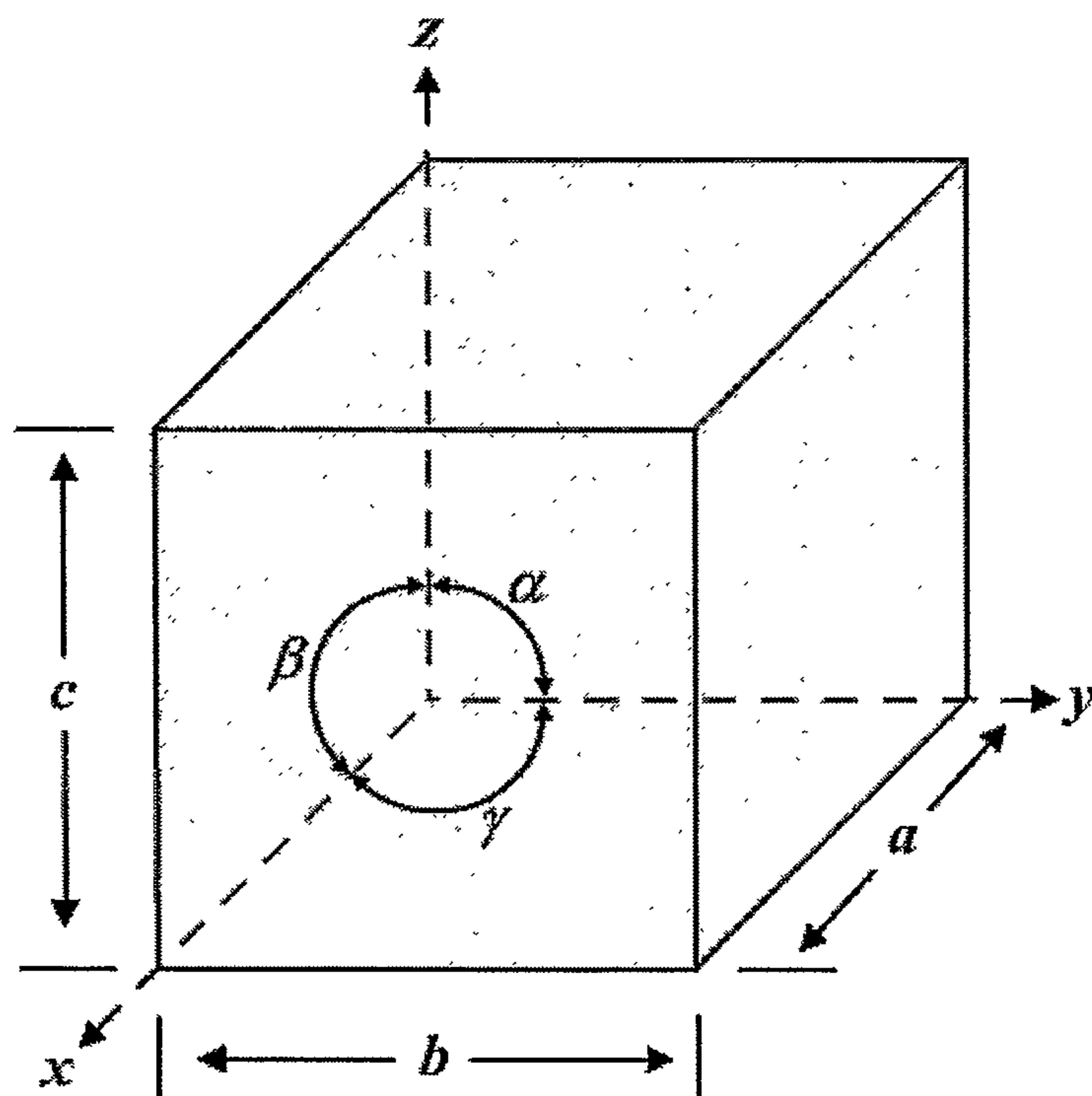
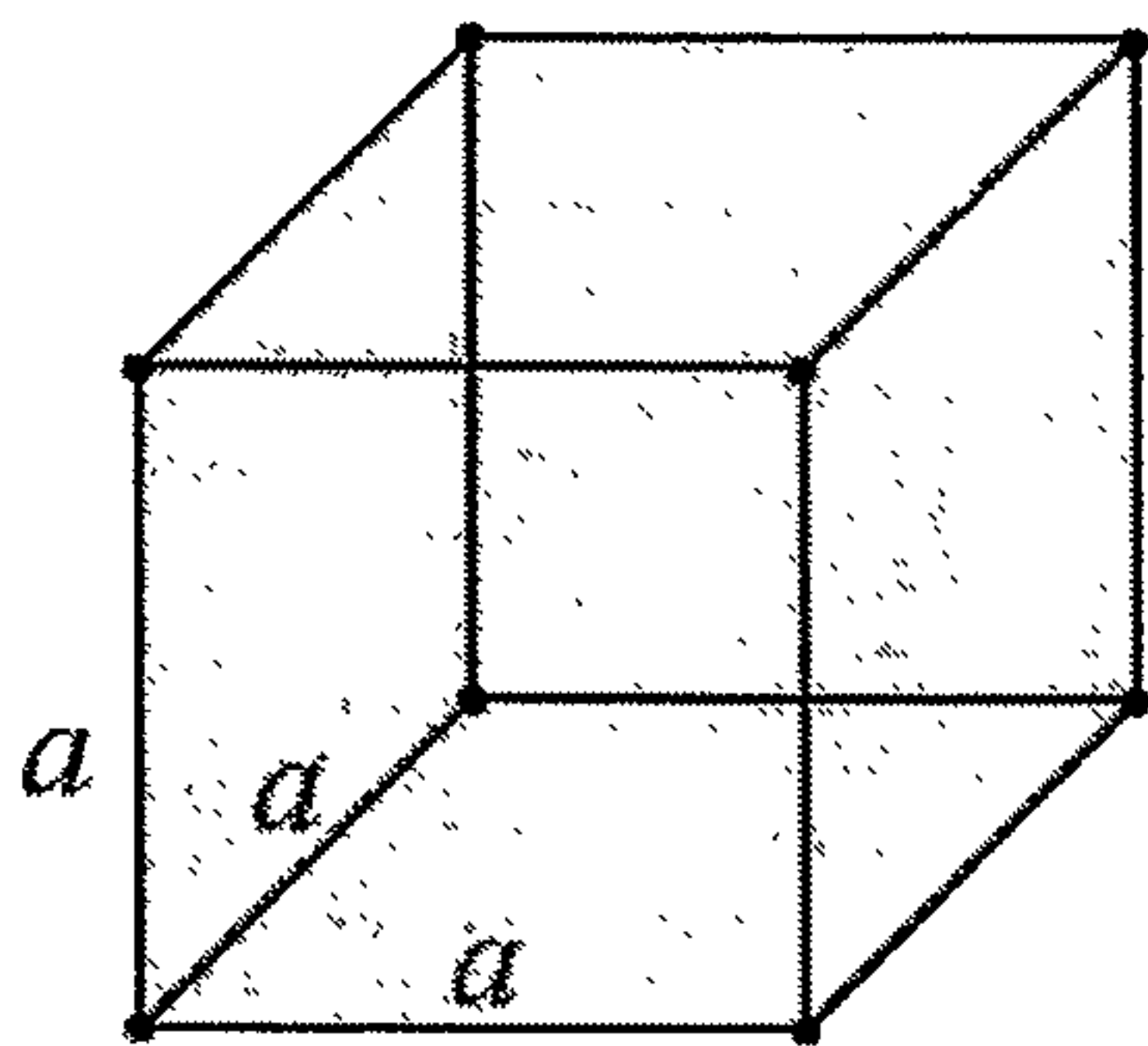


Figure 4.2 A unit cell with x , y and z co-ordinate axes, showing axial lengths (a , b and c), and interaxial angles (α , β and γ) [2].

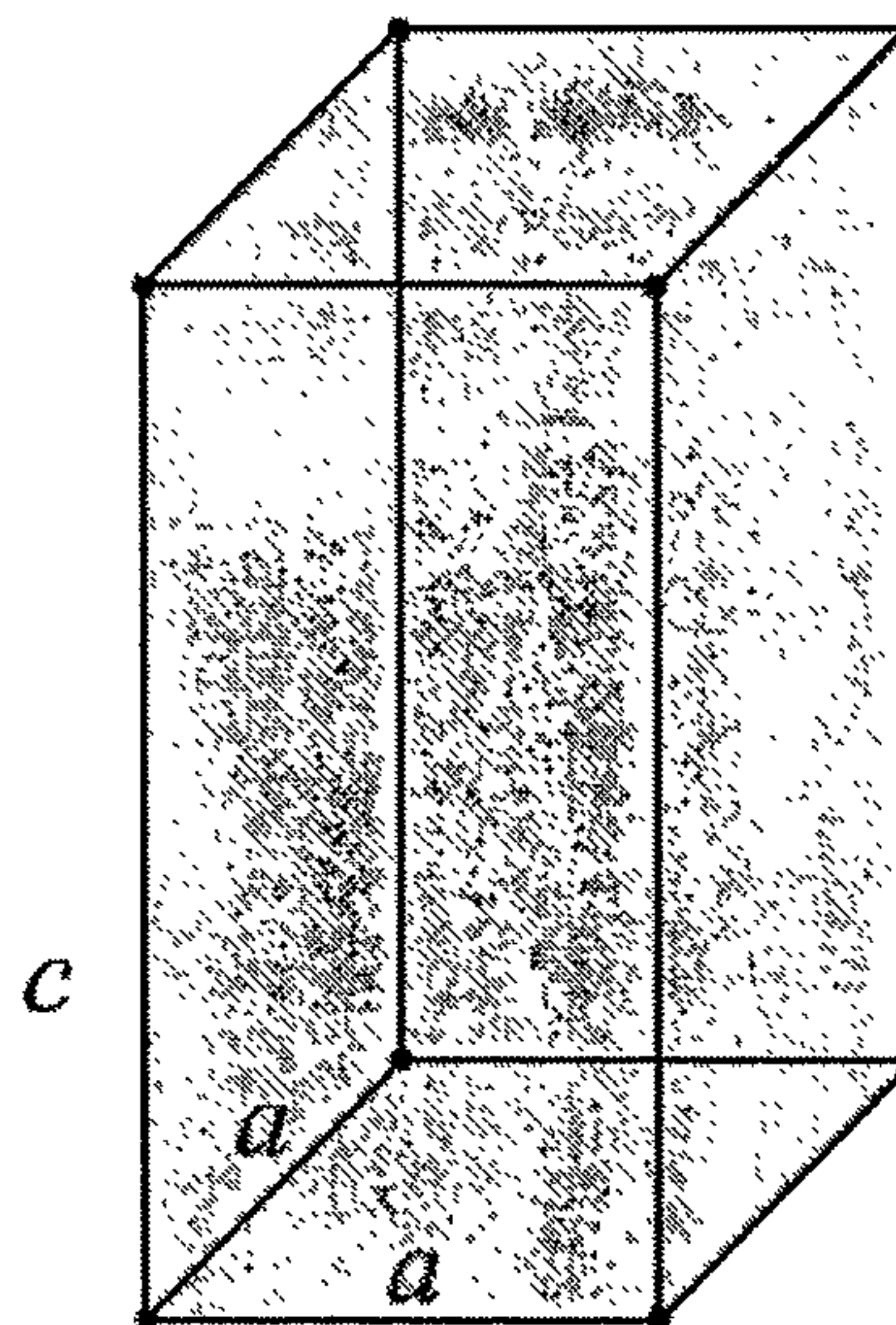
There are seven different possible arrangements of a , b , and c , and α , β , and γ . Each signifies a discrete crystal system. These seven crystal schemes are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic and triclinic. The cubic system has the greatest degree of symmetry where $a=b=c$ and $\alpha=\beta=\gamma$. The triclinic system exhibit the lowest degree of symmetry where $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$. The cubic, tetragonal, monoclinic and orthorhombic crystal systems are displayed in Figure 4.3 [2].



Cubic

$$a = b = c$$

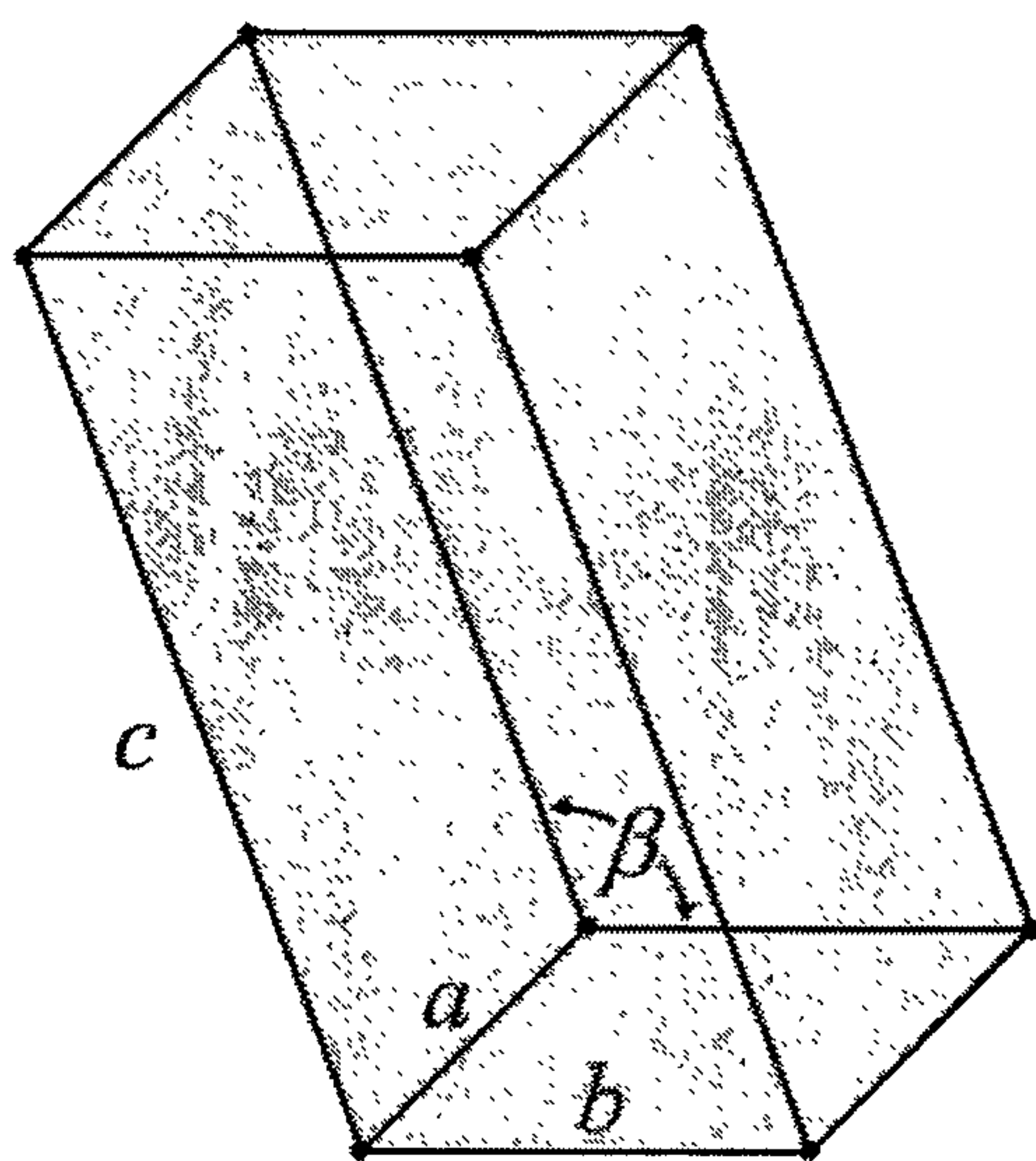
$$\alpha = \beta = \gamma = 90^\circ$$



Tetragonal

$$a = b \neq c$$

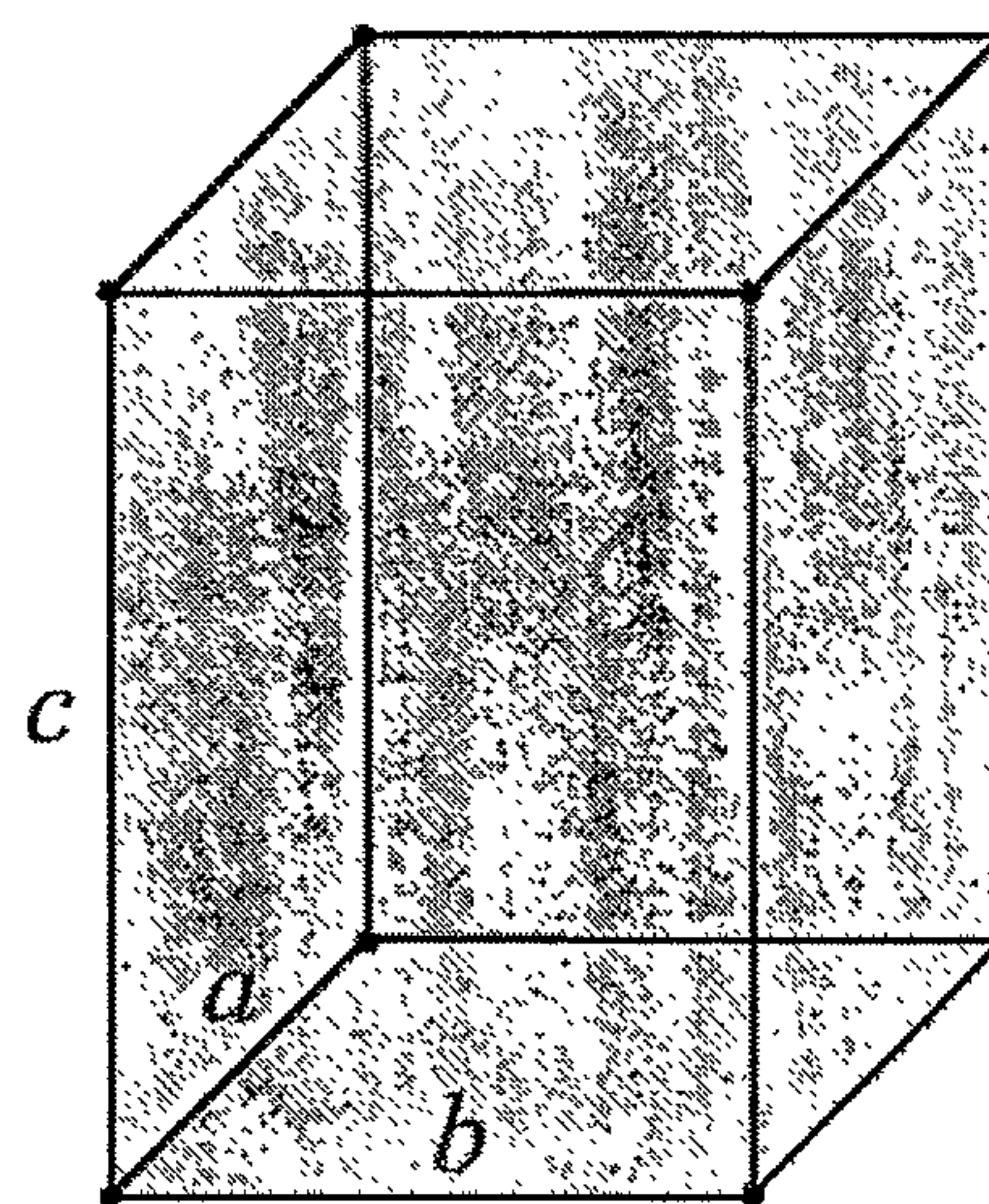
$$\alpha = \beta = \gamma = 90^\circ$$



Monoclinic

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ \neq \beta$$



Orthorhombic

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

Figure 4.3 Lattice parameter relationships and figures showing unit cell geometries for the cubic, tetragonal, monoclinic and orthorhombic crystal systems [2].

4.1.4.1 Crystallographic directions

When studying crystalline materials, it is often necessary to identify a particular point within a unit cell, crystallographic direction or planes of atoms. Three numbers or indices are used to indicate point locations, directions and planes. The unit cell is the foundation in determining the index values, where a right-handed co-ordinate system comprising three axes (x , y , and z) placed at one of the corners and coinciding with the edges of the unit cell (Fig. 4.2). The three axes are not mutually perpendicular in some crystal systems, such as hexagonal, rhombohedral, monoclinic and triclinic [2].

The line that fits between two points or a vector is defined as the crystallographic direction. The $[100]$, $[110]$ and $[111]$ are common directions; they are drawn in the unit cell (Figure 4.4) [2].

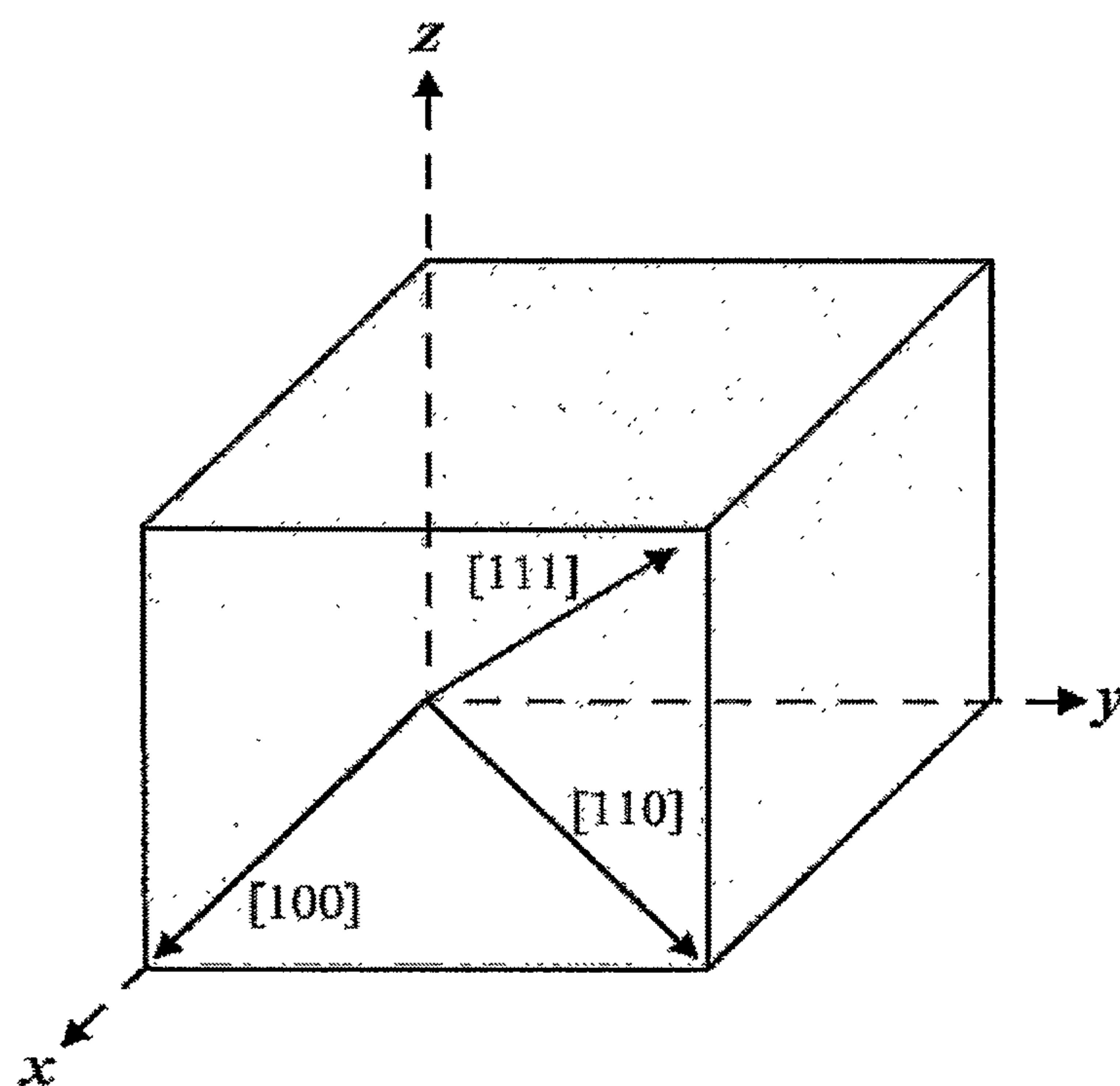


Figure 4.4 The $[100]$, $[110]$ and $[111]$ directions within a unit cell [2].

4.1.4.2 Crystallographic planes

The Planes orientations of a crystal structure are determined by considering the unit cell as the basis with the three-axis coordinate system shown in Figure 4.2.

Crystallographic planes are specified by three Miller indices as (hkl) . If two planes are parallel to each other, they are considered equivalent with identical indices [2].

Some examples of crystallographic planes are shown in Figure 4.5.

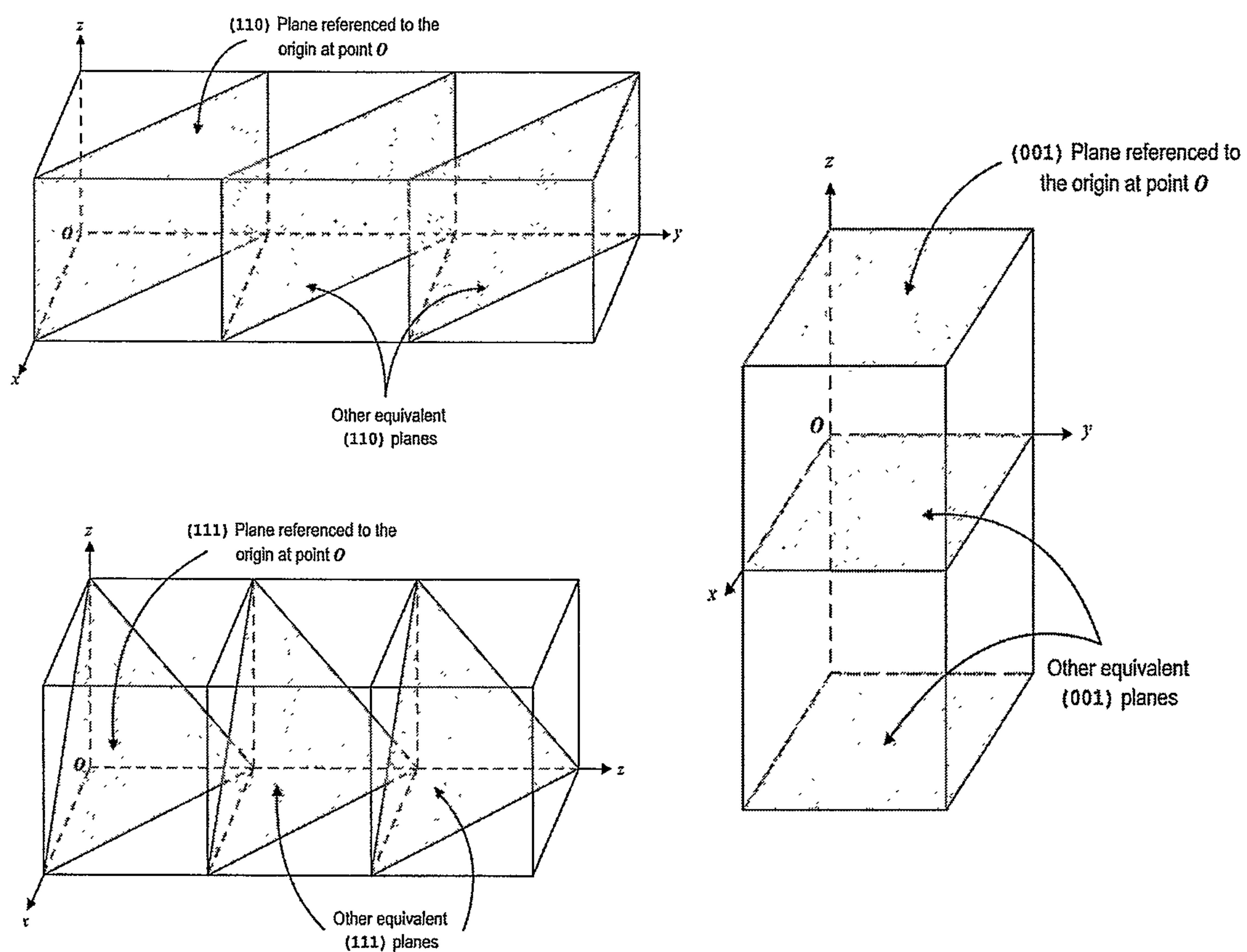


Figure 4.5 Series of crystallographic planes, (a) $[001]$, (b) $[110]$ and (c) $[111]$ [2].

4.2 X-ray Diffraction (XRD)

4.2.1 Introduction

In 1895 Roentgen, a German physicist, discovered X-rays [5]. The properties of these rays were unidentified that time. However, it was well known that X-rays travel in

straight lines and affect photographic films in a similar manner to light. Unlike the light, X-rays were invisible and more penetrating. Therefore, they could easily pass through the human body, metal, wood and many other opaque objects. If a source of X-ray is placed on one side of an object and a photographic film on the other side, a shadow picture (radiograph) can be made. In this way, a crack point in a bone or in a piece of metal can be located. Both physicians and engineers benefit from this advantage and the value of X-ray usage increased [5].

The exact nature of X-rays was established in 1912. In the same year, X-ray diffraction by crystals was discovered, which proved the wave nature of X-rays. This provided a new method for exploring the fine structure of matter [5].

4.2.2 Definition and Use

X-ray diffraction is a major tool used to investigate structure at the atomic scale dimension of matter [1,5]. In addition to the simplicity of this technique, it provides accurate information on interplanar spacings and atomic positions. Initially, it was used for the determination of crystal structure. Other uses were developed later on to include chemical analysis, stress measurements, phase equilibria and crystal orientation [5].

The interference mechanism (wave interaction) is necessary to understand the concept of X-ray diffraction. When waves of the same amplitude are in phase, the alignment of their maxima and minima results in a wave twice of the amplitude of its components. This is known as constructive interference. However, if one of the two

waves is shifted by a distance of half a wavelength, this results in a wave equal to zero at all points (destructive interference) (Figure 4.6) [1].

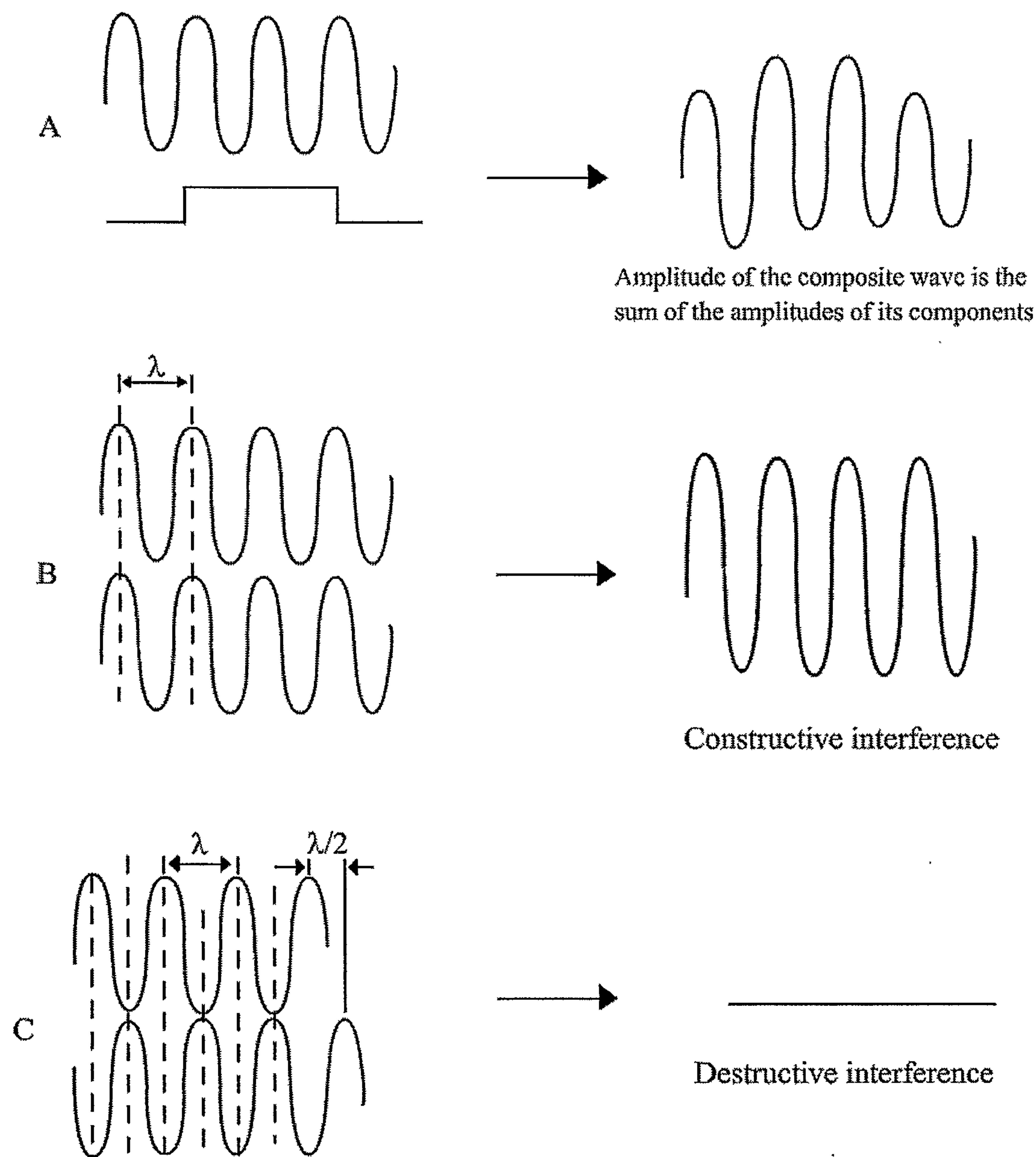


Figure 4.6 Wave interferences: (A) the general case, (B) constructive interference and (C) destructive interference [1].

If we consider a beam of two parallel X-rays impinging upon a surface of a crystal, the wavelength of the radiation is λ , the angle of incidence is θ , and the

perpendicular distance between parallel planes (the interplanar spacing) is d . The first wave is reflected from the top of the atoms, and the second is reflected from the next lower parallel plane of atoms (Fig. 4.7). The difference in distance from a source to a detector between the X-rays beams 1a and 2b is given by the following formula:

$$AB + BC = 2d \sin \theta \quad (2)$$

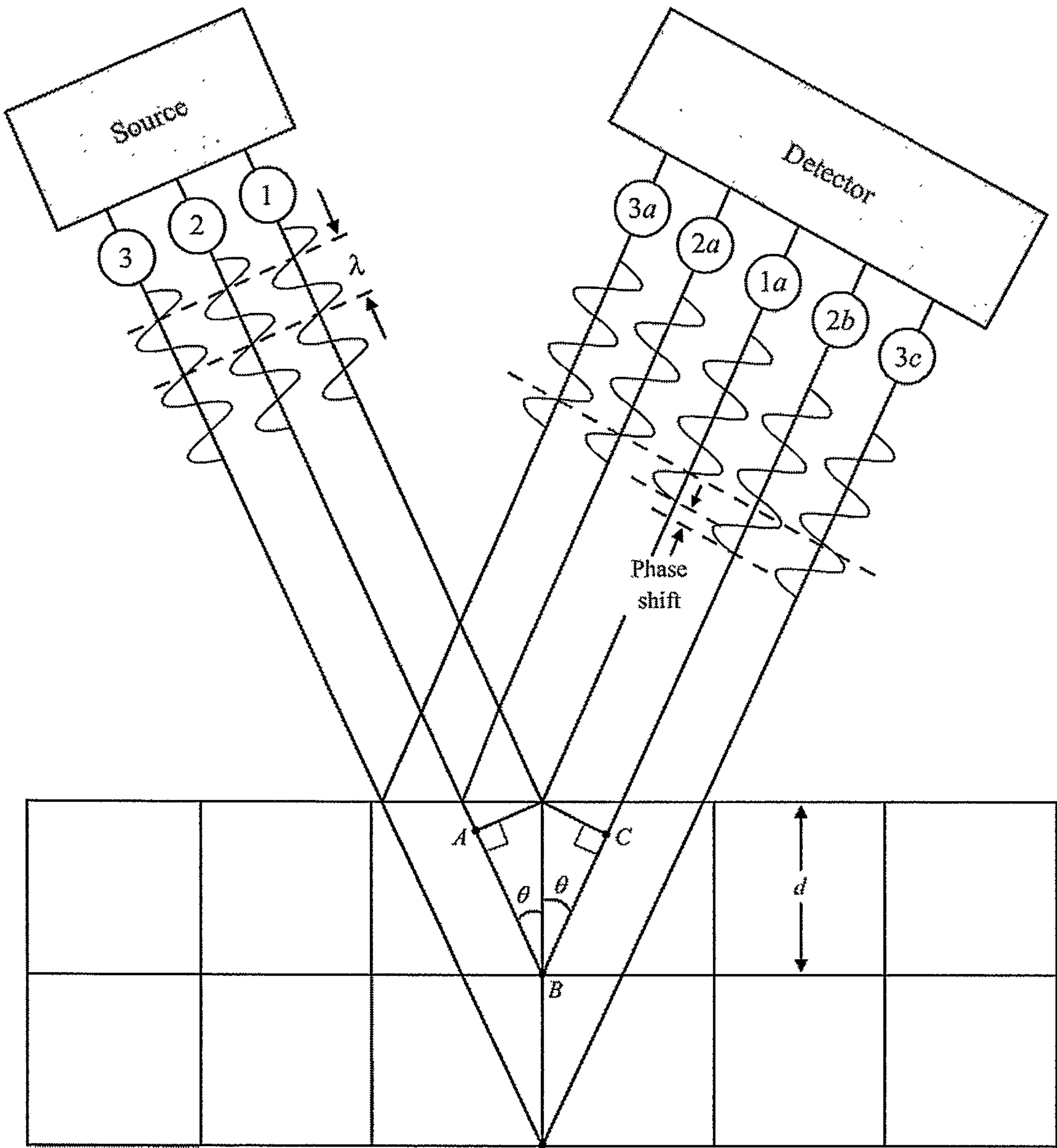
AB and BC represent the length of the line between the indicated points. As a result of this difference, there is a space shift between the two X-rays at the time they reach the detector. The two waves interfere constructively only if the path length difference is an integral of the X-ray wavelength. When the constructive interference occurs in an X-ray experiment, it is called the diffraction and the diffraction condition is represented by the following equation (Bragg's Law) [1]:

$$2d \sin \theta = n \lambda \quad (3)$$

where n is an integer. Bragg's law states that the diffraction occurs at particular values of θ , where θ is determined by the wavelength of the radiation and the interplanar spacing.

This can be summarised as follows. When an X-ray strikes an atom, it is scattered in all directions. In crystalline materials most of the beams scattered by the atoms interfere destructively. However, under some conditions the interference is constructive resulting in these reflected X-ray beams being detected in diffraction experiments. The conditions under which X-rays constructively interfere requires the angle to which the X-ray is scattered to equal the angle of incident X-rays, and the

difference in the path length of the two waves to be an integral number of wavelength ($n\lambda$).



Pathlength 2a – Pathlength beam 1a = 0
 Pathlength 2b – Pathlength beam 1a = AB + BC
 Pathlength 3c – Pathlength beam 1a = 2 (AB + BC)

Figure 4.7 The geometry of X-rays reflected from parallel atomic planes. The angle of incidence is θ , the wavelength of the x rays is λ , and the spacing between parallel planes of atoms is d [1].

4.2.3 Purpose

The present study adopted the X-ray diffraction technique for the following objectives.

1) Crystalline phases play an important role in the mechanical properties of brittle materials [6]. Therefore, X-ray diffraction was used to identify the crystalline phases in the materials studied, Empress 1, Empress 2 and an experimental ceramic.

2) Empress 1 and Empress 2 are glass ceramics and submitted to different heat treatment during fabrication processes in the dental laboratory, such as heat-pressing, colour firings (staining) and glazing. There was a concern, accordingly, as to whether these treatments trigger further crystallisation and subsequently affect the mechanical properties of these materials. X-ray diffraction was utilised to assess the effect of heat-pressing and further heat treatment on the crystalline phases of these investigated materials.

3) The present study also evaluated the effect of second heat-pressing (repressing) on the flexural strength of the investigated materials. X-ray diffraction was used to assess the effect of second heat-pressing on the crystalline phases of the investigated materials.

4.2.4 Specimen preparation.

For crystalline phase identification, several machined discs measuring 11.2×1 mm of new ingots of Empress 1 and Empress 2 (before pressing), and discs measuring 14×1 mm after pressing, and after all further heat-processing procedures, and after repressing were used. All samples were placed in the holder of a Siemens

diffractometer and scanned using Cu K α X-ray from 20° to 40° 2 θ degrees; a step size of 0.04° and 5 s-step interval were used.

4.2.5 Results

4.2.5.1 Empress 1

Before pressing, X-ray diffraction patterns of Empress 1 showed that leucite was the main crystalline phase, with the background intensity signals indicating the presence of an amorphous phase, the glass matrix. The main leucite peaks were detected at 2 θ values of 25.89°, 27.22°, 30.41°, and 31.36° with the dominant peak (highest intensity) at 27.22° matching the (400) crystallographic plane of the tetragonal phase (Figure 4.8). The X-ray diffraction standard file of leucite is 15-0047. The lattice parameters for the leucite tetragonal systems were as follows: $a=13.01$ Å, $b=13.01$ Å, $c=13.82$ Å and $\gamma=\alpha=\beta=90^\circ$.

After heat-pressing, similar X-ray diffraction pattern was achieved (Figure 4.9) and the major peaks were detected at the same diffraction angles. The same result was also achieved after further heat treatments, and after repressing, which denotes no alteration in the crystalline content (Figures 4.10 and 4.11).

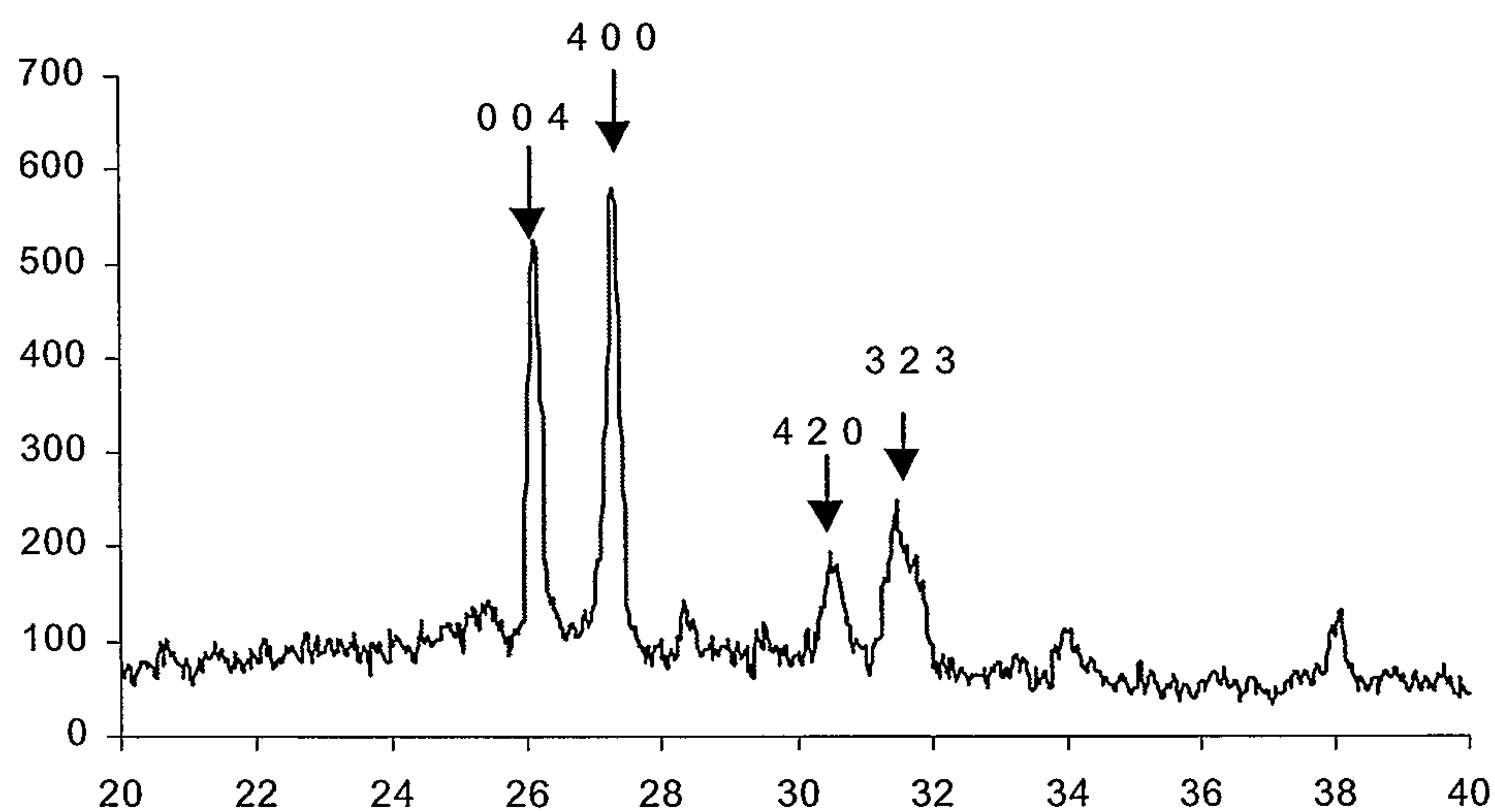


Figure 4.8 X-ray diffraction pattern of Empress 1 before heat-pressing, showing leucite peaks (arrowed) at 2 Theta values of 25.89, 27.22, 30.41, and 31.36 degrees

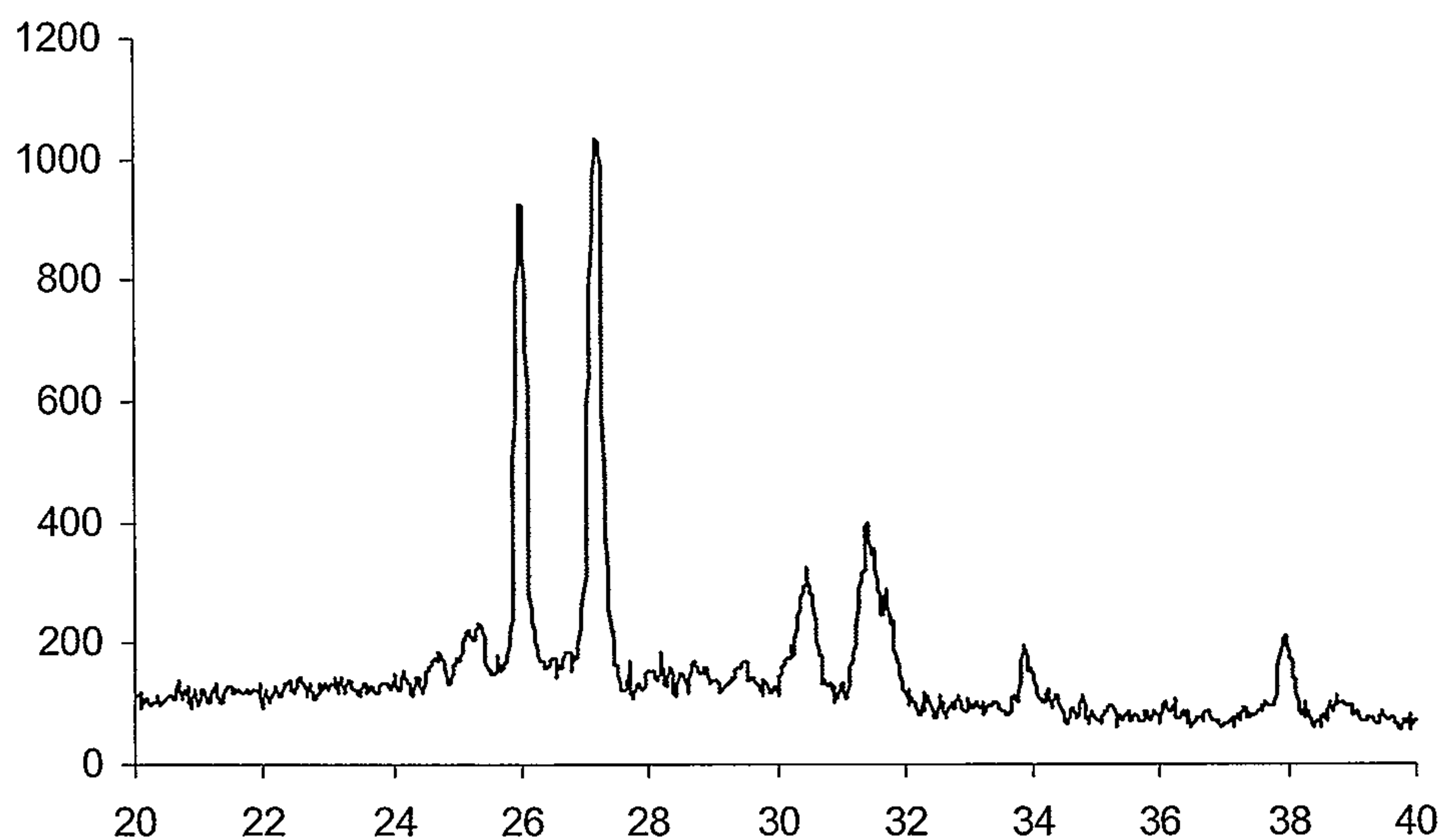


Figure 4.9 X-ray diffraction pattern of Empress 1 after heat-pressing, showing a similar diffraction pattern to the pattern achieved before pressing.

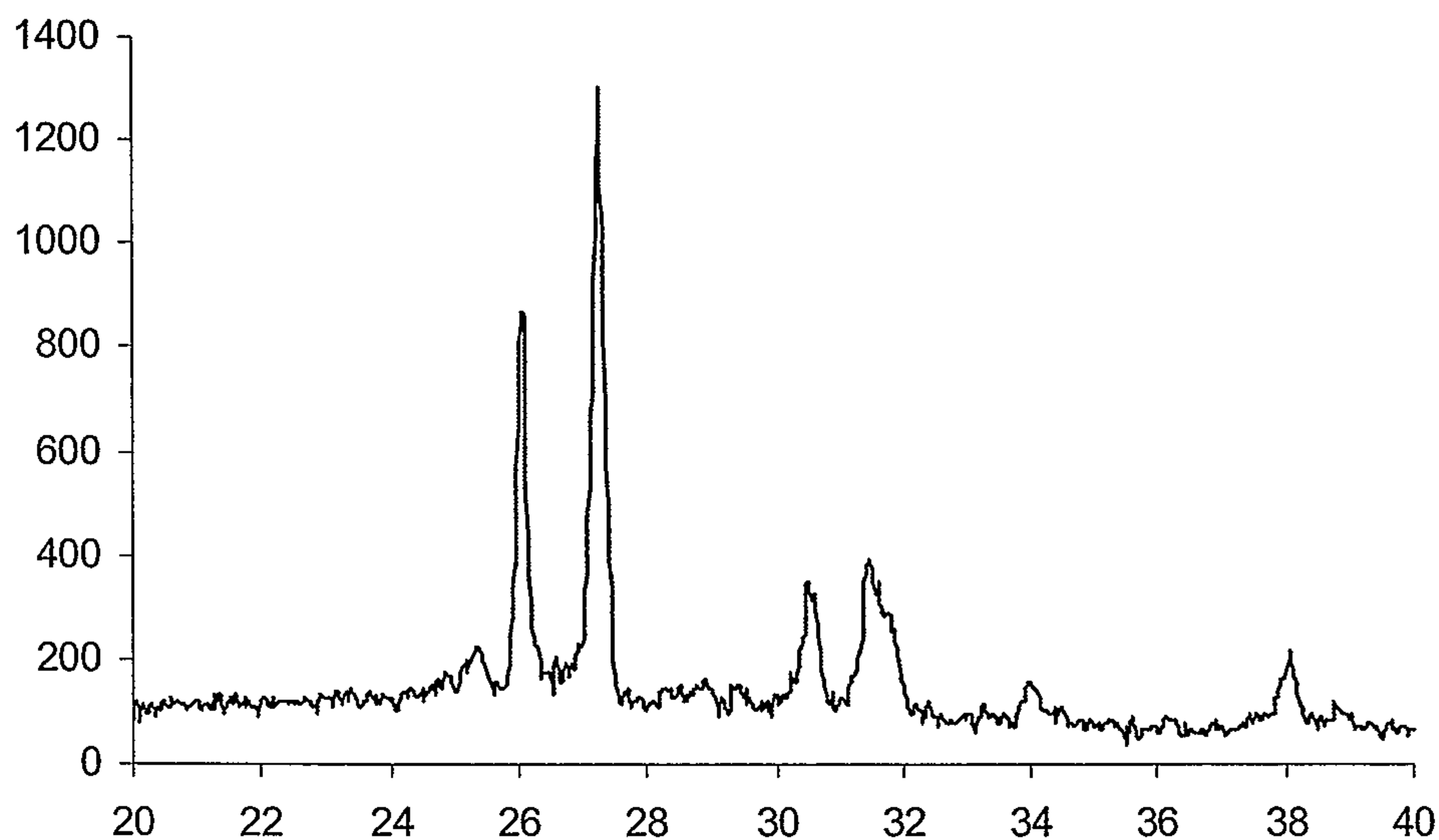


Figure 4.10 X-ray diffraction pattern of Empress 1 after further heat treatments, showing a similar X-ray diffraction pattern to those patterns achieved before and after heat-pressing.

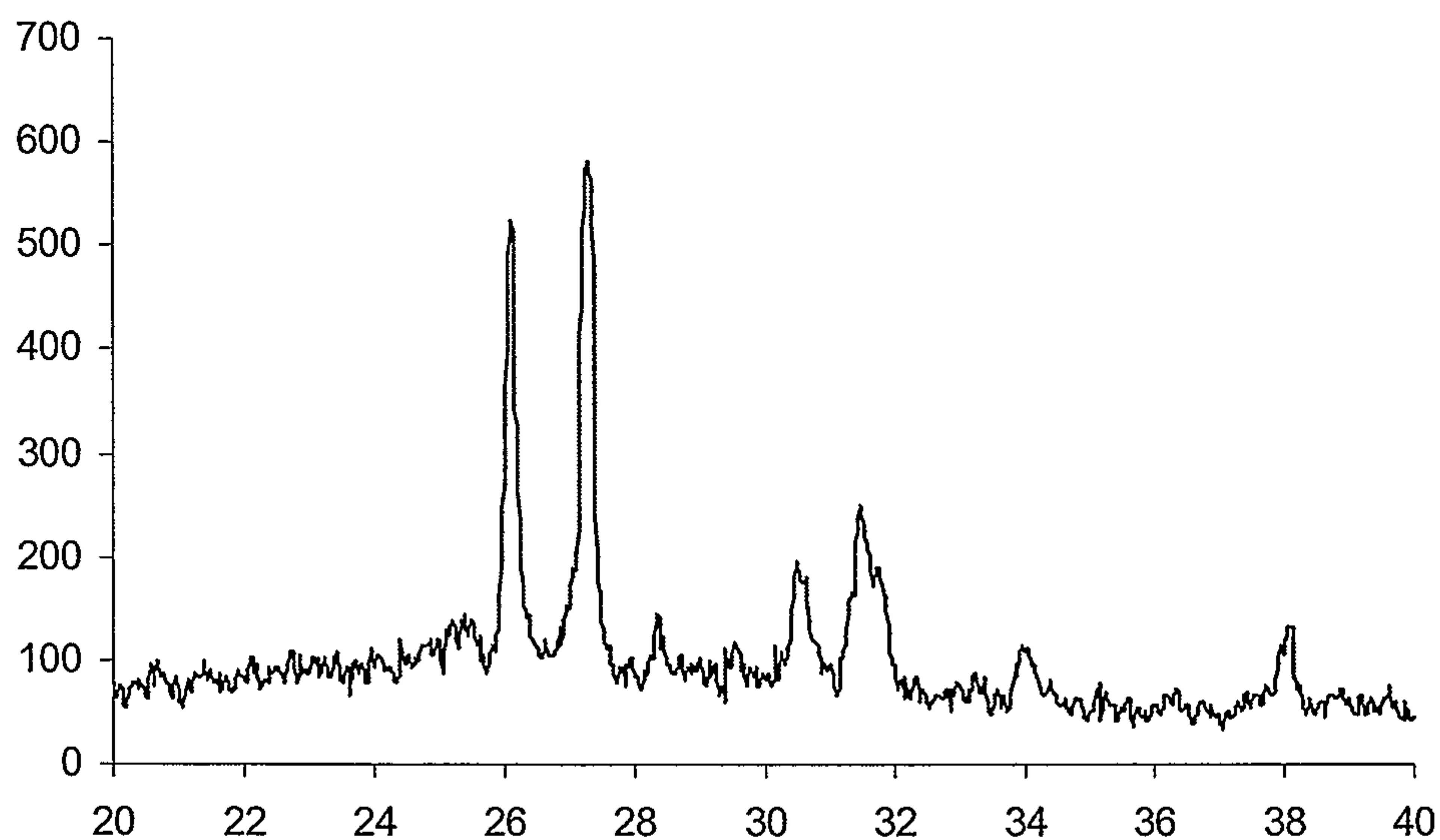


Figure 4.11 X-ray diffraction pattern of Empress 1 after repressing, showing similar results to those achieved before and after pressing, and after further heat treatment.

4.2.5.2 Empress 2

Before pressing, the X-ray diffraction pattern of Empress 2 showed that it is also a glass-containing ceramic material. The pattern is almost identical with the expected intensities for the JCPDS diffraction data of lithium disilicate crystals randomly aligned. The main peaks of the lithium disilicate were observed at diffraction angles of 23.9, 24.45, 25, 30.5, 30.7, 33.3, 37, 37.8, 38.3, and 39.4 degrees (Figure 4.12). The dominant peak (highest intensity) was detected at 25 degrees, which corresponded to the (111) crystallographic plane of the monoclinic phase as predicted from the X-ray diffraction standards file (40-0376) lithium silicate. The lattice parameters for the orthorhombic systems are as follows: $a=5.822 \text{ \AA}$, $b=14.6 \text{ \AA}$, $c=4.775 \text{ \AA}$, and $\gamma=\alpha=\beta=90^\circ$

The two minor peaks that were detected at diffraction angles of 22.3 and 23.1 corresponded to the lithium orthophosphate, Li_3PO_4 standard peaks predicted from the X-ray diffraction file (15-0760).

After pressing, no additional peaks were observed and similar X-ray diffraction was observed. However, different crystal orientations may have occurred upon pressing as all major peaks changed their relative intensities. Another feature evident after pressing was a minor decrease in the background intensity of X-ray diffraction, which might be due to better homogenous dispersion of the crystals or further crystallisation of the glassy matrix. Minimal alteration in the positions of minor peaks was also noticed (Figure 4.13).

After further heat treatments, the X-ray diffraction pattern was quite similar to that achieved after pressing. However, a further background intensity decrease, and minimal positional alteration for the minor peaks were observed (Figure 4.14).

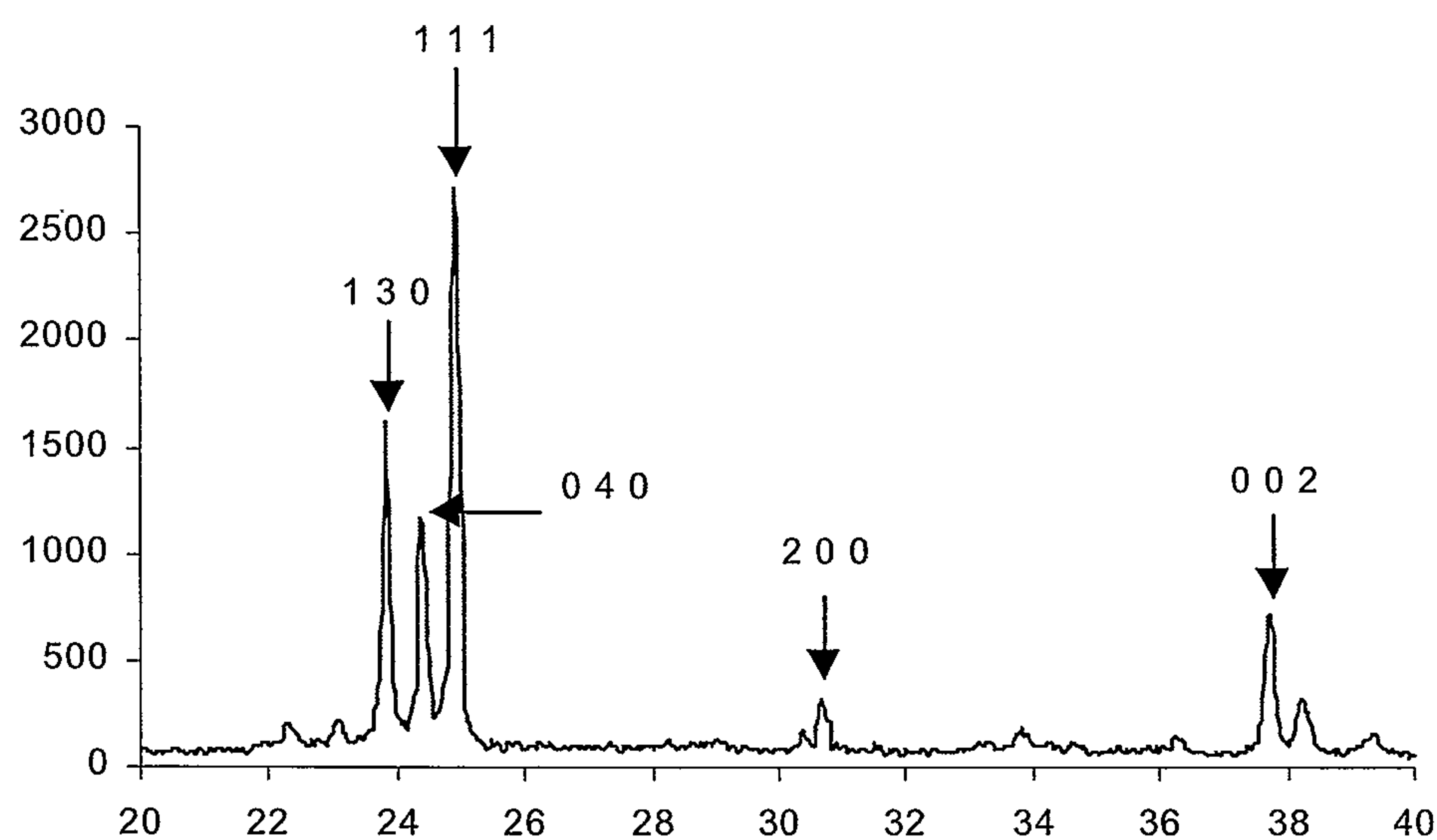


Figure 4.12 X-ray diffraction pattern of Empress 2 before heat-pressing, where arrows indicate the highest three peaks (at 23.9, 24.45 and 25 degrees) of the lithium disilicate.

After repressing, peak positions and heights were almost identical to those achieved after pressing (Figure 4.15).

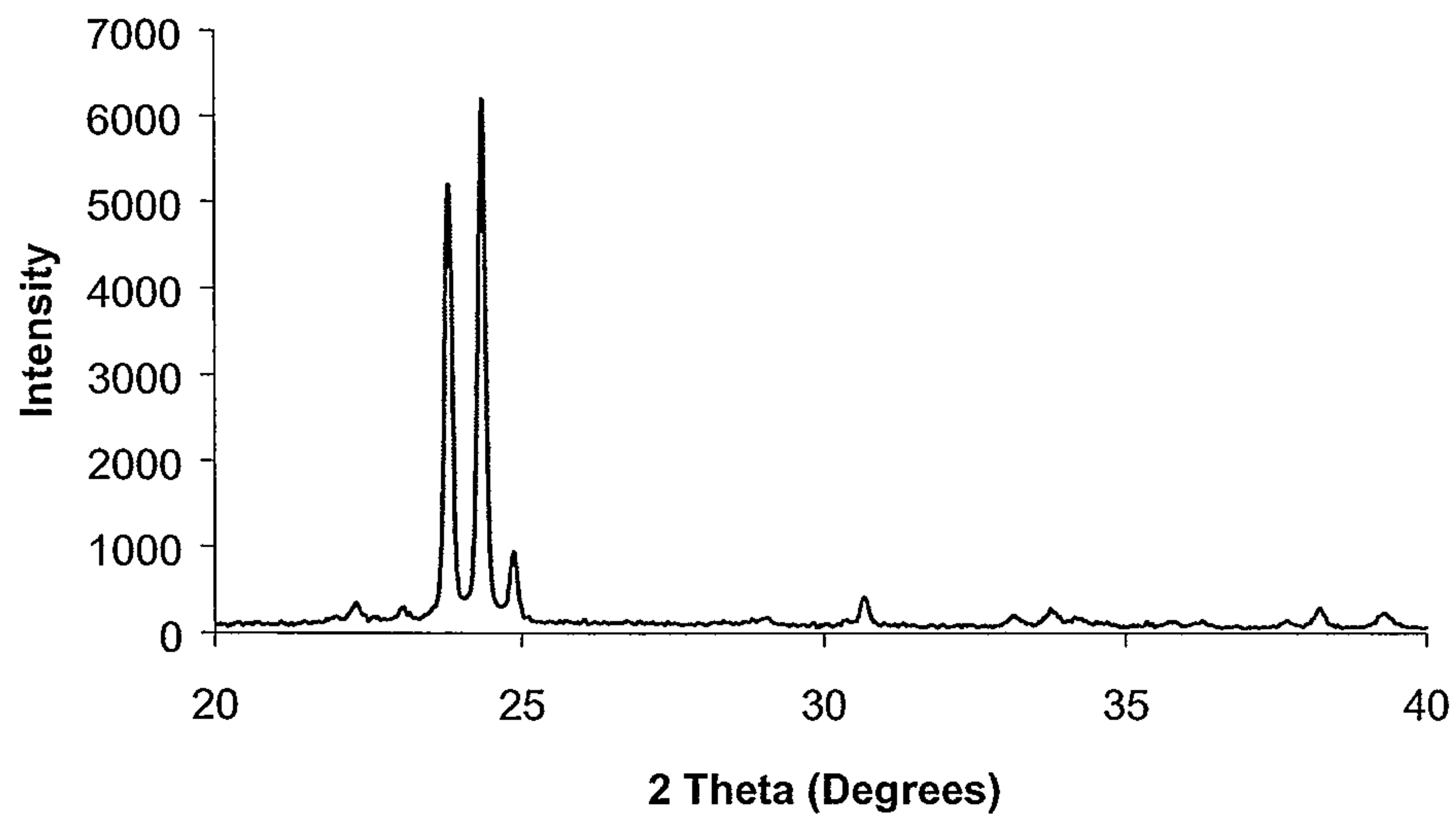


Figure 4.13 X-ray diffraction pattern of Empress 2 after heat-pressing, showing different lithium disilicate peak positions and intensities.

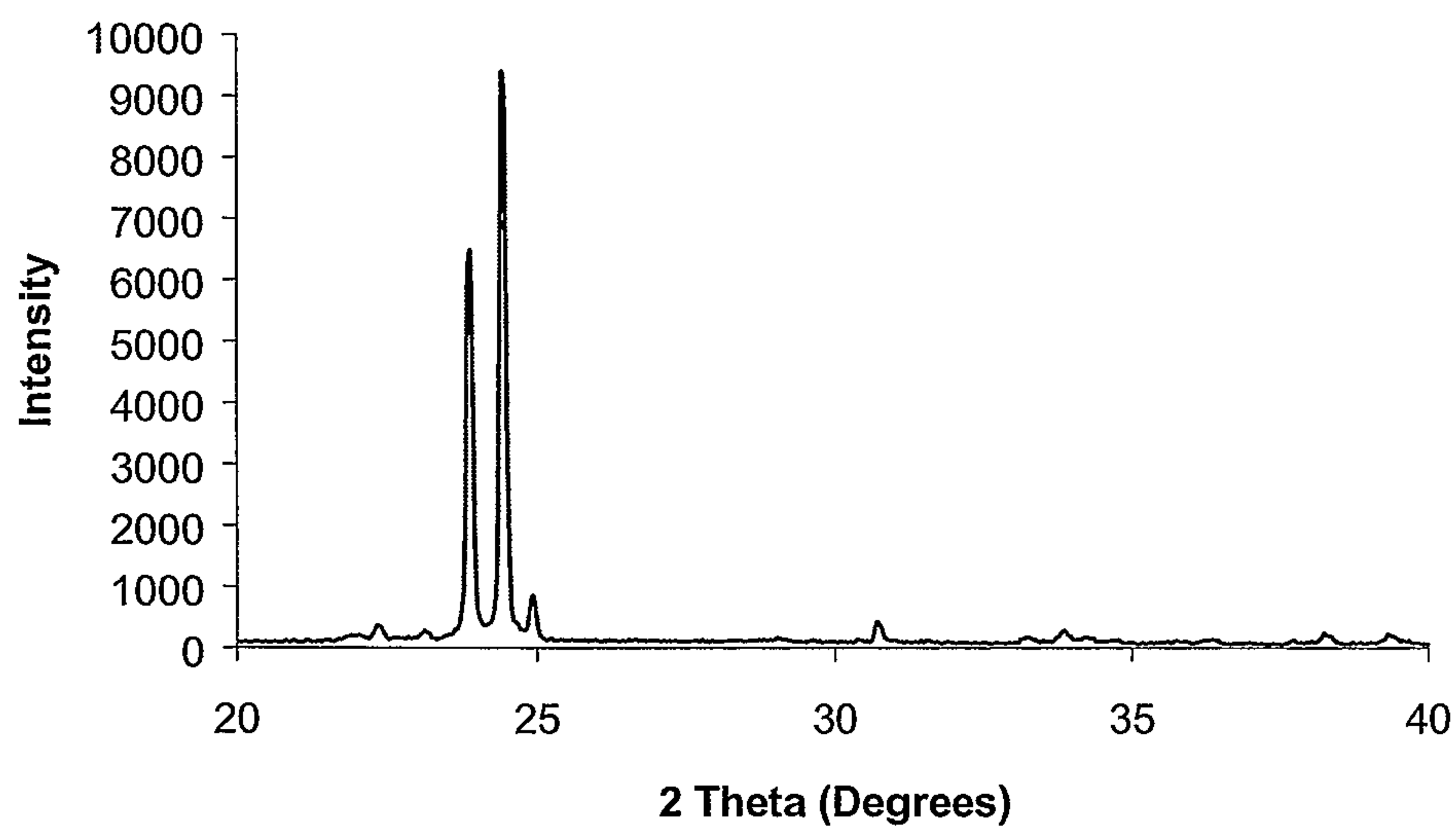


Figure 4.14 X-ray diffraction pattern of Empress 2 after further heat treatments, showing a further background intensity decrease.

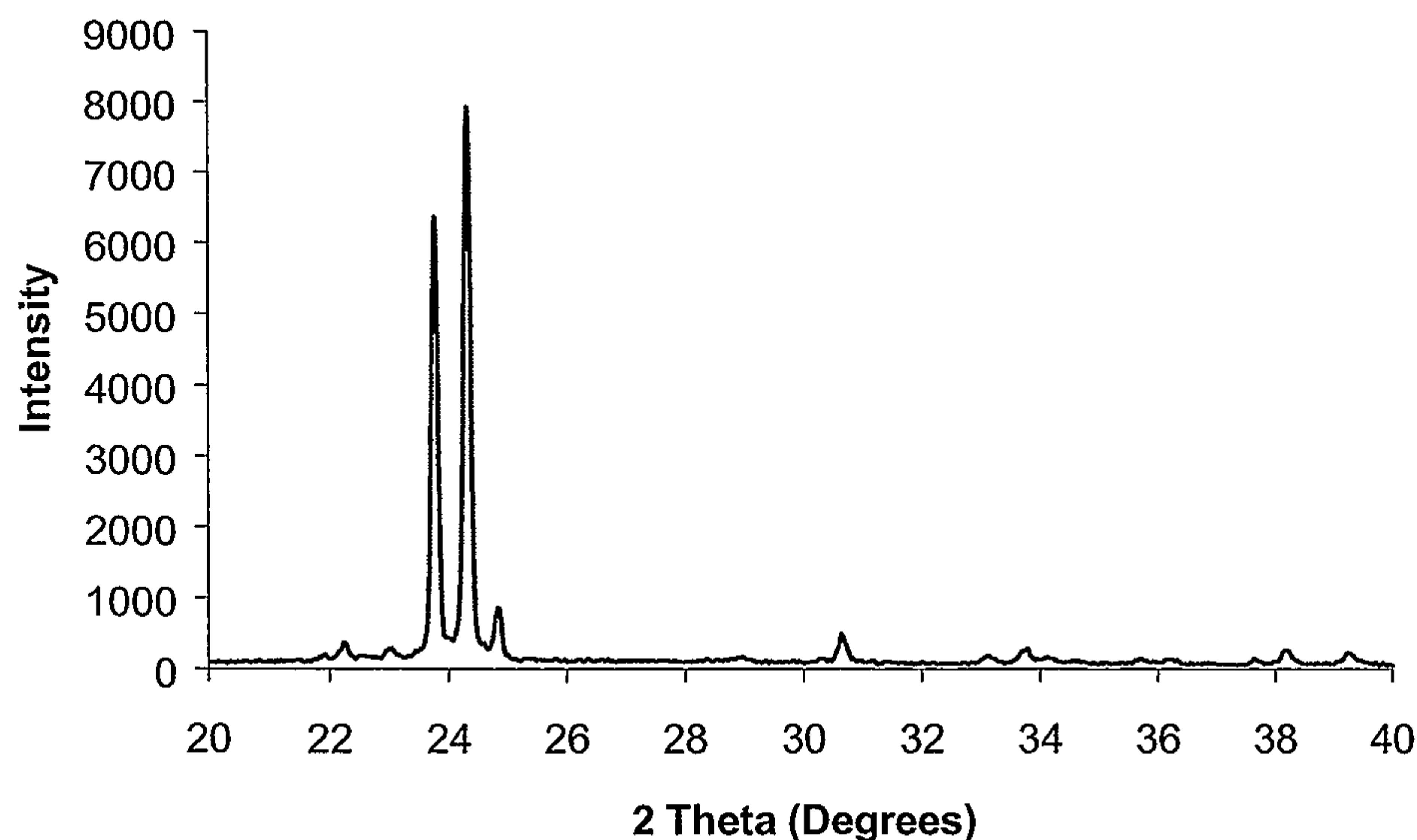


Figure 4.15 X-ray diffraction pattern of Empress 2 after repressing, showing an identical pattern to that observed after first pressing.

4.2.5.3 Experimental ceramic

Because this material was supplied by the manufacturer in the pressed state, the X-ray diffraction was performed only after pressing. The X-ray diffraction pattern of this material showed that it is a glass ceramic material and the lithium disilicate is the main crystalline phase. The main peaks of the lithium disilicate were observed at diffraction angles of 23.85, 24.35, 24.9, 30.4, 30.8, 33.2, 37.5, 37.8, 38.3, and 39.3 degrees. The dominant peak (highest intensity) was detected at 24.9 degrees, which corresponded to the (111) crystallographic plane of the monoclinic phase as predicted from the X-ray diffraction standards file (40-0376), lithium silicate (Appendix 4.2). The lithium orthophosphate peaks were also detected at diffraction angles of 22.3, 23.1 degrees. Apart from the main lithium disilicate positions of the experimental ceramic and Empress 2, their X-ray diffraction patterns are almost identical (compare Figures 4.13 and 4.16).

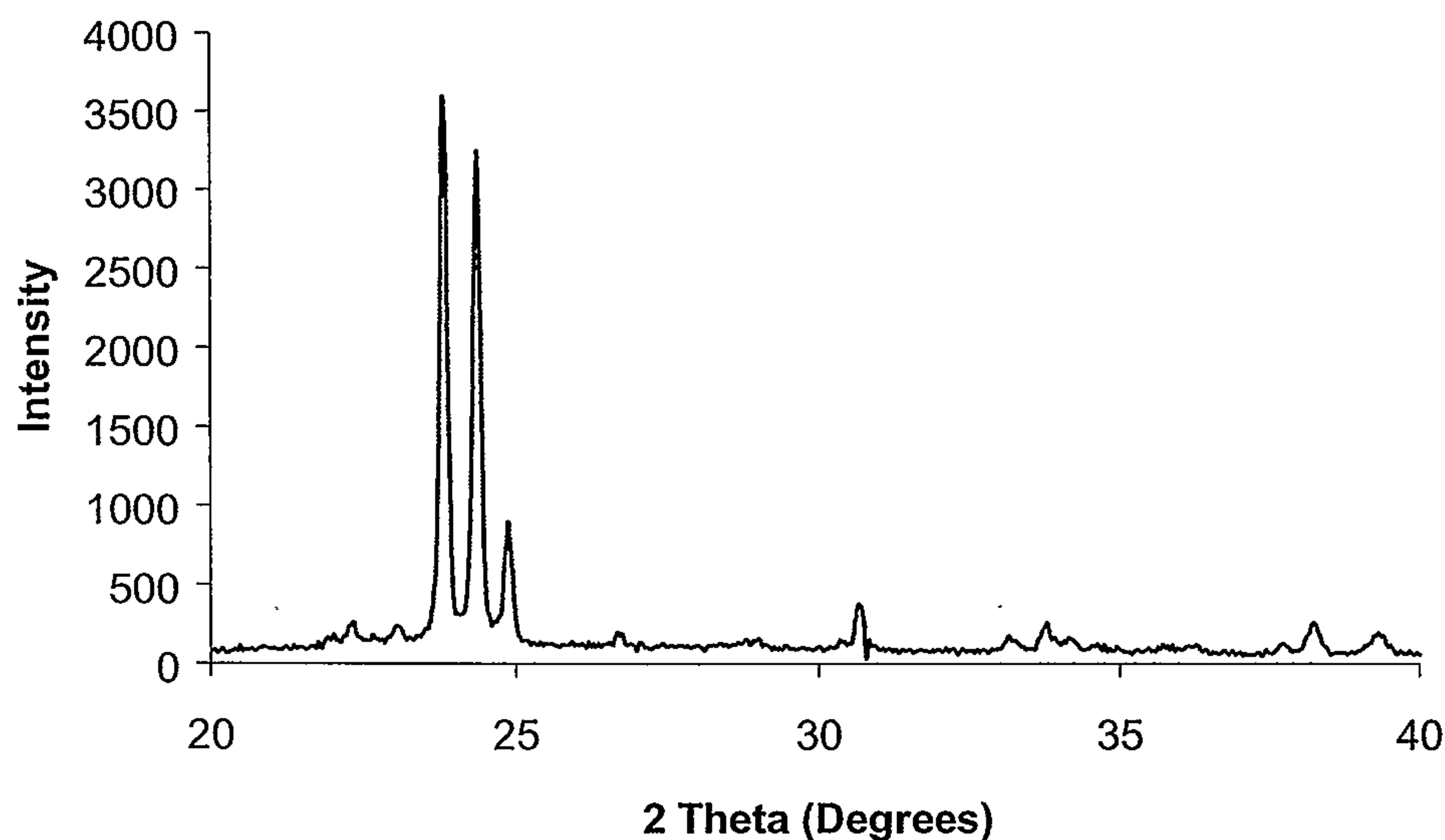


Figure 4.16 X-ray diffraction pattern of the new experimental ceramic, showing a similar pattern to Empress 2.

4.2.6 Discussion

X-ray diffraction results showed that all materials in this study are glass-ceramic systems. Leucite is the main crystalline content in Empress 1. This system demonstrated no change after pressing, heat treatment or repressing. This is very consistent with the mechanical properties results, which showed no change after such treatments. This is further explained in Chapters 6 and 7.

The main crystalline portion in both Empress 2 and the experimental ceramic is lithium disilicate, as all main peaks of the two materials corresponded to the lithium disilicate standard peak positions in the X-ray diffraction file. Different positions and relative intensities of the Empress 2 major peaks were observed after heat-pressing, which was attributed to the texture developed by alignment of the highly acicular monoclinic lithium disilicate crystals. During pressing, the flow within the sprue and mould may have assisted in aligning these grains, thereby resulting in a non-random

crystal orientation and the long axis of the of these crystals was oriented parallel to the surface of the disc. After additional heat treatment, Empress 2 showed a further decrease in background intensity decrease, which might be a result of further homogenous crystallisation within the glass matrix. The effect of such variations on the mechanical properties are appraised in Chapter 6.

4.2.7 Conclusion

From the X-ray diffraction study, it can be concluded that:

- 1) Empress 1 is a glass-containing ceramic material and leucite is the main crystalline content.
- 2) Empress 1 demonstrated no change upon pressing, further heat treatments or repressing. This denotes that this material might have reached the maximum crystallisation during fabrication processing in the factory.
- 3) Empress 2 and the experimental ceramic material are also glass ceramic materials and the main crystalline phase is lithium disilicate.
- 4) X-ray diffraction analysis revealed the similarities of Empress 2 and the experimental ceramic and showed that pressing significantly influenced the texture of the lithium disilicate crystals.

4.3 Microstructural investigations

4.3.1 Introduction

When studying the properties of materials, it is important to examine the structural elements, and defects that might be present. This will allow the proper understanding of a relation between defects, structural elements and properties. Once this is established, a better understanding of materials' properties is possible. The structural investigations are usually performed at macroscopic or microscopic levels [4].

4.3.2 Macroscopic investigation

Macroscopic investigations are those used on the overall composition of a material. The features investigated are large enough to be seen by a human eye or low-power microscope. Despite allowing the examination of only the gross features of a material, this type of examination is very helpful and may obviate the need for more complicated techniques. This is because more sophisticated techniques may be costly and require more time for a material's preparation [4].

4.3.3 Microscopic investigations

Most materials have constituent grains that are of microscopic dimensions and may be in the range of microns. These must be investigated using specific microscopes, and the features examined are termed microstructural. Microstructural examination discloses of a material's structure in greater detail. However, special specimen preparation, mounting and equipment are necessary [4]. The microscopes that are used in such examination are either of transmitted light or reflected light. Thin sections of rocks or wood, for example, are examined under a transmitted light

microscope. Because of metals' opacity, they must be examined using reflected light microscopes [4].

4.3.4 Scanning Electron Microscope

The scanning electron microscope is an extremely useful tool for microstructural investigation. A specimen's surface for such an examination may be polished and etched. More importantly, the surface must be electrically conductive. For nonconductive materials, a very thin metallic surface coating must be applied. The surface is then scanned with an electron beam, and the reflected or back-scattered beam of electrons is collected then displayed at the same scanning rate on a cathode ray tube. The resultant image represents the features of the specimen's surface and can be photographed [2].

4.3.5 Purpose

In the microstructure section the following issues were investigated:

- 1) The microstructural features of Empress 1, Empress 2 and the experimental ceramic material, which include the crystals' size, shape, and distribution.
- 2) The same microstructural features after pressing and repressing.

4.3.6 Specimen preparation

Several finely polished specimens were cleaned with ethanol and etched with HF acid. The etching procedure for microstructural observations was different according to the material investigated. Empress 1 was etched with 0.2 vol% of HF acid for 1

minute; Empress 2 and the experimental ceramic were etched with 10 vol% HF acid (a range of time from 2 to 20 minutes).

4.3.7 Results

4.3.7.1 Empress 1

A microstructural investigation of Empress 1 before pressing showed a dispersal of various shapes and sizes of many small (measuring 0.5 to 3.5 μm in diameter) tetragonal leucite crystals embedded in a glass matrix. Twinning and fracture within crystals can be seen in some individual crystals (Fig. 4.17). Clusters of leucite crystals and vacant sites of glass matrix were also observed (Figs. 4.18 and 4.19).

After pressing, similar microstructural features were noticed. However, a more uniform distribution of leucite crystals within the glass matrix was noticed, (compare Figures 4.18 and 4.20, which have been taken at the same magnification). Extensive twinning of the leucite crystals was repeatedly observed in both small and large leucite crystals (Figure 4.21). Some images showed signs of microfracturing within the glass matrix and surrounding the leucite crystals (Figure 4.22). Noticed in a few images the presence of accumulated microcracking damage within a glass matrix, which results from scratching damage during either grinding or polishing (Figure 4.23).

The microstructural features after repressing were identical to those found after pressing (compare Figure 4.21 and Figure 4.24). Also, there was no better crystal distribution than that observed after pressing (compare Figure 4.25 and Figure

4.26). Similar to the material after pressing, areas of extensive glass microcracking were also observed (Figure 4.27).

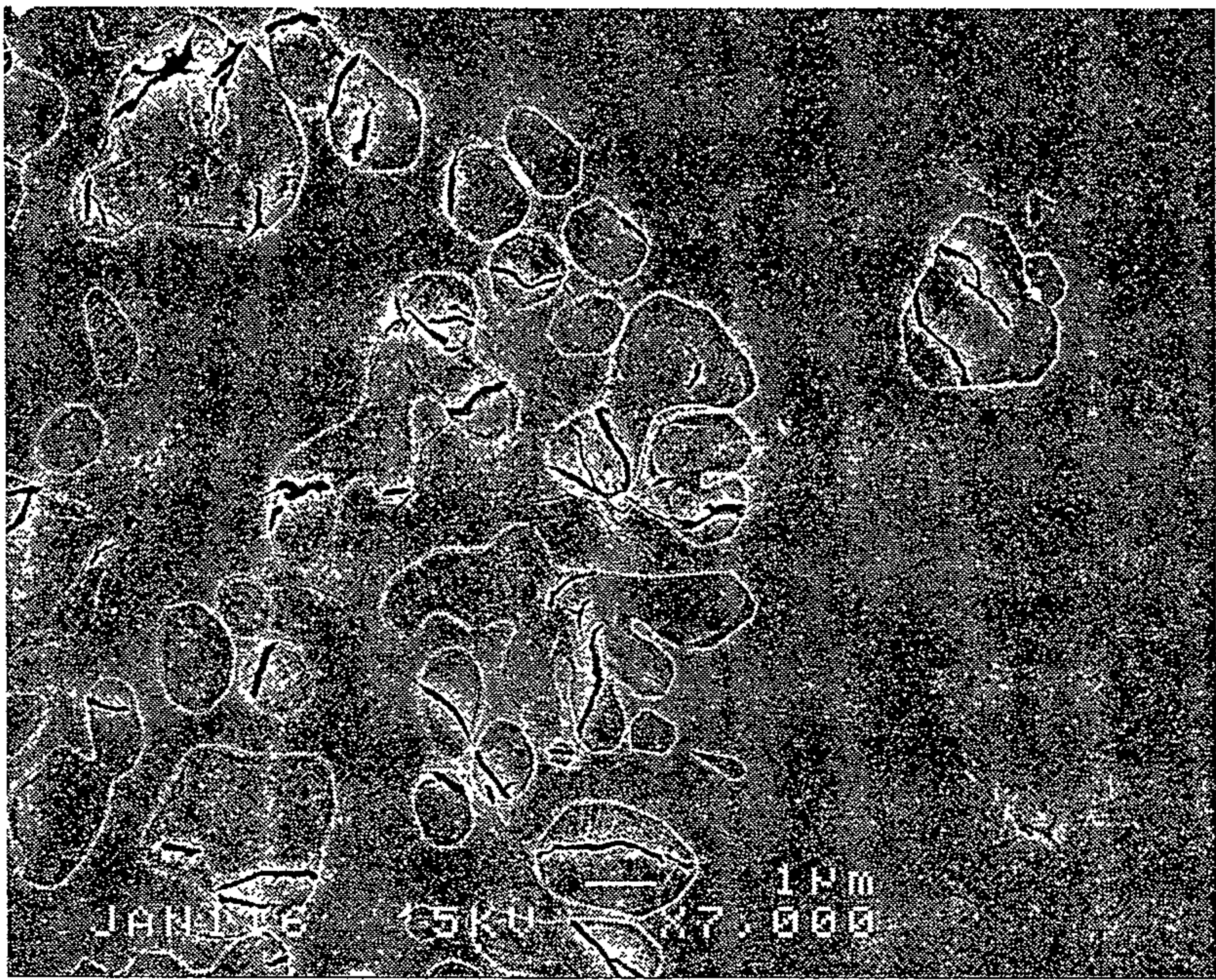


Figure 4.17 Small leucite crystals are embedded in a glass matrix of a specimen before pressing, where some crystals appeared cracked and others are twinned.

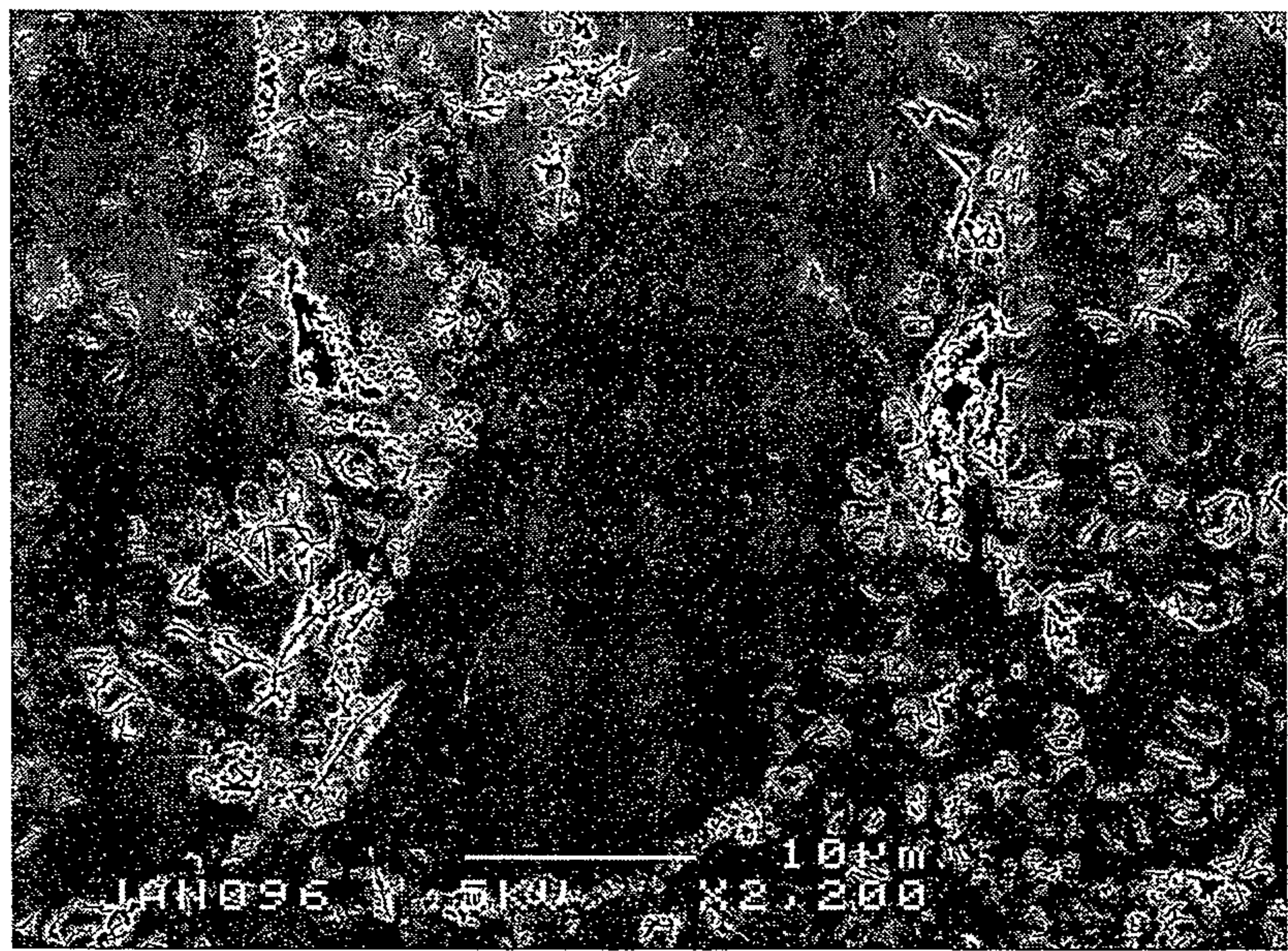


Figure 4.18 Clusters of leucite crystals in Empress 1 and vacant sites of glass matrix before pressing (magnification x 2, 200).

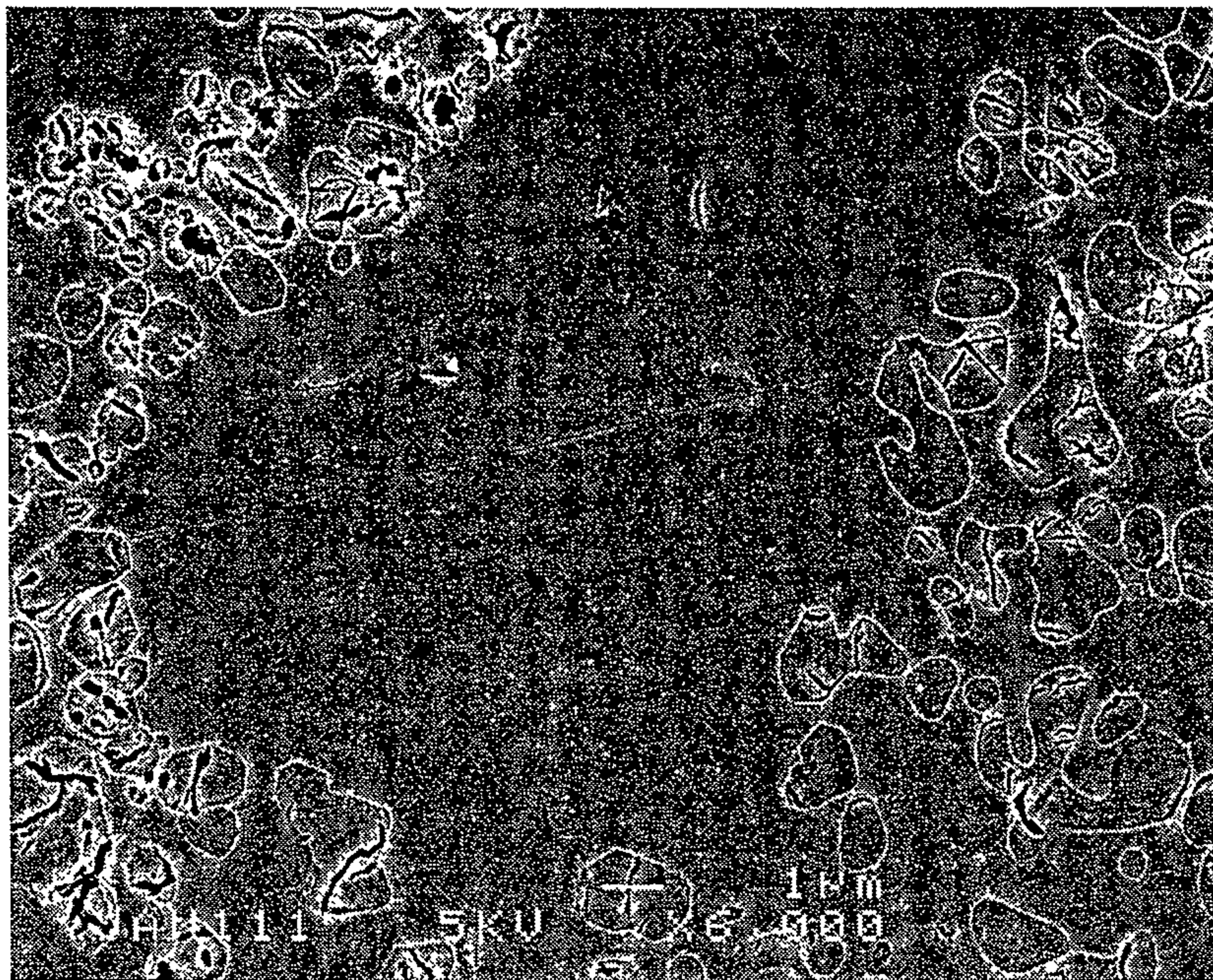


Figure 4.19 Clusters and cracking of leucite crystals before pressing.



Figure 4.20 Better distribution of leucite crystals than that observed before pressing (magnification 2200 x).



Figure 4.21 Extensive twinning of leucite crystals after pressing (magnification 8000 x).

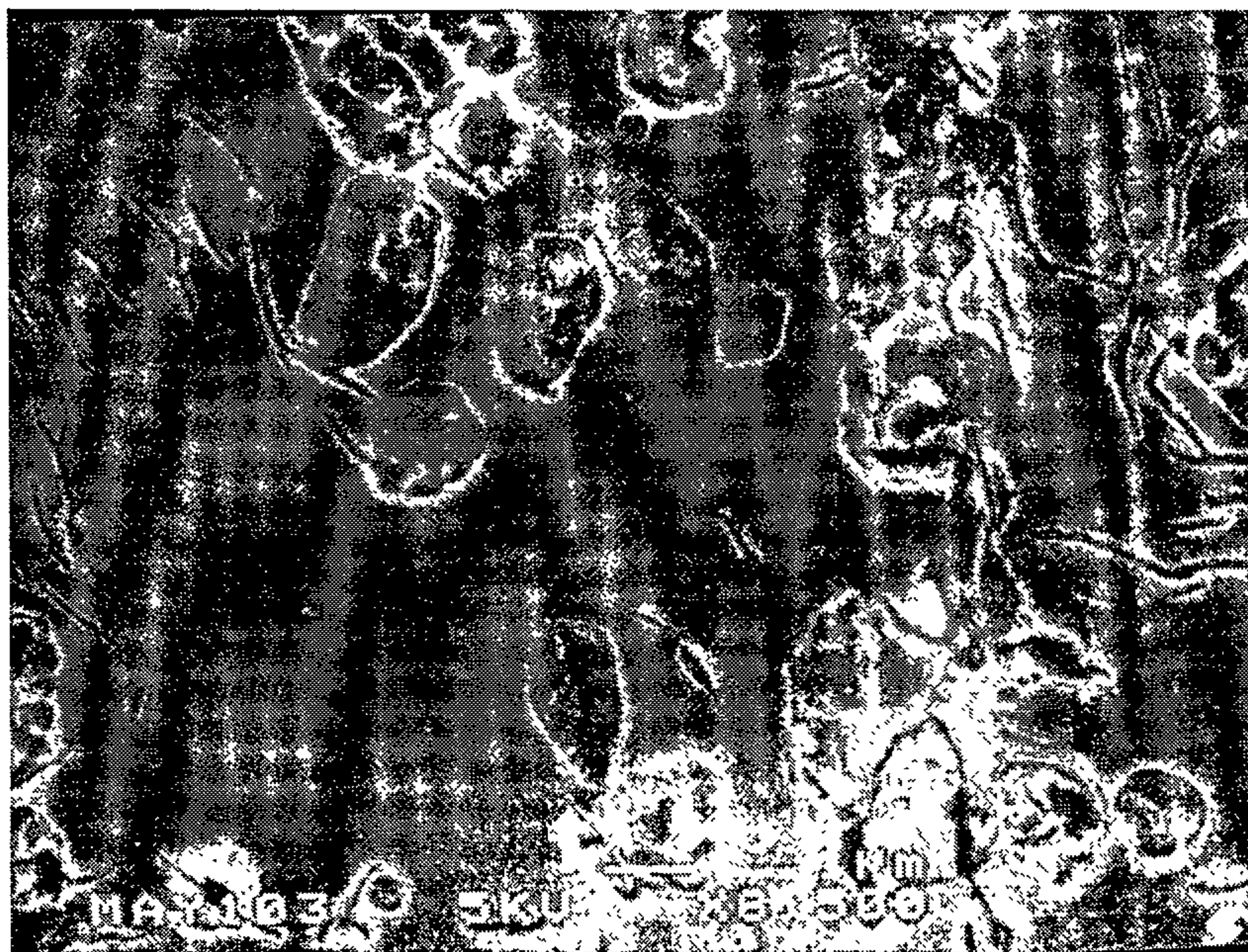


Figure 4.22 Microfracturing within the glass matrix and surrounding the leucite crystals was observed in some images.

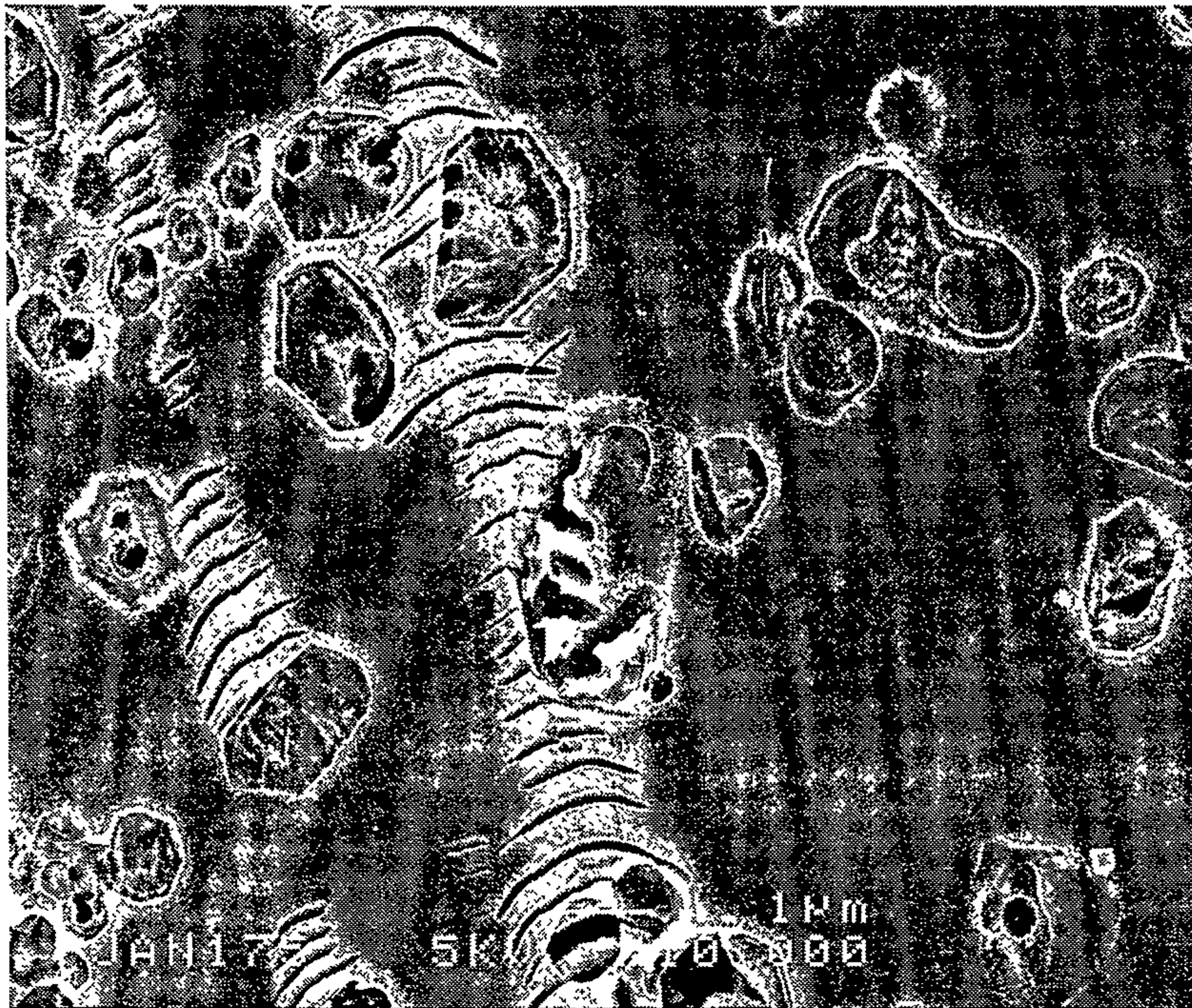


Figure 4.23 Areas of accumulated cracks resulted from scratching damage during polishing or grinding after pressing (10000 x).

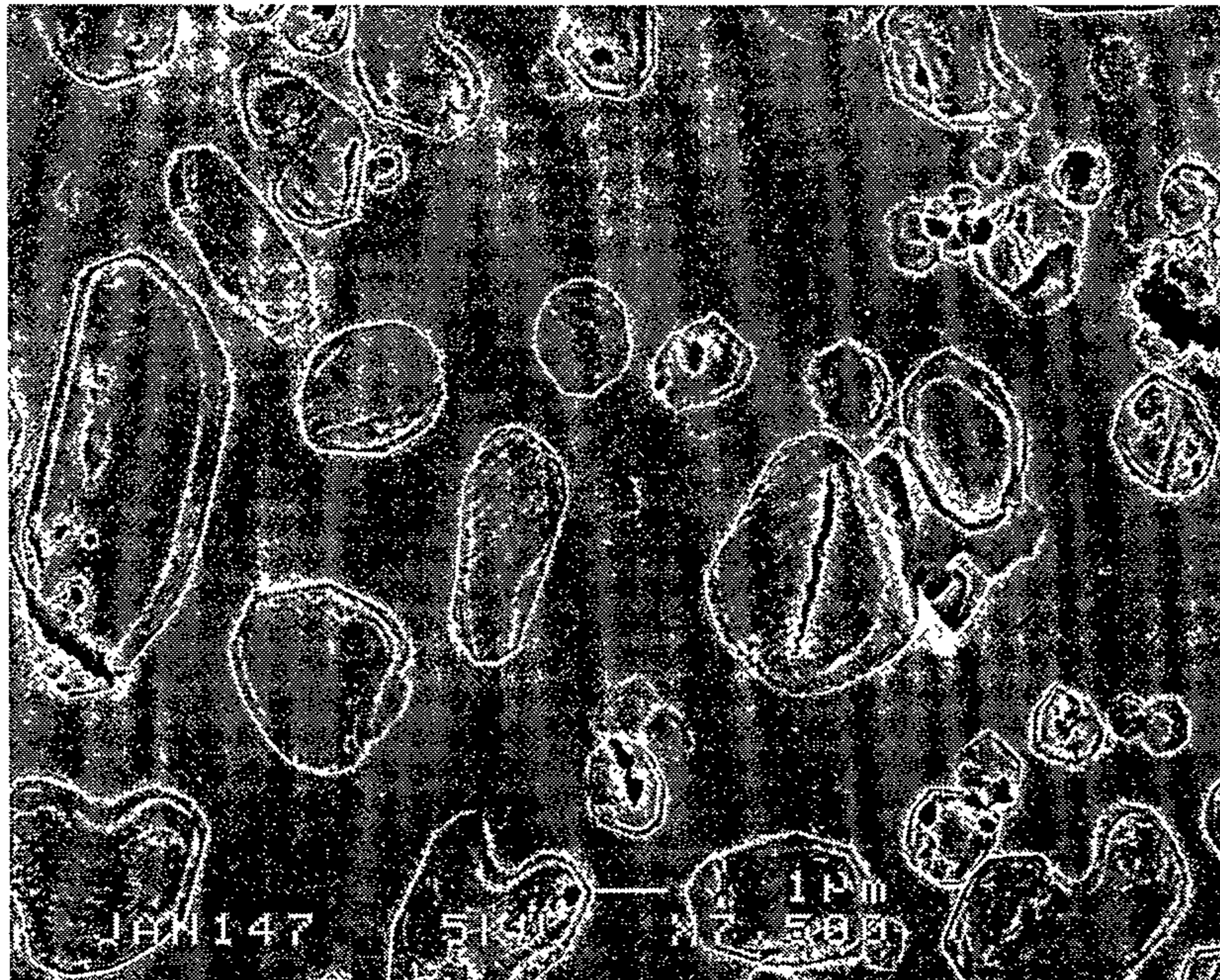


Figure 4.24. Microstructural features of Empress 1 after repressing were similar to those after pressing, where glassy areas, leucite crystals and twinning can be seen.

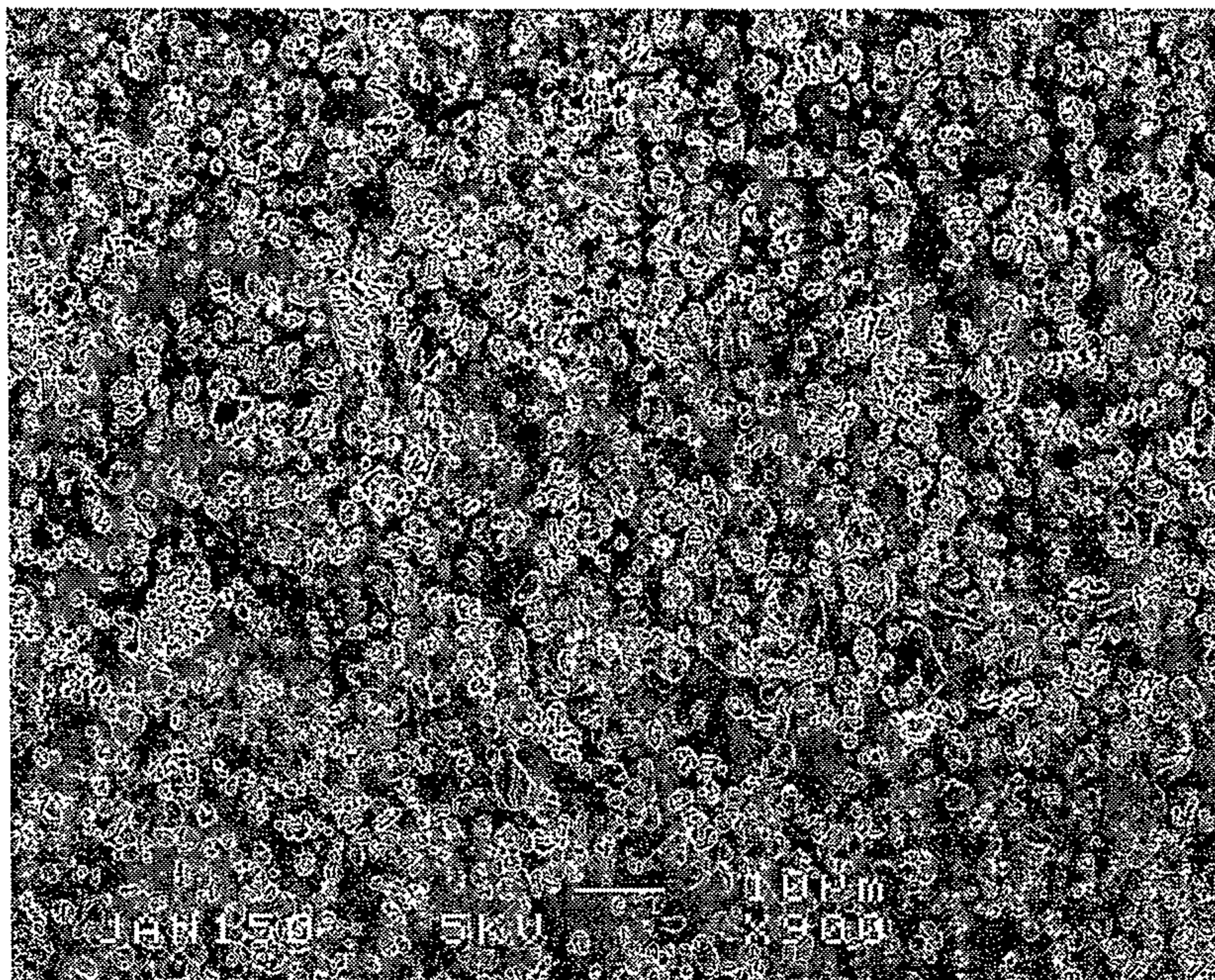


Figure 4.25 Homogenous distribution of leucite crystals in a glass matrix after pressing.

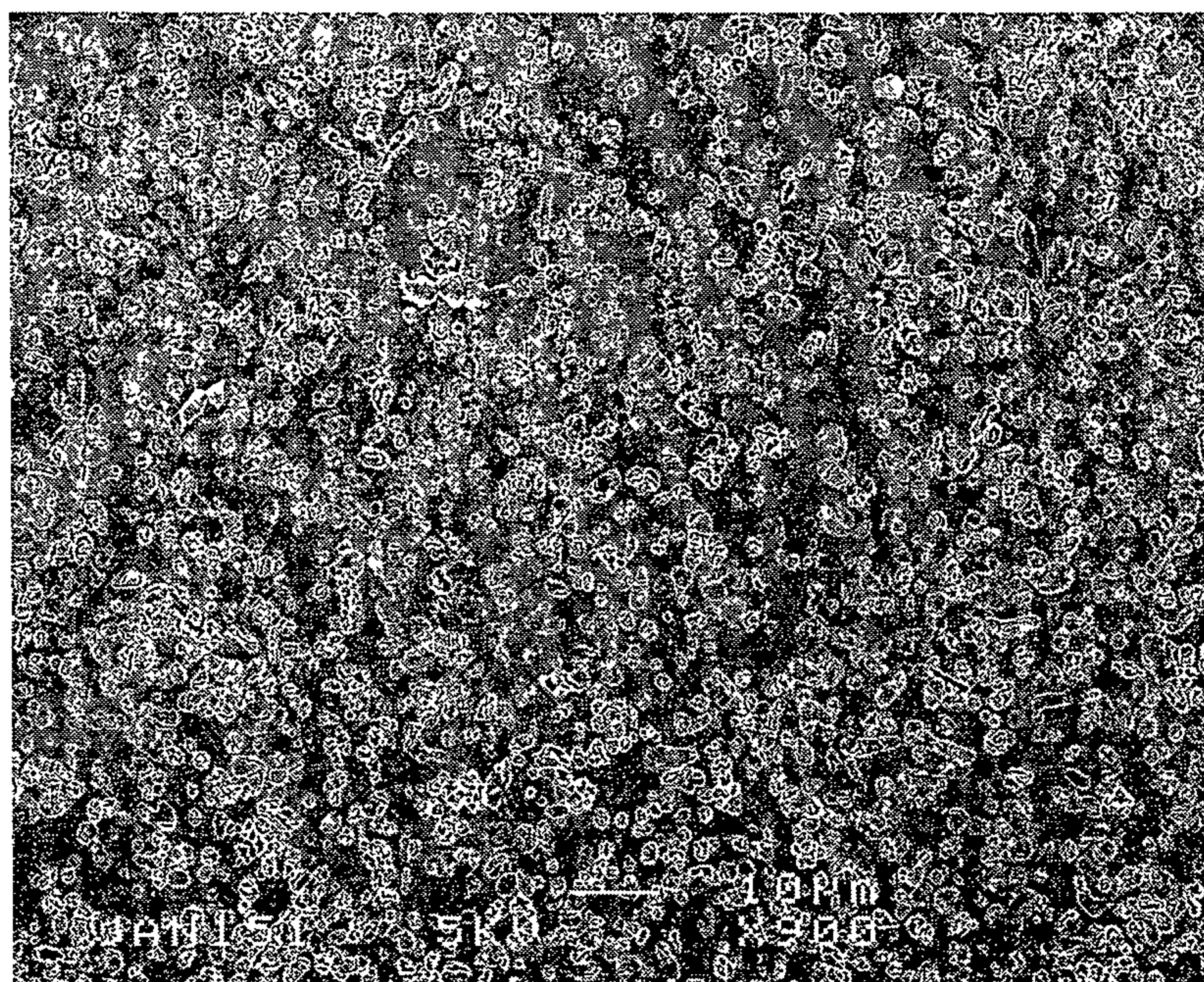


Figure 4.26 Similar homogenous crystal distribution was also observed after repressing.

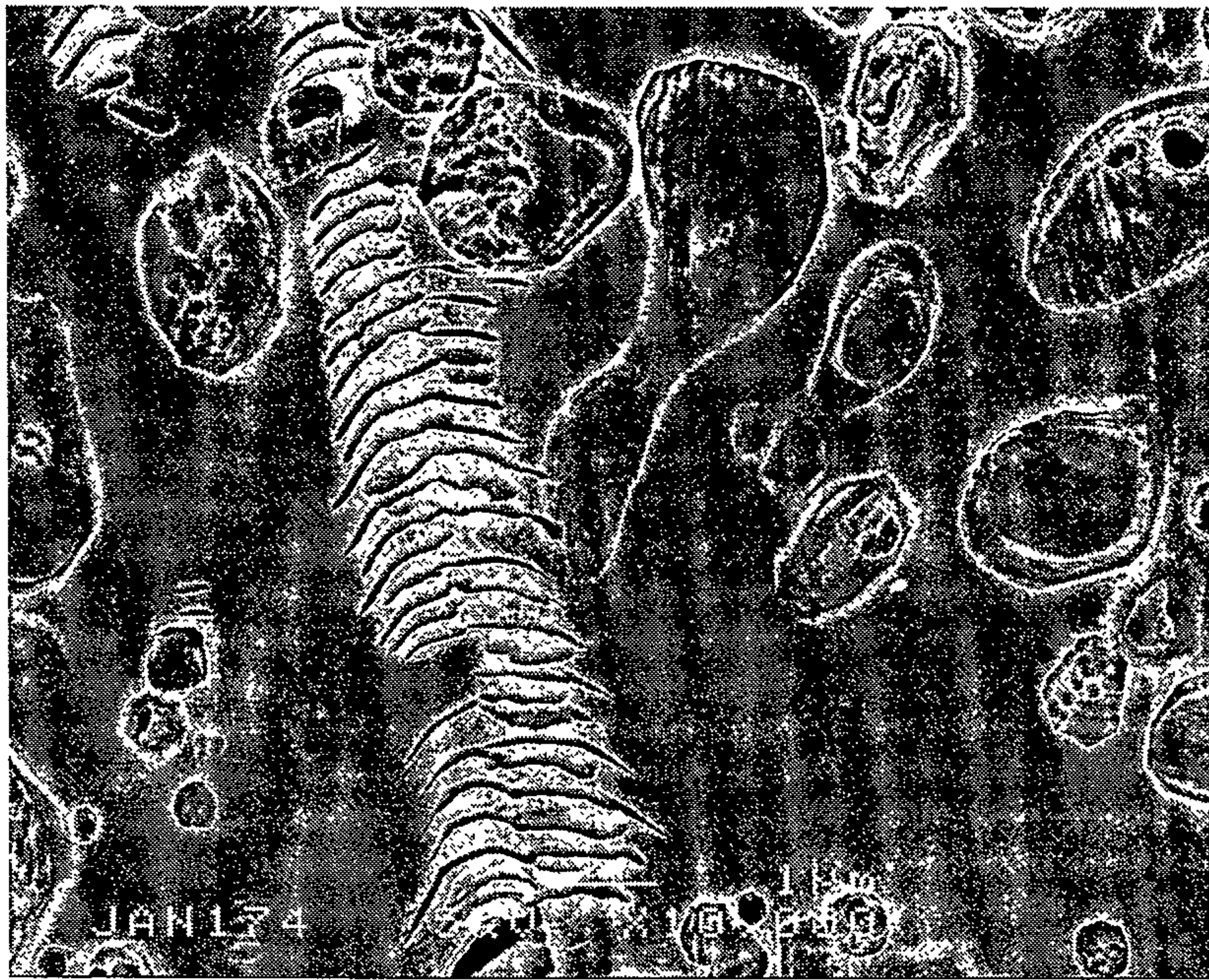


Figure 4.27 Area of extensive glass microcracking after grinding and polishing of a repressed sample of Empress 1 (10000 x).

4.3.7.2 Empress 2

The microstructure of Empress 2 is composed of dense numerous elongated lithium disilicate crystals. These crystals are homogenously distributed in a multi-directional manner within a glass matrix. The size of these crystals ranged from 2 to 4.5 μm in length, and were approximately 0.8 μm in diameter (Figure 4.28). The other crystalline phase, lithium orthophosphate crystals detected using the X-ray diffraction, could not be observed, which might be due to its greater solubility upon acidic etching.

A similar microstructure was noticed after pressing. However, the lithium disilicate crystals became more aligned, as crystals appeared oriented in one direction, that is, parallel to the pressing direction. This alignment was very prominent in bar-shaped specimens, used for the 3-point bending test (Figure 4.29) and in the sprue

specimens (Figure 4.30). In disc-shaped specimens, the preferred orientation of crystals can also be seen in some areas of the disc, but some crystals are clamped together with slightly different directions (Figure 4.31). Crystals also appeared larger than before pressing; the mean crystal size was $7\mu\text{m}$.

Repressing resulted in an alignment of the lithium disilicate crystals as noticed after first pressing. The crystals alignment in disc-shaped specimens, where crystals are aligned in groups that have different directions is given in Figure 4.32. In bar-shaped specimens the alignment of most crystals appeared in a single direction (Figure 4.33). In addition, the crystals were larger than those crystals found before and after first pressing (Figure 4.34). The approximate mean crystal size was $9.7\mu\text{m}$.

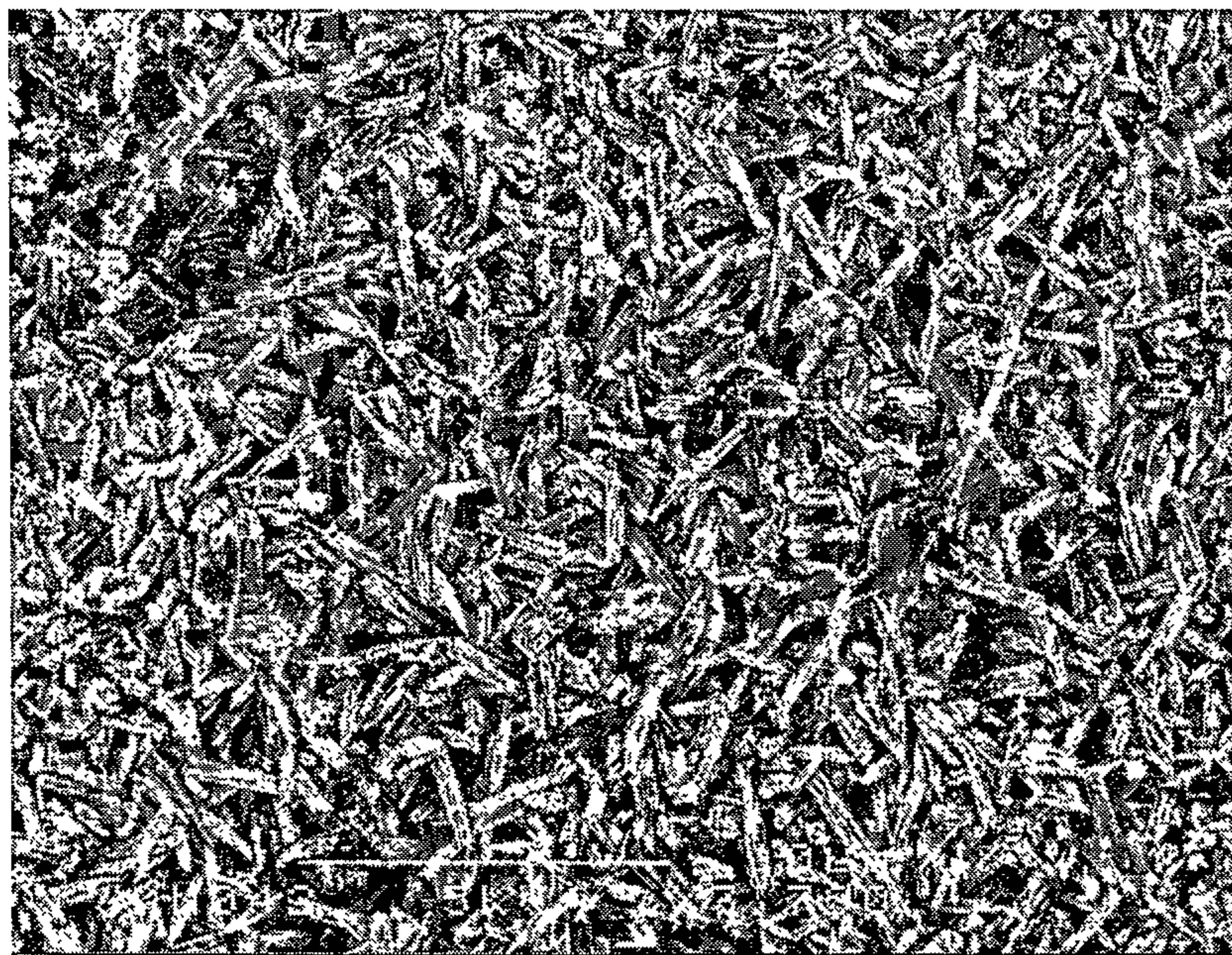


Figure 4.28 Microstructure of Empress 2 before pressing, showing homogenous distribution of many elongated lithium disilicate crystals (magnification 3700 x).

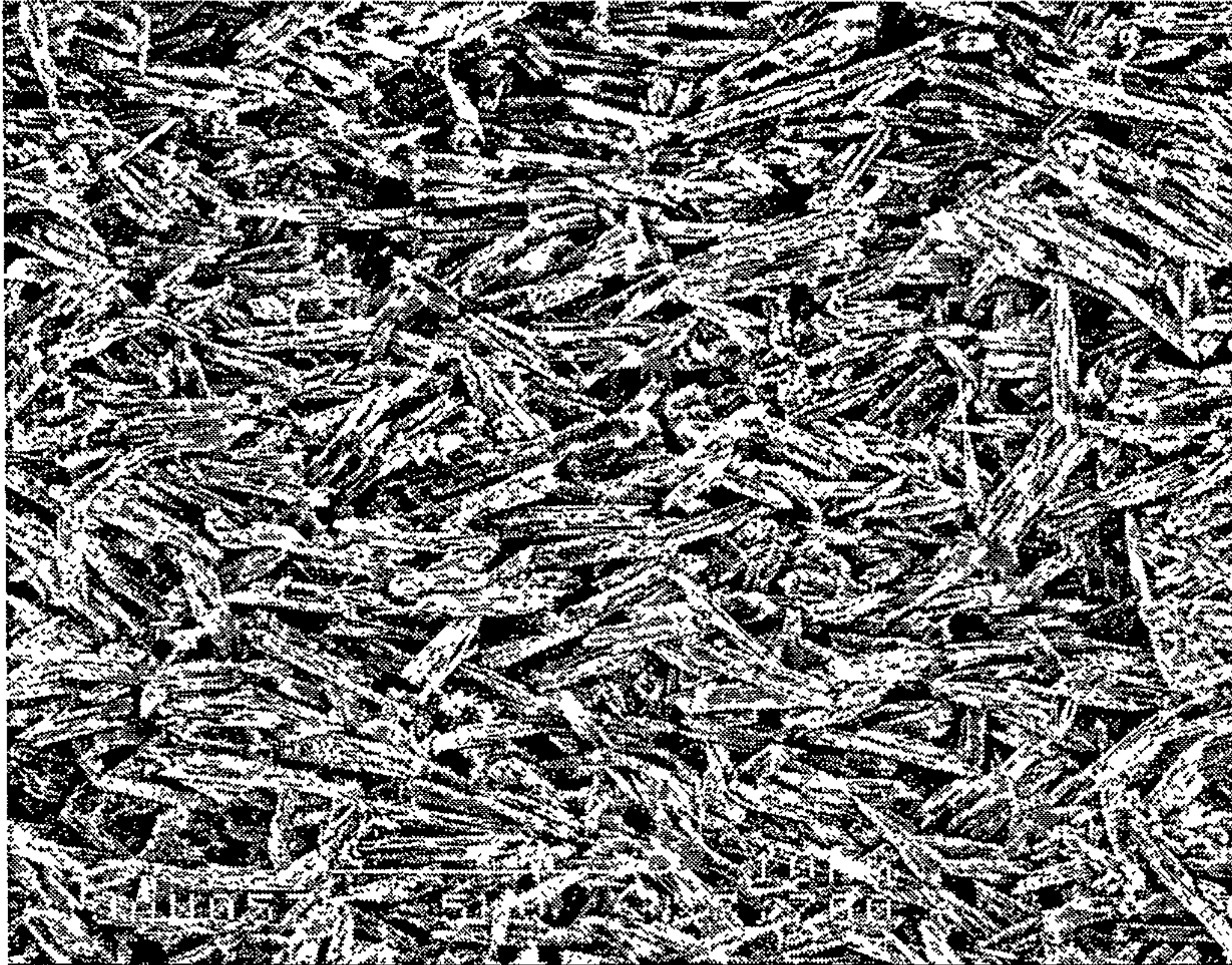


Figure 4.29 Microstructure of Empress 2 after pressing, observed at the same magnification (3700 x), showing larger lithium disilicate crystals than those found before pressing, and the crystals' alignment in a bar-shaped specimen.



Figure 4.30 Alignment of lithium disilicate crystals in a sprue, where most crystals are oriented with their long axis parallel to the pressing direction (magnification 3700 x).

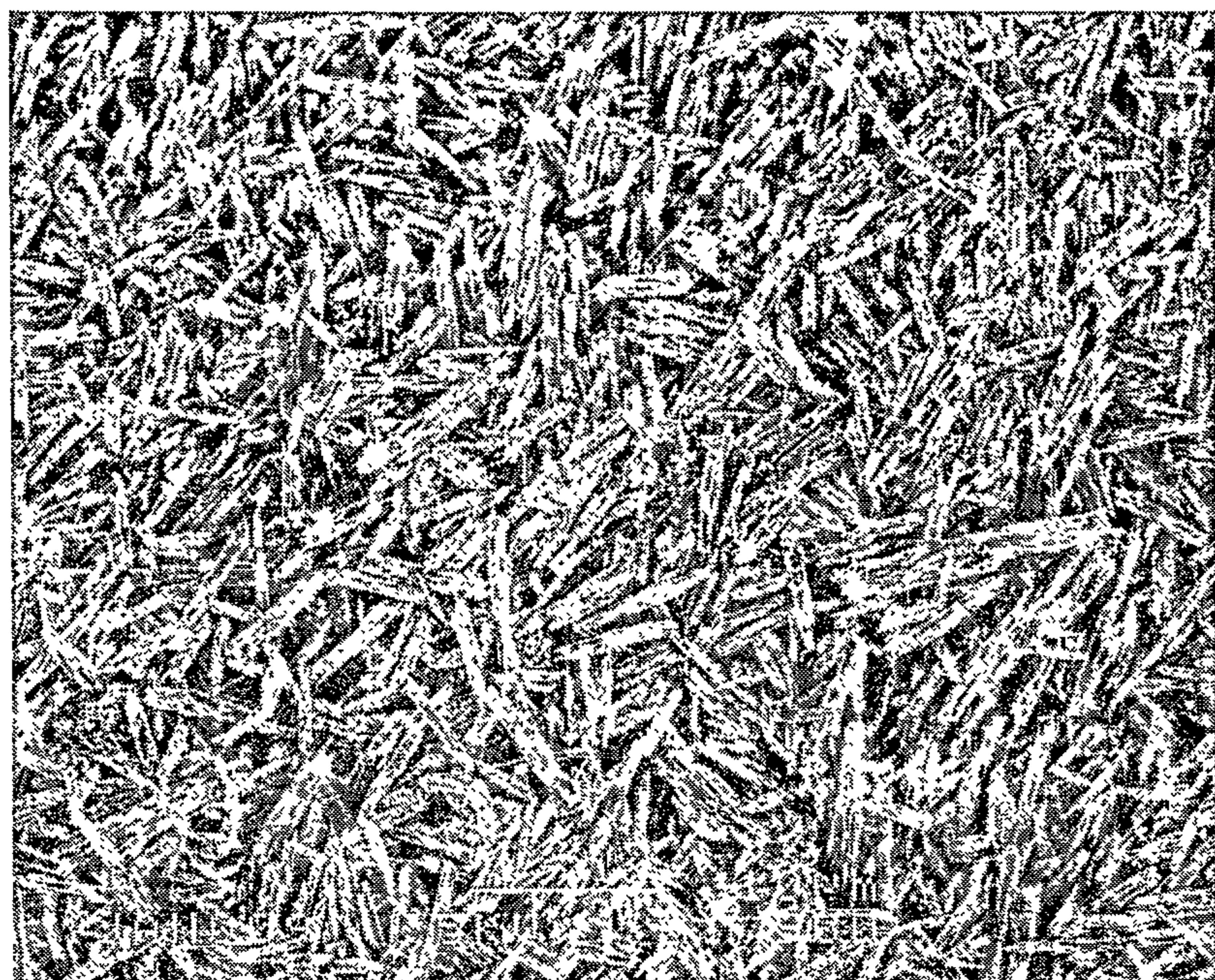


Figure 4.31 Lithium disilicate crystals in a disc-shaped specimen, showing crystals with slightly different directions (Magnification 1900x).



Figure 4.32 Microstructure of Empress 2 after repressing, showing clusters of lithium disilicate crystals that oriented in slightly different directions in disc-shaped specimen (Magnification 3300x).



Figure 4.33 Lithium disilicate crystals in a bar-shaped specimen after repressing, where most crystals are aligned in the Y-axis direction, which is parallel to the pressing direction.



Figure 4.34 Lithium disilicate crystals after repressing appeared larger than those found after pressing, where clusters of crystals can also be seen.

4.3.7.3 Experimental ceramic

Similar microstructure features to those of Empress 2 were found for the experimental ceramic material (Figure 4.35). However, the lithium disilicate crystals of the experimental ceramic material were smaller than those of Empress 2. The approximate size of these crystals was 3.4 μm . This material was not investigated before pressing or after repressing because it was submitted in the pressed state by the manufacturer.

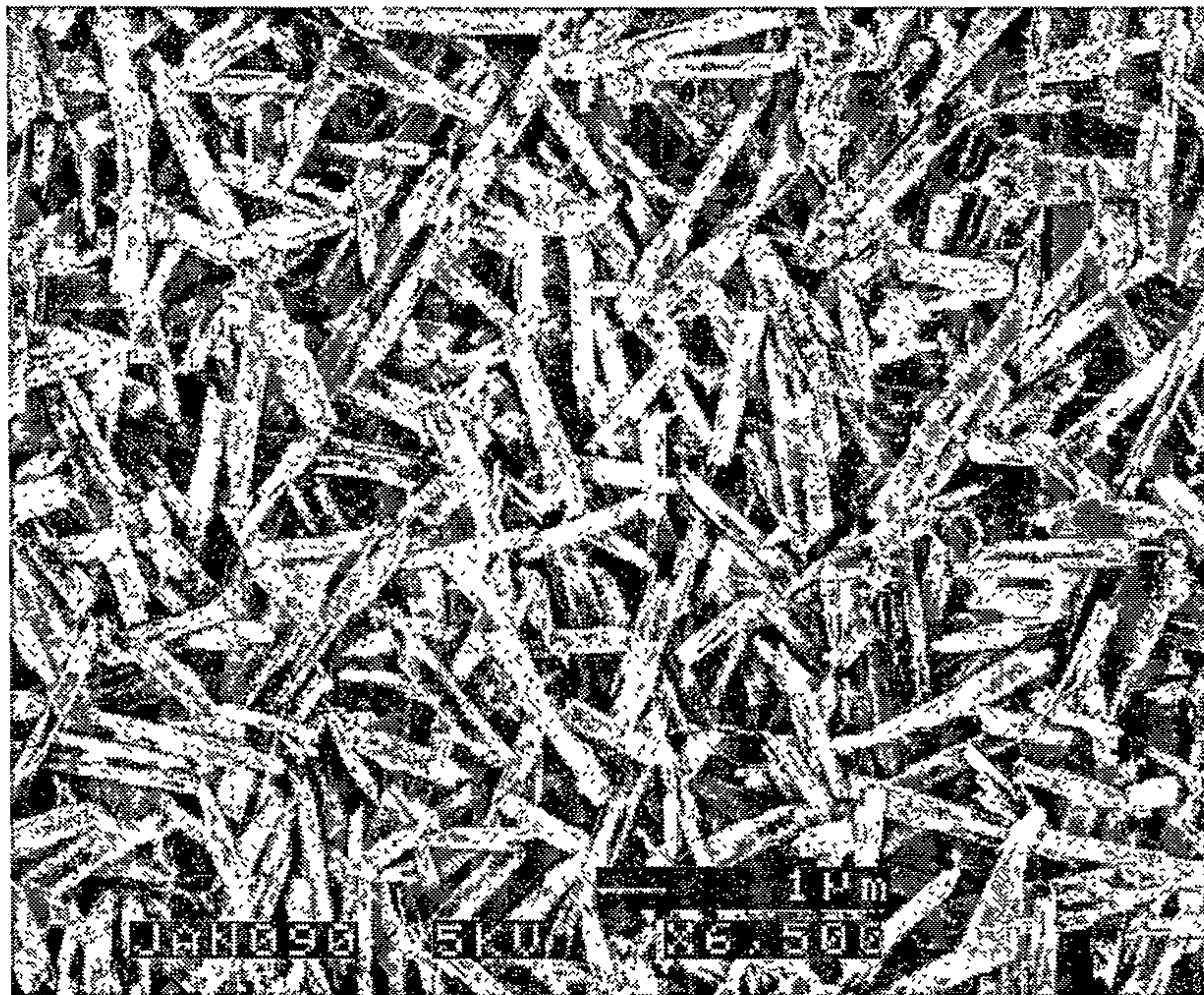


Figure 4.35 Lithium disilicate crystals of the new an experimental ceramic material, showing an interlocking pattern of crystals.

4.3.8 Discussion

Microstructural investigations revealed the presence of small sphere-like leucite crystals contained within a continuous glassy matrix in the Empress 1 material before pressing. The size or orientation of leucite particles didn't appear to change following pressing or repressing. However, a better crystal distribution within the glass matrix

can be seen, which was noticed previously [7]. It was reported that the agglomerated crystals were dispersed during heat pressing, when forcing the softened ingot through a small diameter in the sprue [7]. Repressing didn't cause a better distribution than that observed after the initial pressing. The size and shape of the tetragonal leucite crystals were very similar before pressing, after pressing and repressing.

The pressed and repressed material of Empress 1 showed microcracking within the glass matrix, which was more prominent surrounding leucite crystals (Figure 4.22). Such damage has been linked to the significant difference in the coefficient of thermal expansion between leucite crystals and the glass matrix. This creates internal tension within the crystals and compensating compressive stresses within the glass matrix upon cooling.

Some areas in the pressed and repressed materials showed severe glass cracking and damage (Figures 4.23 and 4.27). Such damage is thought to result from sliding deformation and damage of individual particles of the SiC grit paper with Empress 1 surface during grinding or polishing. This creates relatively small partial Hertzian cone cracks behind the sliding grit contacts [8], which became more visible with the aid of acidic etching. The significant residual stress accrual in this material during cooling, due to the prominent thermal expansion mismatch between leucite crystals and the glass matrix, can also cause localised damage within the glassy matrix surrounding these crystals, and particularly around larger leucite crystals.

Twinning of leucite crystals was observed in most specimens examined before pressing, and was extensive after pressing and repressing. This was attributed to the

shear deformation associated with relief of the shear strains during the transformation from the cubic to tetragonal phase at 625° C [9]. Many previous studies showed that twinning, differently shaped leucite crystals, and cracking within the glass matrix and the crystals are common features of the Empress 1 material [10-12].

The similar microstructural features of the pressed and repressed samples may signify that repressing didn't noticeably affect the microstructure of Empress 1. This is consistent with the mechanical properties results of this material, which showed no change after such treatment. These issues and validation of such a linkage are provided in more detail in Chapters 6 and 7, where the flexural strength and fracture toughness are evaluated after these treatments.

Lithium disilicate crystals embedded in a glass matrix were the main composition of the microstructure of Empress 2 before pressing, after pressing and repressing. These elongated crystals appeared to be randomly distributed and form an interlocking pattern before pressing. However, the majority of these crystals became more aligned along one direction after pressing; that is, parallel to the pressing direction. It should be noticed that the alignment was more prominent in the bars used for the 3-point bending strength technique and in sprues. In the discs used for the biaxial strength measurements, the alignment was also noticed but there are some areas where crystals had clamped together and had different direction. During pressing, these crystals are aligned in the small diameter, the sprue, but when they occupy the disc space a degree of dispersion occurs and crystals change their direction.

In fact, the alignment of crystals in lithium disilicate glass ceramics has been previously observed by Atkinson and McMillan [13]. These authors showed that the disilicate phase is morphologically oriented parallel to the extrusion axis. Rüssel (1997) has outlined a number of approaches that may result in alignment of crystallisation in glass ceramics; these include surface crystallisation, assisted by a temperature gradient, and from shear stresses associated with plastic deformation of a partially crystalline melt [14]. However, in lithium disilicate glass ceramics, it was shown by high-temperature X-ray diffraction in a previous investigation that the nucleation of lithium disilicate crystals occurred at 500°C and the amplitude of these peaks continued to increase until this phase began to dissolve at about 960°C [15]. As the pressing temperature is 920°C, some 40°C below the melting temperature, it is considered that the orientation of these crystals during extrusion is a result of shear stresses during pressing [14]. Pressing is a high strain deformation process that can, in needle-like, platelets or fibre-reinforced glass ceramics, result in an oriented glass ceramic [14]. However, it should be noted that crystal alignment during heat-pressing is also affected by crystal shape, amount, size and the viscosity of the glass phase [16]. The images of the repressed material showed almost the same outcomes.

Another feature evident after pressing and repressing of Empress 2 material is the size increase of the lithium disilicate crystals. This behaviour is called Ostwald ripening [17] and is common for all precipitated materials. It takes place when the microstructure coarsens, and liberates surface energy excess due to the solubility of small particles. As a consequence, larger grains are expected to grow at the expense of those small particles. The present results after pressing are similar to previously reported findings by Oh et al. (2000) [18]. These researchers noticed that the lithium

disilicate crystals, after pressing, were approximately double the size of those before pressing.

A statistical approach was used to find the difference in the size of these crystals before pressing, after pressing and repressing. Statistics showed that there was a significant difference in the lithium disilicate crystal sizes among the material before pressing, after pressing and repressing ($p < 0.05$). Plotted in Figure 4.36 is a statistical illustration of the size of lithium disilicate crystals before pressing, after pressing and after repressing. Plotted also in Figure 4.37 is the effect of pressing time on the size of lithium disilicate crystals.

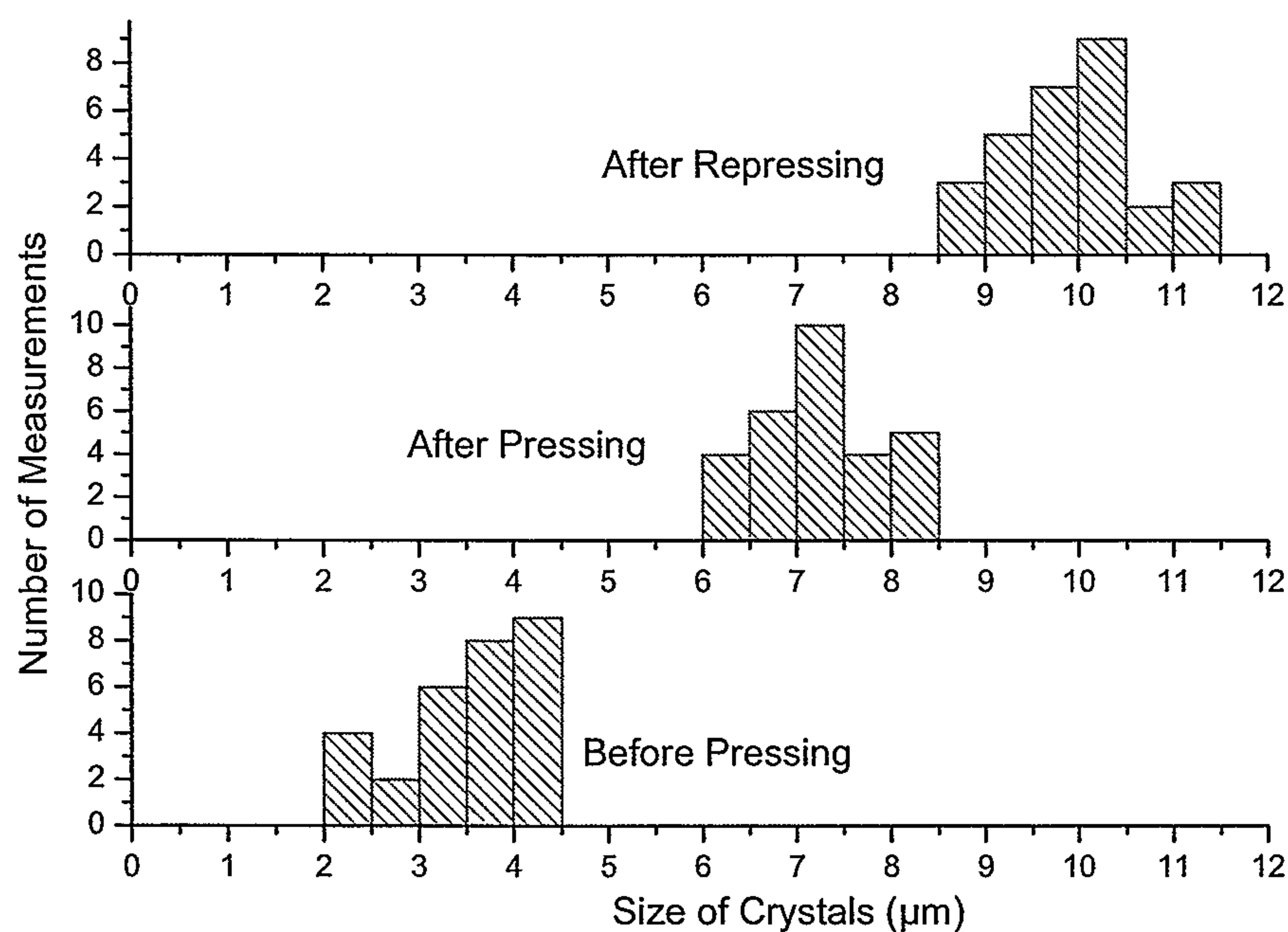


Figure 4.36 Illustration of a statistical plot of the size of lithium disilicate crystals (μm) before pressing, after pressing and repressing. Pressing took place at 920°C.

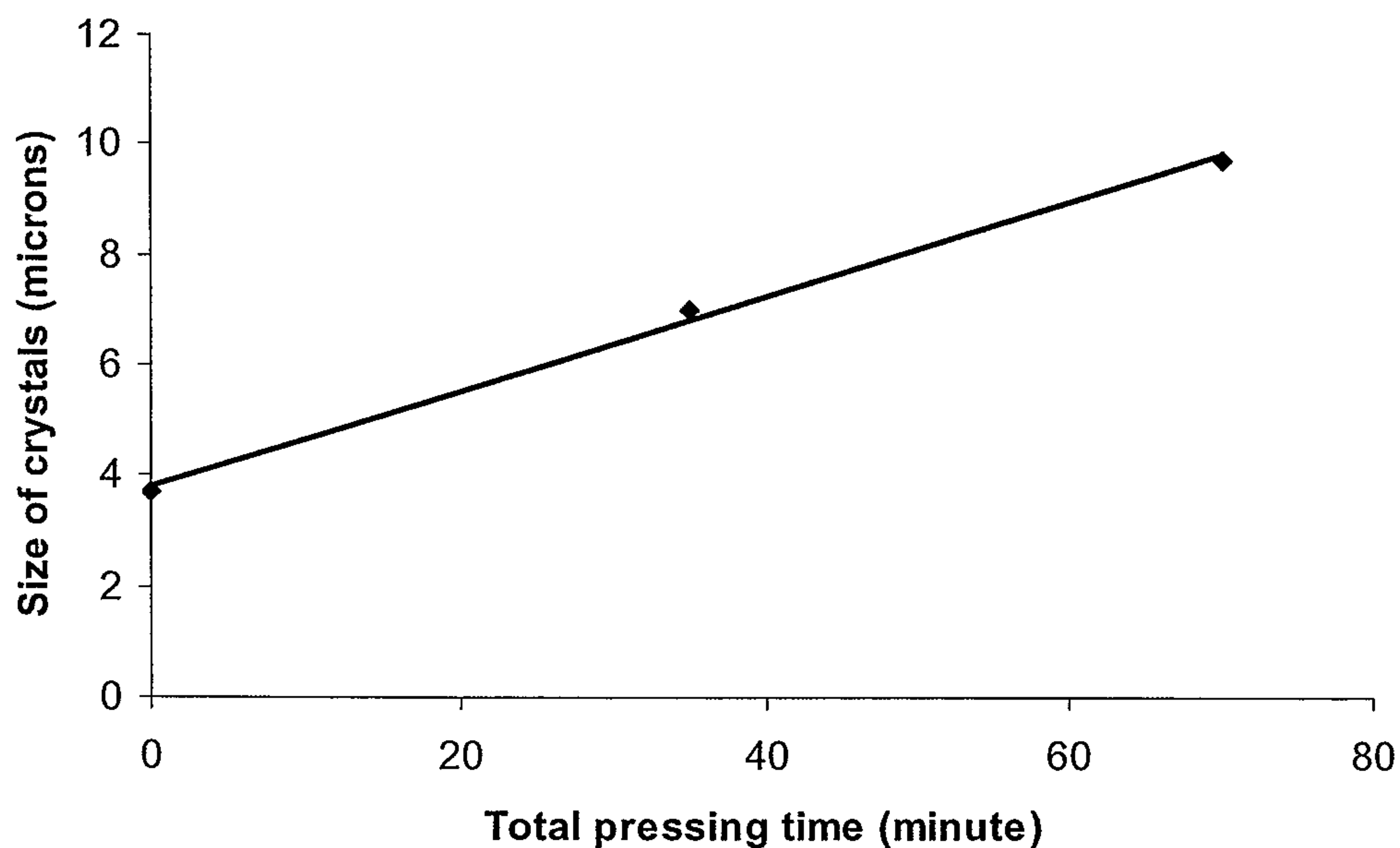


Figure 4.37 Illustration of the effect of pressing time (minutes) at 920°C on the size of the lithium disilicate crystals (μm).

4.3.9 Conclusion

From the present study the following conclusions can be drawn.

1. The microstructure of Empress 1 is mainly composed of small sphere-like leucite crystals distributed in a glass matrix.
2. Heat pressing plays a significant role in the homogenous distribution of the leucite crystals within the glass matrix.
3. Repressing didn't affect the microstructure of Empress 1.
4. Fracturing within the glass matrix and crystals, and crystal twinning were features found before and after pressing and repressing
5. Empress 2 was composed of many elongated lithium disilicate crystals, randomly (multi-directional manner) embedded in a glass matrix prior to pressing.

6. Alignment and increase in the size of the lithium disilicate crystals were features found after pressing.
7. Repressing caused a further increase in the size of the lithium disilicate crystals. The lithium disilicate crystals of the experimental ceramic material were smaller than those of Empress 2.

4.4 Porosity

4.4.1 Introduction

The porosity of a material reveals the volume of voids or pores pre-existing. It may arise during fabrication processes or accidentally. In ceramics, it mostly occurs as a result of improper casting techniques or because of lack of control in the firing cycles [4]. It is an undesirable property, and generally believed to affect the mechanical properties of ceramic materials [19]. For example, a significant strength reduction is anticipated if an interaction between pores and the microscopic flaws occurs, and also if larger pores are located within areas of high tensile stresses. The detrimental effect of porosity is that it acts as a stress concentrator and also decreases the cross-sectional area over which the force is applied [20]. It also affects the optical properties by scattering light and decreasing translucency [21]. Porosity control is therefore a fundamental consideration during the design or processing of the dental ceramics [21].

4.4.2 Purpose

Empress 1 and Empress 2 materials are claimed to benefit from heat-pressing during laboratory fabrication [22]. Benefits include occlusal accuracy and better marginal integrity (lost waxing technique) [10], better mechanical properties (due to better crystal distribution within a glass matrix after pressing) [7, 18], net-shape forming by pressing, and resultant decreased porosity[22]. This study observed the porosity (shape, size and number) of Empress 1 and Empress 2 before pressing, after pressing and repressing.

4.4.3 Specimen preparation for porosity

Several highly polished specimens before pressing, after pressing and repressing were gold-coated (20 nm) and observed using a scanning electron microscope. Pore size, shape and number were recorded.

4.4.4 Results

4.4.4.1 Empress 1

Spherical pores were found before pressing for the Empress 1 material, measuring approximately from 20 to 86 μm in diameter (Figure 4.38). However, smaller and fewer pores were found after pressing and repressing, measuring approximately from 10 to 35 μm in diameter (Figures 4.39 and 4.40).

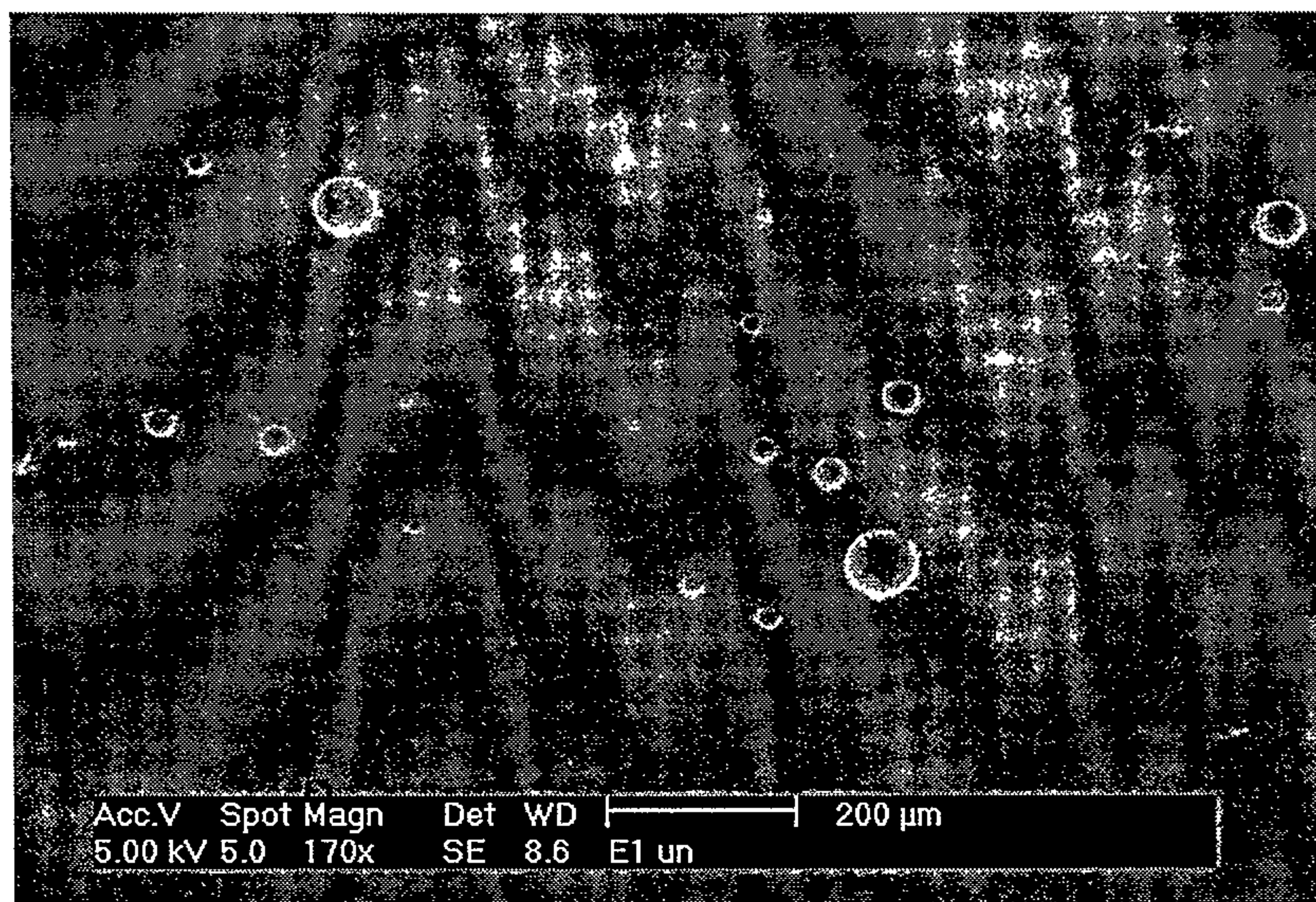


Figure 4.38 Different sizes of many spherical pores are distributed in a finely polished surface of Empress 1 before pressing.

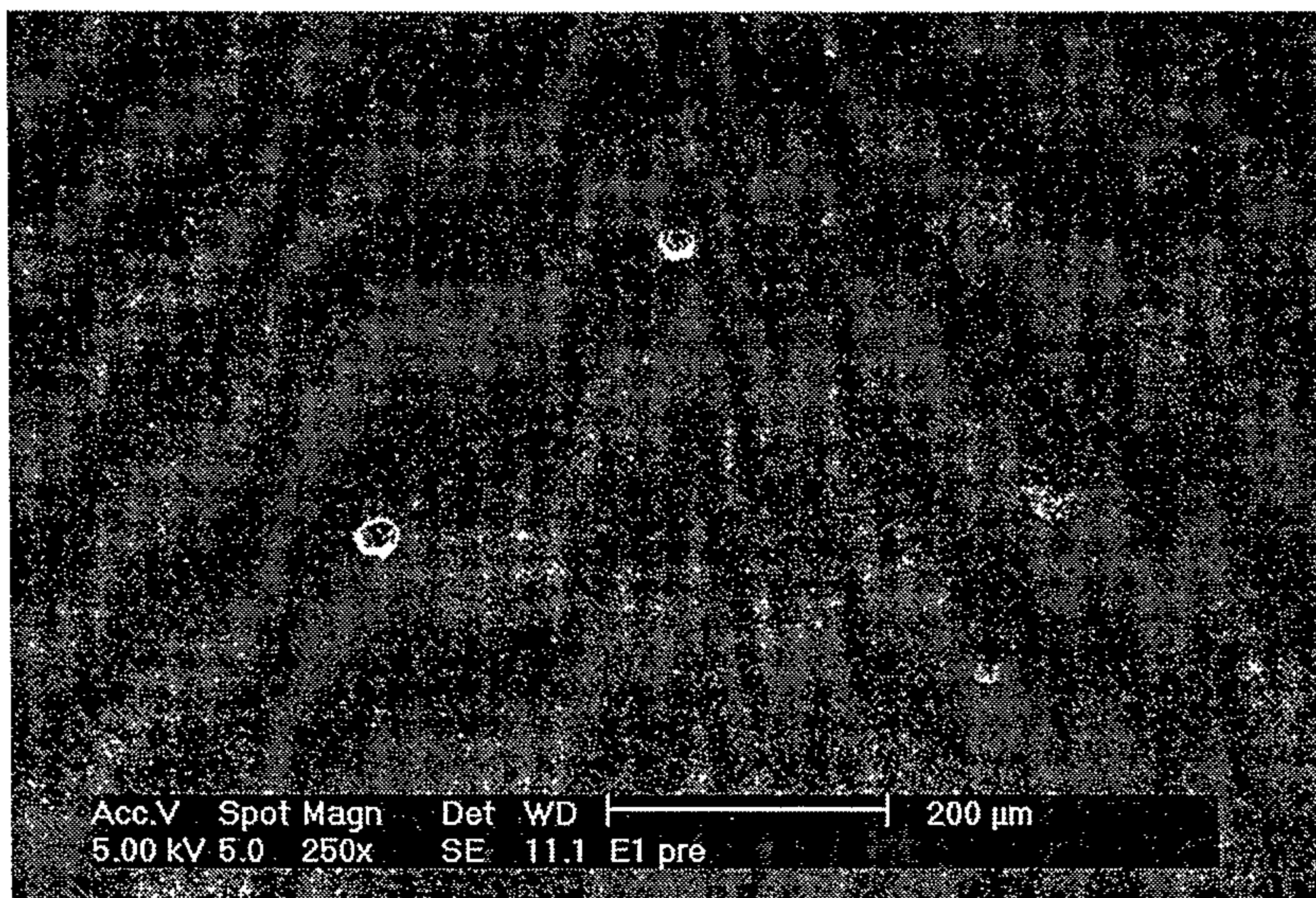


Figure 4.39 A finely polished surface of Empress 1 after pressing, showing fewer spherical pores than those found before pressing.

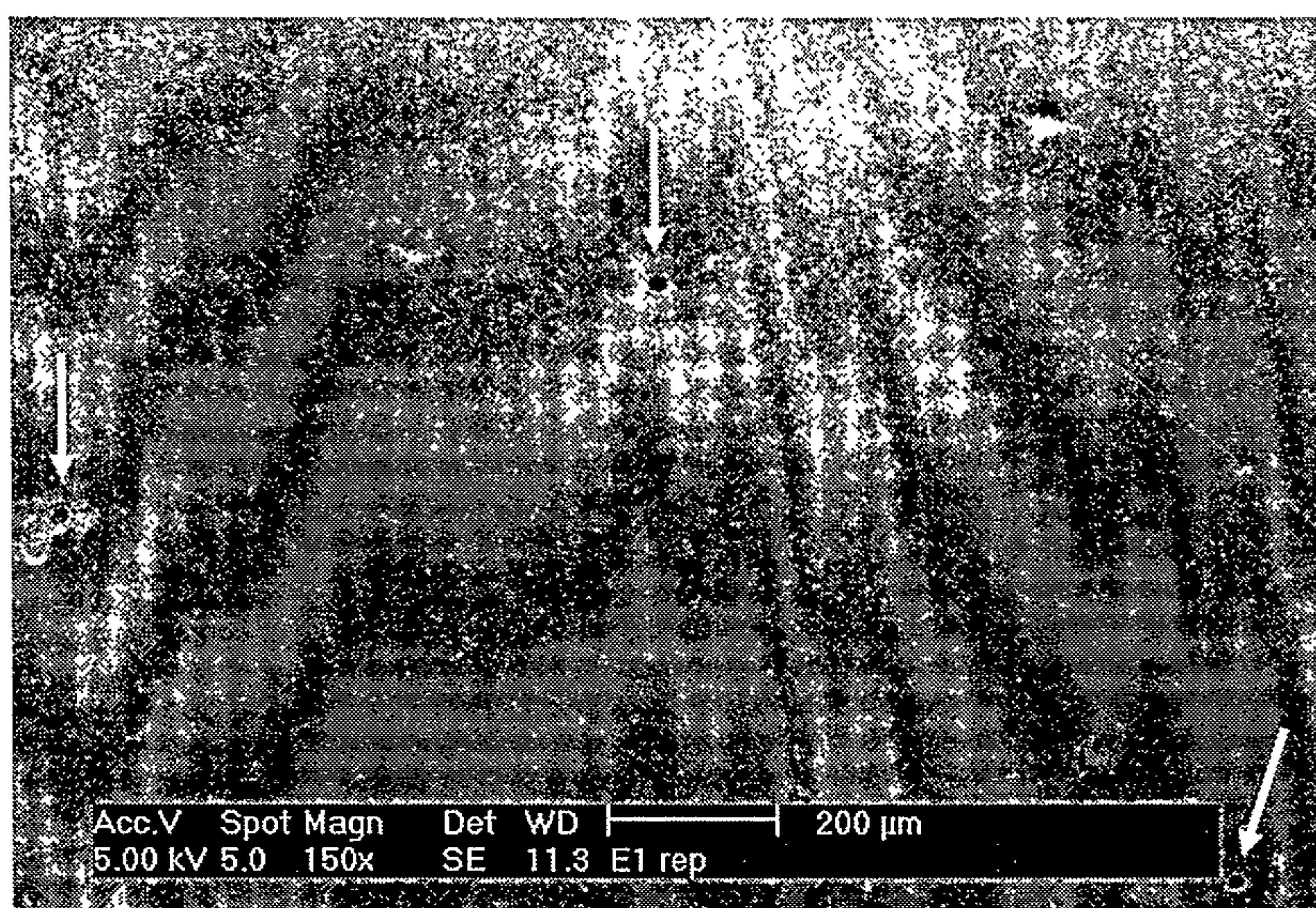


Figure 4.40 A finely polished surface of Empress 1 after repressing showing few spherical pores.

4.4.4.2 Empress 2

The Empress 2 material also showed spherical pores throughout the polished surface, measuring approximately from 5 to 12 μm in diameter (Figure 4.41). Most images observed after pressing were free of pores on the surfaces and some showed very few

pores (Figures 4.42 and 4.43). Images after repressing also showed virtually no pores (Figure 4.44)

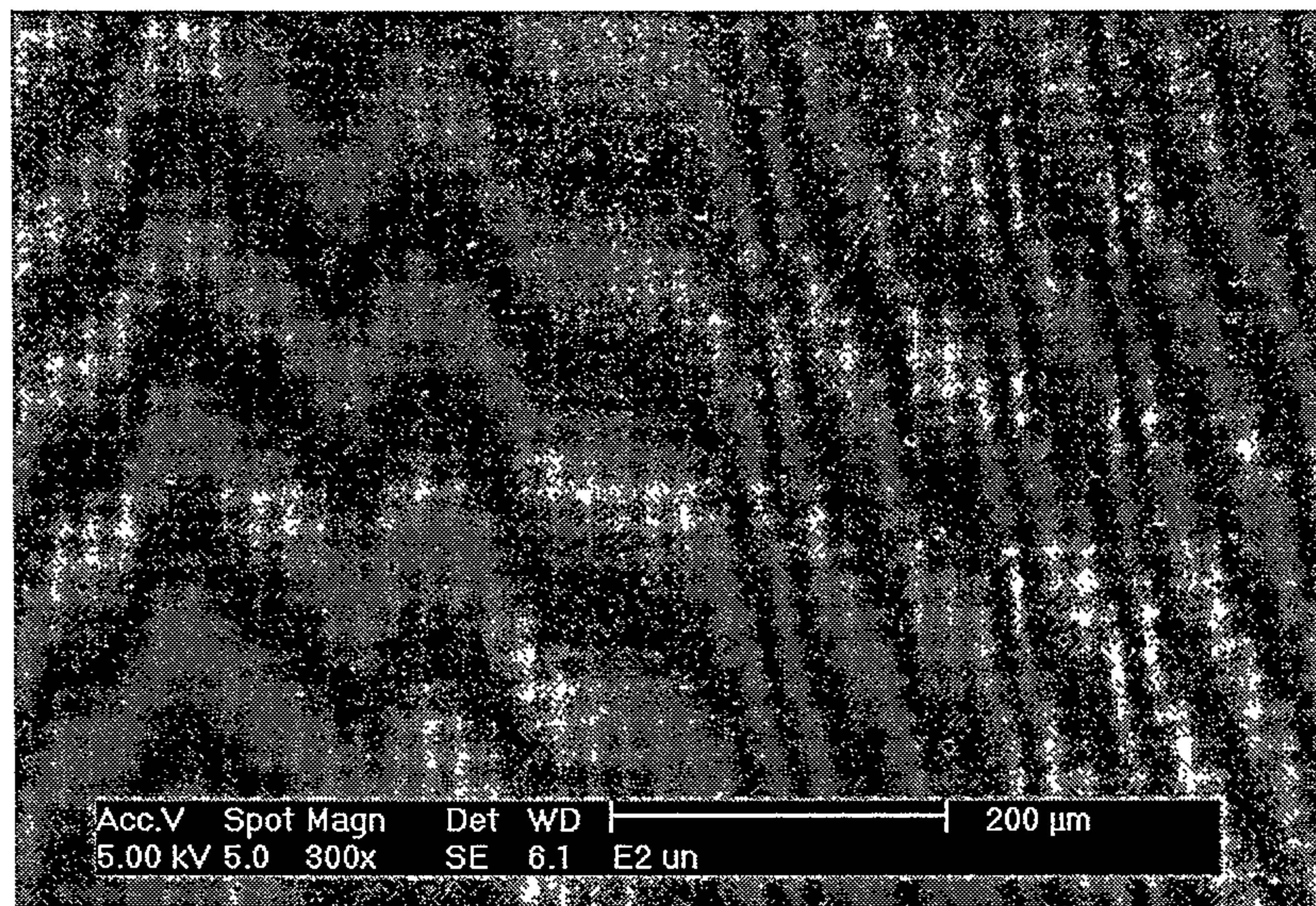


Figure 4.41 Various small spherical pores distributed throughout a polished surface of Empress 2 before heat-pressing.

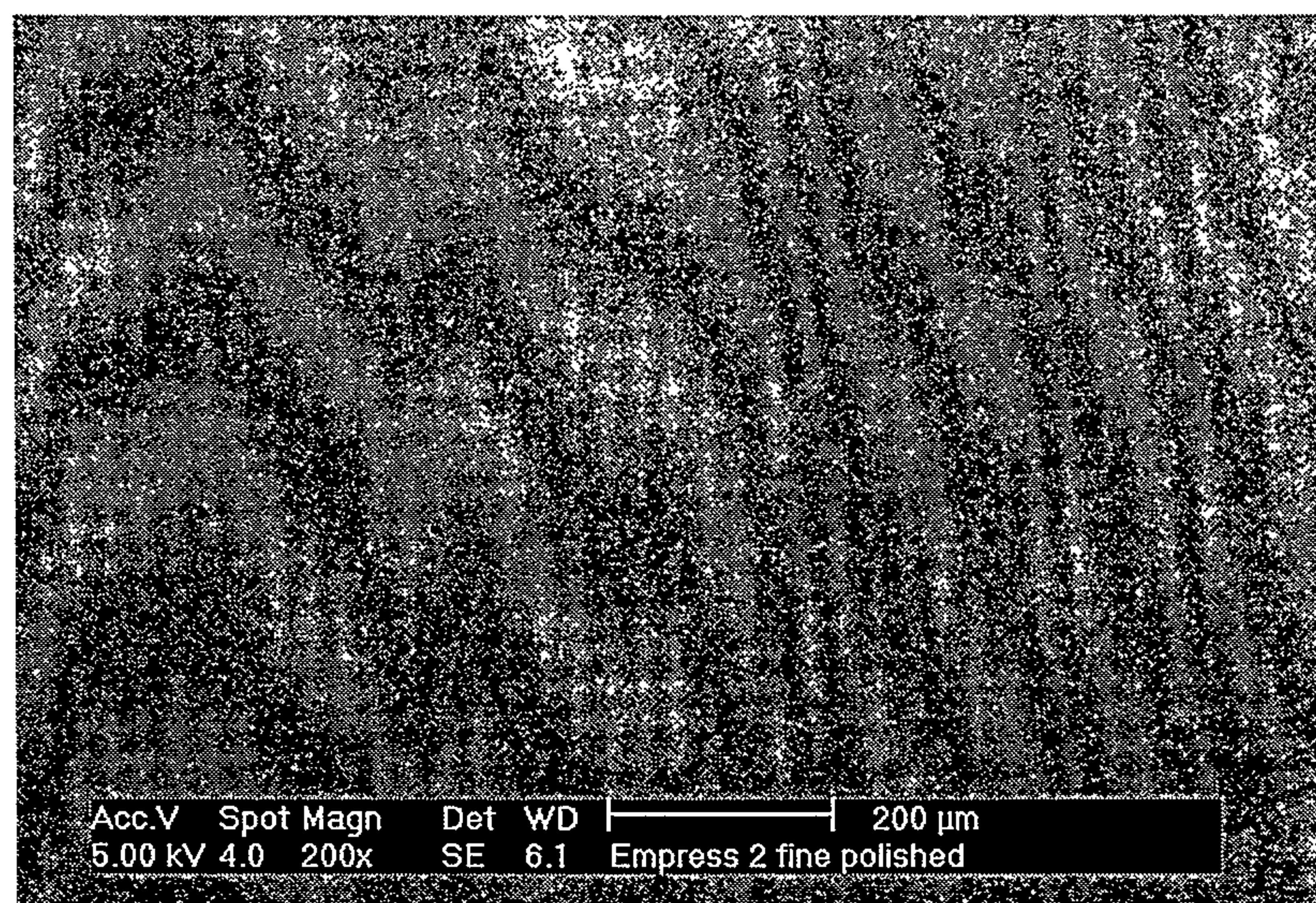


Figure 4.42 A finely polished surface of Empress 2 after pressing, showing very few small spherical pores.

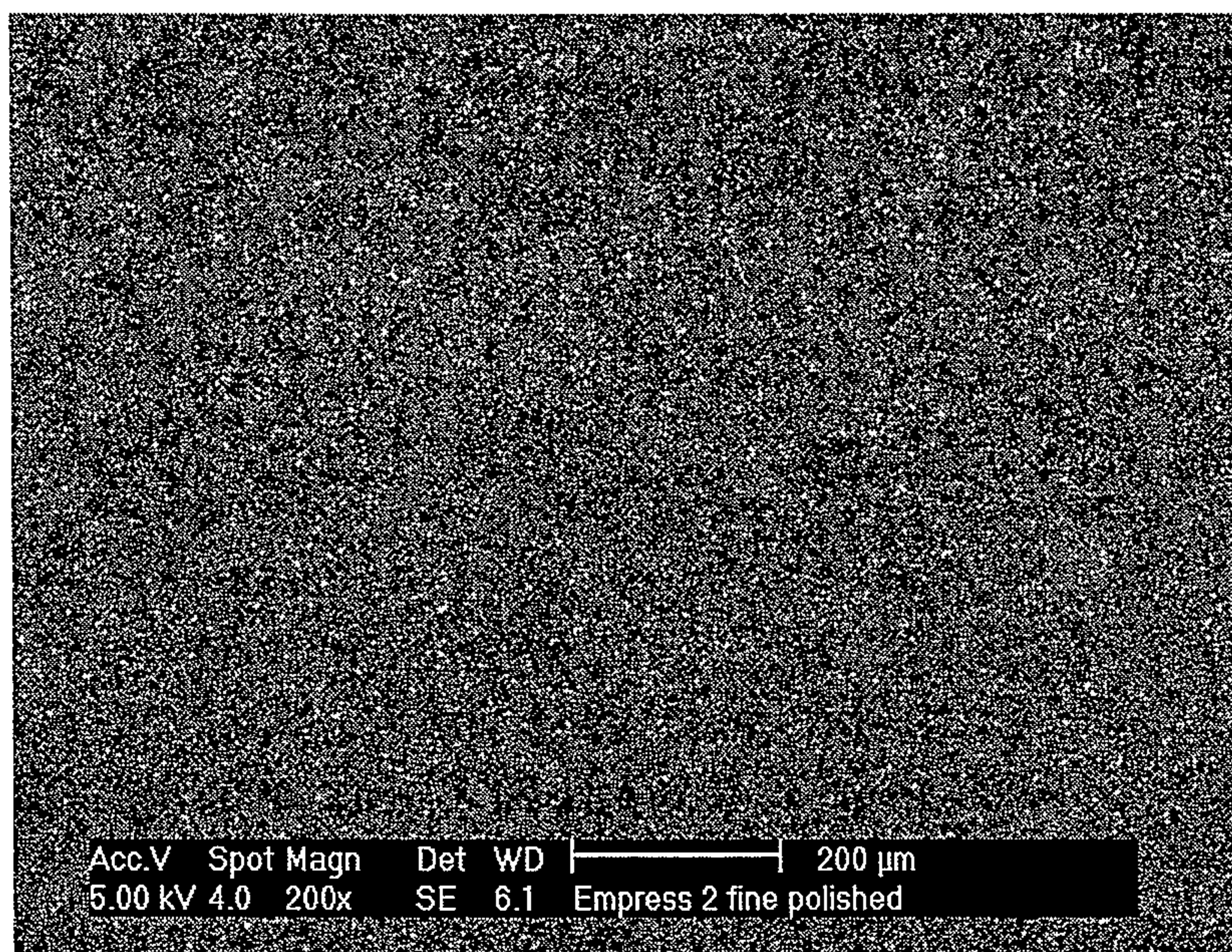


Figure 4.43 Many images showed no pores after heat-pressing.

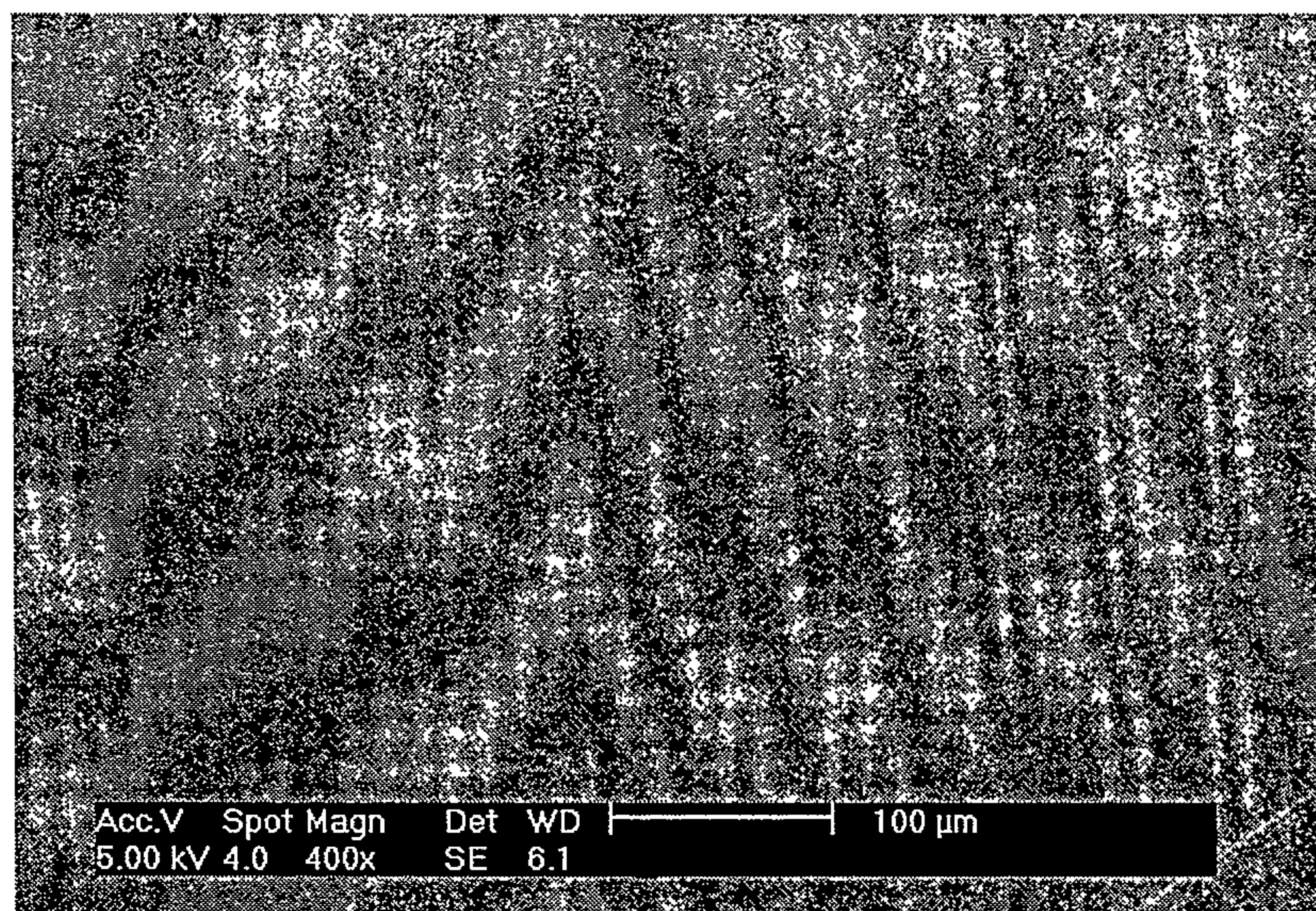


Figure 4.44 Repressed material of Empress 2 showing no pores.

4.4.5 Discussion

Scanning electron photomicrographs showed that pressing significantly decreased the number of pores of both investigated materials. For the Empress 1 material before pressing, various spherically shaped pores were noticed throughout the polished surface. After pressing or repressing, smaller and fewer spherical pores than those

found before pressing were present. For the Empress 2 material, small spherical pores were found at different sites throughout before pressing. After pressing or repressing, the surfaces investigated showed either a minimal number of very small pores or no pores. This might have occurred during heat-pressing when glass is melted. The vacuum and pressure assist in better condensation of the material and subsequently less air bubbles from which most pores are initiated. Since the reduction in the number of pores is essential for materials that requires strength and translucency, such as the present materials Empress 1 and Empress 2, these materials should benefit from these advantages enhanced by heat pressing. This issue is addressed more thoroughly in Chapter 7, where the effect of porosity on the mechanical properties is appraised.

4.4.6 Conclusion

Heat pressing was an effective process in minimising the number and size of pores of the investigated materials, Empress 1 and Empress 2.

4.5 References

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CHAPTER 5

ELASTIC MODULUS, POISSON'S RATIO AND HARDNESS

There are wide ranges of materials that can be used in load-bearing applications (called structural materials); these include ceramics, polymers, metals and composites. In dentistry, materials such as amalgam, dental ceramics or composites can be used as restorations. During chewing, these materials are stressed and may fracture. An appraisal of the mechanical properties of these materials provides both clinician and researcher with useful information for selecting the appropriate material and application technique. It is true that there is generally a lack of sufficient clinical studies regarding the latest generation of dental restorative materials prior to widespread usage. This caused heavy emphasis to be placed on mechanical properties in defining the clinical indications of these materials.

This chapter will focus on three mechanical properties, namely elastic modulus, Poisson's ratio and hardness. The first part (5.1-5.8) will provide a review of the definition, importance and method of measurements of elastic modulus and Poisson's ratio. This will be followed by the specimen preparation, testing, results, discussion and conclusion regarding the elastic modulus and Poisson's ratio of the investigated materials, IPS Empress, Empress 2 and the experimental ceramic.

The second part (5.9-5.14) will focus on the hardness of the investigated materials. Definition, importance, and method of measurements of hardness will be provided firstly followed by the specimen preparation, testing, results, discussion and conclusion.

5.1 Stress and Strain

Stress can be defined as the force intensity at any point in a body submitted to a load [1]. It is a force (F) per unit area (A), and can be expressed by the following relationship:

$$\text{Stress } \sigma = \frac{F}{A} \quad (1)$$

Stresses must be defined according to their magnitude and direction [2]. In relation to the direction, they can be classified into three types:

- 1) Tensile stress. A load that creates a stretch or elongation of a body is termed tensile stress.
- 2) Compressive stress. The internal resistance of a body subjected to a load that tends to shorten or compress it, is called compressive stress. The force in tensile and compressive stresses is applied perpendicular to the area over which they act.
- 3) Shear stress. The resistance to a twisting motion or sliding of one part of a body over another is termed shear stress.

Whenever stress is applied, deformation or strain results. Strain is the response of a material to stress. It can be defined as the ratio between the total deformation in one direction of a specimen and the length of the specimen in the same direction [1]. If the original length is l and the increase in length is e , from definition the strain can be expressed by:

$$\text{Strain } \varepsilon = \frac{e}{l} \quad (2)$$

In response to a mechanical force, materials undergo a change in dimension and this is called deformation. When a material reverts back to its original size and shape

upon stress removal, the deformation is called elastic. If a permanent change in the shape results upon removal of the stress, the deformation is called plastic [3].

5.2 Elastic modulus

Elasticity measurement of a material is termed modulus of elasticity or Young's modulus, and symbolised by the variable E [4]. It represents the stiffness of a material within the elastic range when tensile or compressive forces are applied [5]. It is also an indication of the amount of reversible deformation that will occur in a structure when a load is applied to it. Interatomic or intermolecular forces of a material determine its elastic properties. Because this property is strongly dictated by these forces, a material will have the same elastic modulus value if either a compressive or tensile force is applied. It is also independent of any heat or mechanical treatments [4].

Knowledge of the elastic modulus is clinically relevant, because it may assist with the selection of a restorative material with more similar deformable properties to those of the material it is replacing. For example, when a restorative material has comparable elastic properties to those of tooth structure, the differential deflection, which normally occurs at the tooth restoration interface and is considered harmful to marginal bonding, can be decreased.

Elastic modulus is known as the ratio of stress to strain below the proportional limit. Therefore, the lesser the strain for a given stress, the greater the value of the modulus. From stress and strain definition, elastic modulus can be derived as follows:

$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{\varepsilon} = \frac{F/A}{e/I} = \frac{FI}{eA} \quad [2] \quad (3)$$

Since strain is dimensionless, the unit of elastic modulus is the same unit of stress, force per unit area (MPa). However, in this unit the elastic modulus is enormous, therefore it is usually reported in GPa [6].

5.2.1 Importance

In dental restorations, a high elastic modulus is often required. It is desirable that a material undergoes limited deflection on loading and returns to its original shape after it has been stressed. However, in some instances a material with larger deformation or strain is required with a slight stress, such as in the case of orthodontic wires. This phenomenon is called flexibility [2].

It has been reported that increasing the elastic modulus of a supporting core structure of a dental restorative material might be a way of improving the ability of fracture resistance of all-ceramic dental materials [7, 8]. Accordingly, the elastic modulus might be a basis for selection of a core made out of these materials [7]. At the same time, relatively low elastic modulus is desirable in some treatment cases such as restorative fillings. For example, for cervical cavities (Class V) the filling material (composite resins) must have relatively low elastic modulus. This is important to allow the filling material to deform during tooth flexure. On the contrary, other cavity classes such as I or II must be restored with high elastic filling material to withstand occlusal excessive forces and resist fracture [9].

It is commonly found that the strength of brittle materials scales with the elastic modulus. For example, the flexural strength of feldspathic porcelain range from 70 to 90 MPa, and the elastic modulus is in the range of 70 GPa. Materials with higher elastic modulus such as In-Ceram Alumina (250 GPa) are reported to also have higher flexural strength (400 to 550 MPa) [10].

5.2.2 Measurement of elastic modulus

Various methods can be used to determine elastic modulus. These methods can be divided into two groups: static and dynamic methods [11]. Measuring the deformation of a specimen under a known load such as in a tensile test is known as the static method. Common methods are the non-destructive tests (called the dynamic methods). Some of the dynamic methods are: frequency of oscillation of the rod method, ultrasonic pulse transit-time method, resonant ultrasound spectroscopy, free oscillation torsion pendulum and impulse excitation of vibration [6]. Although dynamic methods require specific equipments for performing tests, they became widely adopted to assess the elastic properties of all-ceramic dental materials. This is because of the simplicity of these tests and the possibility of repeating the same test for a single specimen.

5.3 Poisson's ratio (ν)

Axial loading in tensile or compressive mode is accompanied by a simultaneous axial and lateral strain. If a material is under tensile load, it elongates in the direction of the load and there is a reduction in the cross-section. In the case of the compressive load, there is an increase in the cross-section [4]. Poisson's ratio can be defined as the ratio of the lateral to the axial strain within the elastic range. This mechanical property is

related to the nature and symmetry of the interatomic bonding forces [2]. Most engineering materials have Poisson's ratio values of approximately 0.3 [2]. Brittle materials show little permanent reduction in cross-sectional areas during tensile loads, whereas ductile materials show a higher degree of reduction in cross-sectional areas [4].

5.4 Purpose

The elastic modulus and Poisson's ratio of the investigated materials were evaluated in this study for two reasons. Firstly, these mechanical properties of Empress 2 and the experimental ceramic material were not available in the literature. Secondly, fracture toughness and strength measurement using the biaxial test data require information on the materials such as the elastic modulus and Poisson's ratio [12], which are fundamental properties for a material and essential in dental applications.

5.5 Testing Method

The impulse excitation of vibration method, according to the American Society for Testing and Materials (ASTM, C 1259-94), also called the standard plate resonance test method [13] was used to determine the elastic modulus (E) and Poisson's ratio (ν). This test covers the determination of the dynamic elastic properties of advanced ceramics. Mass, geometry and mechanical resonant frequency of a rectangular or cylindrical geometry of a specimen are used to determine the elastic properties. The elastic modulus is determined using the resonant frequency in the flexural mode of vibration, and shear modulus (modulus of rigidity) is determined using torsional resonant vibration. Elastic modulus and shear modulus are used to calculate Poisson's ratio. This method has several advantages. 1) It is easy to operate and

takes little time, 2) it is non-destructive, 3) it can be used in a wide range of materials
4) it gives reliable results [5].

5.5.1 Test specimen

The rectangular-shaped specimens prepared in Chapter 3, paragraph 3.2.1 measuring 30 mm (length) × 12.75 (width) mm × 1.1 mm (thickness) were used. Surfaces of the specimens were slightly polished until a flat surface was achieved, and the opposite surfaces across the length and width were parallel within ± 0.1%. The same treatment was also performed until the opposite surfaces across the thickness were parallel within ± 0.1%. Lengths and weights of the specimen were determined within ± 0.1%. Width and thickness of the specimens were measured within ± 0.1% at three locations and the average was recorded.

5.5.2 Apparatus

The apparatus used in such experiments consists of an impulser, transducer (to convert the mechanical vibration into an electrical signal), an electronic system (consisting of a signal amplifier), a signal analyser and frequency readout device and a support system. This is illustrated in Figure 5.1.

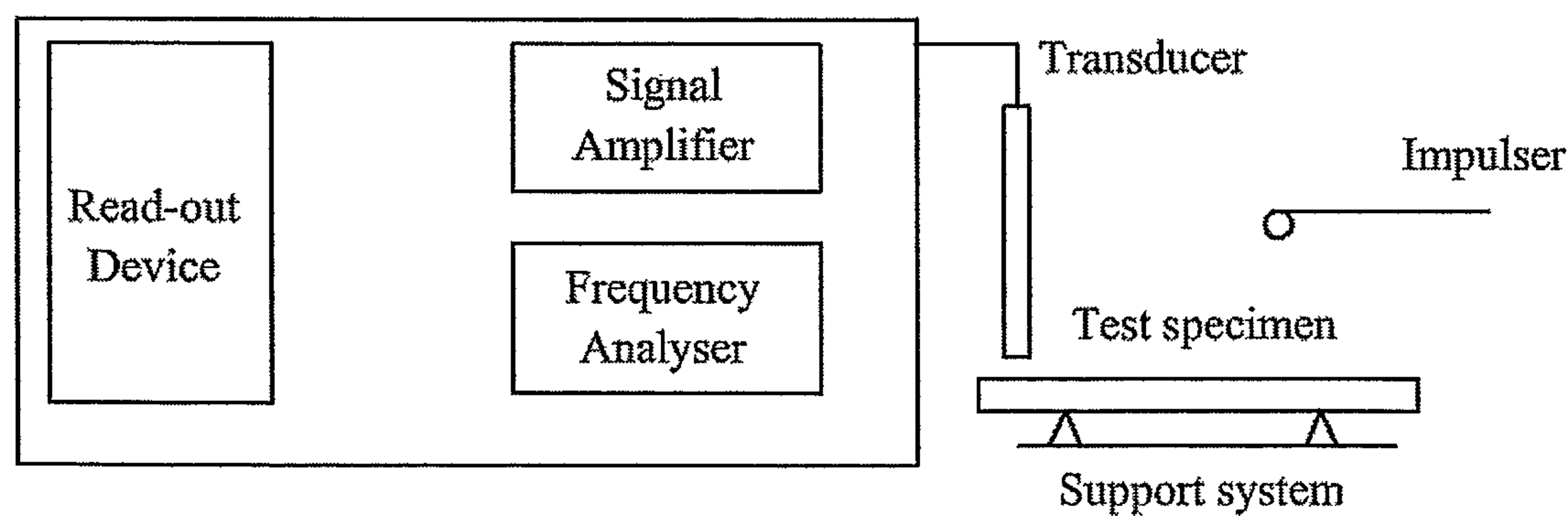


Figure 5.1 Diagram of typical test apparatus (ASTM, C 1259-94).

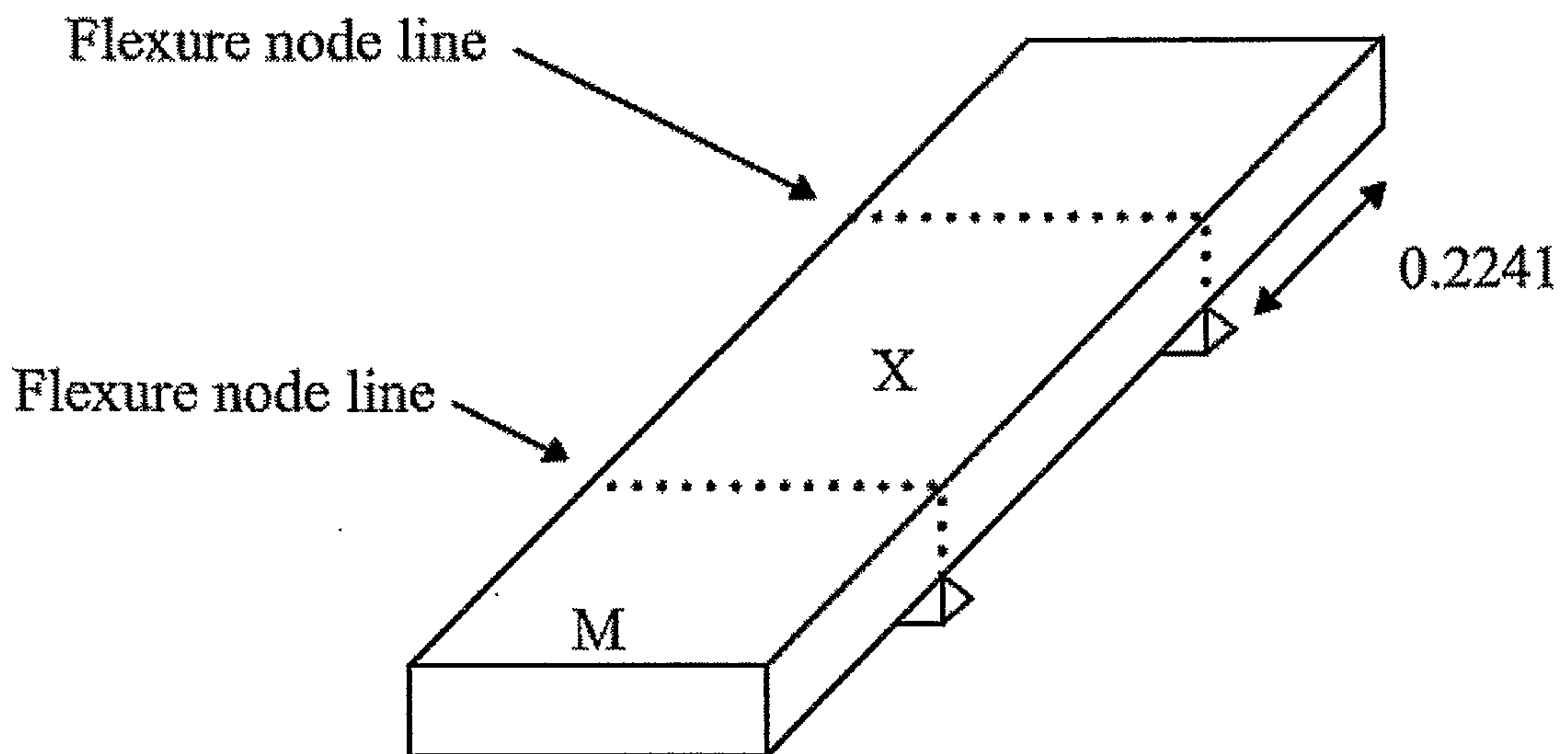
5.5.3 Procedure

The test in the current study was conducted in two ways: 1) the excitation of the fundamental flexural resonant frequency, and 2) fundamental torsional resonant frequency.

5.5.3.1 The flexural resonant frequency

The following steps were carried out to perform this test:

1. Soft foam strips were used as a support system.
2. A specimen was placed on the supports that were located at the nodal points (0.224 of the length of the specimen from each end; Figure 5.2).
3. The microphone was placed close to an antinode point on one side of the specimen, and also oriented so that it would detect the desired vibration.
4. The centre of the specimen was struck lightly and elastically.
5. The test was repeated until similar readings (within 1%), were obtained five times successively.
6. The reading was recorded for elastic modulus determination.



X = impulse point
M = microphone sensor point

Figure 5.2 Specimen oriented for flexural vibration

5.5.3.2 The torsional resonant frequency

The same support was used but placed at the midpoint of a specimen's length and width (Figure 5.3). The vibration was detected at one of the nodal points (0.224 of the length of the specimen from each end) not far from the edge while the specimen was struck at the nodal point diagonally opposite to the microphone position. The test was repeated until the same readings, or within 1%, were obtained five times. The reading was then used to calculate the shear modulus.

The dimensions, masses and the corresponding frequency readings were used to calculate the shear modulus G (GPa), elastic modulus (GPa) and Poisson's ratio (ν). The following expression was used to calculate the elastic modulus [13]:

$$E = 0.9465 \left(\frac{m f_f^2}{b} \right) \left(\frac{L^3}{t^3} \right) T_1 \quad (4)$$

where E = elastic modulus (Pa), m = mass of the bar (g), b = width of the bar, L = length of the bar (mm), f_f = resonant frequency of the bar in flexure (Hz), T_1 = correction factor for flexural mode to account for the finite thickness of the bar, Poisson's ratio, etc.

$$T_1 = 1 + 6.585 (1 + 0.0752\nu + 0.819\nu^2) \left(\frac{t}{L} \right)^2 - 0.868 \left(\frac{t}{L} \right)^4 - \left[\frac{8.340(1 + 0.2023\nu + 2.173\nu^2) \left(\frac{t}{L} \right)^4}{1.0006.338(1 + 0.1408\nu + 1.536\nu^2) \left(\frac{t}{L} \right)^2} \right] \quad (5)$$

where ν = Poisson's ratio (assumed value, according to literature).

Shear modulus was calculated using the following equation [13]:

$$G = \frac{4Lm f_t^2}{bt} \left(\frac{B}{1 + A} \right) \quad (6)$$

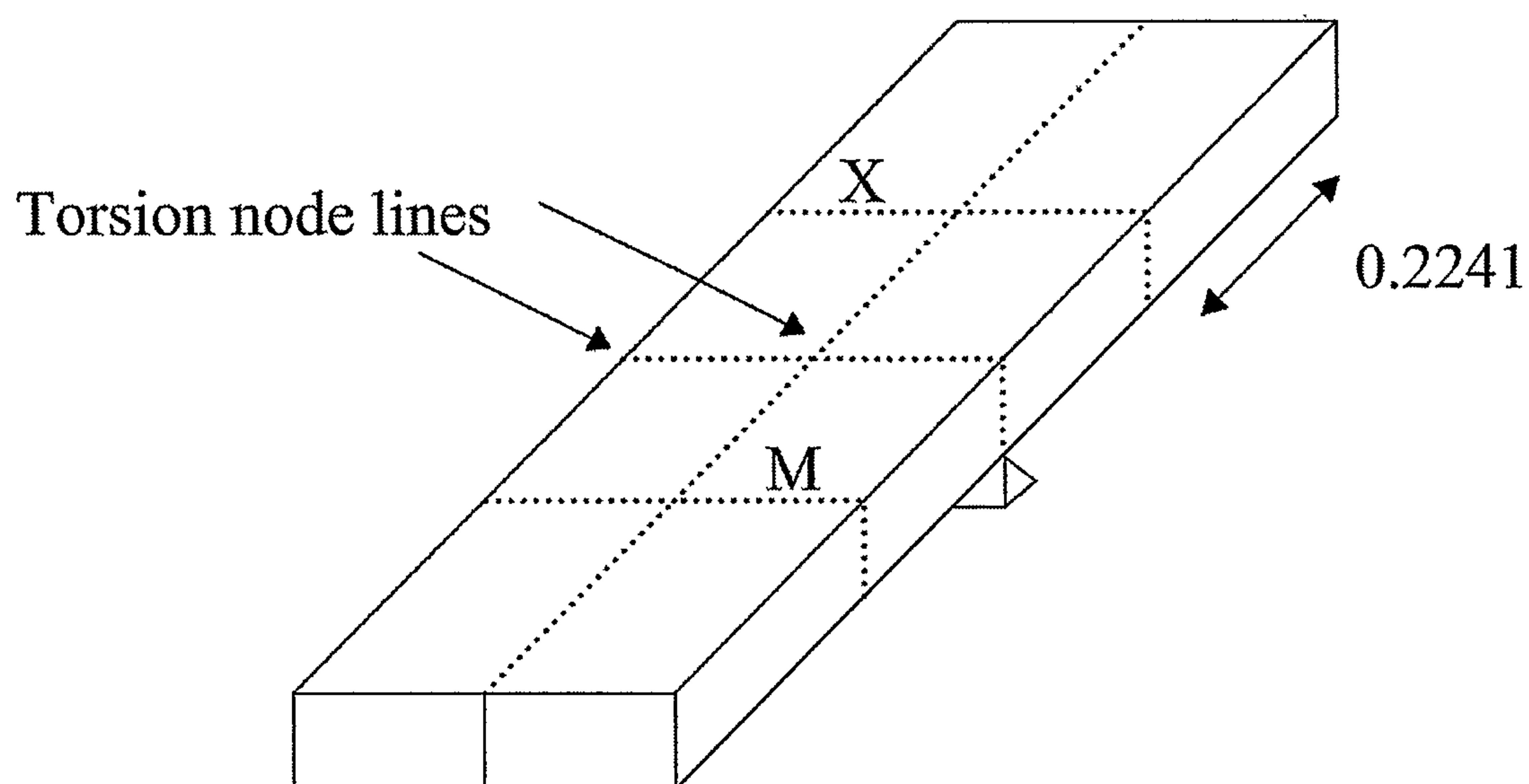
Where G = elastic modulus (Pa), f_t = resonant frequency of the bar in tension (Hz),

$$\text{and } B = \frac{b/t + t/b}{4(t/b) - 2.52(t/b)^2 + 0.21(t/b)^6} \quad (7)$$

And A = an empirical correction factor, which has an effect of $< 2\%$.

The Poisson's ratio was then calculated using the following expression:

$$\nu = \frac{E}{2G} - 1 \quad (8)$$



X = impulse point

M = microphone sensor point

Figure 5.3 Specimen oriented on the support for torsional vibration

5.6 Results

Empress 2 and the experimental ceramic had higher elastic modulus values than Empress 1, but all materials recorded almost the same Poisson's ratio value, as shown in Table 5.1.

Table 5.1 Elastic modulus and Poisson's ratio of the three investigated materials.

Material	Elastic modulus (E) GPa	Coefficient of variation %	Poisson's ratio (ν)	Coefficient of variation %
Empress	65	2	0.23	2
Empress 2	103	4	0.24	3
Experimental ceramic	91	4	0.24	3

5.7 Discussion

The elastic properties of glass ceramic materials are significantly determined by the amount and size of the reinforcing crystals in the glass matrix [14]. The higher the reinforcing crystalline components the higher the elastic modulus and vice versa. This explains the significant difference in the elastic modulus found between Empress 1 and the two lithium disilicate systems (Empress 2 and the experimental ceramic material). In a recent study by Guazzato et al. (2003) it has been reported that the crystalline content (volume fraction of leucite crystals) of Empress 1 is 36%, whereas higher volumes (lithium disilicate crystals) were recorded for both Empress 2 and the experimental ceramic 65 and 67% respectively [15]. The interlocking pattern of these densely backed crystals contributed to the improved elastic modulus of the two materials. The elastic modulus of Empress 2 and the experimental ceramic were 103, 91 GPa respectively, which are very similar to the value of gold alloy [4]. The elastic modulus of Empress 1 was 65 GPa, which falls into the category of feldspathic porcelain, which has typically values of 60-70 GPa and is identical with enamel [14].

Lawn et al. (2001) have recently addressed the significance of evaluating the elastic modulus of dental crown materials [16]. These authors showed that the tensile stresses developed depended upon the ratio of elastic modulus of the ceramic crown and support material as well as the thickness of the crown. Some all-ceramic dental materials, namely Alumina and/or Zirconia-based systems were found to have greater elastic modulus than the present investigated materials. A higher crystalline content, size or shape of these reinforcing systems was also found [17]. The improvements in the elastic modulus have also been accompanied by enhanced flexural strength and

fracture toughness. It is common in brittle materials for strength to scale with the elastic modulus.

The fracture strength of all-ceramic crowns with different core elastic modulus was studied by Lee et al. (2000) [7]. This study reported that the fracture strength of the aluminous porcelain jacket crowns was found to increase with an increase in the elastic modulus of the core material. Accordingly, it was concluded that using cores of high elastic modulus might play a significant role in increasing the fracture resistance of all-ceramic restorations. However, a recent finite element analysis study by Proos et al. (2002) investigated the type of stresses that developed upon using different core all-ceramic materials. Different core substructures made out of the following all-ceramic dental materials: In-Ceram Alumina, In-Ceram Zirconia, In-Ceram Spinel and alumina-based systems were used. Upon loading, the peak radial and hoop tensile stresses were located on the inside of the coping and were proportional to the elastic modulus of the coping [18]. Hence, pre-existing flaws or defects that lie in areas of such high tensile stresses for materials with high elastic modulus are more likely to be areas of catastrophic failure. This may indicate that a material with moderate elastic modulus (100 GPa) and higher fracture toughness may be more reliable than merely greater elastic modulus.

5.8 Conclusion

1. The variation in the Elastic modulus values found between Empress 1 and the two lithium disilicate crystals systems reflects the effect of the structural compositions of these materials.

2. All investigated materials demonstrated similar Poisson's ratio, which may be due to the fact that they are all glass ceramics.

5.9 Hardness

5.9.1 Definition

Hardness is a fundamental mechanical property, which results from the interaction of many properties. It is widely defined as a measure of the resistance to permanent surface indentation or penetration [4].

5.9.2 Importance

Hardness is considered an important mechanical property when comparing restorative dental materials. The significance of measuring hardness in restorative dentistry is that it may delineate the abrasiveness of a material to which the natural dentition may be submitted. It also indicates the ease of finishing a structure and the resistance to in-service scratching [4].

5.9.3 Measurements of hardness

Independent of the type of test, the general procedure for hardness assessment can be summarised as follows: a standardised force or weight using an indenter is applied to a surface of a material. Such force creates a symmetrically shaped indentation (residual impression). The dimensions of the indentation (area, depth or width) are measured at a microscopic level, and entered in a specific hardness formula according to the type of test adopted. These dimensions are normally in an inverse proportion to the material's penetration resistance capability. Therefore, if the same load is applied on a surface of two materials, larger indentation dimensions indicate softer material and vice versa. Hardness values may vary according to the test method used [4].

In fact, various methods are used in evaluating hardness of engineering and ceramic materials. Some of these methods are listed below.

5.9.3.1 Brinell hardness test

This method is one of the oldest methods used to test hardness of metals and alloys of dental applications. A ball-shaped indenter made out of steel or tungsten carbide is used in perform the test. During this test the indenter is left in contact with the surface under the same load for a specific time. This is followed by the measurement of the indentation diameter. The ratio of the applied load to the resultant indentation area is calculated, and the hardness value is called *Brinell hardness number* [4]. A schematic representation of this test is given in Figure 5.4. The Brinell hardness number is given by the following formula:

$$\text{BHN} = L / \frac{D\pi}{2} \left(D - \sqrt{D^2 - d^2} \right) \quad (9)$$

where BHN is Brinell hardness number, L is the load in kilogram, D is the diameter of the ball in millimeters, and d is the diameter of the indentation in millimetres. The units of BHN are kg/mm^2 .

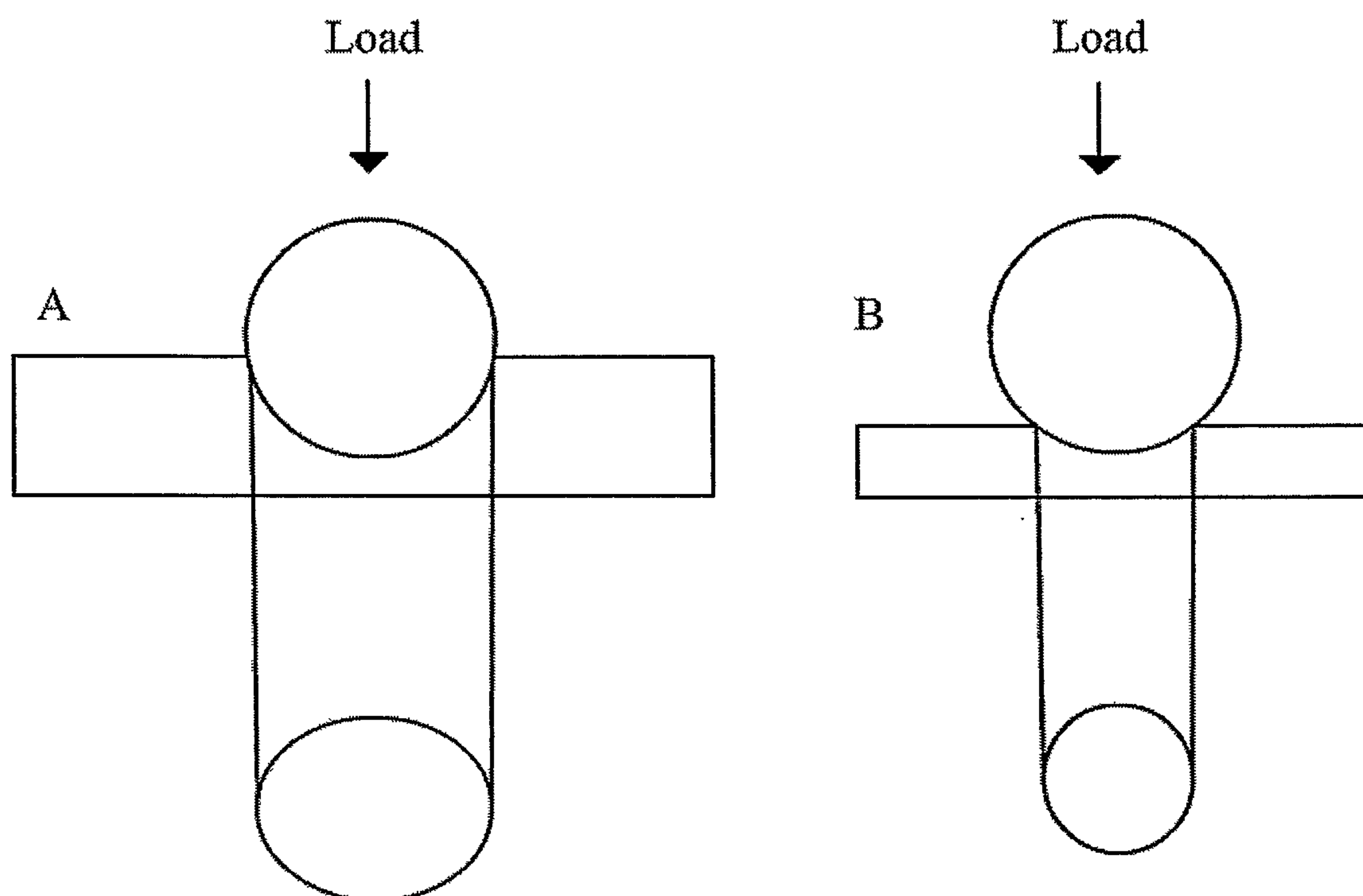


Figure 5.4 Schematic illustration of Brinell hardness test. **A** is an indentation in a soft material and **B** is an indentation in a harder material [4].

5.9.3.2 Knoop hardness test

The need for a hardness test using the micro-indentation method was the main purpose of developing this test. As with the Brinell hardness test, a load is applied to a carefully prepared surface of a material using a pyramid-shaped diamond indenter, and the resultant impression diagonals are measured. Various loads can be applied to the indenter, and hence different impressions can be produced according to the load applied and the nature and hardness of the material. This method has been widely used in assessing both enamel and dentine hardness. The main disadvantage of this test is the time it consumes, and the need for a highly polished and flat surface, which might be a difficult task with very tough and hard materials such as zirconia- or alumina-based materials. The Knoop hardness number (KHN) is given by the following formula:

$$\text{KHN} = \frac{L}{I^2 C_p} \quad (10)$$

where L is the load applied, I is the length of the long diagonal of the indentation and C_p is a constant relating I to the projected area of the indentation. The units for this test are kg/mm^2 [4].

5.9.3.3 Vickers hardness test

This test is very similar in principle to the Brinell and Knoop hardness tests. However, it utilises a 136-degree diamond pyramid indenter (Figure 5.5). The resultant indentation is a square-shaped indentation. Higher loads can be used in this test, and hence it is normally suitable for measuring the hardness of small areas and very hard materials [4].

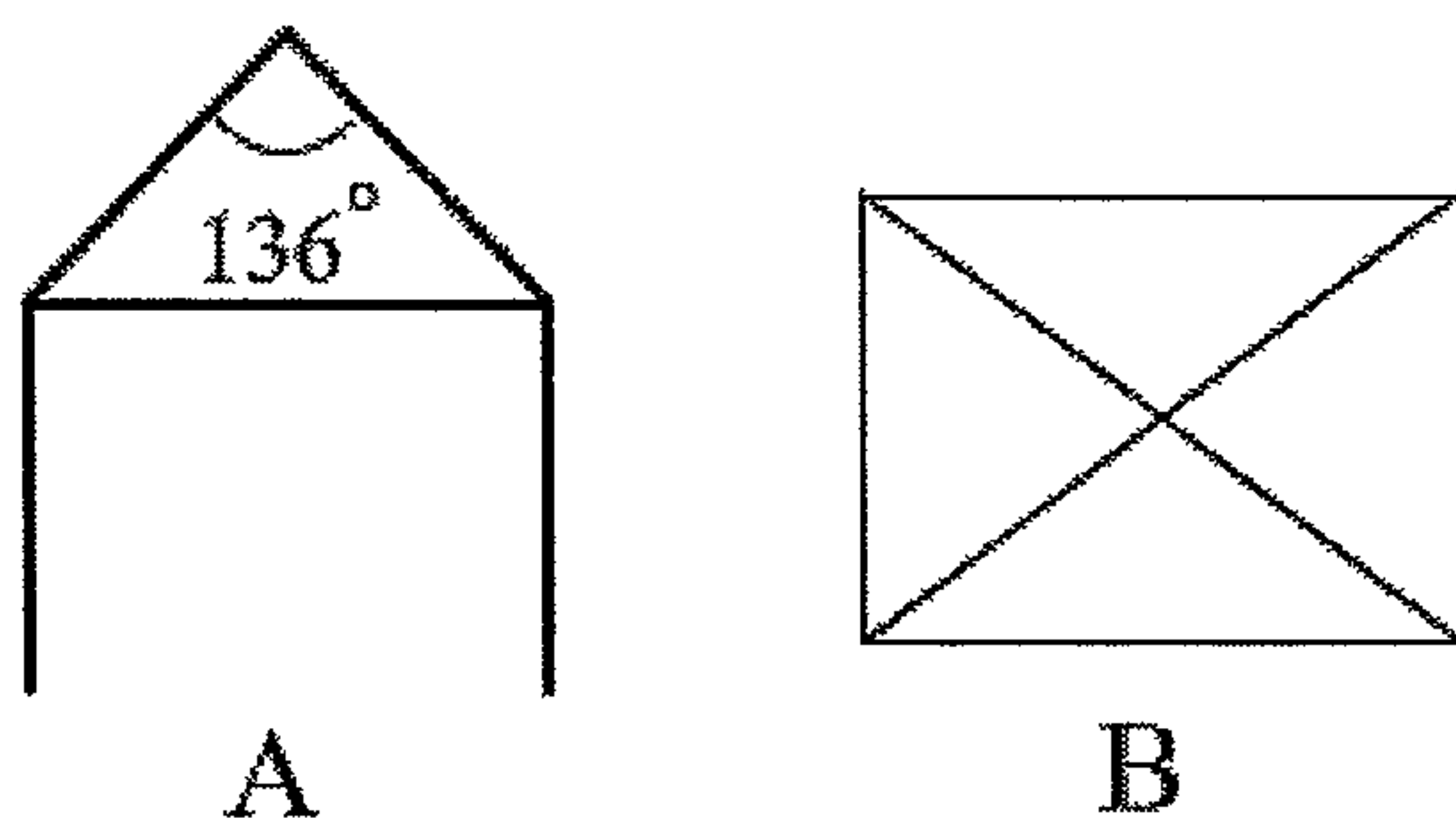


Figure 5.5 Schematic illustration of Vickers indenter, (A) is a side view of the indenter, and (B) is a top view.

There are other techniques that can be used to measure the hardness of materials that have different properties. For example, Rockwell and shore hardness tests are used to measure the hardness of softer dental materials such as plastics, and elastomers.

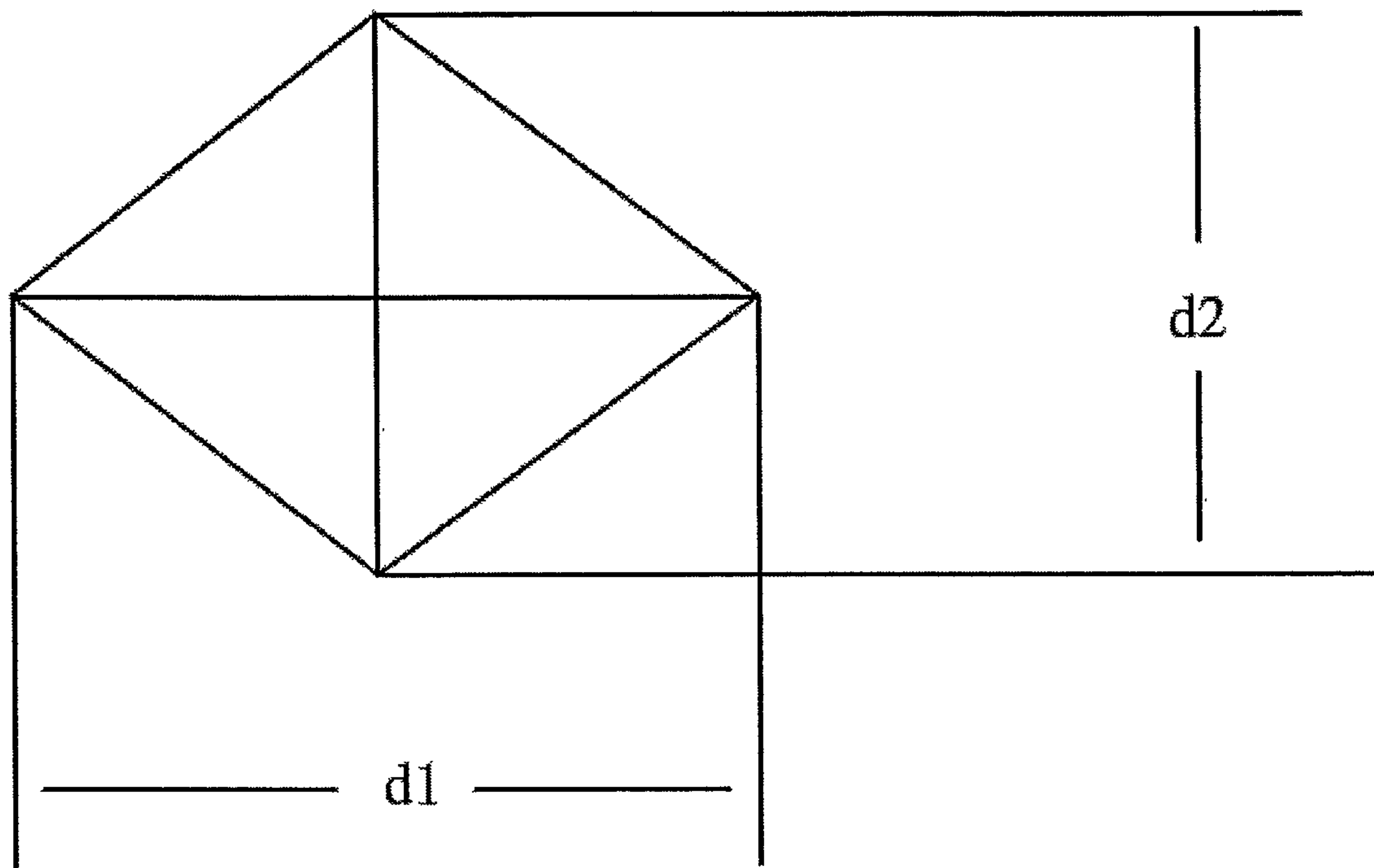


Figure 5.6 Schematic illustration of resultant residual impression following indentation; d_1 and d_2 are horizontal and vertical diagonals.

5.10 Purpose

The present study evaluated the hardness of the three investigated materials, Empress 1, Empress 2 and the experimental ceramic for the following reasons: 1) hardness values of Empress 2 and the experimental ceramics were not available in the literature, 2) measuring the fracture toughness of these materials using the indentation fracture and the indentation strength techniques requires knowledge of their hardness values.

5.11 Preparation of Specimens

This study adopted the Standard Test Method for Vickers Indentation Hardness of Advanced Ceramics according to the American Society for Testing and Materials, designation: C 1327-99 [19].

Two highly polished (mirror-like surface) disc specimens of each material were gold-coated (20 nm), mounted on a universal testing machine (Shimadzu Autograph AG-G series, Kyoto, Japan), and indented with a Vickers diamond pyramid indenter at a series of loads (range from 10 to 80 N). The time of application of the full test load was 15 seconds (± 2). A scanning electron microscope (XL 30 Philips, Eindhoven, Holland) and the optical microscope on an ultra micro-indentation system machine (UMIS 2000, CSIRO, Australia) were used to perform the measurements of the diagonals of the resultant indentations. The requirements for acceptance of indentations were as follows: 1) no cracking around the impression, or on tips or sides of indentations, 2) indentations are symmetric and there were no pores on edges or sides, 3) absence of irregularities on indentations, which indicated that the indenter was chipped or cracked [19].

Twenty-five indentations for each material were made, and ten acceptable indentations were chosen to measure the hardness of each material (Figures 5.7, 5. 8 and 5.9).

The hardness was calculated using the formula suggested by the ASTM, C 1327-99, as follows [19]:

$$HV = 0.0018544 (p/d^2) \quad (11)$$

HV is hardness (GPa), p is load (N), d is the average length of the two horizontal and vertical diagonals (Figure 5.6) of the indentations (mm), and 0.0018544 is a geometrical constant.

5.12 Results

The hardness results were: 6.6, 5.3 and 5.5 GPa for Empress 1, Empress 2 and the experimental ceramic respectively (Table 5.2). The hardness of Empress 1 was statistically greater than those of Empress 2 and the experimental ceramic ($P = 0.001$).

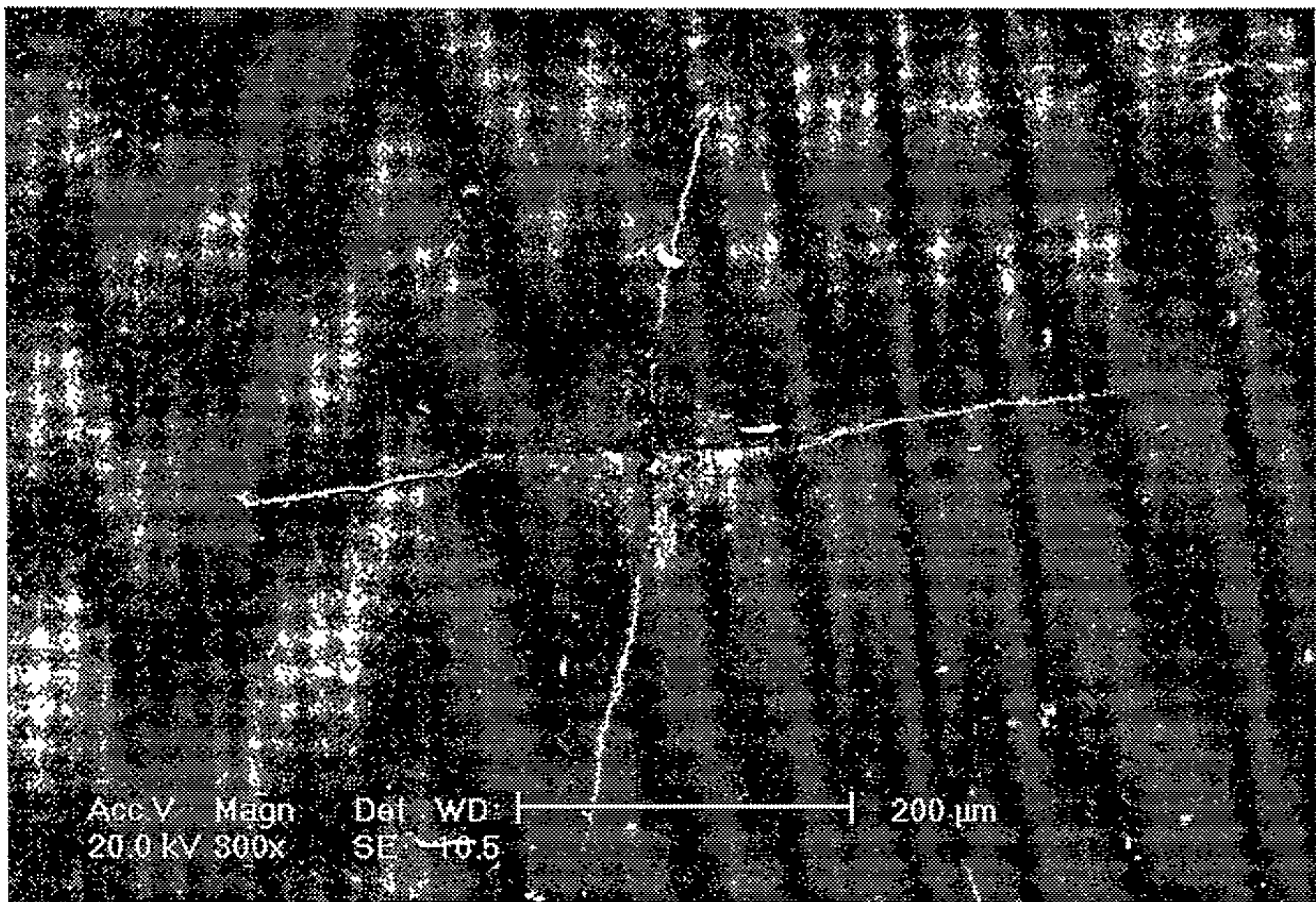


Figure 5.7 SEM photomicrograph of a residual impression of Empress 2 after indentation, used for hardness measurements.

Table 5.2 Hardness results (GPa) of the three investigated materials; load range was from 10 to 80 N.

Material	Hardness (GPa) (±SD)
Empress 1	6.6 (0.4)
Empress 2	5.3 (0.2)
Experimental ceramic	5.5 (0.2)

SD = standard deviation

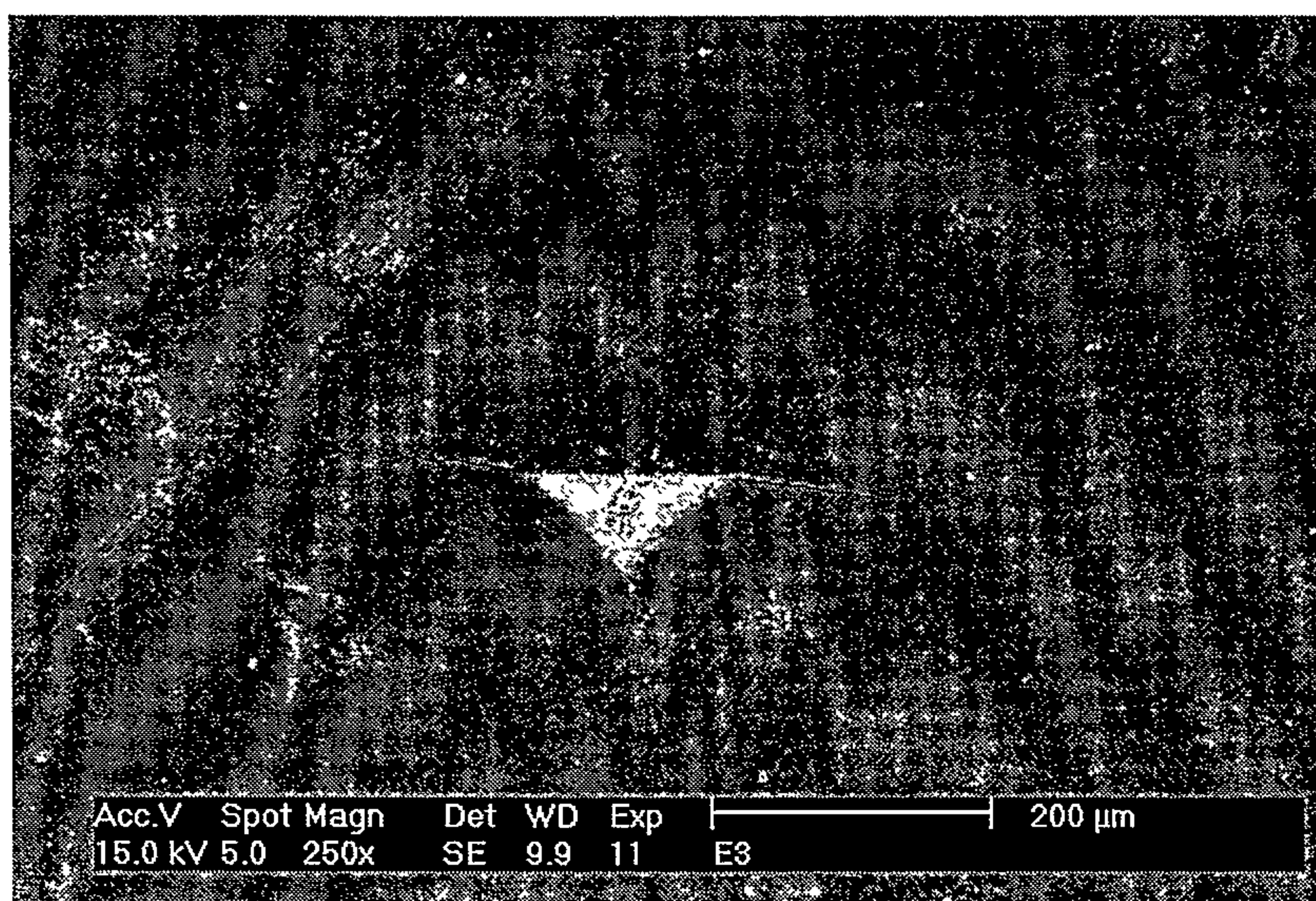


Figure 5.8 SEM photomicrograph of a residual impression of the new experimental glass ceramic after indentation.

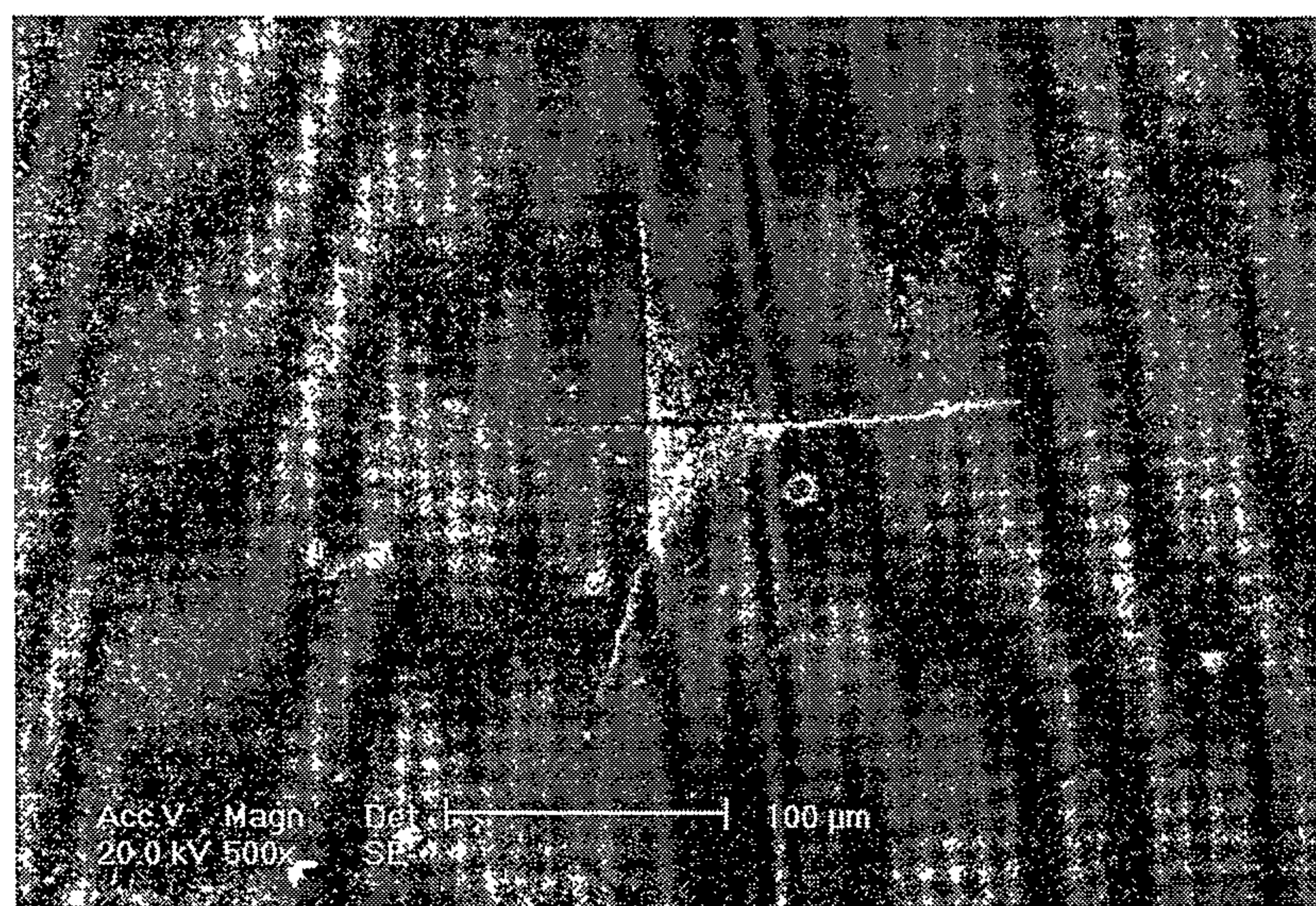


Figure 5.9 SEM photomicrograph of a residual impression of Empress 1 following indentation, used for hardness measurements.

5.13 Discussion

Hardness results of the present study showed that Empress 1 had the highest hardness value. This result is in good agreement with results found in the literature [20, 21]. In

fact, the use of Empress 1 (staining technique) in single units such as veneers, onlays, inlays, where the direct contact of the occlusal surface of a tooth is expected, would indicate the importance of hardness. This is because hardness might delineate the wear that natural dentition might be submitted to during contact (occlusion). Krejci et al. (1993). studied the wear characteristics of Empress 1 and found that these are similar to those of natural dentition [22]. This minimises the harmful effect of abrasion, which might take place during contact with the natural dentition. However, although resistance to abrasion normally increases as the hardness increases, this is not always true when brittle materials are considered. Brittle fracture can occur resulting in many hard abrasive particles, which can speed up the abrasion process. Therefore, fracture toughness, as the ability of resisting crack propagation, should play a very important role in this regard. Lawn stated that lateral cracks, resulted from repetitive particulate contacts, are the main agents for surface removal and subsequently wear. He also reported that materials that have improved fracture toughness, but not necessarily better hardness, should possess the greatest wear resistance capabilities [23].

The lithium disilicate materials, Empress 2 and the experimental ceramic, demonstrated lower hardness than Empress 1. As expected, and based on their similar crystalline content, both materials had similar hardness values. No comparative data in the literature were found for both materials. The hardness values of these materials are similar to that of enamel (4.9 GPa) [24]. Hence, both materials might be more compatible during direct contact with the natural dentition than Empress 1. These materials are used to build up core for fixed partial dentures and hence are covered with porcelain veneer material. Even so, the direct contact with the natural dentition

may occur in non-aesthetic areas, where the bulk of core materials can be exposed in areas that require additional strength, such as the connector regions.

5.14 Conclusion

1. Empress 1 had higher hardness than Empress 2 and the experimental ceramic.
2. Empress 2 and the experimental ceramic had similar hardness values, which was attributed to the similar chemical composition (same crystalline content).
3. Lower hardness of Empress 2 and the experimental ceramic might be beneficial for the wear characteristics of opposing teeth.

5.15 References

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CHAPTER 6

FRACTURE TOUGHNESS

The study of forces and stresses on teeth and dental restorative materials is a very important aspect of dental materials science [1]. Crack propagation and subsequent fracture has been cited as the major problem that leads to ultimate structural failure. Fracture mechanics concepts have been applied recently to characterise the fracture mode of dental materials [1]. To substantiate the ability of brittle materials to bear load and stresses and also appraise the liability to fracture, the mechanical properties must be assessed. Fracture toughness is one of the most important mechanical properties that delineate the fracture behaviour of a specific material. It has gained wide acceptance as a technique suitable for the assessment of ceramic materials' ability to resist crack extension.

In this chapter, fracture toughness of the investigated materials Empress 1, Empress 2 and the experimental ceramic will be presented. In the first part (6.1-6.5), definition, importance, measurement methods and purpose of evaluating fracture toughness of these materials will be given. The second part (6.6-6.10) will outline the methods adopted in the present study, experiments, results, discussion and conclusion. Finally, the effect of heat pressing on the fracture toughness of the same materials will be introduced in the third section.

6.1 Introduction

Most brittle materials fail in tension because of their limited ability to absorb a substantial amount of elastic strain energy before fracture [2, 3]. Dental ceramics are brittle materials, and the major shortcomings of these materials are manifested in their sensitivity to flaws and defects, low tensile strength, and propensity to catastrophic failure [2]. Microscopic surface flaws and defects, which may develop as a result of thermal, chemical or mechanical processes, act as localised stress concentrators [4]. These applied stresses can cause cracks to originate from the defect sites and propagate, leading to catastrophic failure. Efforts to improve the longevity of all-ceramic materials have been directed towards improving their strength and fracture toughness [5].

6.2 Definition

Fracture toughness is defined as the critical stress intensity level at which a given flaw starts growing, and indicates the ability of a material to resist rapid crack propagation and its consequent catastrophic failure [6]. It is considered an intrinsic property and an appropriate parameter that can indicate the structural performance of brittle materials. Unlike strength, it is a genuine characterisation of a mechanical behaviour, as it is normally independent of the size or density of surface flaws [2, 7, 8].

6.3 Importance

Measurement of the fracture toughness of a specific ceramic material not only imparts insight into the ability of a material to resist crack propagation, but also influences the thermal shock resistance [9]. Another important feature of fracture toughness is its ability to indicate a material's serviceability in the oral cavity [10, 11]. Furthermore,

when studying fracture behaviour and toughening mechanisms of brittle materials, fracture toughness data often produce useful information concerning the role played by the crystalline phase within the glass matrix. In fact, reliance entirely on the mechanical properties appraisal is not sufficient to draw a valid prediction for the long-term clinical success and performance of brittle materials [12]. However, it has been stated that materials with high fracture toughness may demonstrate improved clinical performance and these are consequently regarded as more reliable than low fracture toughness materials [13].

6.4 Measurements of fracture toughness

Various methods and techniques have been used for the determination of the fracture toughness of brittle materials. Some of these techniques are conventional fracture mechanics that utilise notches and secondarily induced precracks. Examples of these methods include: compact tension [14], double cantilever beam [15], single-edge-notched-beam [16], single-edge-precracked-beam [17], and chevron notch [18]. Some other techniques utilise diagnostic microcracks introduced by Vickers or Knoop indenters. These techniques are: indentation fracture (IF) [19], and indentation strength (IS) [20][21].

The application of the indentation fracture technique (IF) in studying the behavior and properties of brittle materials is specifically appropriate because only small dimensional specimens are required and the crack growth parameter is similar to those cracks expected in clinical conditions [22]. Utilising this technique, an approximate determination of relative fracture toughness is assessed by introducing flaws of controlled size, shape and location into a sample, in order to characterise the

fracture process (Figure 6.1). This is followed by the direct measurement of the radial crack formed by a Vickers indentation. This technique is simple and requires only a few specimens for testing, however, it results in high dispersion as a result of difficulties inherent with the accurate measurement of crack length and subcritical slow crack growth [6, 22].

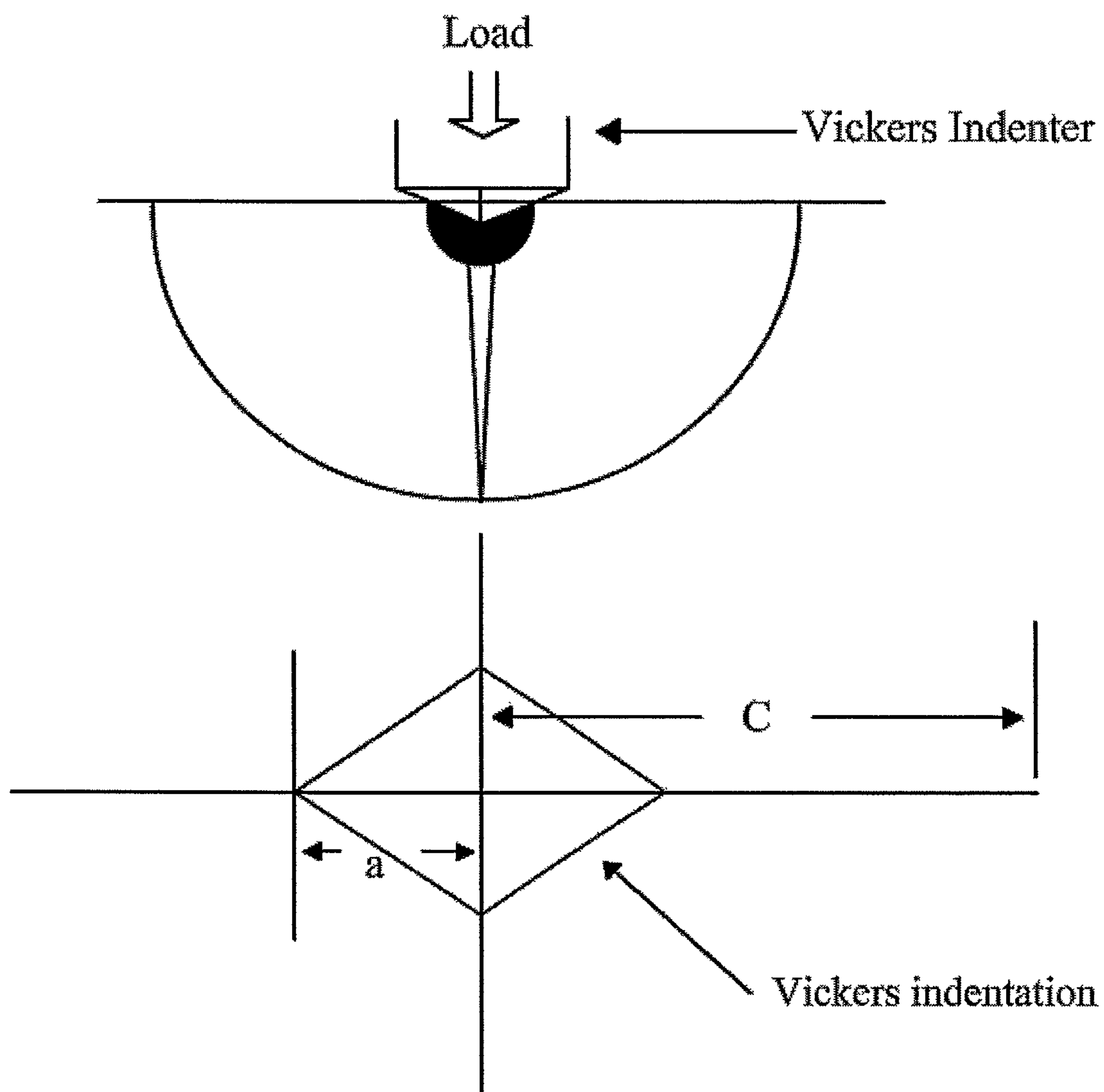


Figure 6.1 Schematic representation of Vickers-produced indentation fracture system, where a is half diagonal and C is radial crack measured from the middle of indentation.

The indentation strength technique (IS) has been less frequently used than the indentation fracture (IF). It is performed by introducing a flaw into a specimen with an indenter (Knoop or Vickers) followed by the application of tensile stress on the indented surface of the specimen until fracture in either a three- or four-point bending, or biaxial flexure test. The measurement of the crack length is not required in this test because the crack will propagate as a response to the external load until it reaches a critical size and catastrophic failure occurs [20].

6.5 Purpose

Before the release of a new all-ceramic dental material into the market, mechanical assessments, which includes the fracture toughness measurement, should be carried out. This provides clinicians and researchers with valuable information in selecting the appropriate material and technique and enables comparison with peer materials. In the present study, the fracture toughness of the three materials was appraised for the following reasons:

- 1) The manufacturer of Empress 1 and Empress 2 (Ivoclar, Schaan, Liechtenstein) was about to release a new all-ceramic dental material (experimental ceramic material), which is stated to be suitable for the fabrication of core substructure for three-unit fixed partial denture. This material is claimed to possess improved mechanical properties over that of Empress 1 and Empress 2. Thus, this material was supplied by the manufacturer for mechanical property comparison with Empress 1 and Empress 2.

- 2) Fracture toughness of Empress 2 was not available in the literature and only a few reports conducted by the manufacturer's team of researchers are available.
- 3) Consistency of fracture toughness using different fracture toughness techniques was also verified.

6.6 Test methods

This study utilised two techniques, indentation fracture (IF) and indentation strength (IS). The IS technique was adopted in biaxial flexural strength, and in three-point bending methods.

6.6.1 Indentation fracture (IF)

Several disc specimens were gold-coated (20 nm), mounted on a universal testing machine (Shimadzu Autograph AG-G series, Kyoto, Japan), and indented with a Vickers diamond pyramid indenter at loads of (40, 60, 80, 100, and 120 N). Three acceptable indentations for each load were chosen. The suitability of the indentations was based on the following requirements [6]: 1) presence of only four radial cracks, with the crack length (measured from the middle of an indentation) 2.3 times longer than half the diagonal of an indentation, 2) symmetrical indentation, 3) absence of chipping or ragged edges, 4) absence of pores at either the tips or the perimeter of an indentation. A scanning electron microscope (XL 30 Philips, Eindhoven, Holland) and the optical microscope on an ultra micro-indentation system machine (UMIS 2000, CSIRO, Australia) were used to perform the measurements of the radial cracks within a few hours after the indentation. The fracture toughness was calculated using the following formula [19]:

$$K_{IC} = 0.016(E/H)^{1/2} (P/c^{3/2}) \quad (1)$$

where 0.016 is a material-independent constant, E is the elastic modulus (GPa), H is the hardness (GPa), P is the indentation load (N) and c is the crack length (m) measured from the middle of the Vickers indentation.

6.6.2 Indentation strength (IS)

A drop of oil was placed on a mirror-like surface. Using a universal testing machine, a Vickers diamond pyramid indenter was used to introduce an indentation at the centre of fifteen disc specimens and fifteen bar specimens at loads of (4, 8, 16, 32, and 64 N). The disc specimens were then subjected to biaxial flexural strength testing (piston on three ball method) (Chapter 7, 7.6.2) and the bar specimens subjected to the three-point bending tests (Chapter 7, 7.6.1) by exerting tensile stress on the indented surfaces until fracture. The biaxial test was performed with a crosshead speed of 0.5 mm/min. The stress at fracture was calculated according to the equation suggested by ASTM (F 394-78), as follows [23]:

$$S = -0.2387 P (X-Y) / d^2 \quad (2)$$

where S is the maximum tensile stress, -0.2387 is a numerical constant ($3/4\pi$), P is the load at fracture and d is the specimen thickness at fracture origin.

Poisson's ratio (Chapter 5, 5.8), the radius of the support circle, the radius of the tip of the piston and the radius of the specimen were used to determine X and Y (Chapter 7, 7.6.2). The three-point bending test was performed with a crosshead speed of 0.5mm/min and span length of 14 mm. The stress at fracture (S_f) was calculated using the following equation as follows [24]:

$$S_f = \frac{3WL}{2B D^2} \quad (3)$$

where W is the breaking load (N), L is the span length (m), B is the specimen's width (m) and D is the specimen's thickness (m).

All specimens were examined to confirm that the fracture occurred from the indentation site. The fracture toughnesses for the bar and disc specimens were then calculated as follows [20]:

$$K_{IC} = 0.59(E / H)^{1/8} (S_f P^{1/3})^{3/4} \quad (4)$$

where 0.59 is a geometrical constant, E is the Elastic modulus (GPa), H is the hardness (GPa), S_f is the stress at fracture (MPa), and P is the indentation load (N).

For the crack-microstructure interaction, one finely polished sample of each material was etched, carbon-coated (20 nm) and indented, using a Vickers indenter, at various loads (range from 10 to 50 N). The field emission scanning electron Microscope was then used to observe the crack-microstructure interaction.

6.7 X-ray Diffraction

In order to verify the difference in the crystal orientations between the bars used for the three-point bending test, the discs used for the biaxial test and the sprue button, the following specimens were prepared. Several fractured surfaces of the bars and also of the discs were attached to each other to form relatively flat surfaces. For the sprues button, several sprues (2.5 mm diameter) were glued together and a slice orthogonal to the cylindrical axis of the sprues was cut with a diamond saw and polished. The X-ray diffraction patterns of these samples were collected following the same procedure adopted in the X-ray diffraction section (Chapter 4, 4.2.4). Also

illustrated in Figure 6.2 are the shapes of specimens that were used to collect X-ray diffraction.

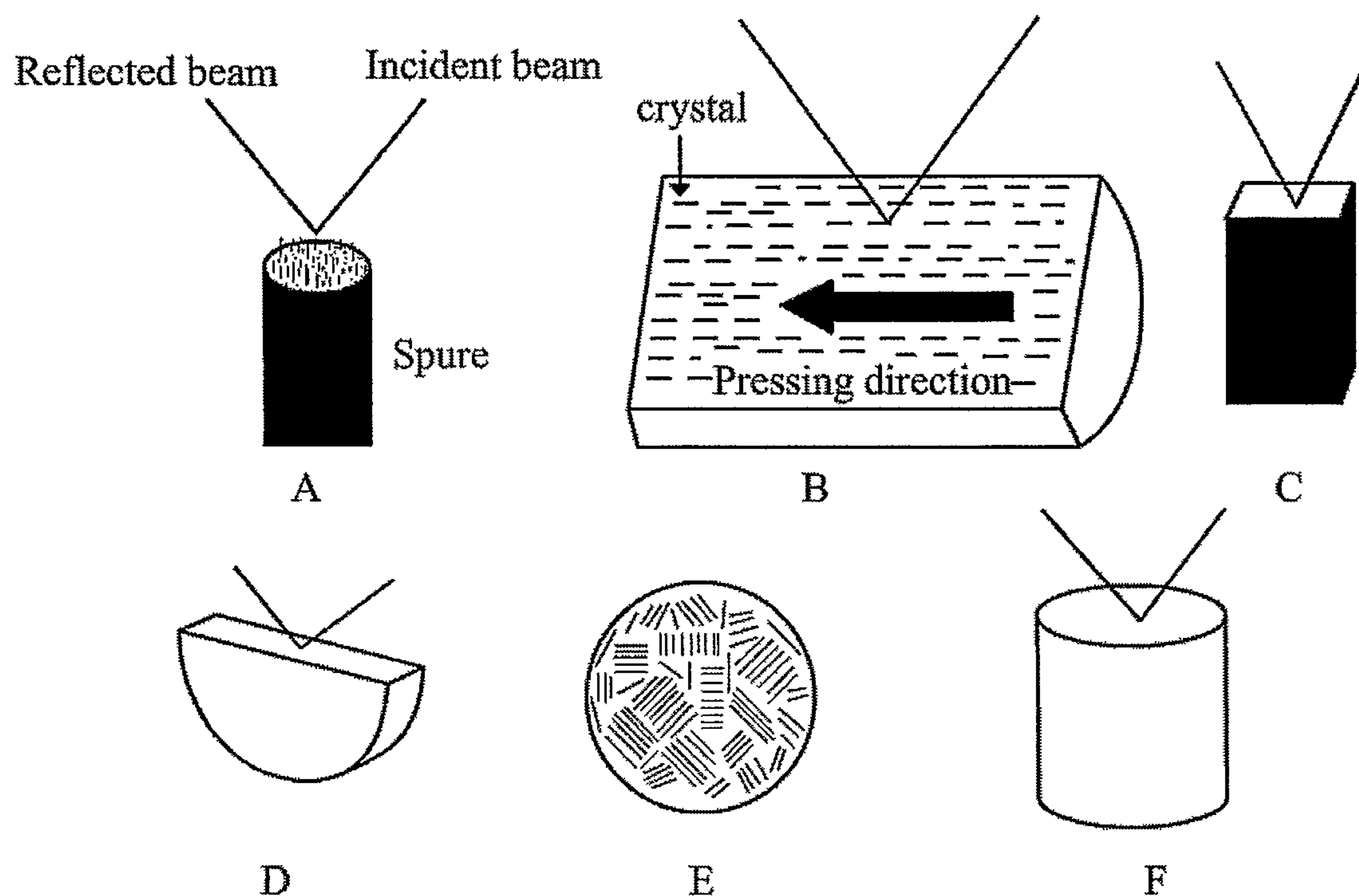


Figure 6.2 Schematic illustration of specimen shapes that were used to collect X-ray diffraction. A represents the sprue where the beam reflected from the tip of lithium disilicate crystals; B is a cross section of a sprue showing the way in which most lithium disilicate crystals are aligned; C is a fracture surface of a bar; D is a fracture surface of a disc; E is a disc showing the way in which the lithium disilicate crystals are aligned; F is a block prior to pressing.

6.8 Results

Fracture toughness results using all testing methods are listed in Table 6.1 and also charted in Figure 6.3. There was no statistically significant difference in fracture toughness, using all techniques, between Empress 2 and the experimental ceramic ($P > 0.05$). Using the IF technique, the indentations were found to generate orthogonal cracks for Empress 2 and the experimental ceramic (Figures 6.4 and 6.5), which had

remarkably different crack lengths. Thus, two values for IF technique were reported for Empress 2 and experimental ceramic. The cracks propagating perpendicular to the lithium disilicate crystals demonstrated significantly higher fracture toughness than those that propagating parallel to these crystals ($P = 0.008$). No statistically significant difference was found among all Empress 1 fracture toughness results ($P > 0.05$), whereas the four fracture toughness results of Empress 2 and the experimental ceramic varied significantly ($P = 0.001$). IS (three-point bending) demonstrated the highest fracture toughness value and IF (long cracks) the lowest. Both materials had significantly higher fracture toughness results than those of Empress 1 ($P = 0.001$), except the IF long crack values which showed no significant difference when compared with Empress 1 values ($P > 0.05$). The Vickers indentation of Empress 1 is shown in Figure 6.6; note the similar crack lengths emanating from the corners of an indentation, and less defined edges than those noticed for Empress 2 indentations.

Table 6.1 Fracture toughness (MPa·m^{1/2}) results of the three pressable materials.

Material	IS 3 point bending (SD)	IS Biaxial (SD)	IF Short cracks (SD)	IF Long cracks (SD)
Empress 1	1.39 (0.3)	1.32 (0.3)	1.26 (0.1)	NA
Empress 2	3.14 (0.5)	2.50 (0.3)	1.53 (0.2)	1.16 (0.2)
Experimental ceramic	3.32 (0.6)	2.43 (0.3)	1.67 (0.3)	1.15 (0.2)

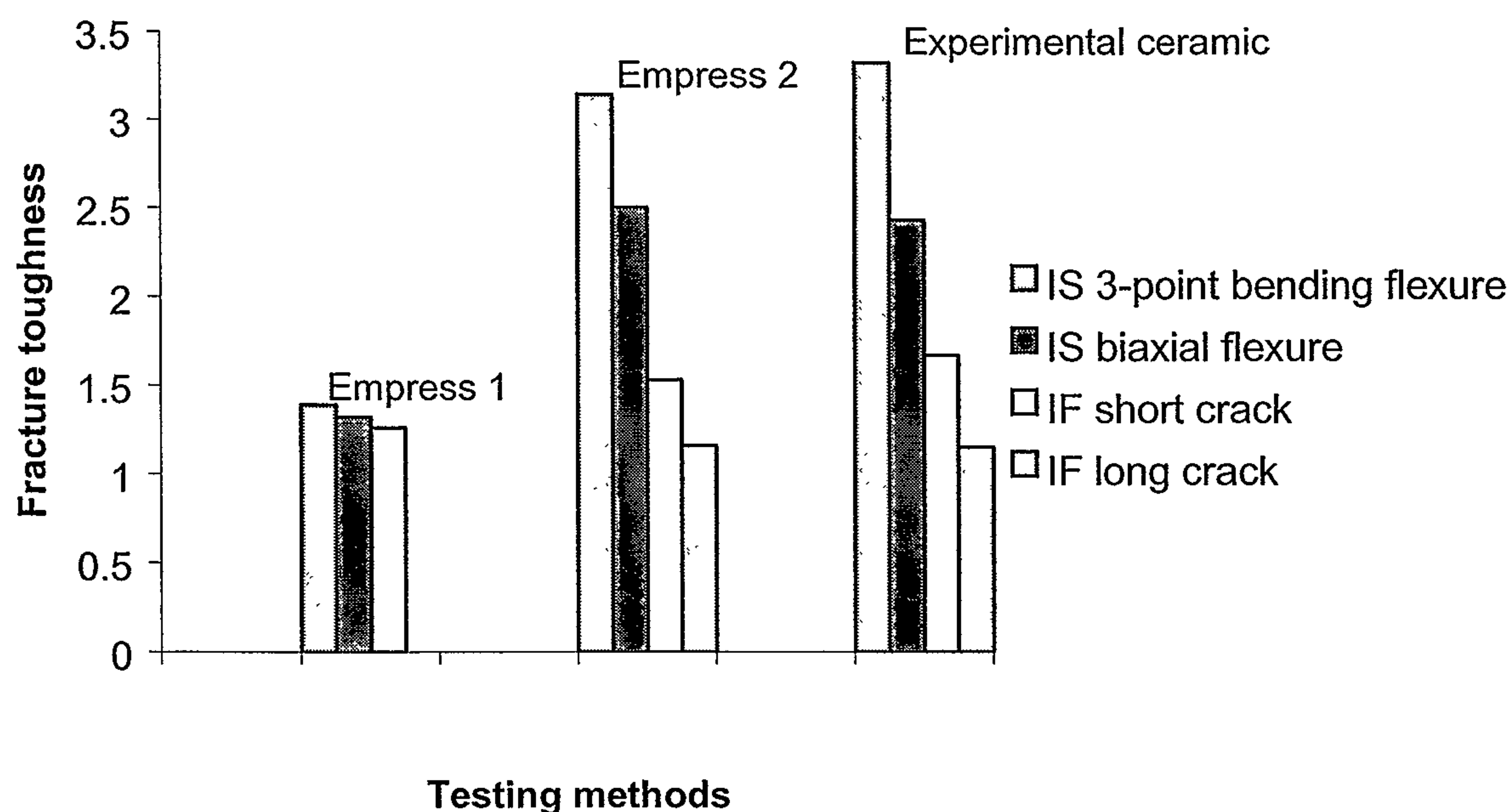


Figure 6.3 Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$) of the three materials versus different testing techniques.

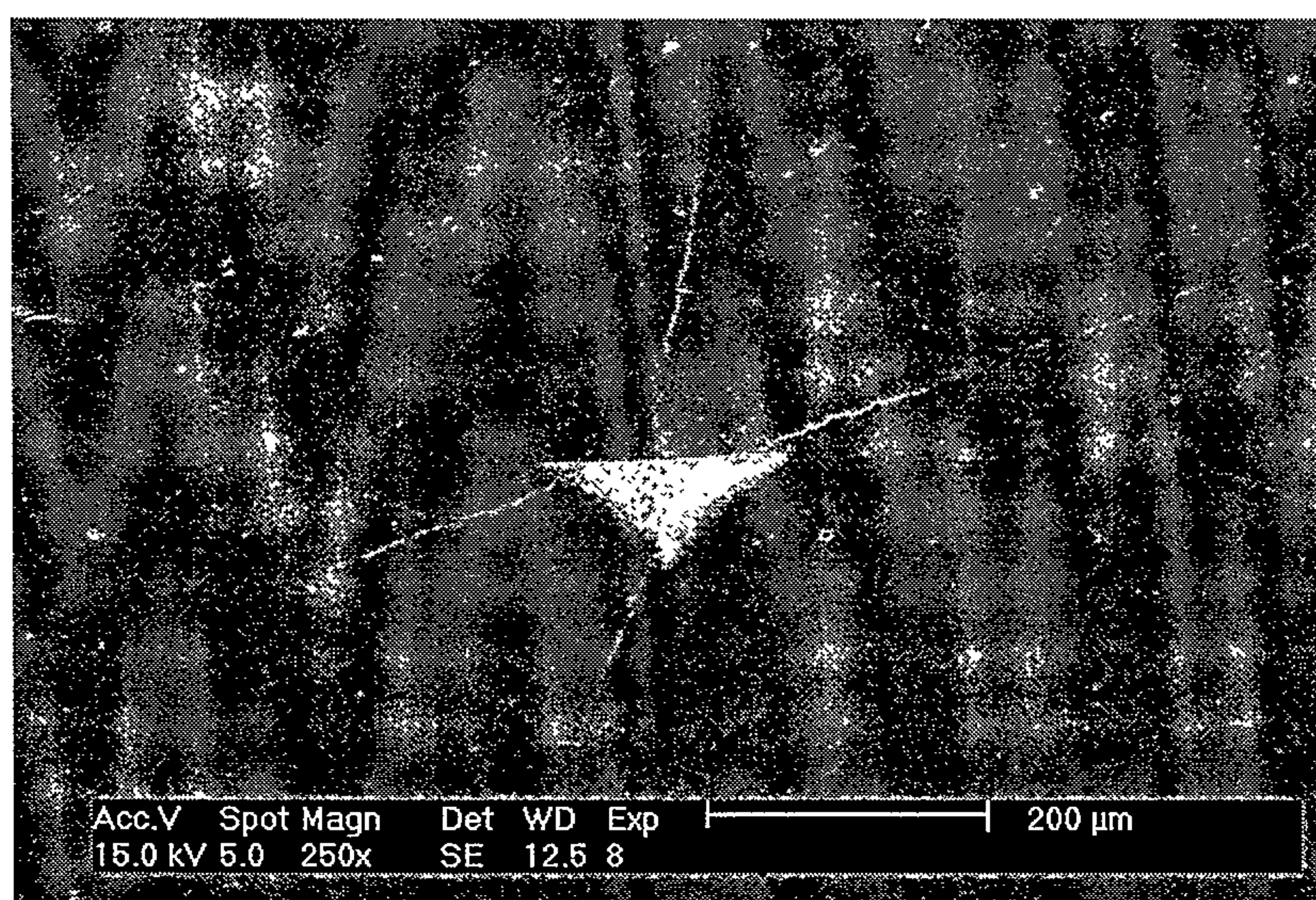


Figure 6.4 SEM photomicrograph of orthogonal cracks emanating from the corners of an indentation of Empress 2 with different crack lengths along the X- and Y-axis.

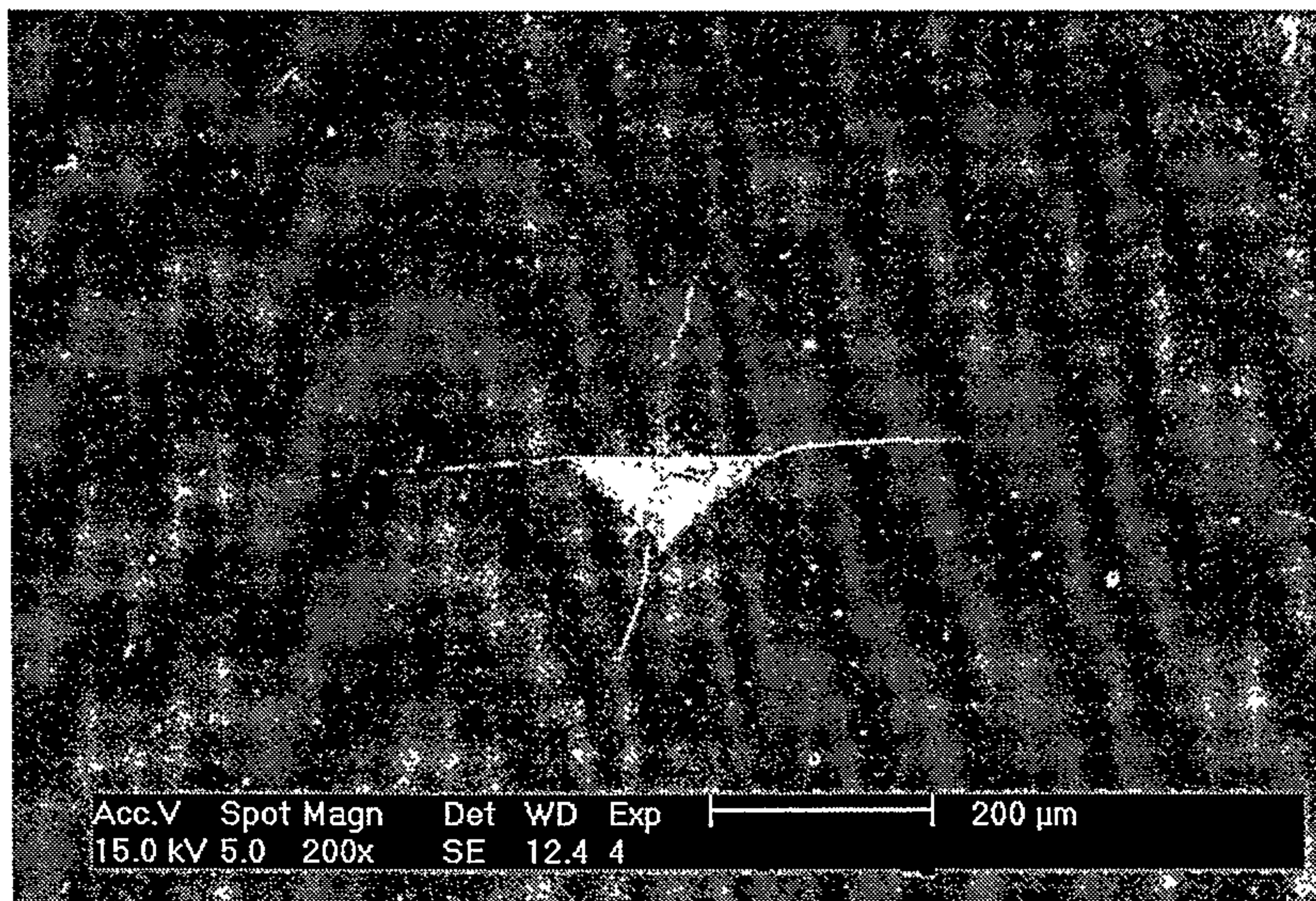


Figure 6.5 SEM photomicrograph of orthogonal cracks emanating from the corners of an indentation of the experimental ceramic with different crack lengths along the X- and Y-axis.

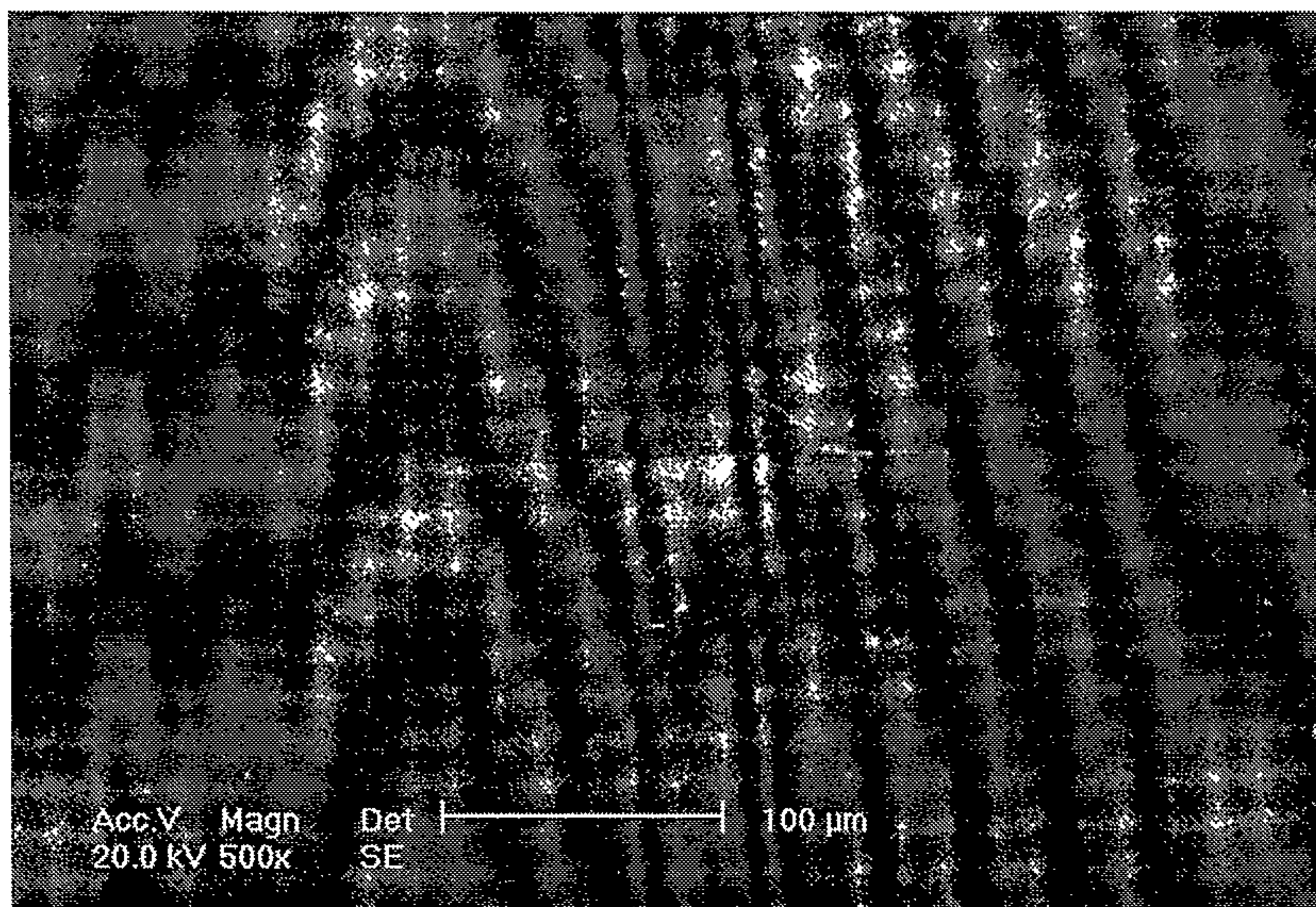


Figure 6.6 SEM photomicrograph of an indentation of Empress 1 showing similar cracks emanating from the corners of the indentation.

In Figure 6.7 the diffraction pattern of Empress 2 before pressing (A) is compared to that of the fractured surfaces of the discs (B), and the sprue (C) is compared to the fractured surfaces of the bars (D). No difference in the X-ray diffraction patterns was

observed between Empress 2 and the experimental ceramic. The X-ray diffraction pattern of Empress 2 before pressing is almost identical with the expected intensities for the JCPDS diffraction data of lithium disilicate crystals randomly aligned. The most intense peak is the (111) of the monoclinic α -Li₂Si₂O₅ crystals. However, for the sprues the intensity of the (002) plane, which is perpendicular to the long axis of the monoclinic crystals, is of comparable intensity to the (111) plane. The fracture surfaces of the discs and bars showed X-ray intensity patterns similar to those of the unpressed and sprue surfaces respectively. This issue will be considered more in the discussion section.

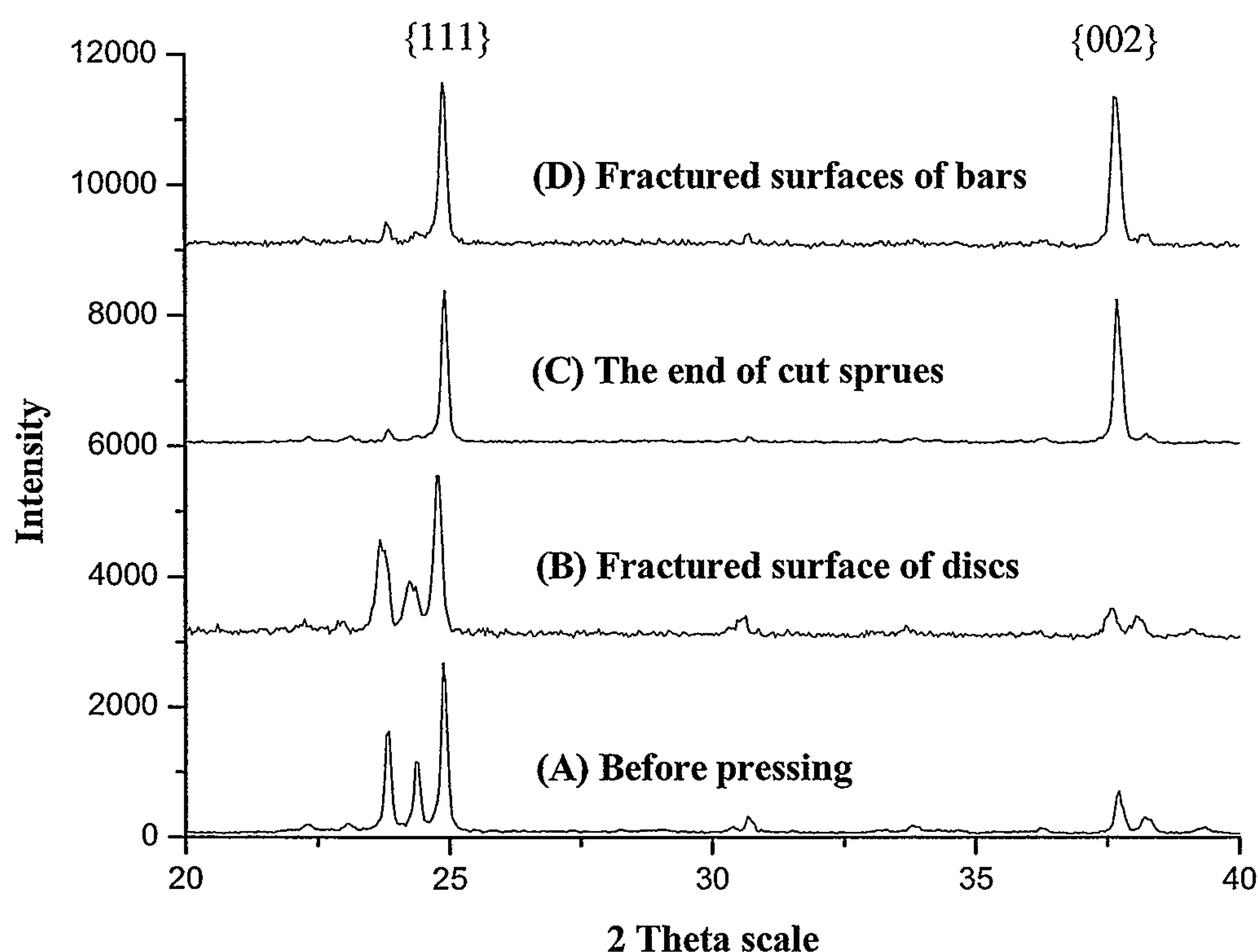


Figure 6.7 X-ray diffraction patterns of Empress 2: (A) before pressing (block), (B) fractured surfaces of discs, (C) the end of cut sprues, (D) fractured surfaces of bars.

$\{111\}$ and $\{002\}$ are the two crystallographic planes with the dominant peaks diffracted from for the fractured surfaces of the bars and the sprues.

6.9 Discussion

6.9.1 Fracture toughness results

Fracture toughness in the present study was evaluated using three different techniques to verify the consistency of the toughness results for the studied materials. Empress 1 demonstrated similar toughness values using all techniques. This result was somewhat surprising, as sub-critical crack growth associated with the IF technique generally leads to a lower value of fracture toughness than the IS method, where the presence of oil on the residual impression reduces this effect. It is usual that the IF technique results in lower values of toughness than the IS and other techniques. This is generally attributed to the shortcomings of the IF technique including the incorrect measurement of the radial crack length, assumption about residual stresses associated with the indentation and, most importantly, the subcritical crack growth by the presence of moisture during the time interval between indentation and crack length measurement. The similarity of the IF and IS techniques may arise because of the significant residual stresses within the material due to the higher thermal expansion of leucite. These residual stresses can influence not only the crack extension behaviour but also the nature of the overall residual stress state around the indentation impression. The high shear stresses and strains that develop within this deformed zone about the indentation will assist in the formation of many small microcracks within and about the leucite crystals. This deformation will release much of the residual stresses and reduce the size of the radial cracks on the surface surrounding the impression.

The IF results for Empress 2 and the experimental ceramic indicate that differences up to 23% and 31% can be observed for these materials depending upon the orientation used to take the measurements. These indentations (Figures 6.4 and 6.5), with different crack lengths, may have been introduced into sites of highly agglomerated crystals that are aligned parallel to each other (Chapter 4, Figure 4.30). A schematic illustration of the alignment of acicular lithium disilicate crystals is shown in Figure 6.8. It is suggested that cracks propagating parallel to the path of aligned lithium disilicate crystals were longer than those cracks extending perpendicular to the crystals and resulted in a lower estimated fracture toughness. Cracks propagating across the crystals are hindered by the aligned crystals as a result of the bridging and crack deflection toughening mechanisms and consequently required more energy to continue propagating, resulting in higher fracture toughness values. It was also noticed in some indentations that cracks did not extend parallel to the diagonal directions of the Vickers indentation but almost parallel to the indentation edges (Figure 6.4). The edges of the residual impression about the Vickers indentations of Empress 2 and the experimental ceramic materials are well defined with sharp plastic-like deformation.

The present study found a significant difference in the fracture toughness measured according to the short crack and long crack for both Empress 2 and the experimental ceramic, and obviously the two materials demonstrated higher fracture toughness values for cracks propagating perpendicular to the aligned crystals (short cracks). These findings are similar to the outcomes reported by Breder et al. (1990) [25] for whisker-reinforced ceramics. These investigators found that fracture toughness anisotropy occurs as whiskers are aligned orthogonal to the heat-pressing

direction. Accordingly, toughening mechanisms such as bridging cannot be applicable if a crack propagates perpendicular to the heat-pressing direction. Therefore, measuring fracture toughness in that direction, that is, parallel to the whiskers, resulted in 30% lower values than those measured with a crack propagating parallel to the heat-pressing direction. A recent study by Denry et al. (2002) [26] found a significant difference in the crack lengths perpendicular or parallel to the heat pressing direction of mica glass ceramic, which was a result of the preferred orientation of these elongated crystals along the heat-pressing direction. The alignment of crystals in lithium disilicate glass ceramics has been explained in Chapter 4, (section 4.12).

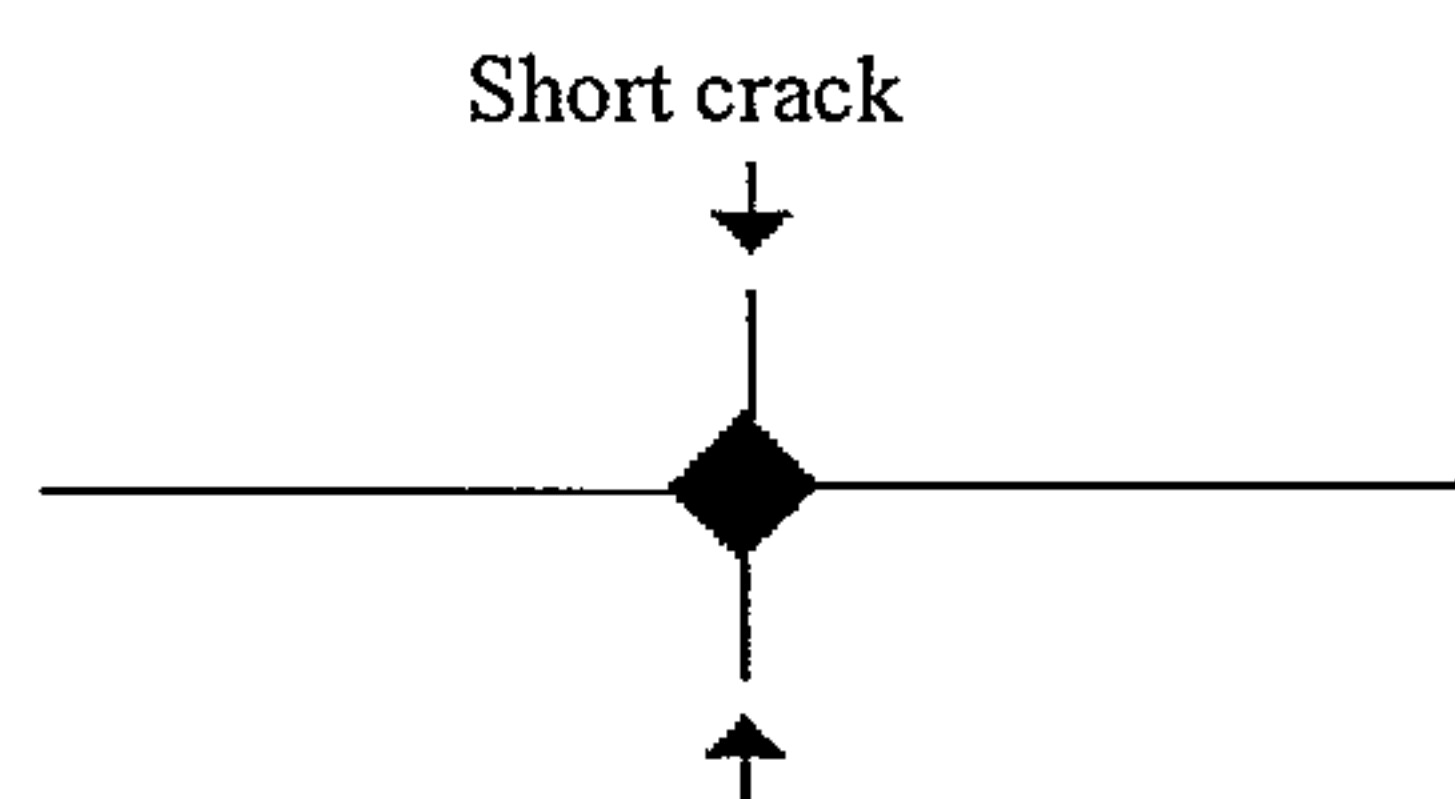
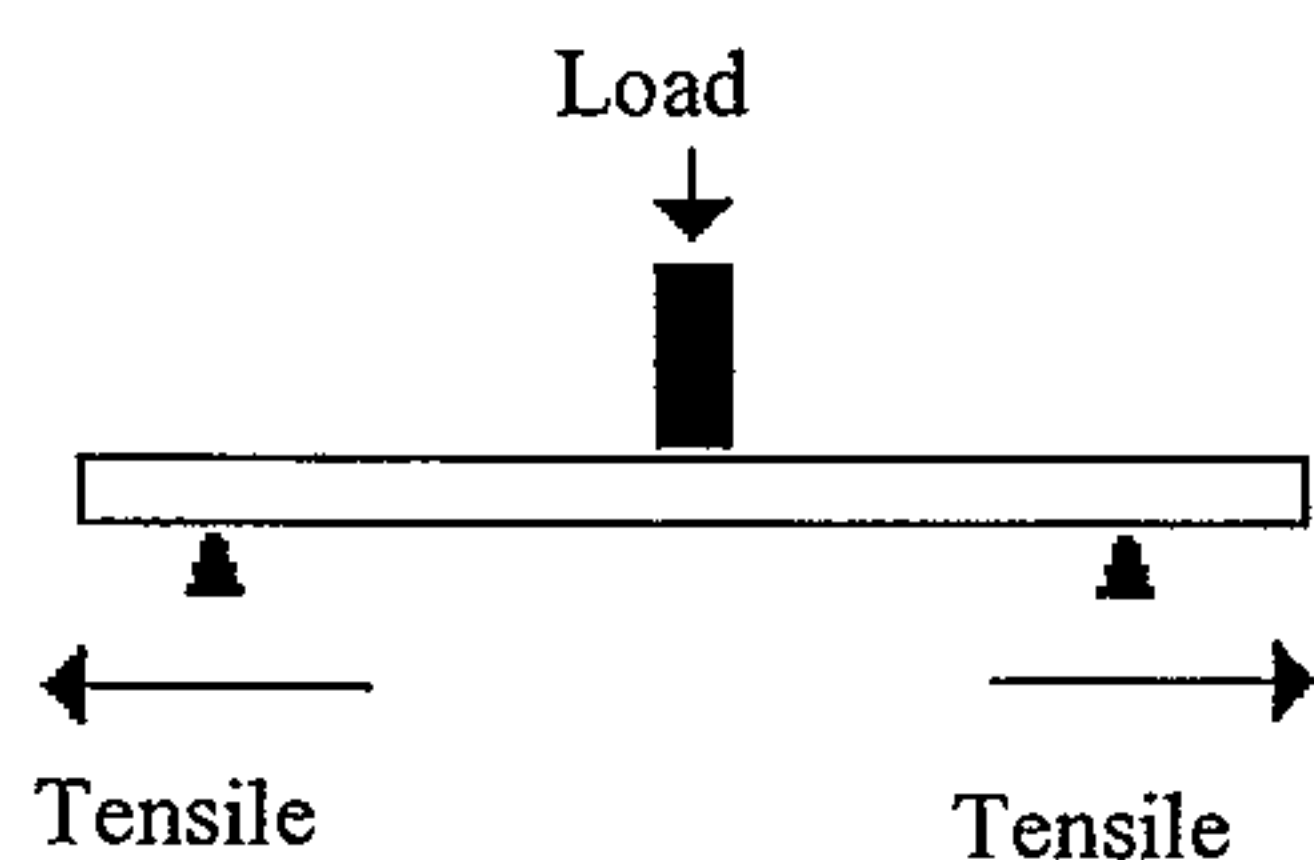
For the IS method, both Empress 2 and the experimental ceramic material had significantly different fracture toughness values for the biaxial and three-point-bending tests. In both instances the three-point bending results were higher than the biaxial tests. Two factors were considered relevant in this regard. In the case of the three-point bending tests on the bars, the cracks generated by the indenter were longer parallel to the bar length and shorter perpendicular to the stressing direction, as shown schematically in Figure 6.8. As indicated in this figure, the shorter cracks had a more tortuous path, cutting through and deflected by the lithium disilicate crystals. Furthermore, during loading, these crystals would have continued to interfere with crack extension and led to a higher value of fracture toughness. In the case of the biaxial test on the disc specimens, the crack length in some orientations was observed to be longer than others because of the localised orientation of the lithium disilicate crystals. The uniformity of the tensile hoop and radial stresses in this test arrangement would ensure that longer cracks in a direction of lower resistance, that is,

parallel to the crystals, would extend at lower stresses and hence result in a lower fracture toughness. There was a concern about the difference in the lithium disilicate crystal orientation and the manner of the crystals' alignment in the bars and discs. X-ray diffraction (Figure 6.7) showed that these crystals are not randomly aligned but have a preferred orientation depending upon the geometry of the specimen they are pressed into. The fractured surfaces of the bars (Figure 6.7 D) showed that the diffraction pattern of these crystals, which was quite similar to the pattern of the sprues (Figure 6.7 C), was diffracted from the aligned crystals in the sprues or the bars. The similarities of the diffraction patterns of the sprues and the fractured surfaces of the bars confirmed the similar crystal orientation of these shapes. The dominant peaks of these surfaces occurred at 2θ value of 24.8° and 37.6° deflected from the crystallographic (111) and (002) planes respectively, as predicted from the X-ray diffraction JCPDS file 40-0376 on (lithium disilicate). The alignment of these elongated crystals occurred in the bars and the crack must have cut across these crystals, resulting in the higher fracture toughness. The fractured surfaces of the discs showed that the beam deflected from randomly oriented crystals (Figure 6.7 B), which was similar to the X-ray diffraction pattern of the unpressed material (Figure 6.7 A), where the random orientation is also expected. As was shown in (Chapter 4, 4.2.6) the surface of the discs had an X-ray diffraction pattern that was not random but the long axis of the crystals was parallel to the surface and not necessarily parallel to each other as observed with the sprues and bars. However, the similarity of the diffraction pattern from the fracture surfaces of the discs and the unpressed blocks indicated a random alignment of these crystals.

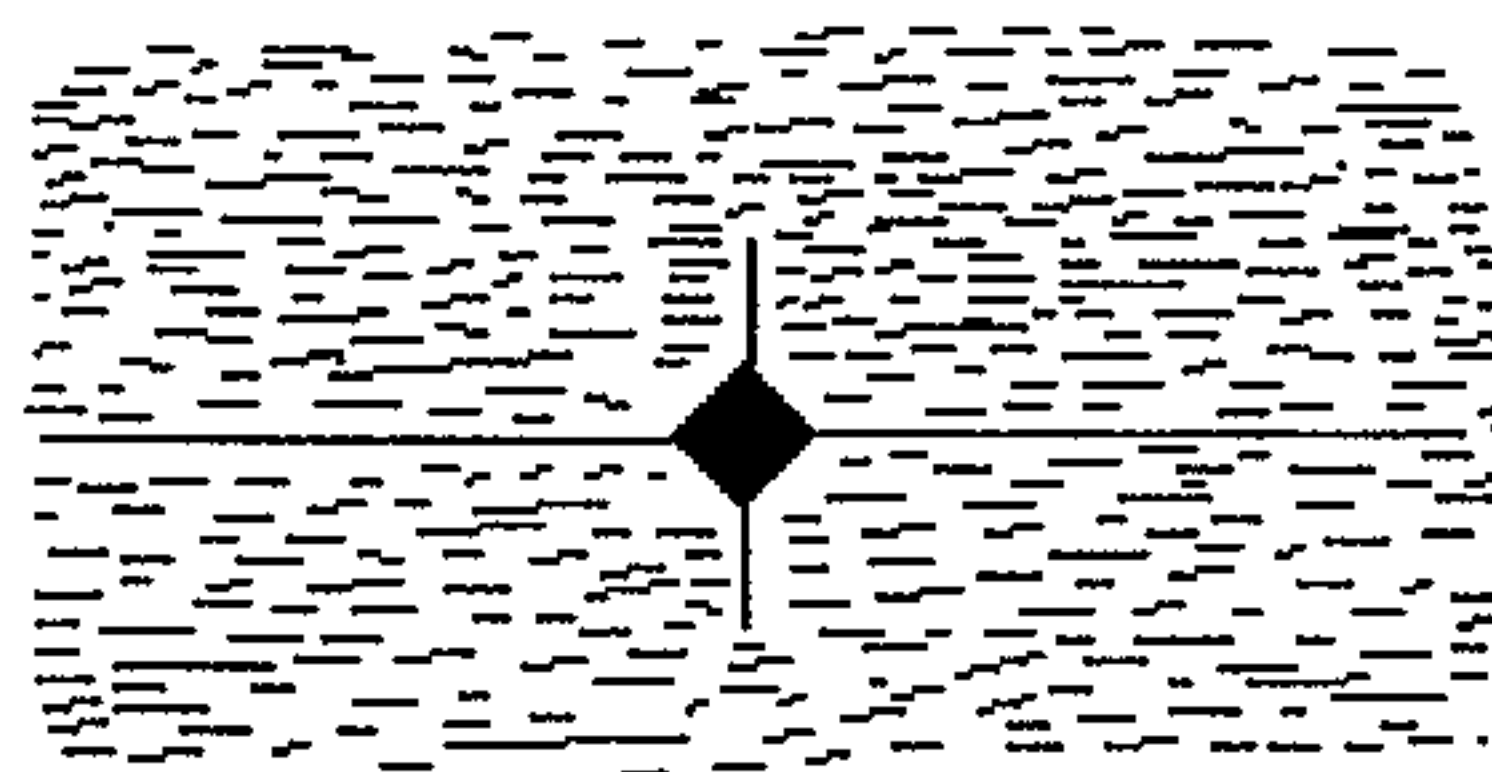
This study showed that the IS technique demonstrated higher fracture toughness results than the IF for Empress 2 and the experimental ceramic materials only. It has been stated that 30% - 40% reduction in the IF fracture toughness values obtained may occur as a result of continued subcritical crack extension associated with the indentation residual stress field [19]. This may explain the significant reduction in the IF fracture toughness which occurred for both Empress 2 and the experimental ceramic.

A comparison of IF technique with the bending method (single-edge-v-notched-beam) (SEVNB) for several ceramic materials was conducted by Fischer et al. (2002) [13]. These investigators reported a fracture toughness of Empress 2 similar to the current observations, using both techniques. They also concluded that the indentation fracture method (IF) is not an accurate method for the determination of fracture toughness and can only be used for a rough estimation of unknown material fracture toughness. However, it does provide clear evidence of anisotropic fracture resistance of a material as seen in Figures 6.4 and 6.5. In the present study, it is shown that the IS (in biaxial flexure) technique demonstrated very comparable values to the (SEVNB) method adopted in that study. However, it also clearly established that testing of the bars (three-point bending) gave an optimistic estimate of toughness, as the fracture toughness of Empress 2 and the experimental ceramic is crystal orientation-dependent.

3-point bending test

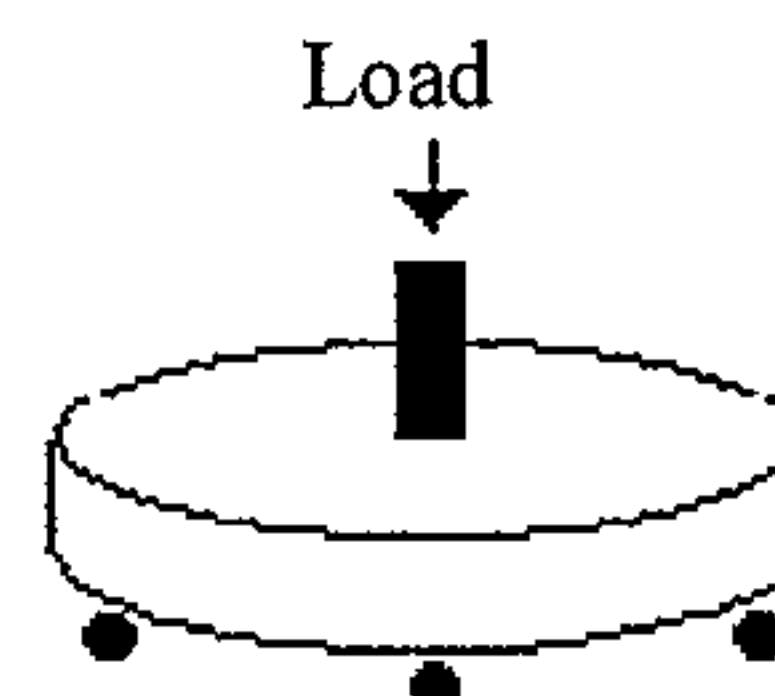
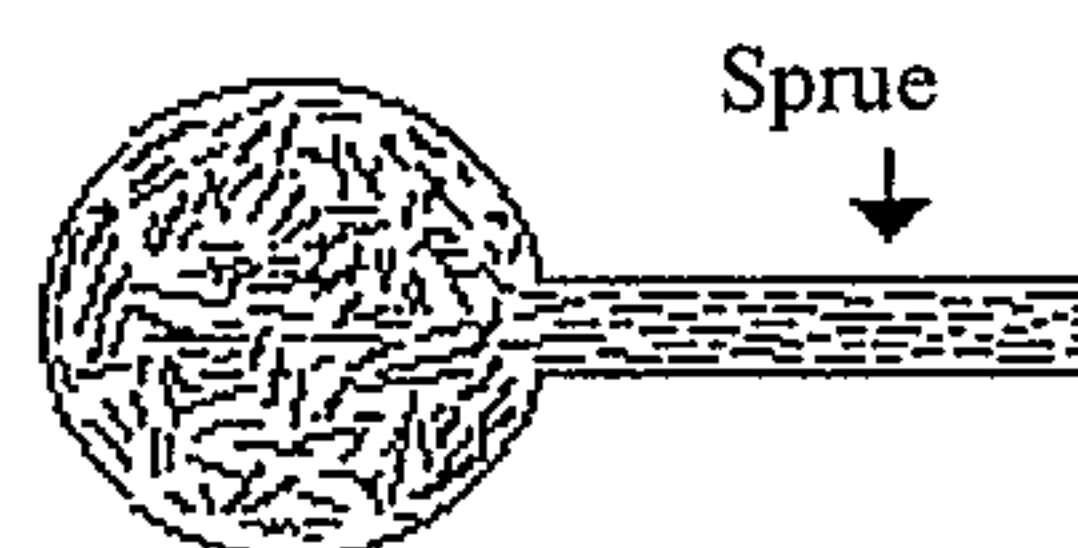


Tensile stresses develop short cracks extension from the indentation extending perpendicular to the tensile stresses.

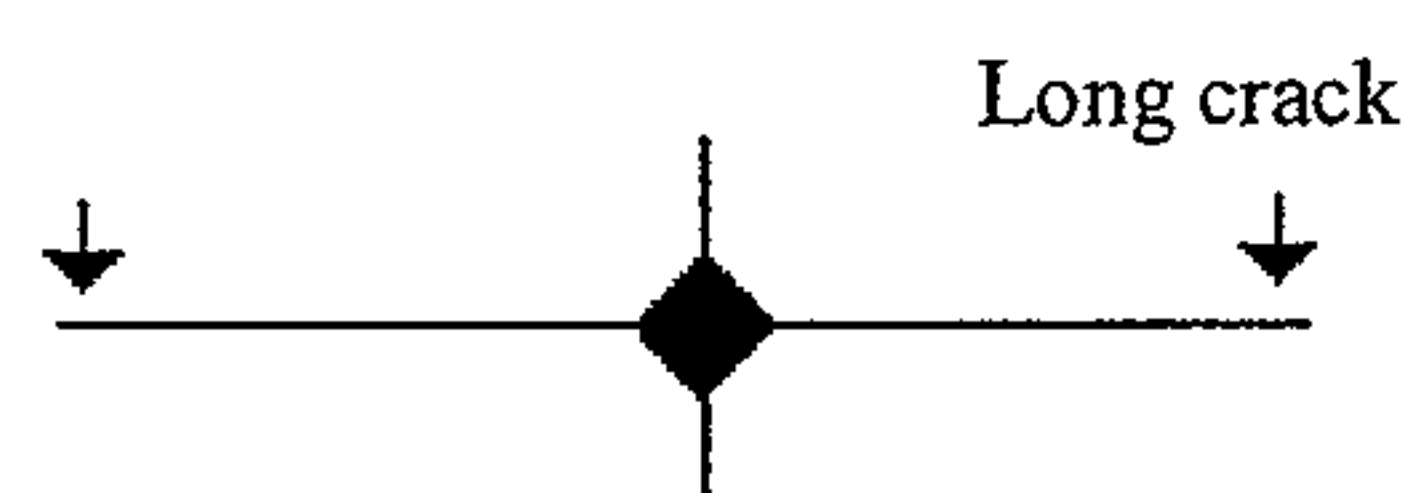


Cracks propagating from the corners of an indentation resulting in different crack lengths.

Biaxial flexure test



Stresses distribute evenly at the centre of a disc used for the biaxial strength.



Uniform distribution of the stresses makes longer cracks propagate catastrophically faster than shorter cracks.

Figure 6.8 The influence of pressing of bars and discs on the orientation of the lithium disilicate crystals in Empress 2 and the experimental material, plus the different distribution of stresses in the biaxial and 3-point bending test and the crack interaction with the lithium disilicate crystals.

6.9.2 Toughening mechanisms of the current ceramics

In the literature, the thermally induced microcracking, crack bridging and crack deflection were described as the most frequently observed toughening mechanisms for lithia-disilicate glass-ceramics [27]. In fine grain size ceramic materials (less than 20 μm), microcrack toughening was suggested as a possible mechanism. Therefore, it is a possible mechanism in Empress 2 and the experimental ceramic [27]. However, observation of microcracks and the estimation of their contribution to the ultimate fracture toughness require an approach somewhat more complicated than that used in the present study. Examination of crack behaviour upon indentation (using IF technique) provides some indications of the toughening mechanisms involved in Empress 2 and the experimental ceramic materials. The deflection of the crack along the crystals into the lower elastic modulus glassy matrix was noticed in the Empress 2 material (Figures 6.9 and 6.10). The increment of the fracture toughness results from the dissipation of the crack driving force as the crack plane is repeatedly reoriented away from the applied tensile stresses. Although the crystal sizes of the experimental ceramic are smaller than those of Empress 2 (Chapter 4, 4.11), this did not result in any significant difference in the fracture toughness between the two ceramics. This is consistent with the statement that crack deflection mechanism is independent of particle size [28].

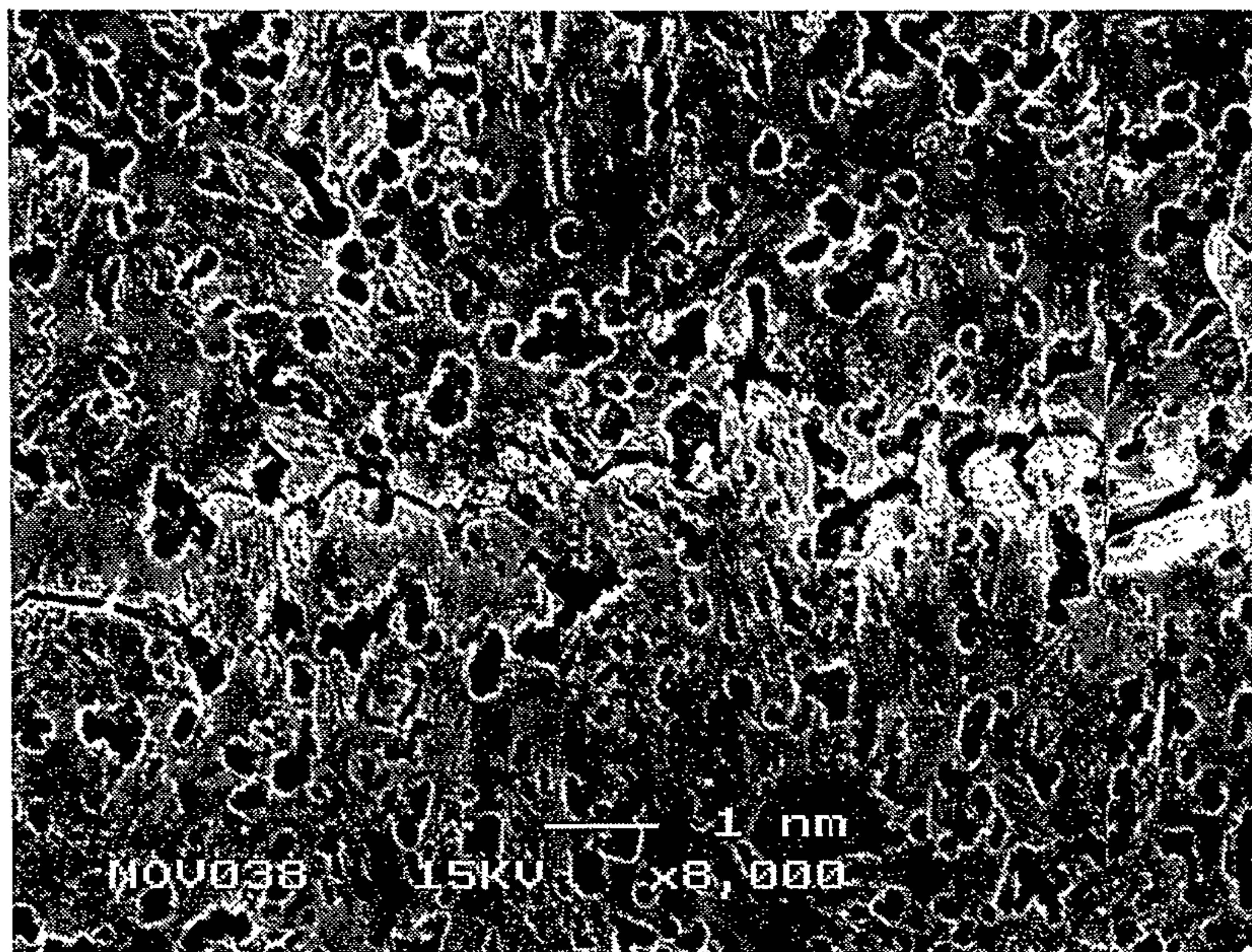


Figure 6.9 Crack is assumed to propagate across the preferred orientation of the grains, which results in a shorter crack path, and consequently greater fracture toughness.

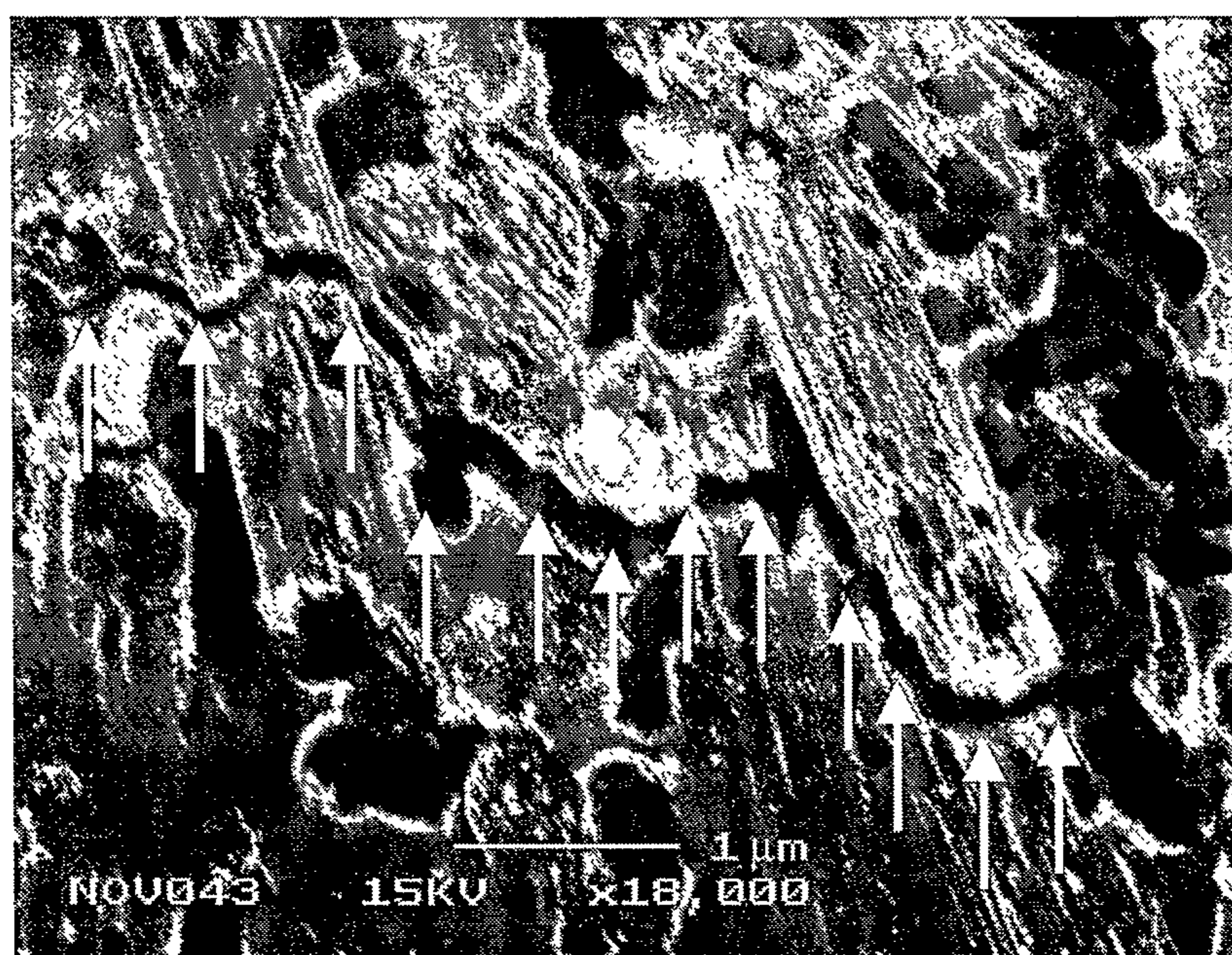


Figure 6.10 Crack is deflected by the needle-shaped crystals of lithium disilicate, giving a mixture of transgranular and intergranular crack patterns (arrows indicate the crack path).

The microscopic observations reported in this study for Empress 1 (Chapter 4, section 4.11) agree with the previous assumption regarding the toughening mechanism of this system. It was stated that the uniform distribution of the leucite crystals and the microcrack toughening due to the mismatch of the coefficient of thermal expansion between the crystalline and glassy phases are the most effective toughening mechanisms [29-32]. There is some controversy with regard to the role of the microcracks in glass-ceramics (Figures 6.11 and 6.12) as a mechanism that toughens ceramics. It has been proposed that the microcracks can contribute to deflecting a crack and dispersing its energy, which results in an increase in both strength and fracture toughness [27]. However, crystals may cluster and subsequently microcracks tend to combine, forming a crack, and surround the cluster (decoupling of leucite particles). This can cause significant degeneration of the strength and fracture toughness [33]. In Empress 1, however, pressing contributes to generating a uniform dispersion of the leucite crystals [31], which plays an important role in avoiding such a phenomenon. Even so, these proposed mechanisms appeared to scarcely toughen Empress 1. Furthermore, a previous investigation reported that Empress 1 is not stronger than some feldspathic veneering porcelains [34]. The remarkable clinical success of this material, reported in the literature, can be attributed to other factors such as glazing and/or staining, which prevent further acidic etching of leucite crystals. Adhesive cementation has also been suggested to improve the durability of the in-service restoration of this material [35].



Figure 6.11 Microcracks and twinning of leucite crystals in the glassy matrix of Empress 1.

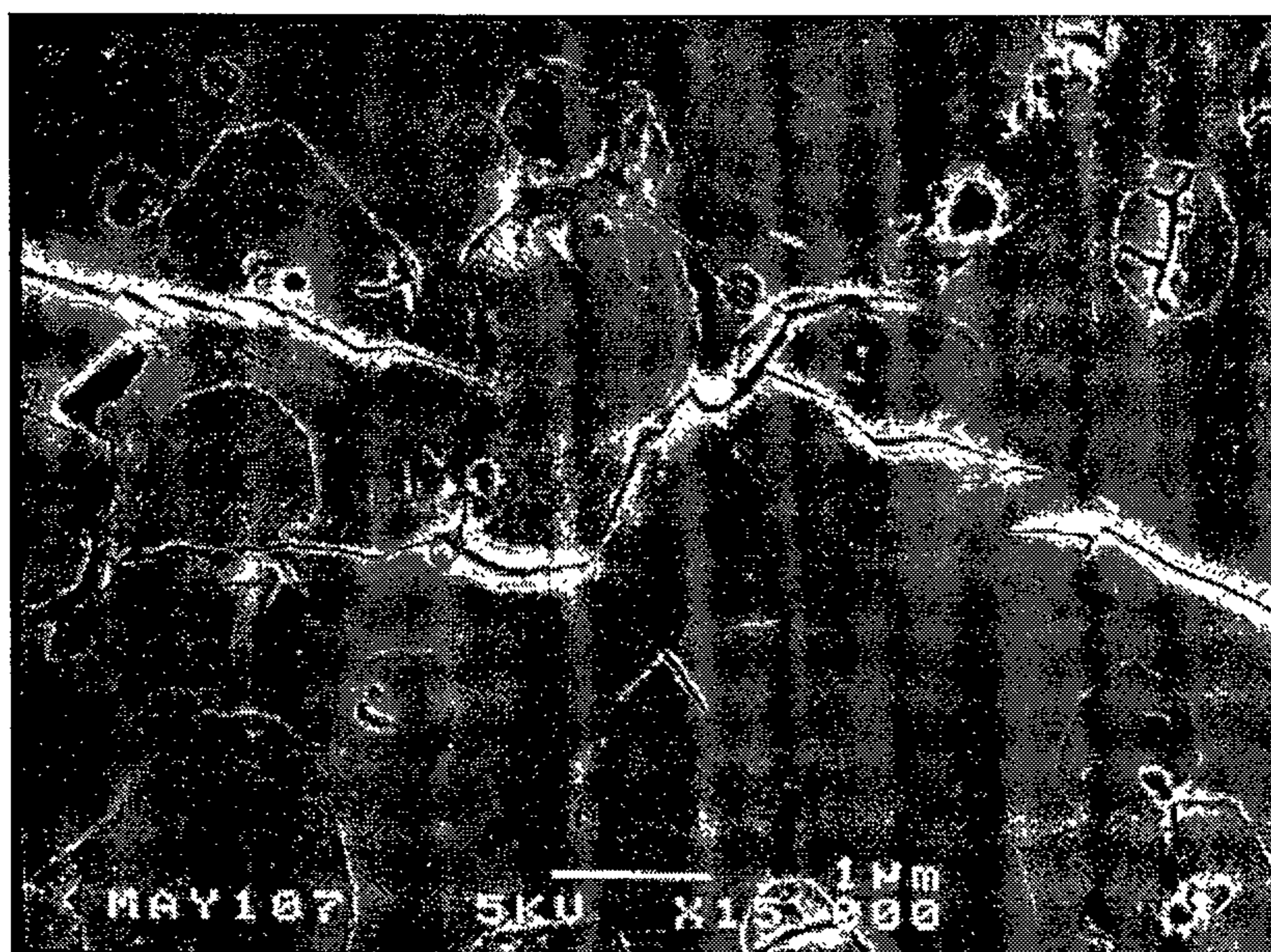


Figure 6.12 The crack propagates through both the crystals and the glassy matrix after indentation of Empress 1 (crack-microstructure interaction).

6.10 Conclusion

This study showed that Empress 1 had consistent fracture toughness results using all techniques. The lithium disilicate-based materials Empress 2 and the experimental ceramic materials demonstrated different fracture toughness results using different techniques. These significant differences were attributed to the different crystal orientations and the orientation dependence of the tensile stresses developed in biaxial and three-point bending techniques. X-ray diffraction provided a significant understanding of the difference in fracture toughness demonstrated by the IS toughness results. The improved fracture toughness of both materials over that of Empress 1 should be beneficial for the clinical application of these materials.

6.11 Effect of heat pressing on the fracture toughness of Empress 1 and Empress 2.

6.11.1 Introduction

The effect of heat pressing on the flexural strength of the pressable materials Empress 1 and Empress 2 has been addressed previously [31, 36]. Two previous studies reported a significant increment in the flexural strength after pressing for both materials. In both instances it was suggested that the better dispersion of the crystalline components, nominally enhanced by heat pressing, is responsible for the significant improvement in strength. The better distribution of the crystalline phases within a glass matrix is thought to minimise the susceptibility of the brittle glass matrix phase to fracture, and enhances a degree of residual stress isotropy within the microstructure, to which this increment in strength might be related. However, these two previous studies utilised specimens that were machined from blocks and compared their strength to that of pressed specimens. The machined samples might have contained irregular or spherical voids and/or detrimental defects introduced during machining. Fracture toughness therefore, as an intrinsic mechanical property, may be a more appropriate approach to determining whether the strength increased as a result of better crystalline phase distribution or together with a reduction of porosity which occurred after heat pressing (Chapter 4, 4.17). The effect of heat pressing on the fracture toughness of these pressable materials has not been previously reported in the literature.

In the previous part of this chapter, the fracture toughness was appraised after pressing only as this value will be very relevant to the situation where the core material is in service in the oral cavity. In this section the fracture toughness was

appraised in block (before pressing) and after repressing for Empress 1 and Empress 2. Although results here might not be relevant to the clinical situations, they can be compared to the results achieved after pressing, and used to evaluate the effect of different crystal orientation occurring after heat pressing and its effect on the fracture behaviour (during indentation) and consequently the fracture toughness.

The hypothesis stating that fracture toughness, like strength, might be accompanied by an incremental improvement after heat pressing, due to enhancement of the toughening mechanisms associated with better dispersion of the crystalline phases is tested here.

6.11.2 Indentation fracture technique

The indentation fracture technique was used to measure the fracture toughness of the same materials before pressing (in a block) and after repressing. The same procedures adopted for the specimens after pressing were followed for the current investigations.

The orientation of the indentations were made for the two materials as follows:

1. In block (unpressed), the indentations were introduced in various positions of a block.
2. In a disc (repressed), a series of indentations was made (beside each other) near the edge (where the sprue was attached, X-axis is parallel to the pressing direction), at the middle of the disc and in other different positions.
3. In a bar and sprue (repressed) specimens, a series of indentations was made near the edge as carried out with the discs, where the long axis of the bar was parallel to the X-axis and also parallel to the pressing direction. Other

indentations were made, but the long axis of the bar was perpendicular to the X-axis.

6.11.3 Results

Fracture toughness for both materials are listed in Table 6.2. The Empress 1 material demonstrated very similar fracture toughness results for the unpressed, and repressed materials: 1.32, 1.3 MPa·m^{1/2} respectively. No significant difference was found between these values using One-way Anova and Tukey's multiple comparison tests ($p > 0.05$). Indentation in the unpressed block of Empress 2 resulted in two similar crack lengths in both X and Y-directions (Figure 6.13). The fracture toughness was 1.9 MPa·m^{1/2} in both directions of an indentation. After repressing, two significantly different crack lengths were found in a bar, disc or sprue (Figures 6.14, 6.15 and 6.16), which resulted in two significantly different fracture toughness values. The fracture toughness values measured from the longer cracks after repressing for bar, disc and sprue were significantly lower than the values measured from the cracks before pressing ($p < 0.05$).

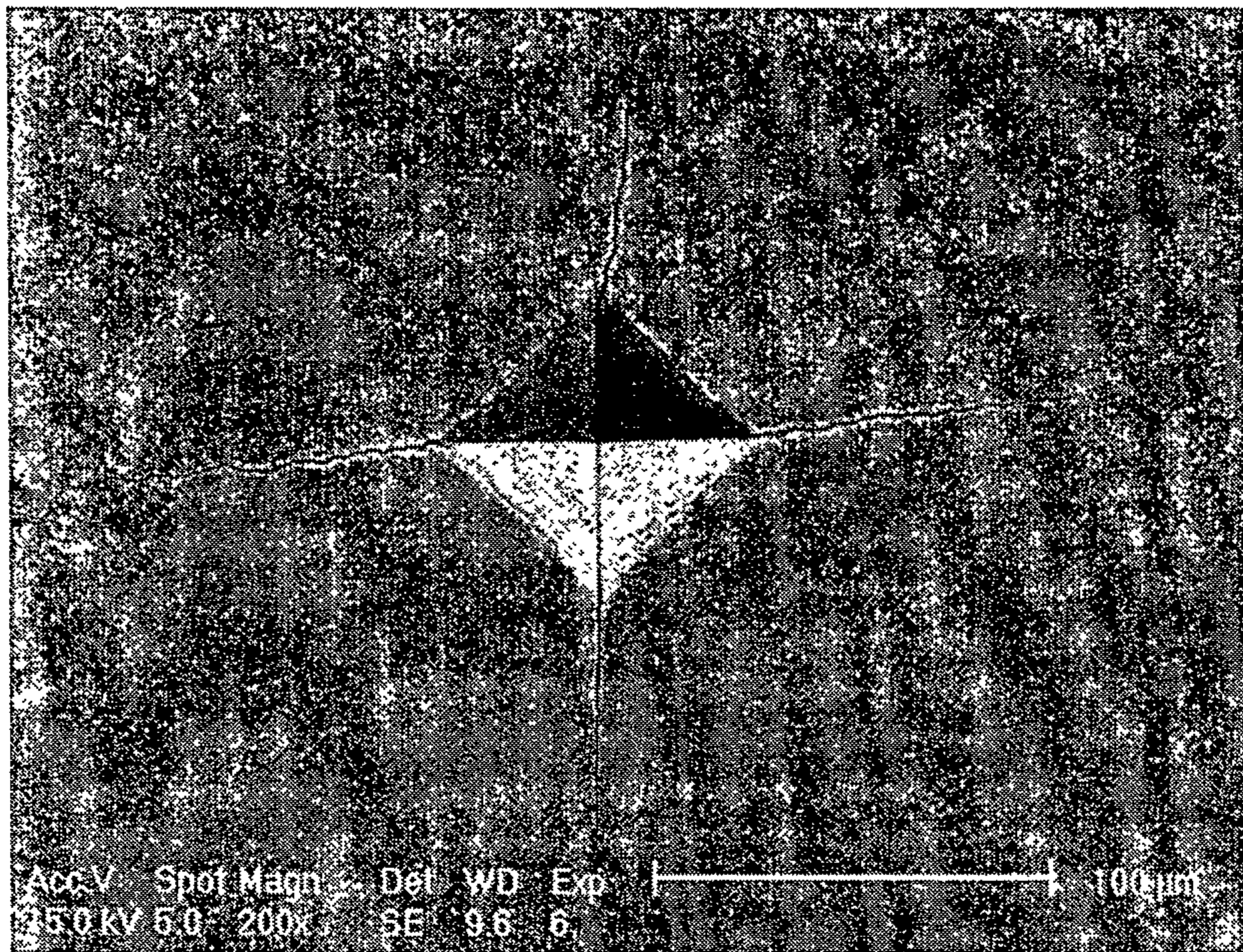


Figure 6.13 Cracks of similar length emanating from the corners of Vickers indentation of Empress 2 material before pressing.

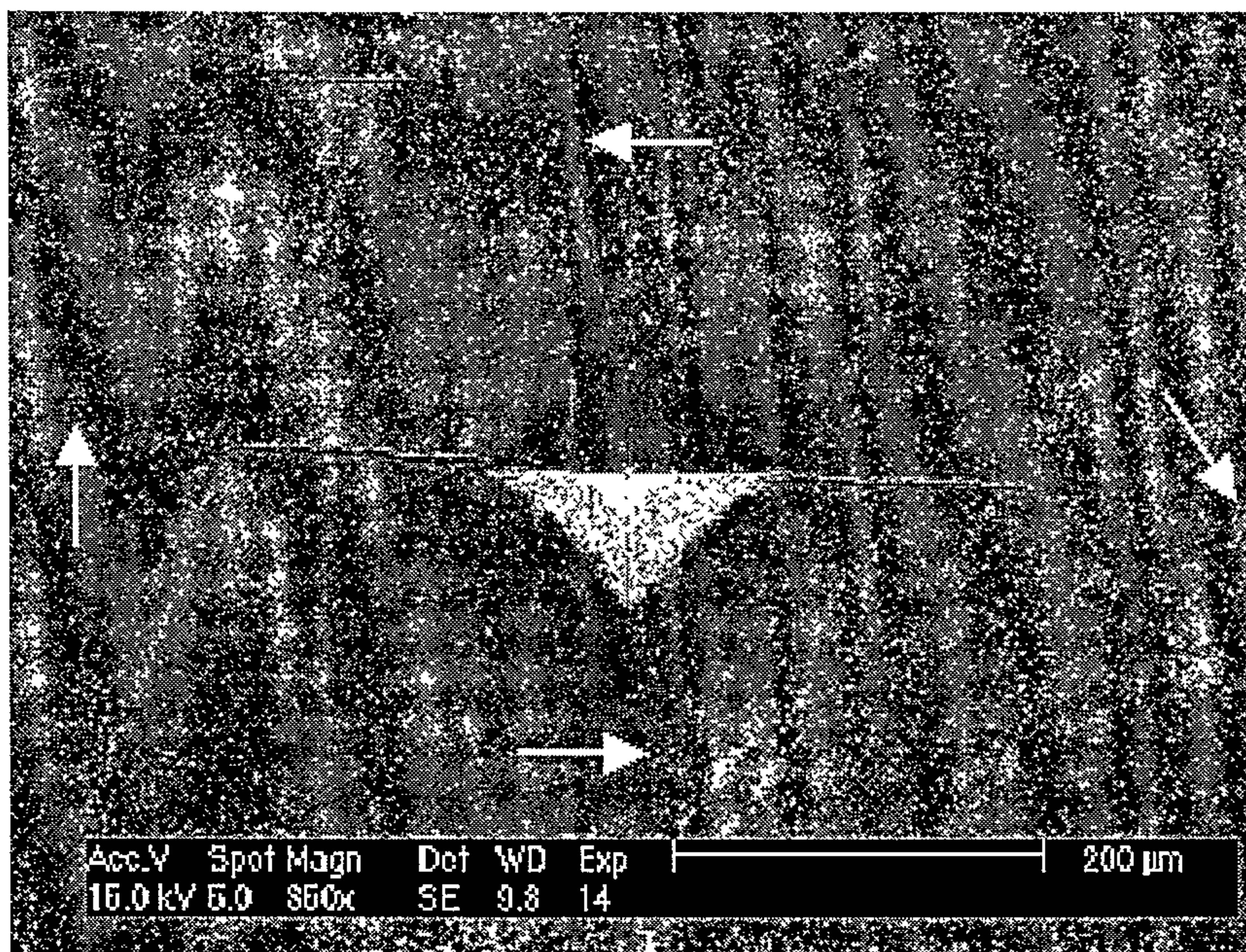


Figure 6.14 Cracks of different length emanating from the corners of Vickers indentation of Empress 2 material in a bar after repressing; long axis of the bar is parallel to X-axis (tips of cracks are arrowed).

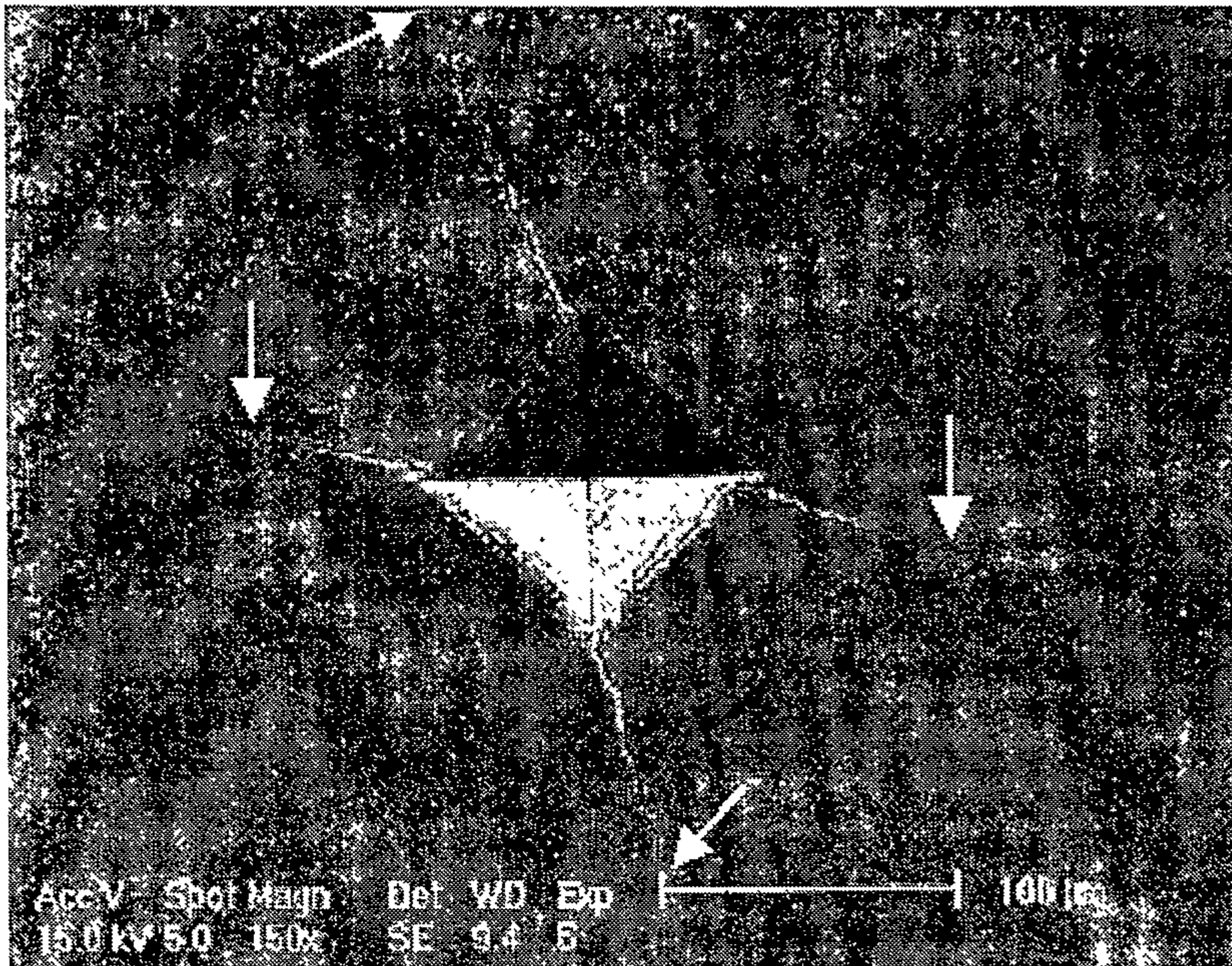


Figure. 6.15 Cracks of different length emanating from the corners of Vickers indentation of Empress 2 material in a disc after repressing (tips of cracks are arrowed).

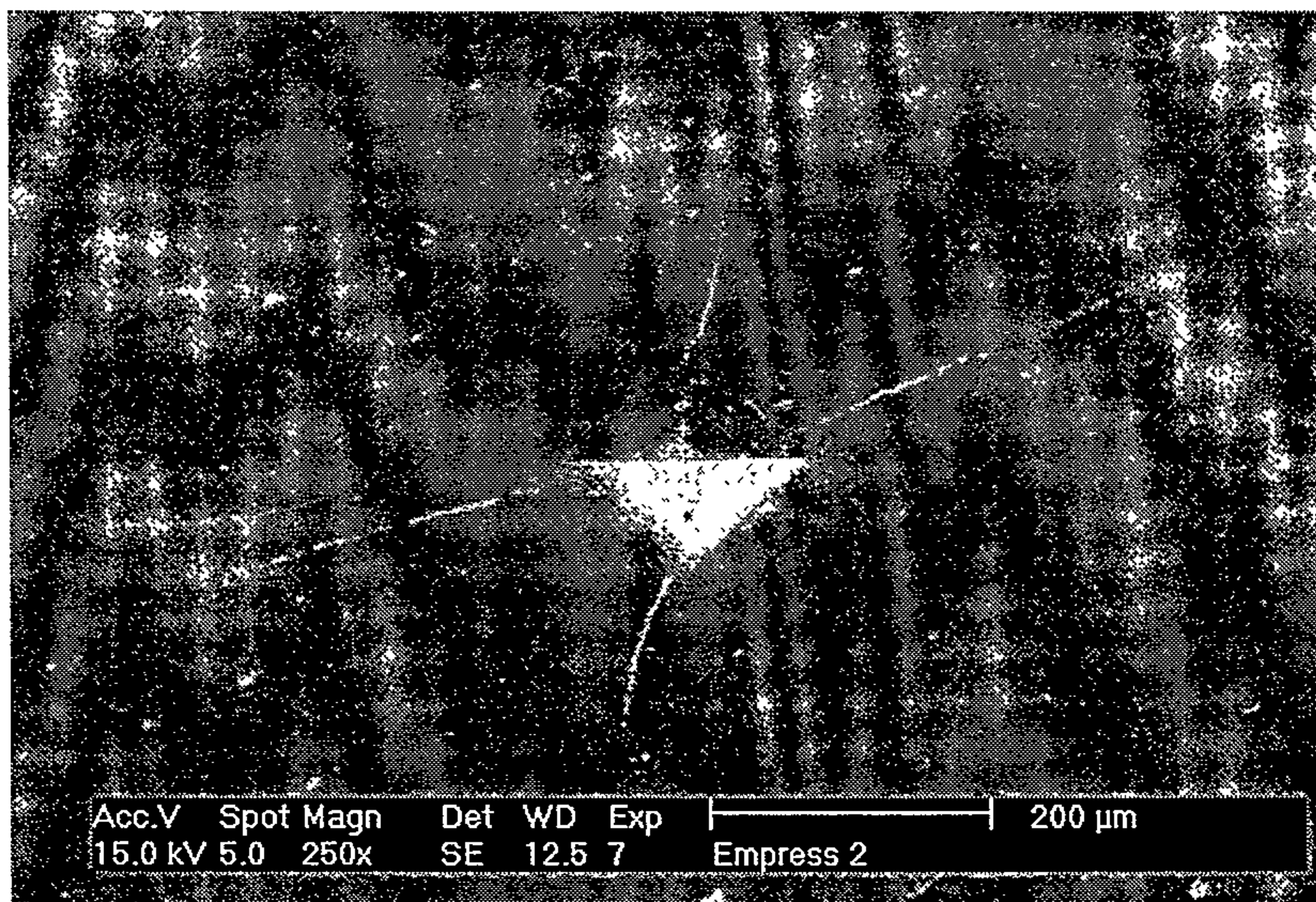


Figure. 6.16 Cracks of different length emanating from corners of Vickers indentation of Empress 2 material in a sprue after repressing.

Table 6.2 Fracture toughness (MPa·m^{1/2}) of the two materials, Empress 1 and Empress 2.

Material	Before pressing (SD)	After repressing (SD)	
		Shrot crack	Long crack
Empress 1	1.32 (0.18)	1.3 (0.11)	—
Empress 2	1.9 (0.2)	—	—
Empress 2 (bar)	—	1.91(0.16)	1.53 (0.13)
Empress 2 (sprue)	—	1.98 (0.20)	1.48 (0.19)
Empress 2 (disc)	—	1.95 (0.11)	1.43(0.12)

6.11.4 Discussion

Observation of the four radial cracks that emanated from the corners of the indentation residual impressions of Empress 2 material indicated the effect of the lithium disilicate crystalline alignment on the fracture behaviour. Firstly, the crystals were homogenously distributed, in an unpressed material (Figures 4.29, Chapter 4), in a randomised multi-directional manner. In such a structure, cracks would extend from the corners of an indentation with comparable lengths, as a result of similar crack paths (Figure 6.13). Crack bridging and deflection are most likely the toughening mechanisms involved (Figure 6.10). The indentation impressions were well defined with sharp plastic-like deformation resulting from the presence of a significant amount of densely packed lithium disilicate crystals.

In the repressed material, similar crack behaviour to that which occurred after first pressing was noticed (Figure 6.14), whereby the crack extended in one direction and was hindered in the other direction. SEM images showed that crystals were also aligned parallel to each other (Figure 4.33, Chapter 4) (in a disc), which appeared to

significantly affect the crack lengths, as also noticed after first pressing. However, in the first investigation crack behaviour was only observed in disc-shaped samples. This investigation introduced indentations in bar-, disc- and sprue-shaped specimens to verify the difference of fracture behaviour among these differently shaped specimens. Results showed similar fracture behaviour in these specimens. In bar- and sprue-shaped specimens, crystals were aligned parallel to each other and to the pressing direction. The crack was hindered perpendicular to the pressing direction (Y direction), and extended longer in the X-direction, that is, parallel to the pressing direction. In the disc specimens, because crystals were clamped in groups that had slightly different directions, the crack would extend longer when parallel to the long axis of these crystals and shorter when perpendicular to their long axis. In all cases the fracture toughness value measured from the short crack was significantly higher than the value measured from the long crack path. These findings were very similar to the outcomes achieved after first pressing as explained in the previous section.

This study attempted also to evaluate the effect of the time interval after indentation on the crack length and subsequently on fracture toughness. Crack length measurements were taken in less than 25 seconds after indentation. Despite this relatively short time to measure the crack lengths, the fracture toughness results didn't reach the values that were achieved using other fracture toughness techniques, 3 and $2.5 \text{ MPa}\cdot\text{m}^{1/2}$, using the indentation strength technique in 3-point bending or biaxial flexural tests. Such results may indicate that the shortcomings of the IF technique, such as accuracy and time dependence of crack length measurement, are unavoidable.

The Empress 1 material showed no difference in fracture toughness values measured in the unpressed and repressed materials. The Vickers indentations examined showed similar residual impressions, crack lengths in both X- and Y-axis (Figure 6.17), and deformation type. Also observed was a multi-layer cracking pattern within a residual impression and less defined edges (Figure 6.18), which are considered to result from the significant amount of microcracking about the residually stressed leucite crystals in the glass matrix. The insignificant difference in the fracture toughness of Empress 1 is probably attributed to the minimal changes found in the microstructure. In addition, the areas devoid of crystals before pressing (glassy areas) (Figure 4.18, Chapter 4), measured approximately 10 to 30 μm , while the size of an indentation introduced by a relatively small load (10 N) is more than 50 μm . This suggests that these isolated glassy regions free of crystals are unlikely to have a significant role in the crack-microstructure interaction, thus resulting in minimal change of fracture toughness.

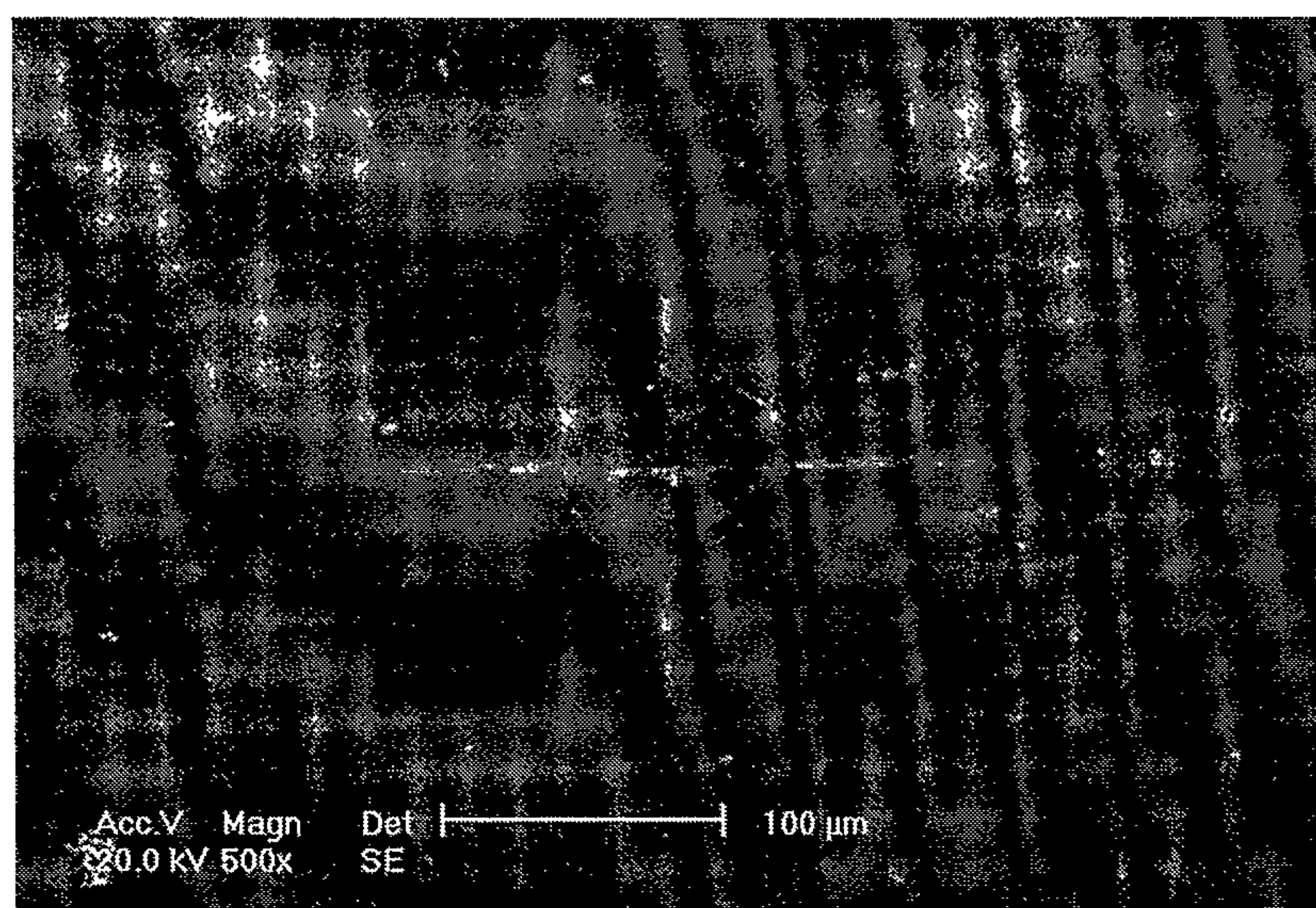


Figure 6.17 SEM of Vickers indentation of Empress 1 showing similar crack length of an indentation.

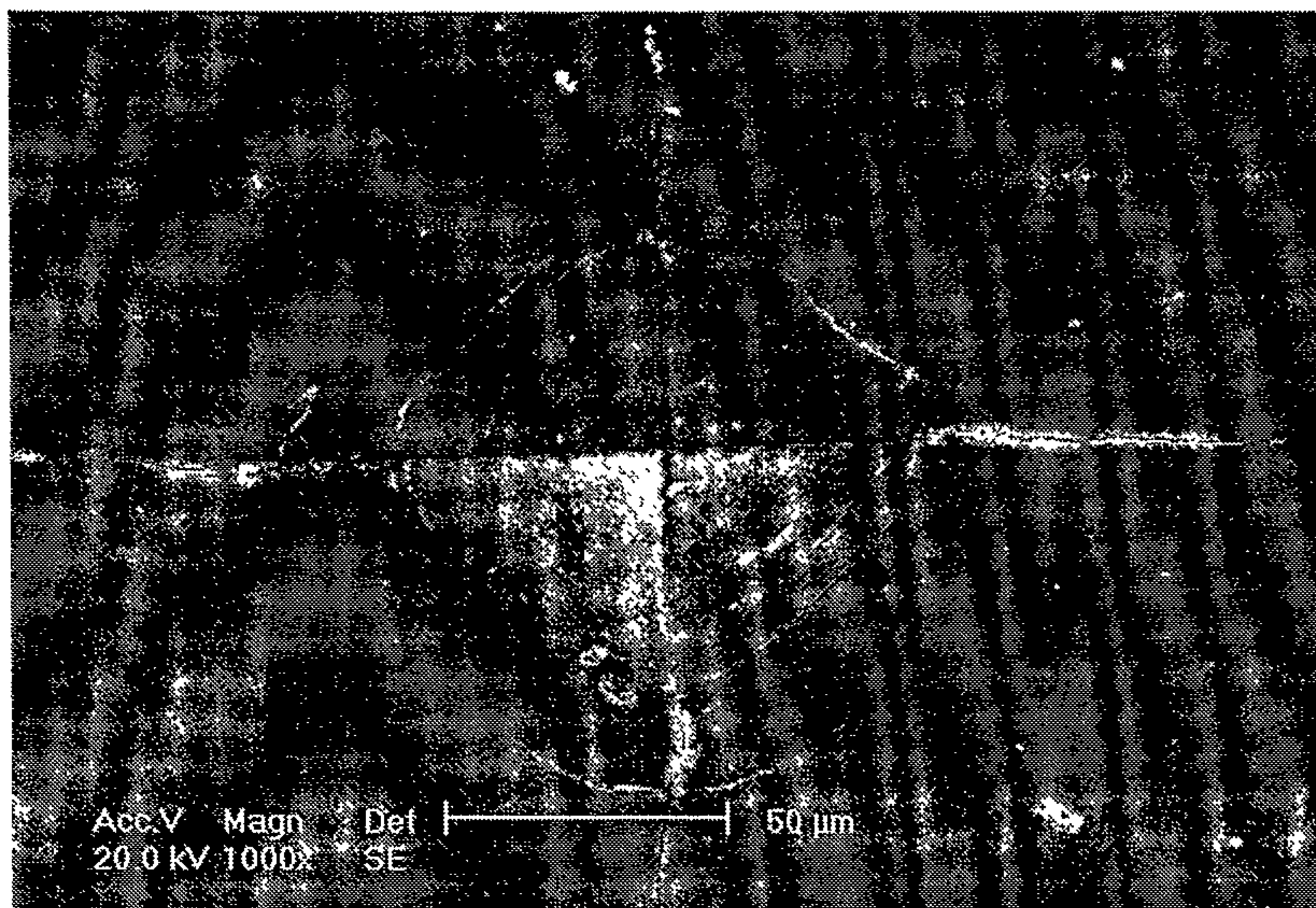


Figure 6.18 Multi-cracking pattern surrounding an indentation of Empress 1.

In Chapter 4, the number and size of pores were found to decrease after pressing and repressing for both materials. This was thought to affect the flexural strength properties of these materials.

Most images showed no pores after pressing, which indicates that the pressing has effectively eliminated these pores. This may also indicate that flaws larger than 12 μm may have been introduced in the unpressed material during the machining of Empress 2 that determines the strength. These outcomes indicate that the strength of the unpressed samples of both Empress 1 and Empress 2 might have been affected by pores and/or defects introduced during machining. As a consequence, lower strength values are expected for these samples as a result of the presence of detrimental defects. This may also indicate that the better crystal distribution after pressing may not be the only factor that determined the improved strength. Other issues, such as pore size, number and location, are also pertinent.

6.11.5 Conclusion

In conclusion, the fracture toughness of the Empress 1 material was not affected by heat repressing. Empress 2 showed two different fracture toughness values, after repressing, as a result of the crystals' alignment that occurred during hot pressing. The strength improvement of Empress 1 and Empress 2 after pressing as a result of better crystal distribution has been proposed in previous studies. However, this study found that the smaller and fewer pores occurring after pressing are considered to have played an important role in strength determination. Therefore, this study concluded that heat pressing enhanced better crystal distribution and also decreased the number and size of pores of Empress 1 and Empress 2, which is considered to increase the flexural strength, but not the fracture toughness for these materials.

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CHAPTER 7

FLEXURAL STRENGTH

Another very important mechanical property that delineates the behaviour of a specific structure under load is strength. Strength testing reveals the failure manner of real components submitted to an external force, and is considered a very useful source of information about how different materials respond to mechanical forces.

The present chapter focuses on the strength properties of Empress 1, Empress 2 and an experimental ceramic material, namely uniaxial flexural strength (3-point bending technique) and biaxial flexural strength (piston on three ball technique).

In the first part (7.1-7.9) a brief outline about strength, definition, importance, method of measurements will be provided. This will be followed by a description of the biaxial flexural, 3-point bending tests, results, discussion and conclusion. Variation in strength results will be assessed by calculating the Weibull modulus of the biaxial flexural strength only.

The second part (7.10-7.14) of this chapter will appraise the effect of different laboratory fabricating processes such as, grinding, polishing, sandblasting and heat treatment (glazing) on the biaxial flexural strength of Empress 1 and Empress 2. The Weibull modulus will also be provided.

7.1 Introduction

Strength is simply known as the stress that causes fracture. Unlike the elastic modulus, it is not a measure of attraction between atoms, but rather it is a measure of the forces over a specific region of a stressed structure [1]. Flexural bending is generally easier to conduct than a pure tensile test, and hence the strength of brittle materials is usually assessed using flexural techniques.

Strength is an important mechanical property that determines the performance of brittle materials [2, 3]. However, microcracks and defects that grow inherently during thermal or mechanical processes can significantly influence strength measurement [4, 5]. Strength is therefore considered a conditional property [4]. Furthermore, many variables, such as testing design, specimen geometry, polishing procedures and testing environments can affect strength measurements [6, 7].

7.2 Definition

Strength can be defined as the maximum tensile stresses that a material can endure before fracture occurs. It might be defined also as force per unit area required to initiate and propagate a crack to the fracture point. The inability of ceramics to reduce the tensile stresses at the tip of the cracks by deformation in an inelastic manner explains why they are much weaker in tension rather than in compression and also why dental restorations normally fail in areas of tensile stresses [1, 8]. Therefore, tensile strength is considered more meaningful compared to compressive strength when testing this property in brittle dental materials [9].

7.3 Methods of Measurements

There is a trend towards the use of flexural tests for strength evaluation of brittle materials. Testing methods need to satisfy some basic requirements to standardise the procedure and to lead to universally acceptable and reproducible results. This indicates that a specific test method should provide precise and reliable results. Different methods are available to assess the strength properties of the ceramic materials. These testing methods include 3-point bending [10-12], 4-point bending [7, 13], the non-destructive test method [14], and the biaxial flexural test, which includes the ring on ring [2], ball on ring [15], and piston on three ball tests [16-18]. It should be noted that strength results derived from different testing methods might be different and hence comparisons under these different conditions or testing parameters may become invalid [2, 19].

7.3.1 3-point bending flexural test

The 3-point flexural test is the standard for strength testing of dental ceramics [20]. It is simple in application and yields reliable results. This test is quite popular and many previous investigators have adopted it for evaluating the relative strength of dental ceramics materials. In addition, it can be used to measure flexure displacement and elastic modulus [9]. The main drawback of this test, however, is the small portion of a specimen that is subjected to the maximum tensile stresses, and also the inherent sensitivity to flaws and defects near sample edges [7, 20]. The latter can make edge defects the origin of premature fracture.

In this test, a standardised bar-shaped specimen is supported close to either end and centrally loaded until fracture occurs. Tensile stresses are induced at one

surface, which is opposite to the loading area, and compressive at the opposite surface (Figure 7.1). The magnitude of the tensile stresses decreases remarkably and can diminish to a zero value at the middle of the specimen. This zone is called the neutral axis where the stresses change from tension to compression. The strength results obtained from this test may be called flexural strength, bending strength, transverse strength [1, 12].

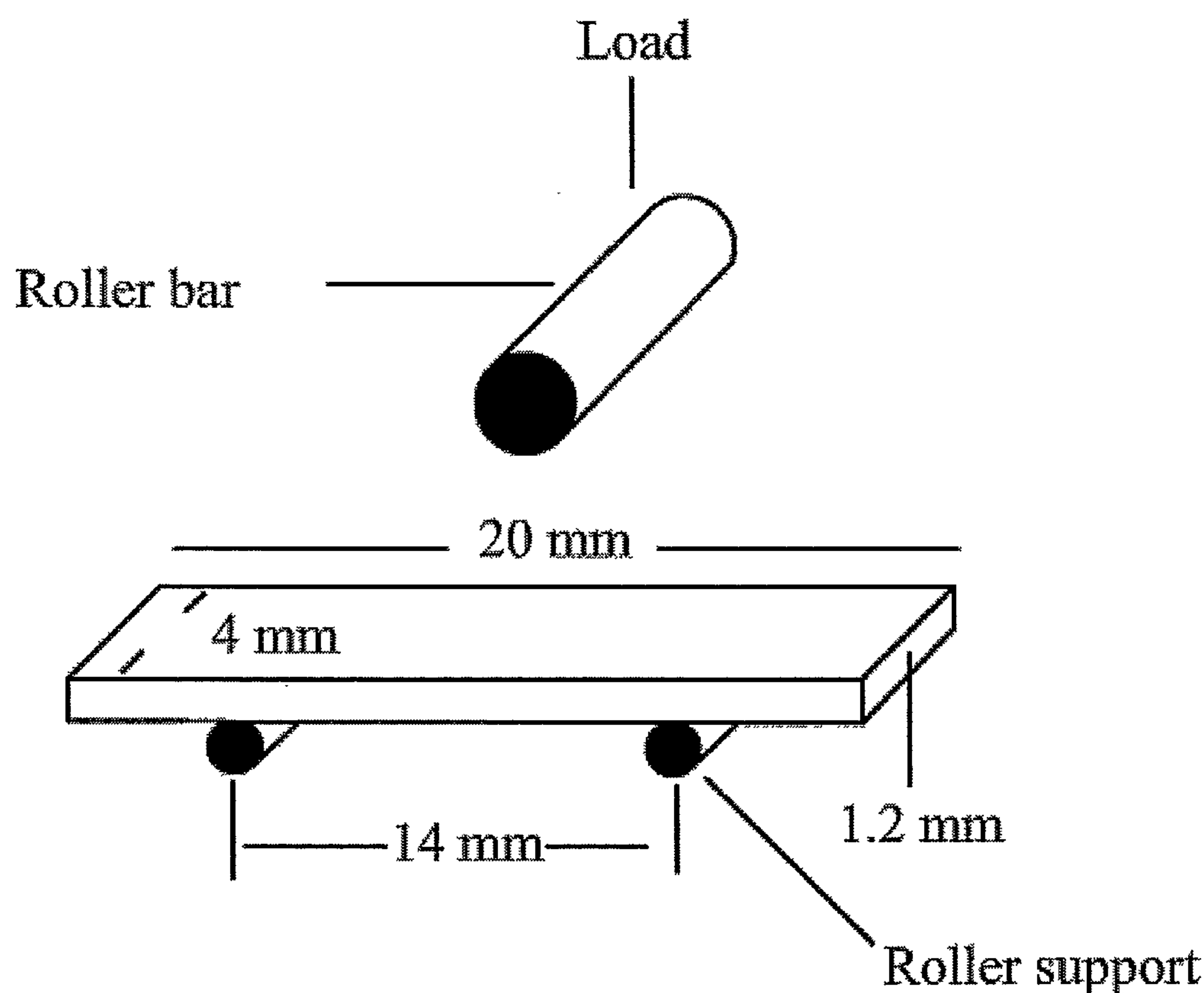


Figure 7.1 Diagrammatic representation of the 3-point bending flexural test.

7.3.2 Biaxial flexural strength

It is well known that strength values obtained from the uniaxial flexural strength significantly depend on the integrity of specimen preparation, polishing procedure and edge status. Therefore, large variations in strength can be expected. To eliminate the

edge effects, the biaxial flexural technique supports a disc sample with three or more points near its periphery and equidistant from the sample centre and loads are applied to the sample at the centre of the other surface. The load induces a biaxial state of stress, radial and circumferential stresses. The maximum tensile stress occurs beneath the stressing area (under the piston.), whereas the edges of the specimens are almost free of stresses. Therefore, the biaxial test should produce less strength variation among samples tested [20]. This flexural strength method has become a widely recognised technique suitable for assessing the flexural strength of brittle materials.

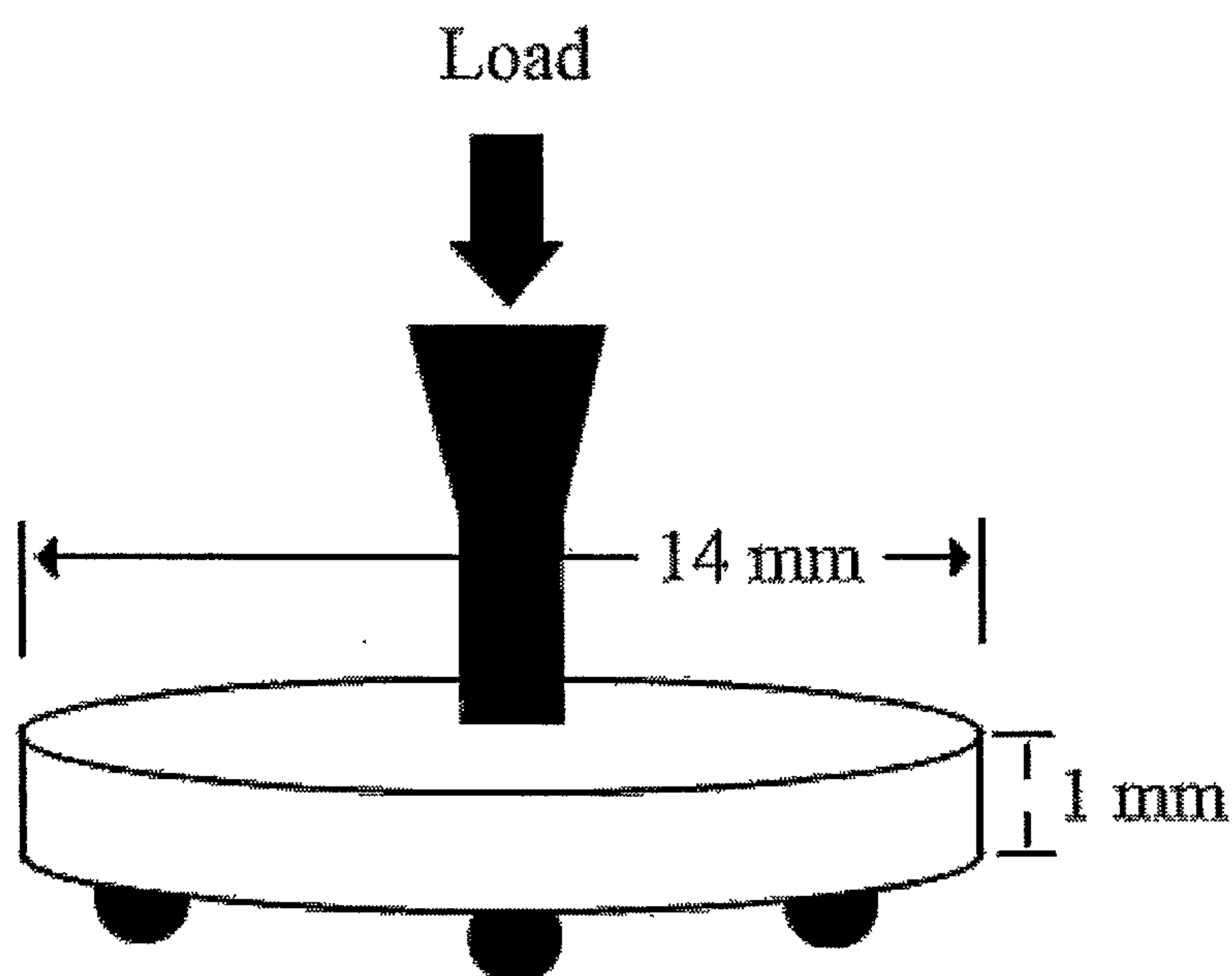


Figure 7.2 Biaxial flexural test diagram, showing a disc-shaped specimen loaded by a piston and supported by three ball bearings.

7.4 Weibull modulus

Materials may contain cracks and defects either in the surface or within the bulk. These defects may grow either inherently, or during processing and following different treatments. Stresses are amplified near crack tips and are detrimental and

may initiate fracture of the specimen. However, this may not happen if stresses are absorbed by local plastic deformation such as in the case of ductile materials. In brittle materials, in contrast, the strong bonding between atoms and grains makes slip difficult and thus plastic deformation at the crack tip is very limited, resulting in limited energy absorption [21].

In dentistry, the statistical measure of strength is the mean strength with standard deviation and coefficient of variation. However, ceramics normally have a large variation in strength as a result of the effect of internal flaws, which sometimes makes the results unpredictable. It is therefore arguable whether mean strength of the brittle ceramic materials is reliable and can portray their actual strength [22, 23].

The most important cause of fracture is the size and shape of a critical pre-existing crack or flaw within the area of maximum tensile stresses. The larger the crack or pre-existing defect size, the lower the tensile strength at which the materials fracture [4, 21].

A further two influential factors during brittle testing are the size and shape of specimens. For example, large samples are more likely to contain larger flaws than those in small samples. As a result, the large flaw is more likely to propagate and the sample fails at lower stresses. This indicates the importance of the sample volume, which is directly relevant to the fracture strength of brittle materials (volume dependence of strength) [21]. The influence of specimen volume was incorporated into strength appraisal when Weibull (a Swedish physicist), proposed the concept of survival probability $P_s(V_0)$, instead of the common average strength, to describe the

strength of brittle materials. The survival probability of samples at an applied stress (σ) having the identical volume (V_0) can be given by the following equation:

$$P_s(V_0) = \exp\{-(\sigma/\sigma_0)^m\} \quad (1)$$

where σ_0 and m are constants and σ is the applied tensile stress [24, 25]. When the applied tensile stress is set equal to zero, the previous expression results in $P_s(V_0) = 1$, and all samples survive. As stress increases, samples fail and then $P_s(V_0)$ becomes smaller. At $\sigma = \infty$, all the samples break and $P_s(V_0) = 0$. If the σ is set equal to σ_0 in the formula the result is $P_s(V_0) = 1/e = 0.37$. So σ_0 is the stress that allows 37% of the samples to survive. The exponent constant m indicates how quickly the strength falls, as σ_0 is approached. This is called the Weibull modulus [9, 21].

The Weibull modulus characterises the distribution or variability of strength data. The lower the value of m , the greater the variability of the strength [21, 23, 24].

7.5 Purpose

The present study evaluated the flexural strength of Empress 1, Empress 2 and the experimental material. Empress 2 was introduced into the market in 1998 as an all-ceramic dental material suitable for the fabrication of three-unit fixed partial dentures. However, few reports about the mechanical properties were available in the literature and some of these reports were conducted by the manufacturer's team of researchers. This study attempted to appraise the flexural strength (uniaxial and biaxial) of this material and compared them to other pressable and advanced all-ceramic systems.

The effect of different laboratory fabrication procedures on the biaxial flexural strength has also been evaluated.

7.6 Tests adopted in the present study

Uniaxial flexural strength (3-point bending) and biaxial flexural (piston on three ball method) have been used in this study to assess the flexural strength properties of the studied materials.

7.6.1 Uniaxial flexural strength (3-point bending test)

Twenty bar-shaped samples for Empress 1, Empress 2 were prepared as discussed in (Chapter 3, 3.3). The bar specimens of the new experimental ceramic were submitted to the same polishing and finishing procedure, as they were supplied by the manufacturer in the pressed state. The final dimensions of all specimens after polishing procedures were approximately 20 mm (length) x 1.2 mm thickness x 4 mm (width).

The uniaxial flexural strength (three-point bending test) was assessed for each material (Figure 7.1) following the requirements of the International Organisation for Standardisation. ISO 6872 [26]. The following equation was adopted to calculate the flexural strength:

$$M = \frac{3Wl}{2bd^2} \quad (2)$$

where M is flexural strength, W is the breaking load (N); l is the test span (m), b is the width of the specimen (m); d is the thickness of the specimen (m). The specimens were tested with a universal testing machine (Shimadzu Ag-50 KNE, Kyoto, Japan), rested on a self-aligning fixture with a span of 14 mm. Tests were conducted at a crosshead speed of 0.5 mm/min at room temperature ($20 \pm 1^\circ \text{C}$) with a relative humidity of $70 \pm 5\%$. Before testing, the edges of the surface of the specimens undergoing tensile stresses were chamfered with a diamond disc (grit size $9 \mu\text{m}$). After testing, the fracture surface of the specimens was observed with an optical microscope to ensure that fracture didn't occur from sample edges. It was found that very few specimens had fractures that originated from an edge. Such samples were discarded and other samples were tested.

7.6.2 Biaxial flexural strength (Piston on three ball method)

Twenty disc-shaped specimens of Empress 1 and Empress 2 measuring 14 mm diameter x 1.1 mm thickness were pressed, ground, polished and heat-treated as discussed in Chapter 3, 3.3. The final dimensions of the specimens were 14 x 1 mm. The disc specimens of the new experimental ceramic material, which were supplied in the pressed state by the manufacturer, were subjected to the same polishing and finishing procedures explained in Chapter 3.

The piston on three ball test was used to determine the biaxial flexure strength of twenty discs of each material. The test was carried out using a universal testing machine (Shimadzu Autograph AG-G, Kyoto, Japan) at a crosshead speed of 0.5 mm/min until failure occurred. The disc specimens were supported on three symmetrically spaced balls (6 mm distant from the centre of the jig). A thin plastic

sheet (0.05 mm thick) was placed between the piston (0.75-mm diameter) and the specimen in order to facilitate an even load distribution. Testing was performed at room conditions (22 °C, and 66% relative humidity). The maximum tensile stress, which corresponded to the biaxial flexure strength, was calculated according to the equation suggested by the test standard ASTM F 394-78 [27], as follows:

$$S = -0.2387 P (X-Y) / d^2 \quad (3)$$

where S is the maximum tensile stress, P is the load at fracture and d is the specimen thickness at fracture origin. X and Y were determined as follows:

$$X = (1 + \nu) \ln(B / C)^2 + [(1 - \nu)/2](B / C)^2 \quad (4)$$

$$Y = (1 + \nu)[1 + \ln(A / C)^2] + (1 - \nu)(A / C)^2 \quad (5)$$

where ν is the Poisson's ratio, A is the radius of the support circle, B is the radius of the tip of the piston, and C is the radius of the specimen.

7.6.3 Weibull Modulus

Strength variation among each group was evaluated by calculating the Weibull modulus (m). An Excel[®] spreadsheet was used to rank the biaxial strength data in ascending order and appoint a rank over the range 1 to N (N is the number of specimens); a straight line was then fitted through the points using the median rank regression method. The following equation was used to calculate the Weibull modulus, as follows:

$$P_f = 1 - \exp [-(\sigma / \sigma_0)^m] \quad (6)$$

where P_f is the failure probability, σ is the strength at a given P_f , σ_0 is the characteristic strength and m is the Weibull modulus. However, since P_f can be identified by the following relation:

$$P_f = j / (N + 1) \quad (7)$$

j is the rank in strength and N is the number of specimens, equation No. 6 can be rewritten as follows:

$$1 / (1 - P_f) = 1 / \exp [-(\sigma / \sigma_0)^m] \quad (8)$$

Accordingly, plotting $\ln \ln [1 / (1 - P_f)]$ against $\ln$ (strength) will provide a slope with the value of the Weibull modulus (m) [7, 17].

7.7 Results

7.7.1 Biaxial flexural test

Biaxial flexural strength results, Weibull modulus, standard deviation, and coefficient of variation for the three materials are listed in Table 7.1. The experimental ceramic material had the highest strength value, 440 MPa, and Empress 1 the lowest, 175 MPa. Empress 2 had a value of 407 MPa. Weibull modulus results were 8.5, 7.5, and 4.5 for Empress 2, the experimental ceramic and Empress 1 respectively. Illustrations of the Weibull plots of the three materials are also provided (Figures 7.3-5)

An Anova test for equality of results of all three populations were significant ($p < 0.0005$). The samples were also compared two at a time using 2-sample t-test. The t-test showed that there was no statistical significant difference between Empress 2 and the experimental ceramic ($p = 0.218575$), whereas both Empress 2 and the experimental ceramic materials were significantly stronger than Empress 1 ($p < 0.05$).

Table 7.1 Biaxial flexural strength (MPa) of the three materials

Material	Biaxial flexural strength (±SD)	Coefficient of variation (%)	Weibull modulus
Empress 1	175 (±32)	20	4.5
Empress 2	407 (±45)	12	8.5
Experimental ceramic	440 (±55)	13	7.5

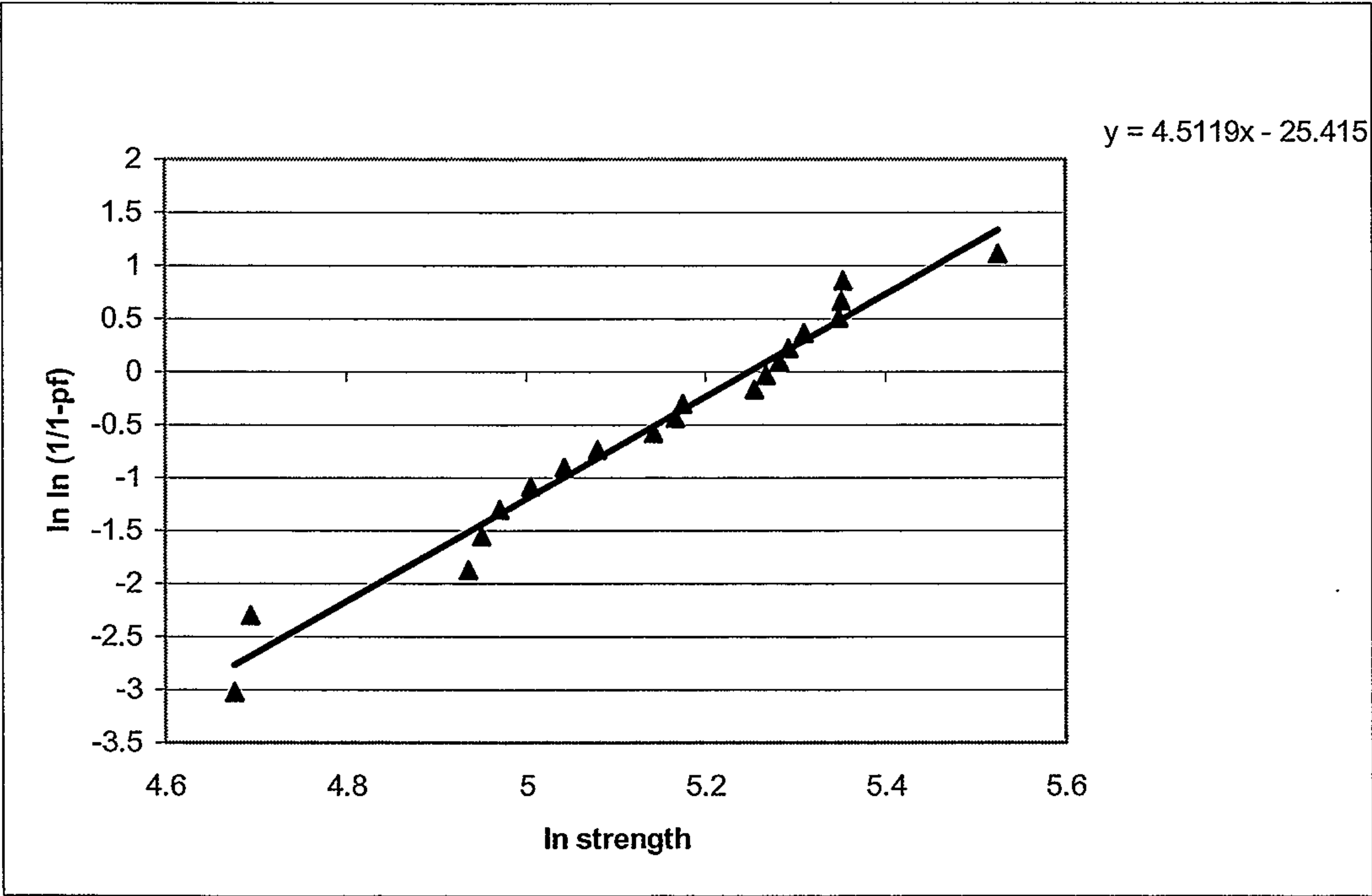


Figure 7.3 Illustration of Weibull plot of Empress 1.

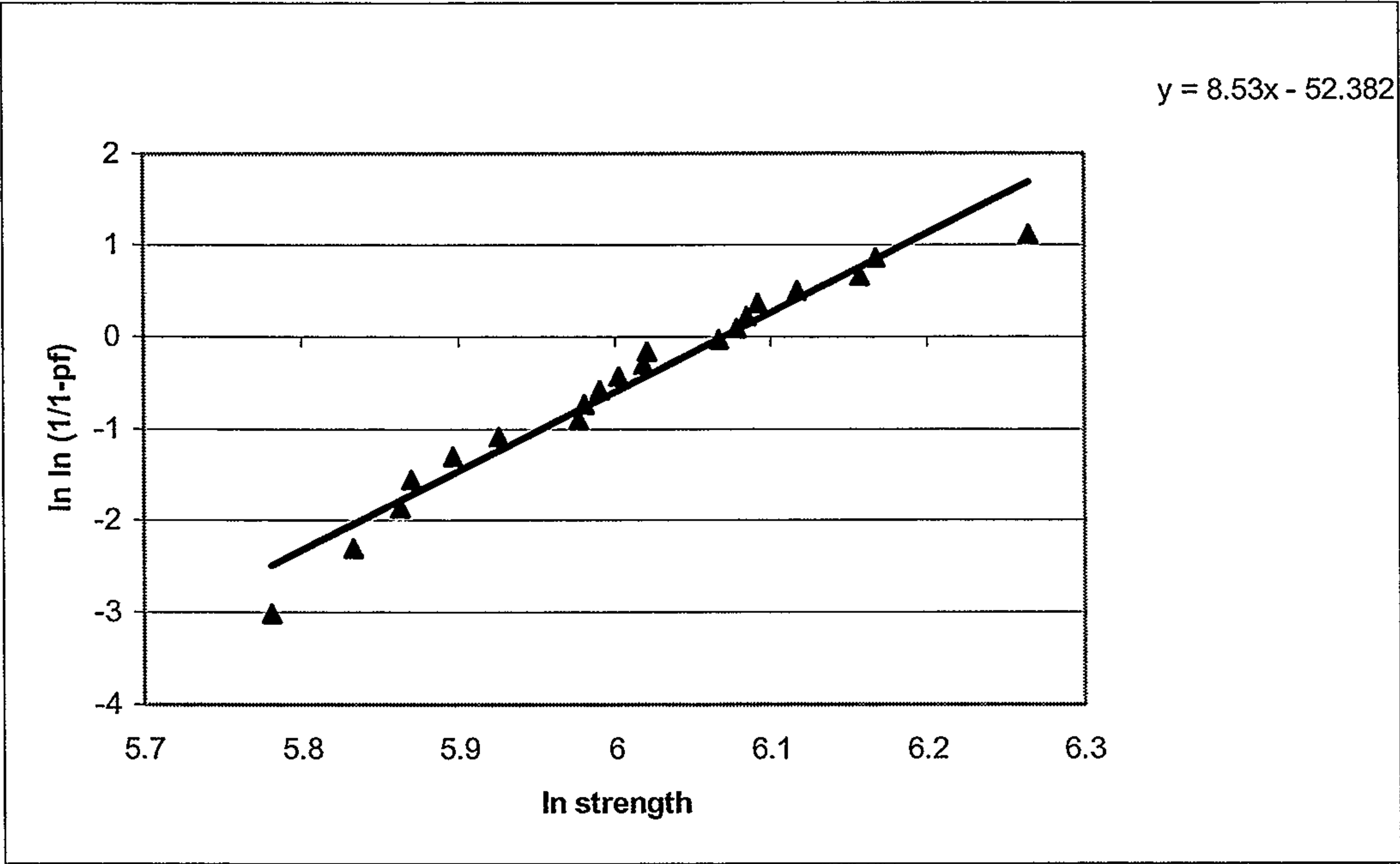


Figure 7.4 Illustration of Weibull plot of Empress 2.

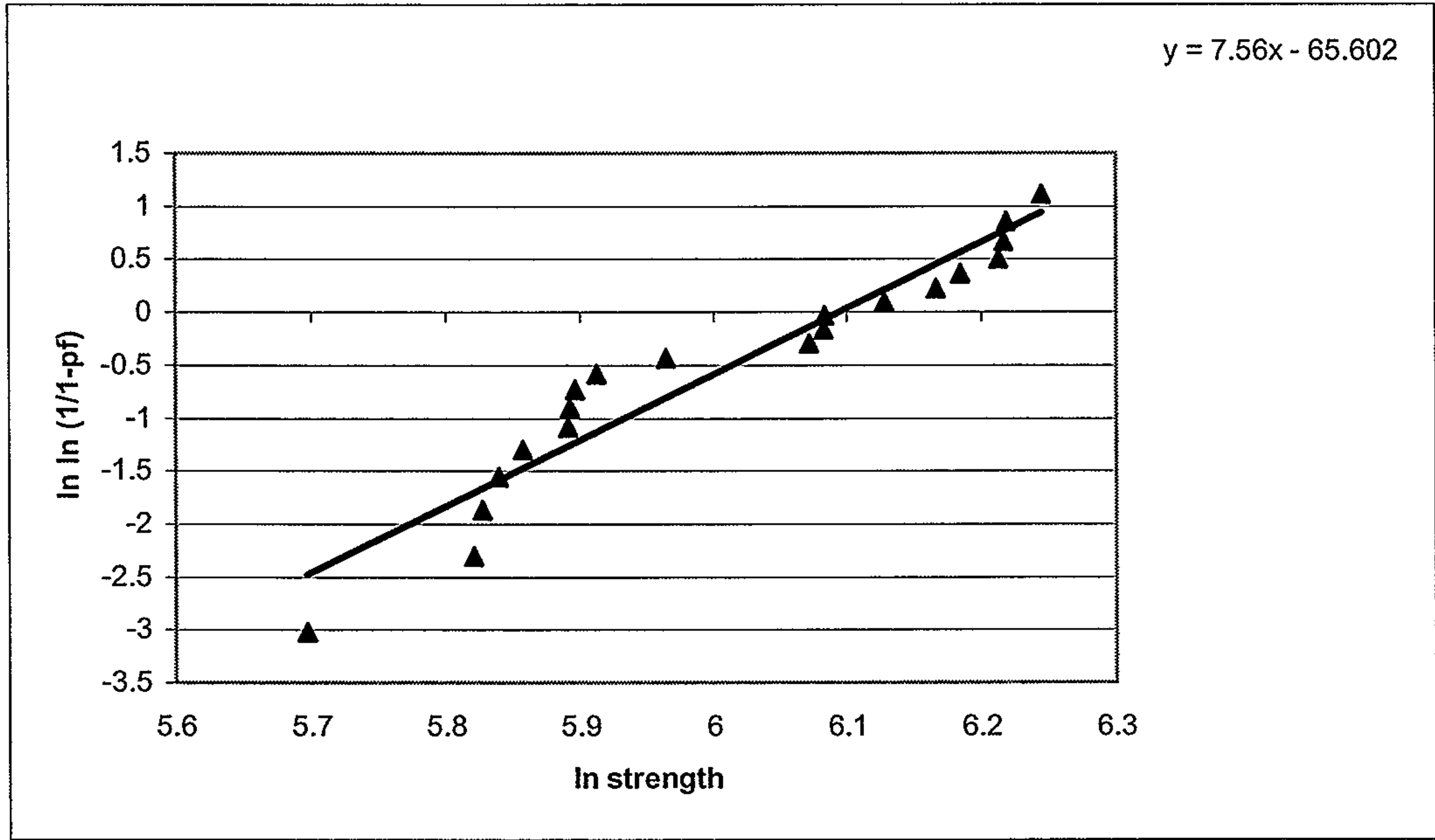


Figure 7.5 Illustration of Weibull plot of the experimental ceramic material.

7.7.2 3-point bending test

Flexural strength results and standard deviation for the three materials are listed in Table 7.2. Empress 2 and the experimental ceramic recorded significantly higher strength values than Empress 1. However, no statistically significant difference was found between them. Results are listed in Table 7.2.

Table 7.2: Uniaxial flexural strength (MPa) of the three materials.

Material	Uniaxial flexural strength (± SD)	Coefficient of variation (%)
Empress 1	106 (17)	15
Empress 2	306 (29)	18
Experimental ceramic	303 (49)	22

7.8 Discussion

The optimum strength of any ceramic is dependent upon the fabrication procedure and minimisation of the content of flaws [28]. Furthermore, several factors can also influence the definitive strength of ceramic materials, including testing methods, dimension of specimens, test environment, polishing procedures, rate of stressing and area of specimen subjected to the stresses.

Empress 1’s biaxial flexural strength value of 175 MPa as reported in this study, is higher than some previous results found in the literature. An explanation for the difference can be ascribed to the testing parameters. Previous biaxial flexural studies [16-18, 20] that reported lower strength values (133 to 136 MPa) used piston tip diameters from 1.3 to 1.6 mm whereas the present study adopted a smaller piston

tip diameter, 0.75 mm. This may have improved the strength values because a smaller area of the specimen was subjected to the maximum tensile stresses. There was subsequently less chance of the specimen having critical flaws in that area, which led to the improved strength [4].

The uniaxial flexural strength of this material is in good agreement with some previous results found in the literature. Cattell et al. (1997) and Seghi et al. (1995) reported strength values of 117 and 97 MPa respectively [11, 12]. On the other hand, Lawn et al. (2001) mentioned, in a review study, a higher value, 160 MPa [29]. Dong et al. (1992) also reported that strength values ranged between 160 and 180 MPa [30]. These strength variations have been attributed to different test parameters and polishing procedures.

A very important concern with a glass ceramic is whether heat treatment, such as that encountered during dental ceramic processing, modifies crystalline content and thereby the mechanical properties. Dong et al. (1992) investigated the effect of heat pressing and/or heat treatment on the Empress 1 system and found that pressing significantly increased the flexural strength [30]. This improvement in the flexural strength was attributed to better crystal distribution within a glass matrix, which is thought to minimise the susceptibility of the brittle glass matrix phase to fracture, and enhances a degree of residual stress isotropy within the microstructure, to which this increment in strength might be related. These investigators also found that further improvement in the strength after additional heat treatments was due to further development of residual stresses within the glass matrix produced by different thermal expansion of leucite crystals and glass matrix.

Shareef et al. (1994) studied the effect of microstructural features on the flexural strength of leucite-reinforced glass ceramic [31]. They noted that particle size and homogenous distribution of the microstructure have a great influence on the strength of these systems. A ball-milling technique was used in that study to decrease the leucite particles' size. The treated ceramics revealed a more even distribution of the leucite crystals and less evidence of cracks within the glassy matrix.

Empress 2 and the experimental ceramic demonstrated higher flexural strength than Empress 1. It was established that the amount and nature of the crystalline components may significantly enhance the mechanical properties [10, 11]. Fischer et al. (2001) attributed the improved mechanical properties of Empress 2 to the interlocking structure of the elongated lithium disilicate crystals [14]. These fibre-like crystals are homogeneously embedded in a glass matrix in an interlocking structure, which plays a major role in hindering the crack propagation and consequently elevating the flexural strength and fracture toughness. Moreover, cracks within such a structure would become trapped by these fibres and extend in a more circuitous manner, imparting a crack growth resistance which usually results in a higher reliability associated with a higher Weibull modulus.

Drummond et al. (2000) evaluated the mechanical properties of several glass ceramic systems [32]. They reported that the strength of an experimental lithium disilicate glass ceramic was twice as strong as the other investigated glass ceramics. Another mechanical properties comparison study by Holand et al. (2000) showed that Empress 2 was four times stronger than Empress 1 [33]. Sorensen et al. (1999) and Schweiger et al. (1999) stated that the 3-point bending test on lithium disilicate glass

ceramic yielded values of 339 and 350 MPa respectively, which are in close agreement with the results found in the present investigation [34, 35].

All-ceramic dental materials rely on their crystalline components to enhance their strength. However, an increase of the crystalline content may also result in an increase of the opacity. In spite of the approximately 60% crystalline content of the new pressable materials, Empress 2 and the experimental ceramic, they still maintain good translucency and offer an acceptable trade-off between strength and aesthetic appearance. The combination of these qualities may be beneficial in solving many clinical situations.

7.9 Conclusion

The similar flexural strength properties of the lithium disilicate-based glass ceramics Empress 2 and the Experimental ceramic is consistent with the similar microstructure and X-ray diffraction characterisation for both materials. This proves that mechanical properties are significantly enhanced by microstructural composition and crystalline phases. Both Empress 2 and the experimental ceramic materials demonstrated an improved flexural strength (uniaxial and biaxial strength values) compared to the leucite-based glass ceramic material, Empress 1. Also, they had higher Weibull modulus values than Empress 1, which indicates that these materials had less strength variations among the specimens tested. Because there are many variables that affect the clinical longevity of all-ceramic materials, mechanical studies are not sufficient to draw a valid conclusion regarding the clinical reliability and high success rate.

7.10 Effect of different fabricating procedures on the flexural strength of Empress 1 and Empress 2

7.10.1 Introduction

All-ceramic materials are subjected to different fabrication procedures in the laboratory, and sometimes must be adjusted clinically to allow either proper fitting or occlusion. The processing procedures and/or clinical adjustments are more likely to initiate subcritical flaws or large defects which, upon clinical loading and/or presence of moisture, may grow to a critical situation, leading to catastrophic failure. In addition, different surface roughnesses formed through different finishing procedures can cause various stress concentrations and consequently may be accompanied by a reduction in strength [36].

The high physical hardness of many ceramic materials makes surface polishing a difficult task and the removal of microcracks is not easily achieved. Moreover, skills of individual dental technicians [37] as well as adherence to the recommendations of a specific dental material's manufacturer can, to a great extent, influence the mechanical performance of all-ceramic materials. For example, pressable materials are submitted to sandblasting during divesting. Sandblasting is a complex procedure which has always been problematic and may lead to damage on a ceramic's surface and growth of microcracks [38]. Wolf et al. (1993) pointed to the importance of several issues during sandblasting which include: the particles' size, shape and mass as well as the kinetic energy of particles as they collide with a ceramic surface [39].

The effect of the processing procedures, polishing, grinding and glazing on the mechanical properties of some dental ceramic materials has been studied by many investigators [13, 36, 37, 40-55]. However, there is controversy concerning the most suitable method that can produce a smooth and strong surface [47].

Concerns have been expressed regarding the effect of different treatments on dental ceramics, during either dental laboratory procedures or clinical adjustments on their flexural strength. Moreover, the difference between the surface and the interior crystalline phase for the Empress 2 material, caused by different surface treatments [56], may act to strengthen this material. This is thought to be due to the creation of a surface layer composed of dense and larger lithium disilicate crystals than the bulk interior [57].

7.10.2 Purpose

During laboratory fabrication procedures and/or clinical adjustments, the pressable materials; Empress 1 and Empress 2, may be ground, polished or sandblasted. These treatments may affect their strength by introducing microscopic flaws and defects. No previous studies that appraised the effect of sandblasting and grinding on the strength of Empress 1 and Empress 2 were found in the literature. The aim of this study was to appraise the effect of different surface treatment procedures, sandblasting, grinding and polishing, on the flexural strength of Empress 1 and Empress 2, and to test the hypothesis that their strength is dependent on the resultant surface roughness.

7.11 Materials and Methods

7.11.1 Samples preparations and treatments

One hundred and forty disc specimens measuring 14 mm diameter and 1.1 mm thickness of Empress 1 and Empress 2 were prepared as discussed in Chapter 3, 3.3. When approaching pressed specimens during divesting, caution was exercised to avoid the impact of the sand particles on specimens, which was achieved by reducing the sandblasting pressure to 2 bars and increasing the distance between the specimens and the tip of the sandblaster nozzle.

Polishing and grinding procedures were different from those used with the specimens of the intrinsic biaxial and uniaxial flexural strength. All specimens were randomly divided into 7 groups of 20 specimens, for each material, and submitted to the following treatments:

Group 1: Specimens were left as pressed, untreated (control group).

Group 2: were wet polished with 220, 320, 500, 800, 1200 grade silicon carbide paper followed by 4, 2 and 1 μm diamond paste mounted on a metallographic lapping machine (Rotopol-22 Struers A/S, Rodovre, Denmark) at a feeding rate of 300 RPM and a force of 22 N. The total polishing time was approximately 3 minutes.

Group 3: were treated as per Group 2 followed by heating samples to the maximum glazing temperature (850° C for Empress 1 and 800° C for Empress 2) and holding temperature for 1 minute in a porcelain furnace (Programat P100, Ivoclar-Vivadent).

Group 4: was submitted to wet grinding with 220 and 180 grade silicon carbide paper mounted on the same lapping machine followed by 110 μm diamond disc (Grinder-Polisher, Buehler, UK L., Coventry, England) at the same feeding rate and force used for polishing, and a total grinding time of approximately 1 minute.

Group 5: were treated as per Group 4 followed by heating samples to the maximum glazing temperature and holding temperature for 1 minute.

Group 6: specimens were mounted on a special sample holder and sandblasted for 20 seconds using 50 μm aluminum oxide at a pressure of 3 bars and a distance of 50 mm from the sandblaster nozzle tip (2 mm in diameter).

Group 7: samples were treated as per Group 6 and followed by heating samples to the maximum glazing temperature and holding temperature for 1 minute.

The thickness of each specimen was measured at three different positions and the mean value was recorded. All specimens were then cleaned using an ultrasonic bath (Ultrasonic cleaner; Unisonics, Manly Vale, Australia) for 15 minutes at 90°C and washed in detergent and boiling water.

The average value of surface roughness R_a of all specimens was measured by means of a profilometer (Tencor P-10, surface profiler, California, USA). Five readings were taken for each specimen, within the centre area of each disc where the maximum tensile stresses are developed, with a travel distance of 2 mm, and the average value was recorded.

7.11.2 Biaxial flexural strength

The piston on three ball method described in paragraph 7.6.2 was adopted to assess the biaxial flexural strength. However, a piston tip measuring 1.5 mm was used. This piston size is similar to the piston sizes used in previous studies [16-18, 20]. The same procedures of the first part were also followed to measure the Weibull modulus and statistical differences among groups.

7.11.3 Scanning electron microscopy observations

Three specimens and several fractured surfaces of each group of Empress 1 and Empress 2 were carbon-coated. They were then examined for surface features using a scanning electron microscopy (XL 30, Philips, Eindhoven, Holland) to assess the effect of different treatment processing.

7.12 Results

Mean biaxial flexural strength, average roughness and Weibull modulus for all groups of the two materials are listed in Table 7.3. The control and sandblasted groups of both ceramics recorded the highest roughness values, however, no statistically significant difference was found between them ($p>0.05$) for each ceramic. The polished groups recorded significantly the lowest roughness and the highest strength values for both materials ($p<0.05$). No significant difference was found in the mean biaxial flexural strength values among the control, sandblasted and ground groups for each ceramic ($p>0.05$). After heat treatment, both ceramics demonstrated similar roughness and mean biaxial flexural strength values of the different treatment procedures. In addition, groups showed no significant difference after heat treatment. The Weibull modulus values for Empress 1 groups varied with different treatments,

showing higher values for polished and untreated groups, which ranged from 8 to 10, and lower values for ground and sandblasted groups, which ranged from 5.5 to 7.5. Empress 2 also recorded lower Weibull modulus values after grinding and sandblasting (6 to 7.5) than those values of untreated and polished specimens (ranging from 9 to 11.5).

Table 7.3: Biaxial strength (SD), Roughness (SD), and Weibull modulus for Empress 1 and Empress 2 following different surface treatments.

Material	Treatment	Strength (SD) MPa		Roughness (R _a) (SD) μ		Weibull modulus (m) (SD)	
		B.H	A.H	B.H	A.H	B.H	A.H
Empress 1	Control	125 (14)	-	1.65 (0.5)	-	9 (0.89)	-
	Sandblasting	121 (23)	121 (21)	2 (0.6)	2.1 (0.5)	5.5 (2.7)	5.7 (0.6)
	Grinding	124 (18)	129 (22)	0.7 (0.3)	0.7 (0.3)	7 (0.96)	6 (0.45)
	Polishing	171 (23)	172 (17)	0.04 (0.01)	0.03(0.01)	8 (1.7)	10 (4.8)
Empress 2	Control	300 (35)	-	1.4 (0.6)	-	9 (1.6)	-
	Sandblasting	279 (40)	295 (40)	1.7 (0.6)	1.65 (0.6)	6 (1.64)	7 (1.1)
	Grinding	294 (36)	297 (41)	0.65 (0.3)	0.6 (0.2)	7.5 (1.16)	7 (1.28)
	Polishing	387 (34)	368 (50)	0.025 (0.01)	0.024(.01)	11.5 (0.55)	9 (2.9)

B.H=before heat treatment, A.H=after heat treatment, SD=standard deviation.

7.13 Discussion

The mean biaxial flexural strengths of Empress 1 and Empress 2 in the current study are in good agreement with previous results found in the literature [16-18, 20, 56]. The assumption reported in the first part (7.8) with regard to the effect of the piston's tip size on the biaxial flexural strength was supported. When a similar piston tip diameter (1.5 mm) to those used in previous studies was used, comparable mean biaxial flexural strength values were found. This clearly shows that mean biaxial flexural strength is affected by testing design. Care is therefore required, as mean strength comparisons under different conditions or testing parameters may become invalid.

In the present study, stress concentrations caused by either roughness, surface defects, or internal stresses are believed to be the main reasons for the mean biaxial strength variations among all tested groups of Empress 1 and Empress 2. Sandblasted, ground, and the control groups for each material recorded similar mean biaxial strength values despite their different roughness values. The insignificant roughness value difference between sandblasting and the control group is expected to be due to submitting the control group to sandblasting during divesting. The low roughness values of the ground groups compared to sandblasted and control groups might be attributed to the multiple contact and lower contact pressure associated with uniform particles during mechanical removal from the surface during grinding, which might have minimised the mean degree of roughness. In contrast, in the case of sandblasting, severe random or localised removal is anticipated due to the impact of the sand particles with the surface, which might have created fracture about the impingement site; various deep grooves and valleys and consequently increased the

roughness values. The cracking associated with such treatments is equivalent to that of a pointed indenter, and leads to the development of median, radial and lateral cracks [38]. It is the median and radial cracks that generate the defects responsible for the strength degradation, whereas the lateral cracks result in the material removal and the resultant surface roughness.

Sandblasted and ground groups recorded lower strength values than the control and polished groups for both materials. During grinding or sandblasting, heat, cracking, chipping and residual stresses may be generated, from which strength-reducing flaws are initiated. Mecholsky et al. (1977) reported that two sets of flaws grow in directions both perpendicular and parallel to the grinding direction, but the tensile orientation during testing determines which set initiates fracture [49]. In the case of the biaxial test, the direction of grinding will not be critical, as stresses develop uniformly within the maximum tensile area, at the centre of a disc, and the cracks developed in this area are more likely to dictate strength. In addition, during these treatments, if a flaw size, sharpness, orientation or distribution changed, the final strength of a ceramic material would be changed [4].

The statistically insignificant difference in strength values between sandblasted, ground, and the control groups for both materials was somewhat surprising. This is because lower strength values are expected after more severe procedures such as grinding or sandblasting. This also indicates that strength reduction of a ceramic material is a consequence of the finishing tools' coarseness and feed rate, which determines the associated defects' size and the amount of compressive stresses developed. It may also depend upon the characteristics of

different ceramics' microstructures. Sandblasting, which is considered a complicated and detrimental procedure to strength, was performed in this study for a short time, 20 seconds, and at a stand-off distance of 50 mm, which might have minimised the effect of sandblasting and subsequently the volume loss. The latter is strongly dependent upon the sand particles' diameter, hardness, elastic modulus and velocity, plus the duration of the procedure [58]. Bigger, harder and stiffer particles and/or higher pressure induce larger median and lateral cracks that can significantly dictate strength. The size of these strength-reducing flaws is also dictated by the fracture toughness of the treated material. Grinding was also carried out in this study for 60 seconds and at a feed rate of 300 RPM. Although grinding and sandblasting involve mechanical removal and a damage of varying degrees, they may be accompanied by development of residual stresses, which can be compressive, depending upon the parameters of the treatment procedure [13]. The compressive layer, formed by surface plastic deformation, may act to prevent the extension of microscopic defects. Consequently, provided no significant median or lateral cracks formed, strength might be improved by grinding or machining [59].

Polishing with the diamond paste material produced the smoothest surface and the highest strength compared to all other groups for the two materials. The ability of polishing to eliminate various defects and flaws from the treated surface is considered responsible for such a strength increment. Moreover, the compression layer formed during polishing is also relevant [13]. The strengthening due to compressive surface stresses is a result of residual stresses, which oppose the applied tensile stresses. However, if a flaw size exceeded the depth of this layer, compression stresses may not have contributed to the strengthening effect of polishing [50]. It has been speculated

that greater than 50% strength increase can be achieved after fine polishing [60]. A recent investigation stated that surface modification of Empress 2 material was enhanced by polishing with 800 SiC grit paper, which instigated a significant strength increase when compared to veneering or different heat treatments [56].

Another concern with the polishing, grinding and sandblasting treatment procedures is the effect of heat treatment (glazing). The present investigation found that submitting these materials to heat treatment that is typically encountered during dental laboratory processing didn't improve the strength. Several reports in the literature also showed that auto-glazing had no effect on strength [46, 52, 55, 56]. It should also be considered that heat treatment after polishing or grinding may degrade strength, which is thought to be a result of releasing compressive stresses that normally develop during polishing or grinding. Oh et al. (2000) investigated the effect of heat pressing and subsequent heat firing on the flexural strength of Empress 2 [61]. They found that heat pressing had a positive influence on the flexural strength. However, the combination of heat treatment didn't increase the strength and, unexpectedly, a similar strength result prior to pressing was achieved.

To elucidate the strength dictating flaws or defect sizes that may grow in brittle materials such as the current ceramics Empress 1 and Empress 2, the expression, which relates the strength (σ), in the absence of residual stresses, defect size (C) and fracture toughness (K_{IC}) was used, as follows [62]:

$$\sigma = K_{IC} / Y (\pi C)^{1/2} \quad (9)$$

where Y and π are constants, 1.12 and 3.14 respectively. The fracture toughness given by the indentation fracture method (IF) (Chapter 6, Table 6.1) for the shorter crack of Empress 1 and Empress 2, namely 1.26 and $1.53 \text{ MPa} \cdot \text{m}^{1/2}$ respectively, were used. Estimates of the defect sizes from the range of strength results for Empress 1 material showed similar values for all treated groups, which ranged from approximately 15 to $55 \text{ } \mu\text{m}$, and from only 8 to $20 \text{ } \mu\text{m}$ for polished groups. The Empress 2 material showed similar outcomes where polished groups had significantly shorter cracks or defects typically from 3 to $8 \text{ } \mu\text{m}$, whereas those of other treated groups were in the range of 5 to $20 \text{ } \mu\text{m}$. These crack lengths for both materials were significantly larger than the roughness values recorded by these materials for all differently treated groups. This might give an explanation for the independence of strength values in this study on surface roughness. The fractured surface shown in Figure 7.6 of the fracture origin of the treated Empress 1 sample shows that either pore or surface defect has initiated the failure. The size of this defect's radius is approximately $50 \text{ } \mu\text{m}$.

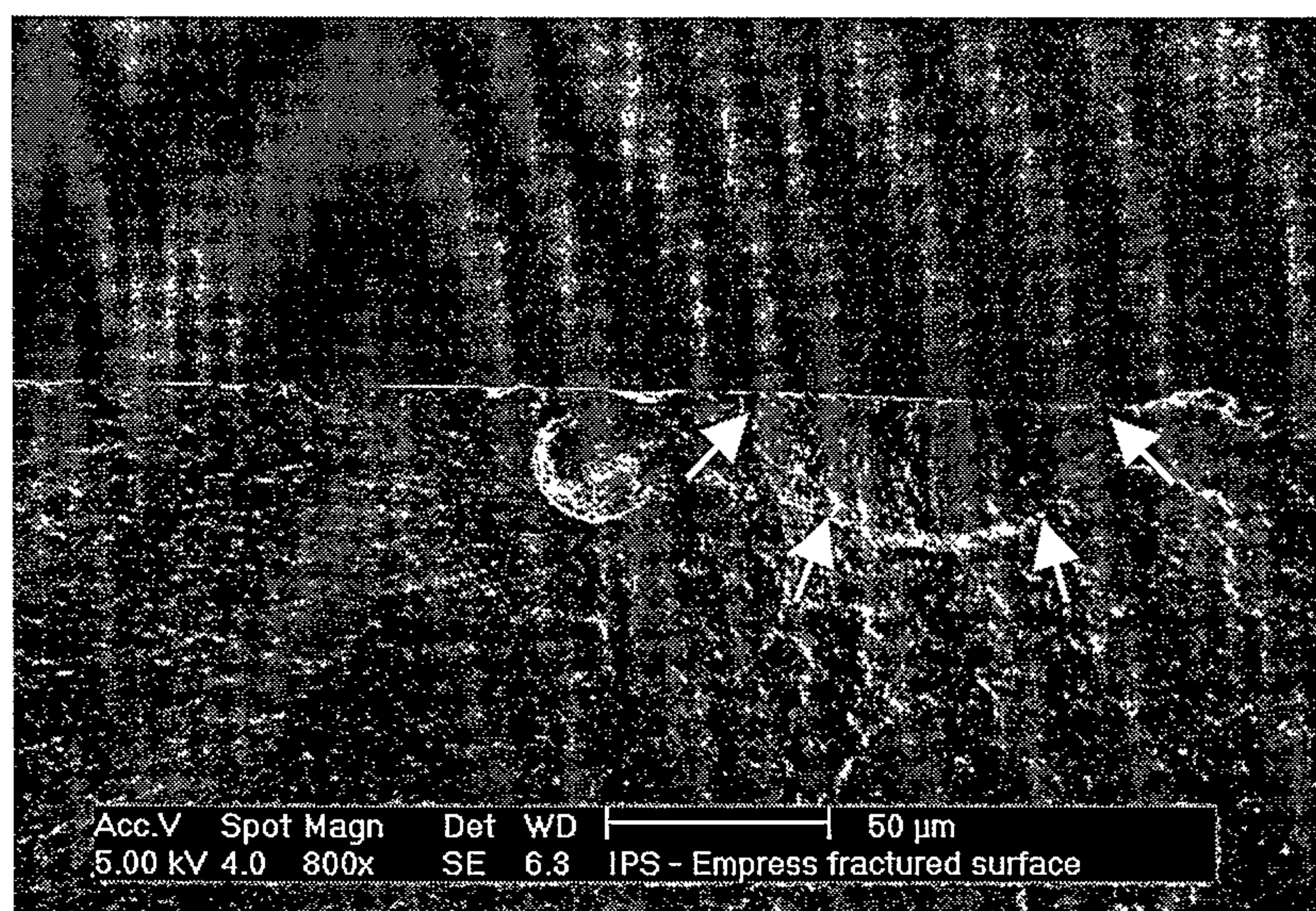


Figure 7.6 SEM photomicrograph of Empress 1: fractured surface of a ground specimen showing spherical porosity site and the fracture origin, which is arrowed.

Weibull modulus values of the polished and untreated groups of Empress 1 and Empress 2 before and after heat treatments showed higher values than ground and sandblasted groups. This indicates less variation in the strength and similar distribution of flaws among samples. The damage and mechanical removal of particles generated by surface cracking damage during either sandblasting or grinding normally introduce wide distribution and different shapes of defects and flaws. Consequently, a wider range of strength values is expected. During testing, some specimens recorded very low load at fracture, and consequently demonstrated lower strength value compared to other specimens. These specimens are expected to be either defected or suffering from detrimental pores that were located within the maximum tension area. Weibull modulus results tend to significantly escalate if these specimens are discarded. More reliable Weibull modulus can be achieved when a larger number of specimens are tested; typically 30 or more are recommended [17]. Weibull modulus results of both materials are in good agreement with results found in the literature, and correspond to the Weibull modulus range reported for most ceramics (5-15) [17, 18, 56, 63].

A scanning electron micrograph of the treated surfaces of these materials showed that fine polishing produced the smoothest surface. However, a dispersion of spherical and irregular types of porosity was noticed throughout the fine polished surface of Empress 1 (Figure 7.7). Fewer spherical pores were noticed in the Empress 2 material (Figure 7.8).

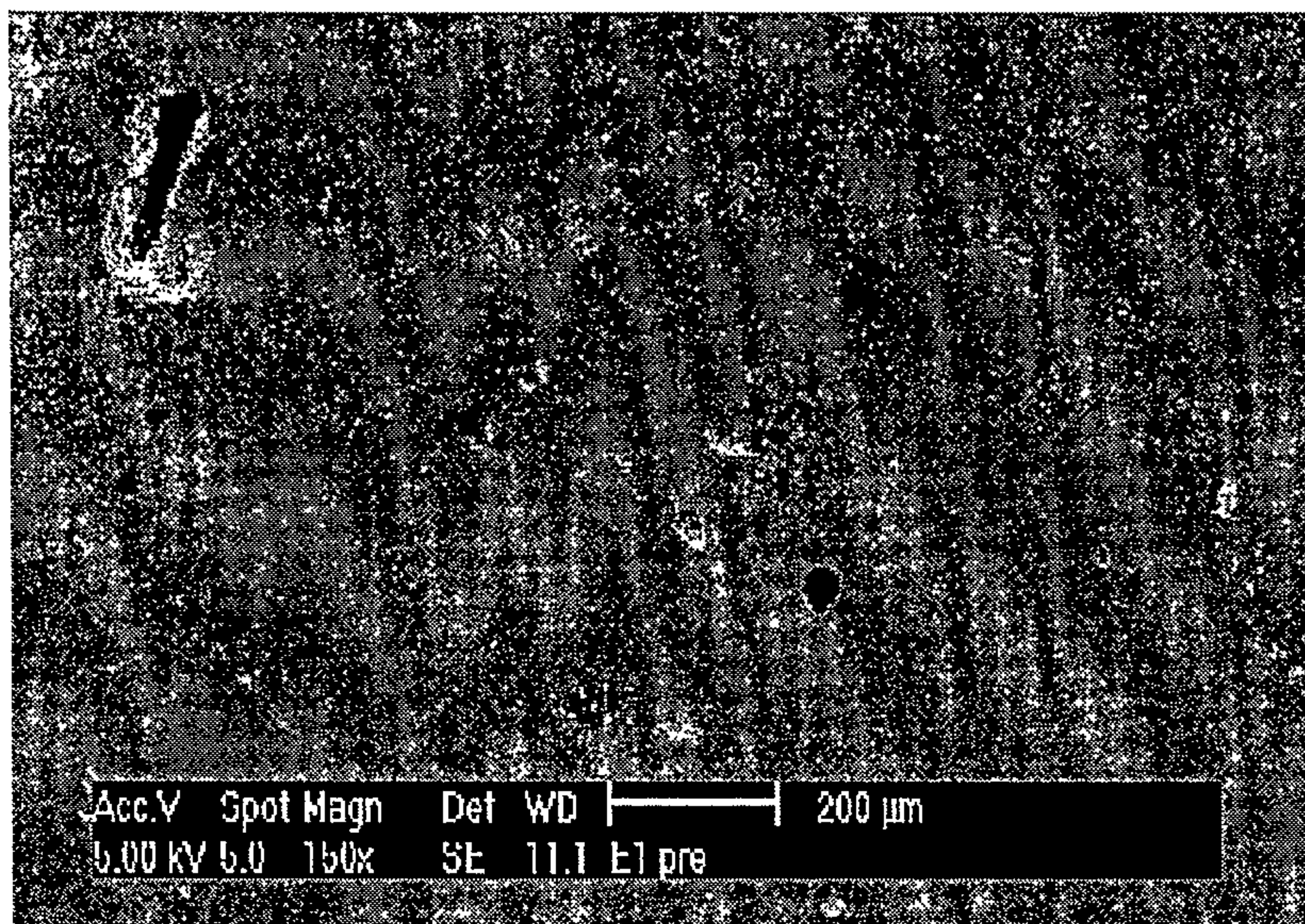


Figure 7.7 SEM photomicrograph of Empress 1 showing the fine polished surface with the associated spherical and irregular shaped pores (magnification 150 x).

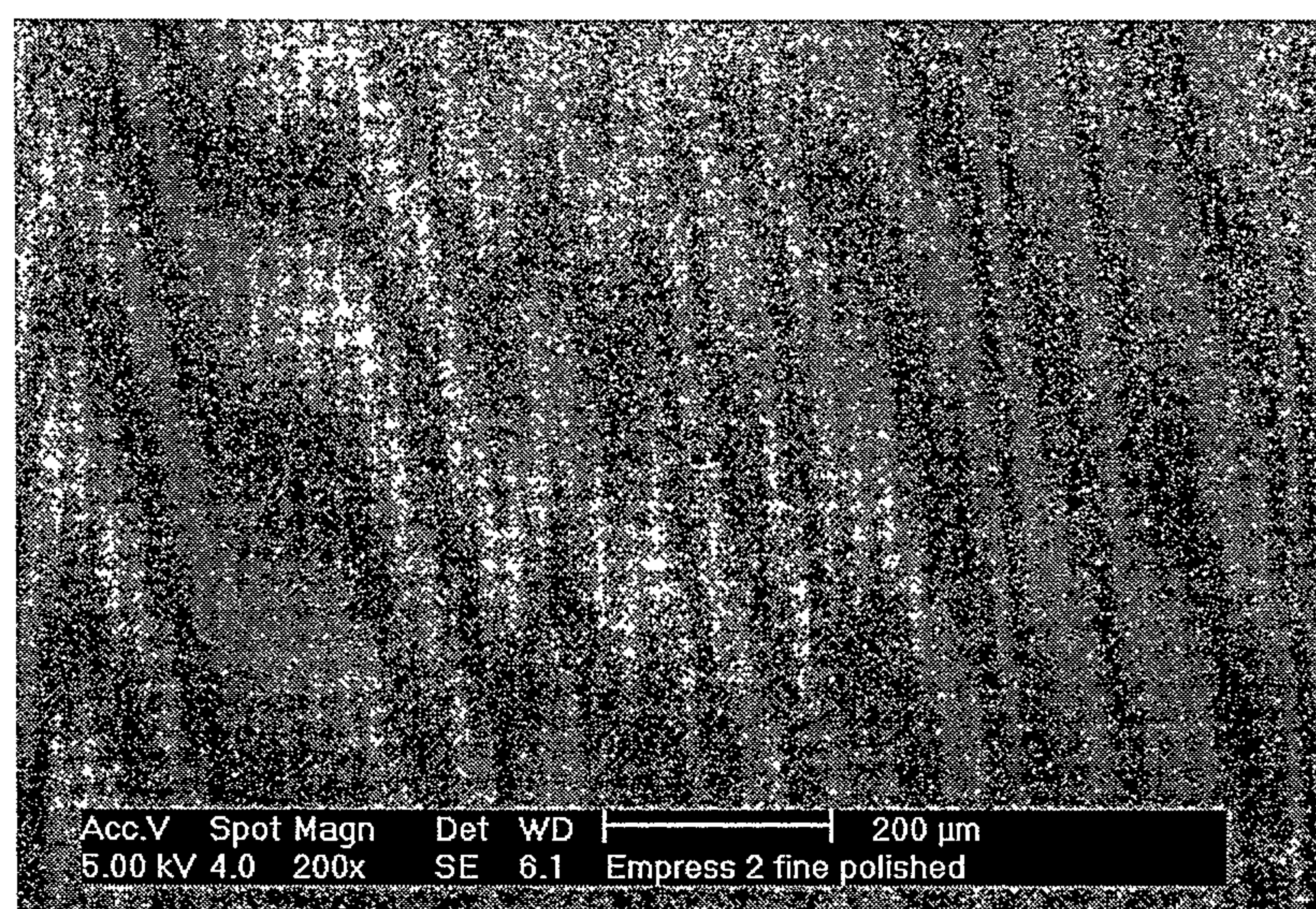


Figure 7.8 SEM photomicrograph of Empress 2 fine polished surface showing very few small spherical pores.

In the Empress 1 material, it is expected that these pores are also present in the other treated surfaces, but they couldn't be visualised due to the severe roughness of these surfaces compared to the polished groups. Fractured surfaces of Empress 1 also

showed some pores (Figure 7.9), which often appeared to be the failure origin sites (Figure 7.6).

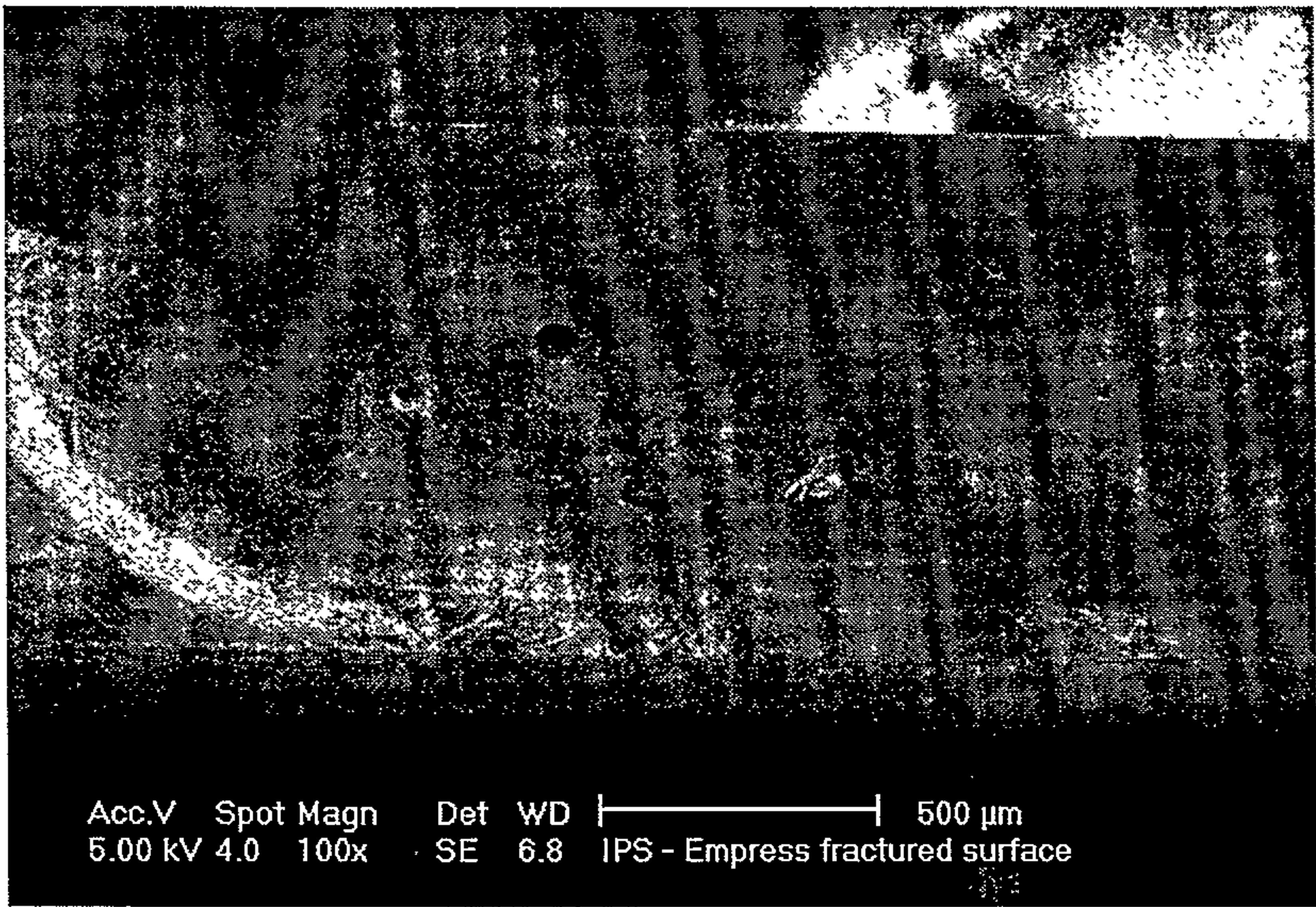


Figure 7.9 Fractured surface of Empress 1 showing some spherical pores.

The fracture surface of Empress 2 did not show such pores, and appeared to be very rough (Figure 7.10). The ground surface of Empress 2 specimens showed coarse scratches in random directions (Figure 7.11).

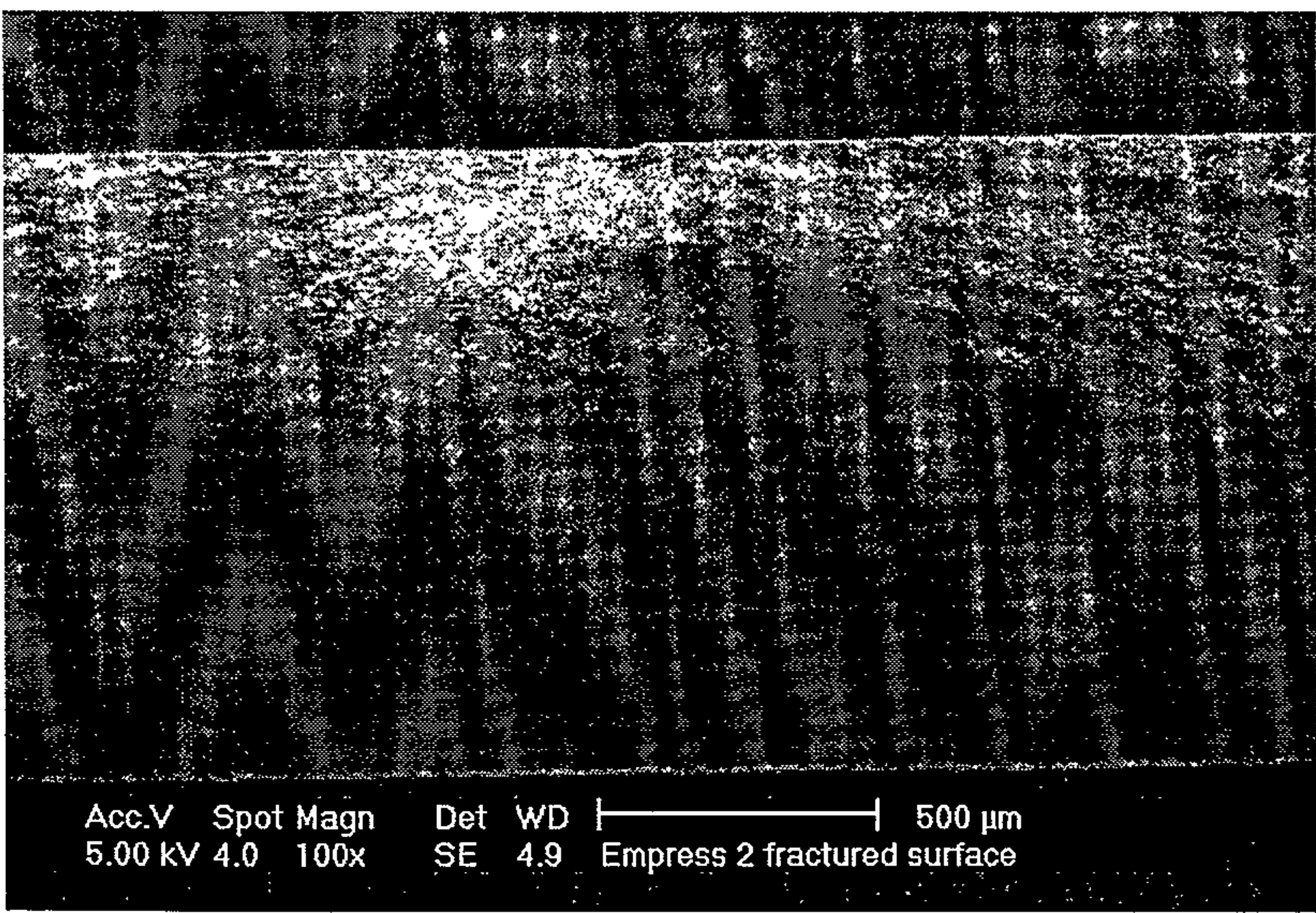


Figure 7.10 SEM photomicrograph of a fractured surface of Empress 2 showing no pores and appearing very rough.

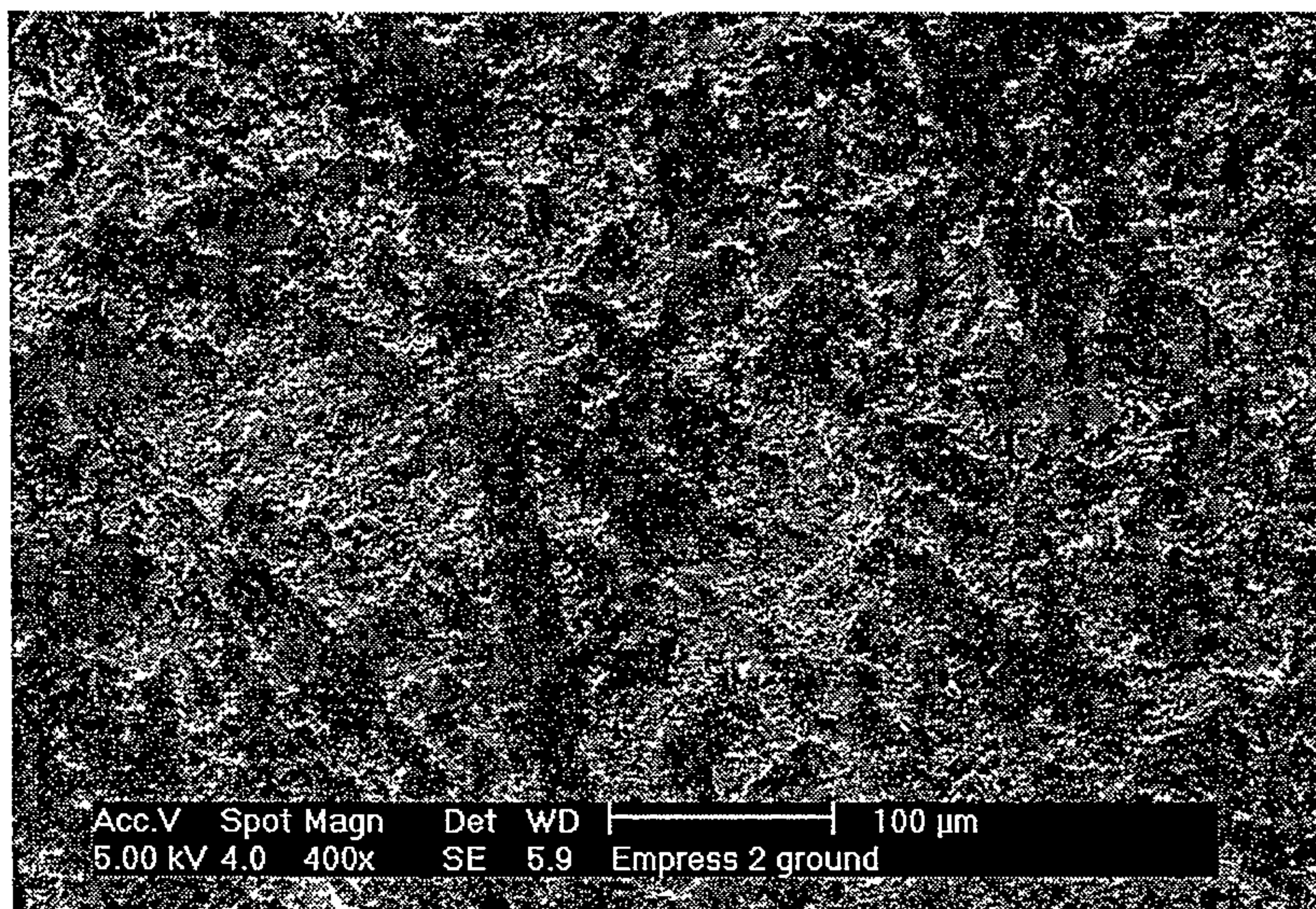


Figure 7.11 SEM photomicrograph of Empress 2 after surface grinding, showing scratches in different directions and associated surface removal.

Such scratches appeared to be deeper in the Empress 1 material, which is thought to be due to the presence of a considerable amount of soft phase, the glass. Rough surface grooves and signs of porosity can also be seen (Figure 7.12).

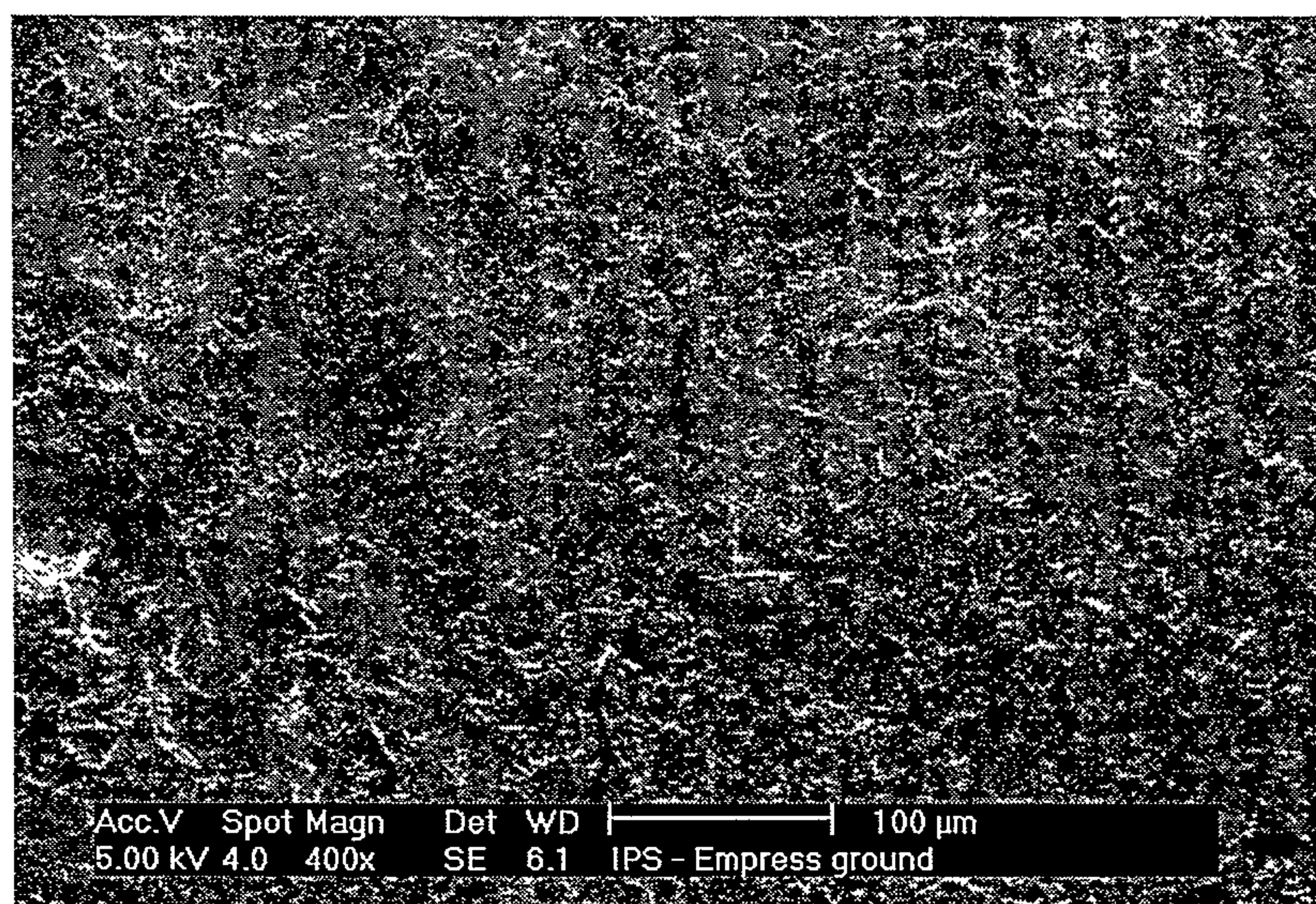


Figure 7.12 SEM photomicrograph of Empress 1 ground surface, showing rough surface with some pores.

Sandblasted surfaces of both materials appear to be very rough and characterised by various deep pits, valleys and irregularly shaped defects (Figures 7.13 and 7.14). The untreated surfaces of both materials showed similar surface characteristics to those of sandblasted surfaces; this is because the untreated surfaces were also sandblasted during divesting, although at lower air pressure; the effect of sandblasting on the surface structure and strength seems to be unavoidable.

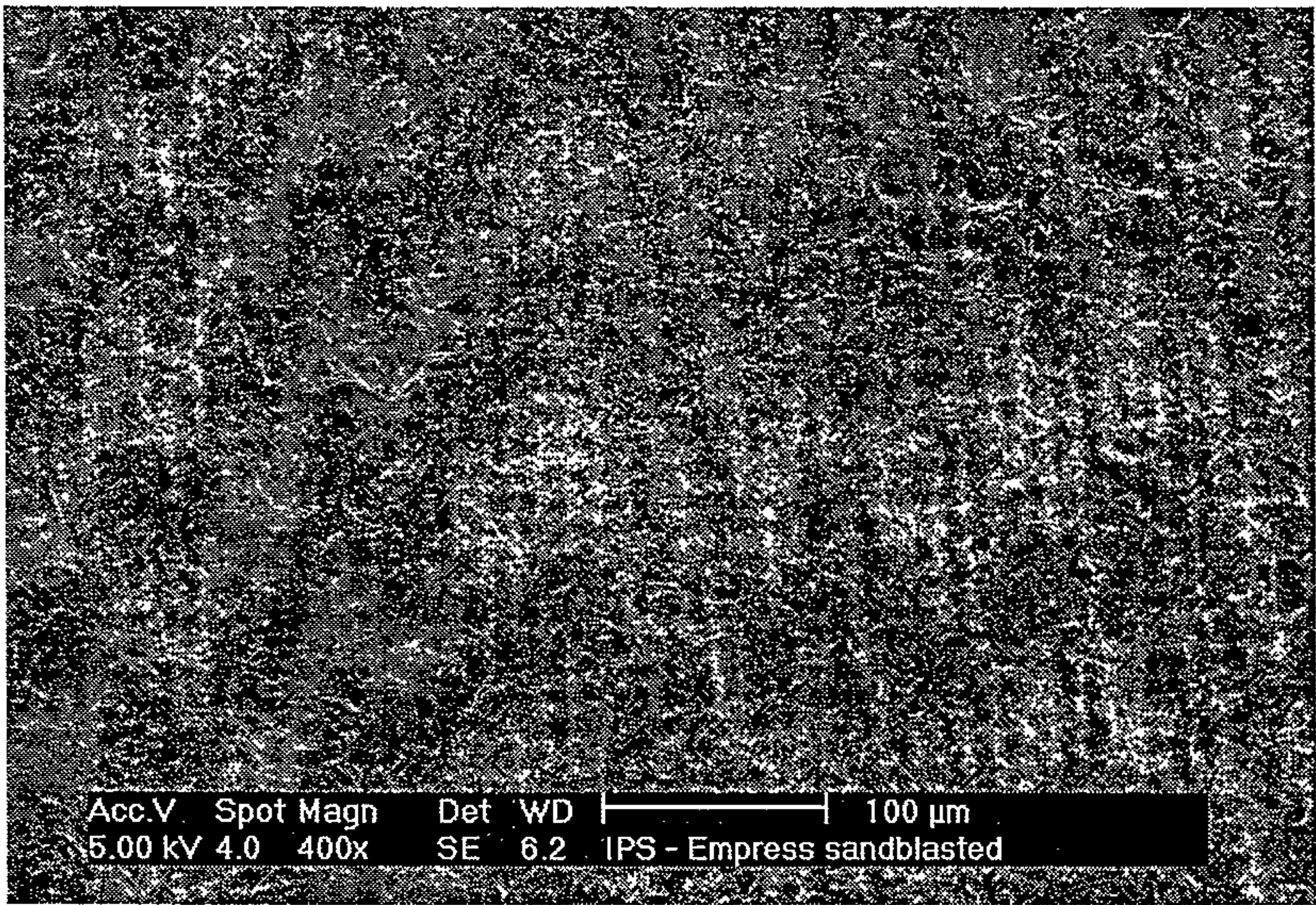


Figure 7.13 SEM photomicrograph of Empress 1 sandblasted surface, showing the rough surface generated. Surface roughness measurements indicated that this surface had deeper pits than other treated surfaces.

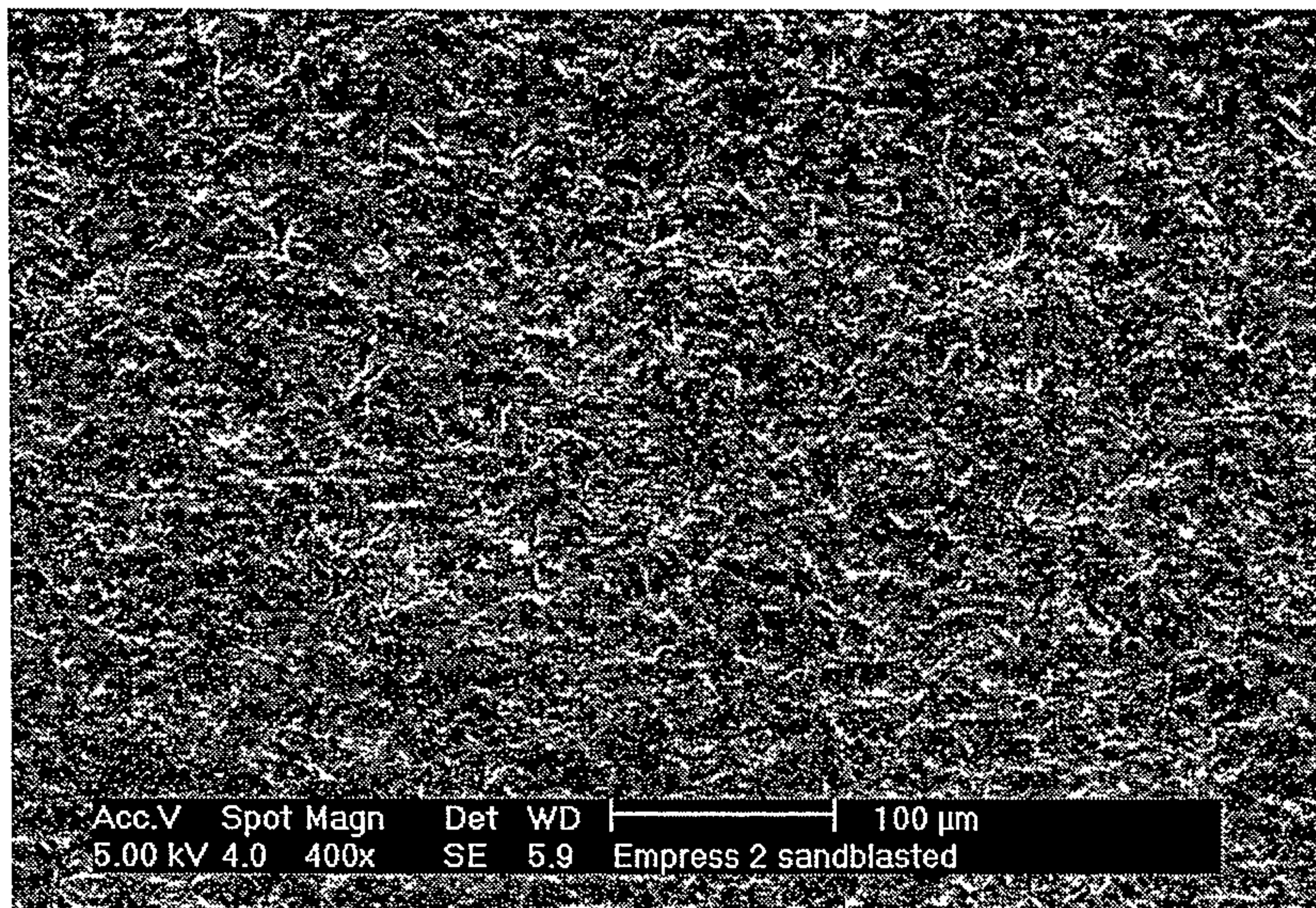


Figure 7.14 SEM photomicrograph of Empress 2 sandblasted surface, showing uniform shallow surface damage and superficial pits.

Based on the results of this study, the hypothesis that the strength is affected by grinding and improved by polishing, and the roughness determines the strength is partly accepted. Stress concentration can be associated not only with surface roughness, but also with other factors, such as internal stresses (within the microstructure), porosity, inherently present or pre-existing cracks and thin sectional areas associated with pores close to tensile stresses at the surface. Thus, surface roughness can dictate strength if no larger stress concentration greater than that due to surface roughness occurs [36]. Kitazaki et al. (2001) reported that surface roughness is not the only factor that determines strength [53]. Furthermore, some ceramic materials exhibit different crystalline concentrations between their surfaces and the internal portions, which may occur as a result of surface nucleation of crystallisation and may act to significantly strengthen materials.

This study showed that sandblasting and grinding didn't significantly decrease strength. Even so, prolonged sandblasting should be avoided or lower pressure is advised, as this will either change the developed crack dimensions or increase the volume loss. Grinding should also be used at low speed and in a wet grinding environment [13]. Polishing has significantly improved the strength in this study, which was related to the ability of polishing to improve the condition of the ceramic's surface and free it from various defects. Polishing or glazing is recommended to counteract the detrimental effects of grinding [55]. However, the present study found no effect on strength after self-glazing. It is therefore suggested that polishing, whenever possible, should follow clinical adjustment or surface modifications in order to minimise the effect of possible harmful defects and flaws. For the Empress 2 material, polishing might be unadvisable in areas where layering porcelain may be added, as this will deteriorate the bond created between the core and layering porcelain. However, in non-aesthetic areas, where the bulk of core material can be exposed, such as the connector regions, polishing can be made carried out. More studies are required to further show the effect of such treatment procedures on the mechanical properties of these materials.

7.14 Conclusion

This study has shown that grinding and sandblasting had no significant effect on the biaxial flexural strength of the materials studied, Empress 1 and Empress 2. Heat treatments that are typically encountered following laboratory fabrication surface treatments also didn't significantly affect strength. However, the lower Weibull modulus values of the sandblasted and ground groups, compared to the untreated and polished groups, were noticed and attributed to the different flaw sizes and/or shapes

among samples during these treatments. Both materials demonstrated significantly improved strength and lower strength variation after polishing. This study also showed no direct correlation between strength and surface roughness, which might be due to the development of higher stress concentration and larger flaws among the microstructure of these materials than that determined by surface roughness.

7.15 References

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CHAPTER 8

MECHANICAL PROPERTIES AND MICROSTRUCTURE OF SEVERAL ALL-CERAMIC DENTAL MATERIALS

This chapter will provide a comparison of the mechanical properties (flexural strength and fracture toughness) of Empress 1, Empress 2 and the experimental pressable ceramic, which have been the prime focus of this thesis, with several modern all-ceramic dental materials. These materials include: In-Ceram Alumina (slip and dry-pressed), In-Ceram Zirconia (slip and dry-pressed), DC-Zircon, and an experimental yttria partially stabilised zirconia material. This mechanical comparative study has been carried out in a collaboration with Dr M. Guazzato, and accepted recently by the Dental Materials Journal. It resulted in two articles, titled "Strength, fracture toughness and microstructure of a selection of all-ceramic materials, Part I: pressable and alumina glass-infiltrated ceramics, and Part II: Zirconia based materials (listed in Journal Publications and Scientific Meetings at the preface of this thesis, Nos. 9 and 10).

Future directions and suggested research studies will also be presented in the second section of this chapter.

8.1 Introduction

The use of all-ceramic dental materials has increased rapidly in the last decade. This, with the improvement in dental material technologies, has stimulated the development of many new all-ceramic dental materials. In order to understand the fracture behaviour, clinical potentiality and limits of such modern materials, the mechanical properties are basically the first parameter investigated. In fact, many mechanical property reports of all-ceramic systems are available in the literature. However, since many of these studies have been conducted under different conditions and methodology, comparing the mechanical properties of all-ceramic materials reported by these studies may not be valid. Furthermore, information regarding the volume of the reinforcing components and the relationship between the microstructures of these materials with the toughening mechanisms is not clearly understood in many instances.

8.2 Aim

For a mechanical properties comparative study with the current pressable materials, six different all-ceramic dental materials have been chosen, namely: In-Ceram Alumina (slip and dry-pressed techniques), In-Ceram Zirconia (slip and dry-pressed techniques), DC-Zircon, and an experimental yttria partially stabilised zirconia material. Their mechanical properties, microstructural features, volume fraction (crystalline content) and the percentage of porosity were assessed and compared with those of the three pressable materials tested in this study. The X-ray diffraction technique was also used to identify their main crystalline phases. In the case of zirconia-based materials, the X-ray diffraction was adopted to determine the relative amount of the monoclinic phase change from the as-sintered to fractured surfaces of

these materials. This was done in order to test the ability of the zirconia-based materials to trigger the very important tetragonal to monoclinic ($t \rightarrow m$) phase transformation process, when stressed and fractured. The $t \rightarrow m$ transformation, which can be induced by external stresses, such as grinding, cooling and impact, results in a 4% increase of volume that causes compressive stresses. These stresses may develop in the vicinity of a crack tip. It is this clamping constraint about the crack tip that must be overcome by the crack in order to propagate, explaining the increased fracture toughness of zirconia compared to other ceramics.

8.3 Materials and Methods

8.3.1 Preparation of specimens

The specimens of In-Ceram Alumina and In-Ceram Zirconia were obtained by cutting bars from either blocks that were already sintered by the manufacturer, or from slip prepared by mixing powder with the corresponding special liquid according to the manufacturer's instructions. The slip of each material was allowed to dry for 24 hours and then sintered at 1100°C for 10 hours in a high-temperature furnace (In-Ceram II, Vita Zahnfabrik, Bad Säckingen, Germany). After drying, the upper part of the slip was smoothly ground with silicon carbide paper until a uniform surface was achieved. Bar specimens were then cut using a diamond blade (Isomet, Buehler Ltd, Lake Bluff, Illinois, USA). The same cutting procedure was used to prepare bars of In-Ceram Alumina and In-Ceram Zirconia dry-pressed (blocks) (In-Ceram Blank for Cerec, Vita Zahnfabrik, Bad Säckingen, Germany). This was followed by the glass-infiltration procedure for each material using a corresponding glass material and heat firings. After glass infiltration the excess glass on the surface of each sample was removed by sandblasting with 50 μm Al_2O_3 at a maximum pressure of 0.25 MPa.

The experimental zirconia material were prepared by sintering some blocks of 3mol% of Y_2O_3 ZrO_2 powder at 1450°C for 1 hour at a heating and cooling rate of 5°/min. The cutting procedure was carried out as explained above. DC-Zircon bar specimens were cut from blocks of fully sintered material, provided by the manufacturer (DCS Dental AG, Allschwil, Switzerland).

All specimens were serially ground and wet polished as done for pressable materials Chapter 3 (3.2.5). Finally, the specimens were cleaned using an ultrasonic bath with acetone at room temperature for 15 minutes. Forty bar samples (twenty samples for each mechanical property) for each material, with final dimensions of approximately 20 mm long, 1.2 mm thick and 4 mm wide, were used to measure the flexural strength with the three-point bending method, as explained in Chapter 7 (7.3.1) and fracture toughness (IS technique), as explained in Chapter 6 (6.6.2).

8.3.2 X-ray diffraction

The same X-ray diffraction procedures carried out for the pressable materials Chapter 4 (4.2.4) were utilised here to identify the crystalline phases of all materials after sintering. In addition, fractured surfaces of all materials were prepared as explained previously in Chapter 6 (6.7). The relative amount (X_M) of monoclinic zirconia was determined with the following expression [1]:

$$X_M = \frac{I_{M(111)} + I_{M(\bar{1}\bar{1}1)}}{I_{M(111)} + I_{M(\bar{1}\bar{1}1)} + I_{T(111)}}$$

where I is the intensity of the peak, the subscripts M (111) corresponds to the monoclinic phase referring to the crystallographic plane (111), T (111) corresponds to

the tetragonal phase referring to the crystallographic plane (111) and M ($\bar{1}11$) corresponds to the monoclinic phase referring to the crystallographic plane ($\bar{1}11$)

8.3.3 Microscopic observations

Several specimens of each material were polished to 1 μm and carbon-coated for SEM observation (XL 30, Philips, Eindhoven, Holland). Additional polished samples were etched and observed with a field emission SEM (JSM 6000 FSEM, Jeol, Tokyo, Japan) after coating with platinum (20 nm). In-Ceram Alumina and In-Ceram Zirconia slip and dry-pressed specimens were etched for 30 minutes with a beam of argon ions (gun current 1.0 mA and gun voltage 5.5 kV) (Dual Ion Mill, Model 600, Gatan Pleasanton, California, USA). DC-Zircon and the experimental zirconia specimens were thermally etched for 10 minutes at 1400°C. Observations of cracks emanating from indentations on the coated surface of selected specimens were also made to investigate the crack-microstructure interaction.

8.3.4 Volume fraction and porosity

Five SEM micrographs taken from five different specimens for each material were used to appraise the volume fraction of each phase and porosity using the point-counting technique [2]. All points of the mesh covering the micrograph were considered to calculate the average and the standard deviation. The Volume fraction and percentage of porosity of the pressable materials were not investigated previously; samples were therefore prepared and the same features were considered.

8.4 Results

8.4.1 X-ray diffraction

X-ray diffraction analysis revealed that both In-Ceram Alumina materials (slip and dry pressed) are primarily crystalline materials with sharp and well-defined peaks. The major peaks were observed at 2θ of 25.7° , 35° , 38° ; their crystallographic planes respectively are (012), (104), (110), which corresponds to the rhombohedral phase (α -alumina), as anticipated from the X-ray diffraction standards file (01-1243), of aluminium oxide (Figures 8.1 and 8.2).

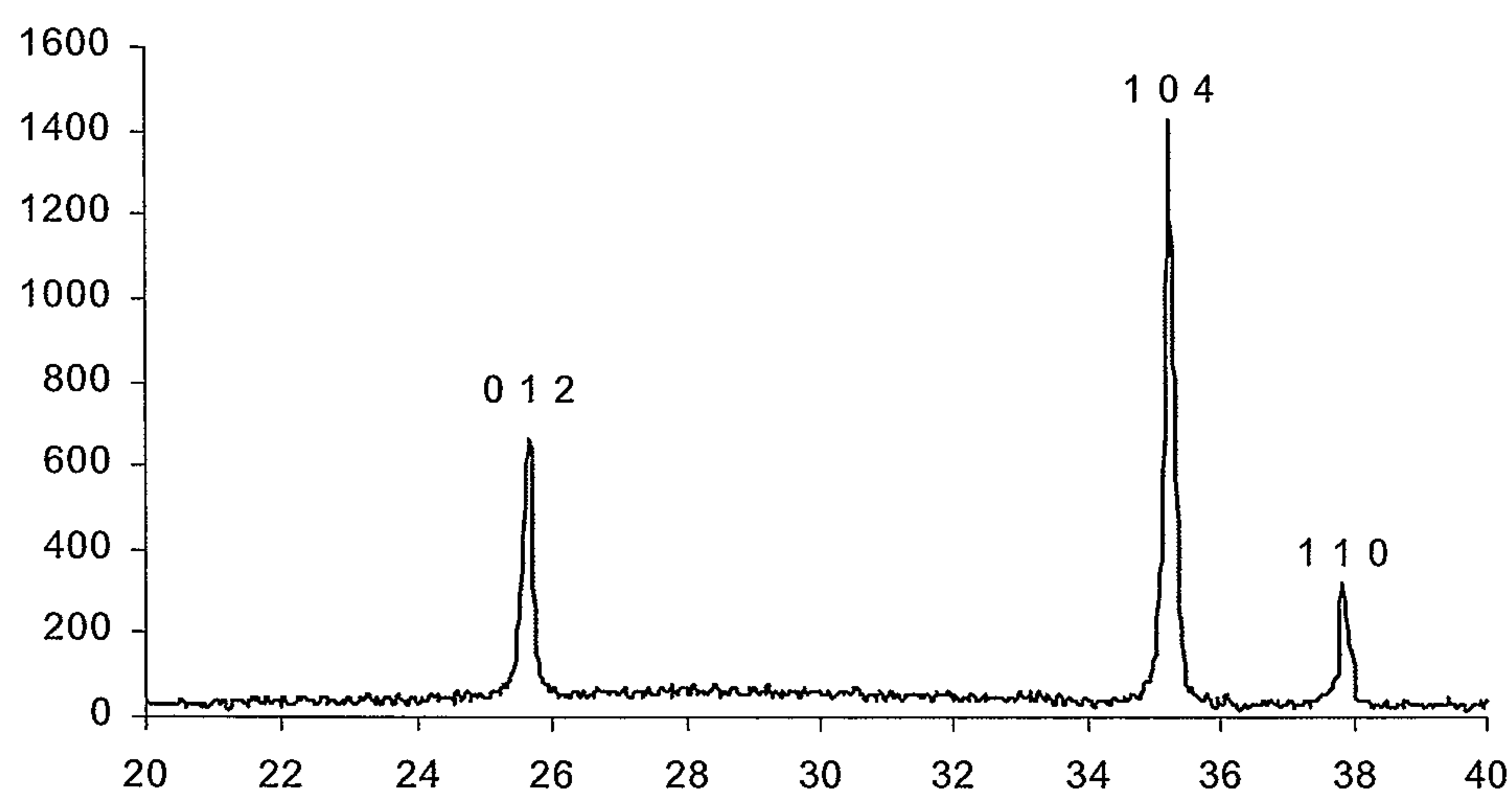


Figure 8.1 X-ray diffraction pattern of In-Ceram Alumina slip.

In-Ceram Zirconia materials (slip and dry-pressed) are also crystalline materials with well-defined peaks of alumina crystals as well as two phases of zirconia, tetragonal and monoclinic. The major peaks of the tetragonal phase (indicated with T above the peaks) in the range 20° to 40° 2θ are 30.01° , 34.5° and 35.2° , with the dominant peak at 30.01° , corresponding to the (111) plane as anticipated from the x-ray diffraction standards file (17-0923) of zirconium oxide.

The monoclinic phase (indicated with M above the peaks) was detected at 2θ values of 28.07° and 31.2° , corresponding to the crystallographic planes (111) and $(\bar{1}\bar{1}1)$ respectively; the X-ray diffraction file is 02-0536. The X-ray diffraction patterns of both materials showed the presence of the peaks corresponding to the alumina crystals (X-ray diffraction standards files 01-1243) indicated with “A” above the peaks (Figures 8.3 and 8.4).

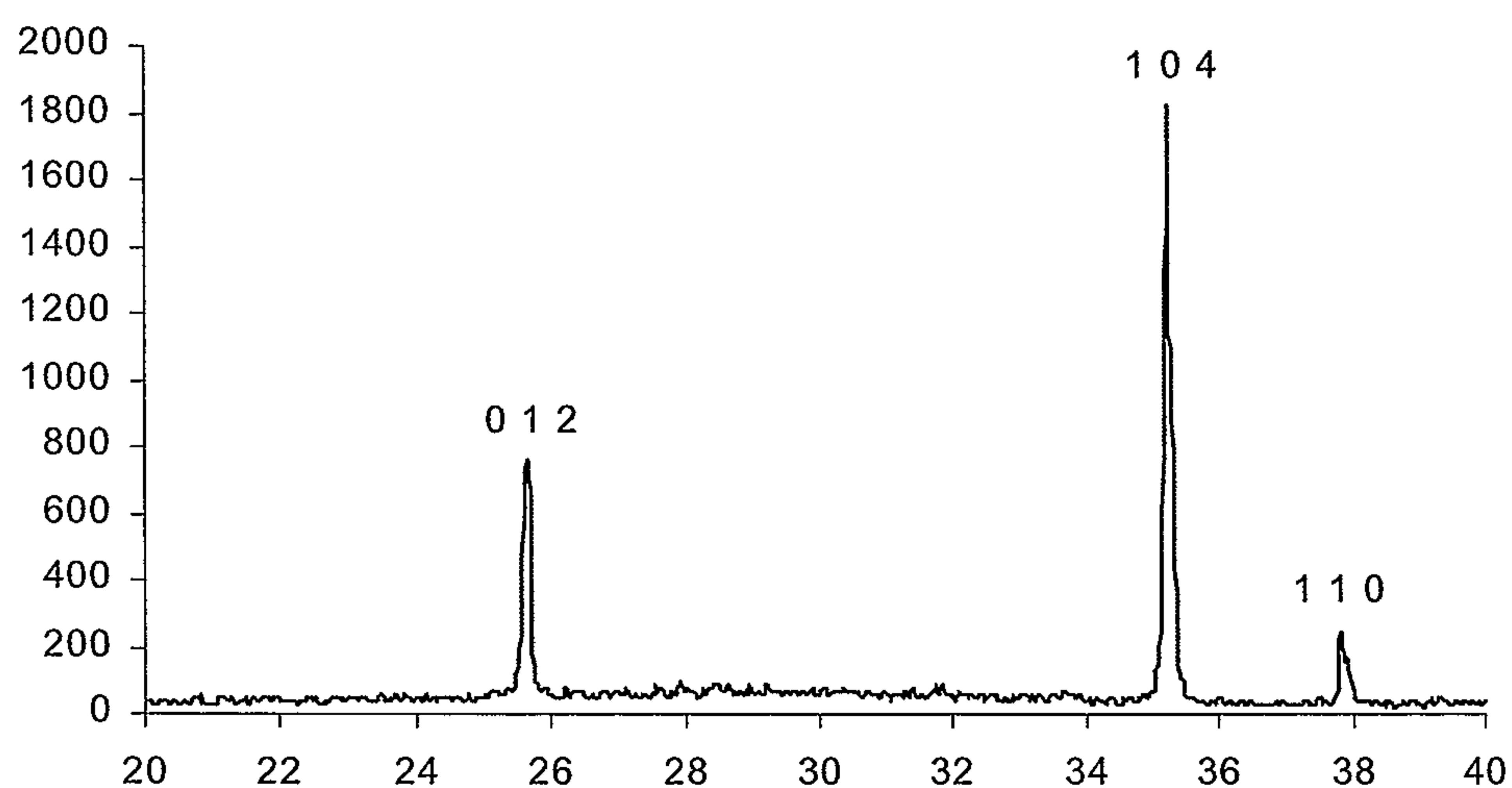


Figure 8.2 X-ray diffraction pattern of In-Ceram Alumina dry-pressed.

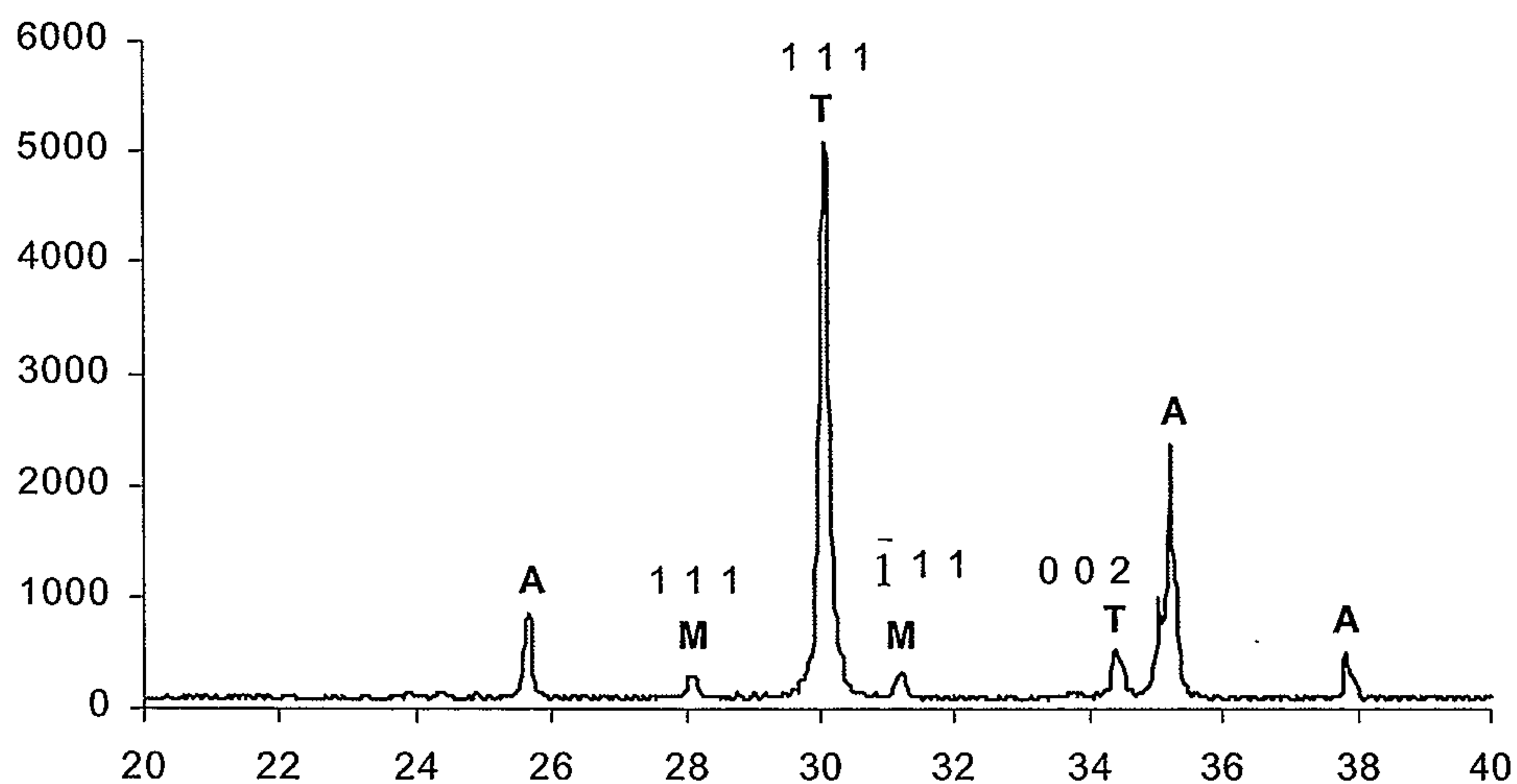


Figure 8.3 X-ray diffraction pattern of the as-sintered In-Ceram Zirconia slip.

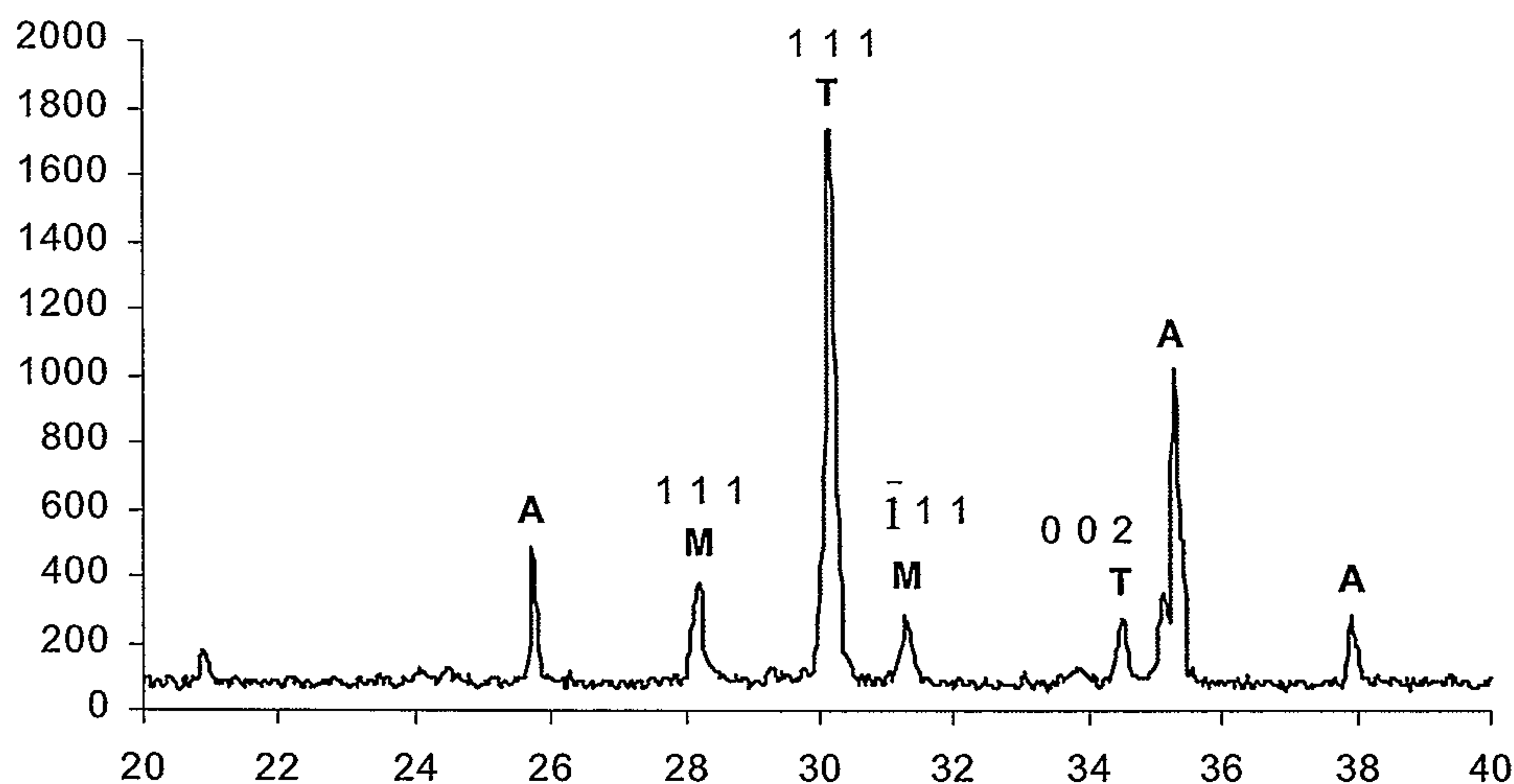


Figure 8.4 X-ray diffraction pattern of the as-sintered In-Ceram Zirconia dry-pressed.

For the D-C Zircon and the experimental zirconia materials the tetragonal peaks were detected at 2θ values of 30.3° , 34.7° , 35.3° predicted from the X-ray diffraction file 14-0534, and corresponding to the crystallographic planes (111), (002) and (200) respectively. For the monoclinic phase, the peaks were observed at 28.07°

and 31.4° corresponding to the (111) and $(\bar{1}11)$ crystallographic planes as anticipated by the X-ray diffraction standard file 05-0543 (Figures 8.5 and 8.6).

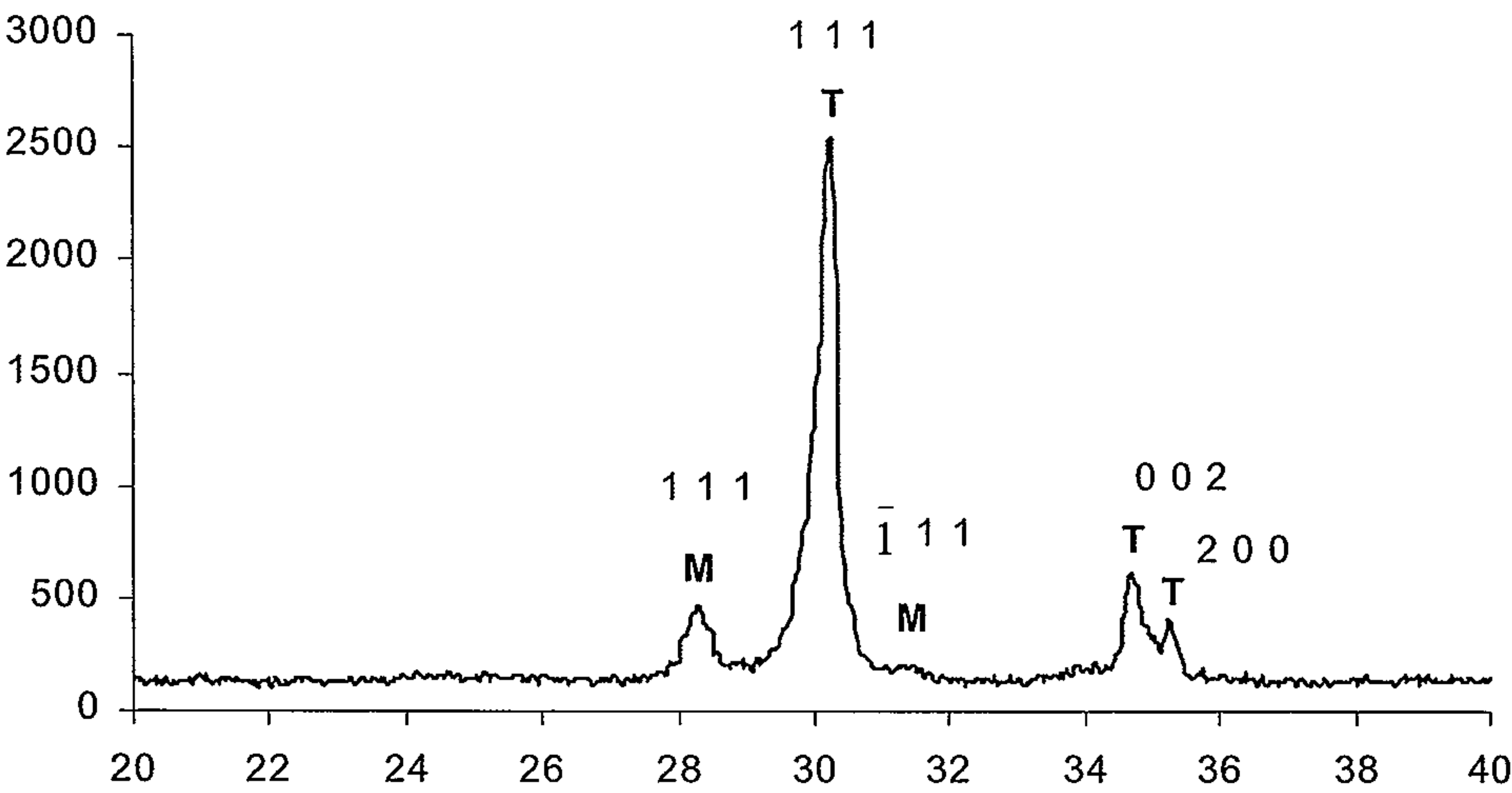


Figure 8.5 X-ray diffraction pattern of the as-sintered DC-Zircon.

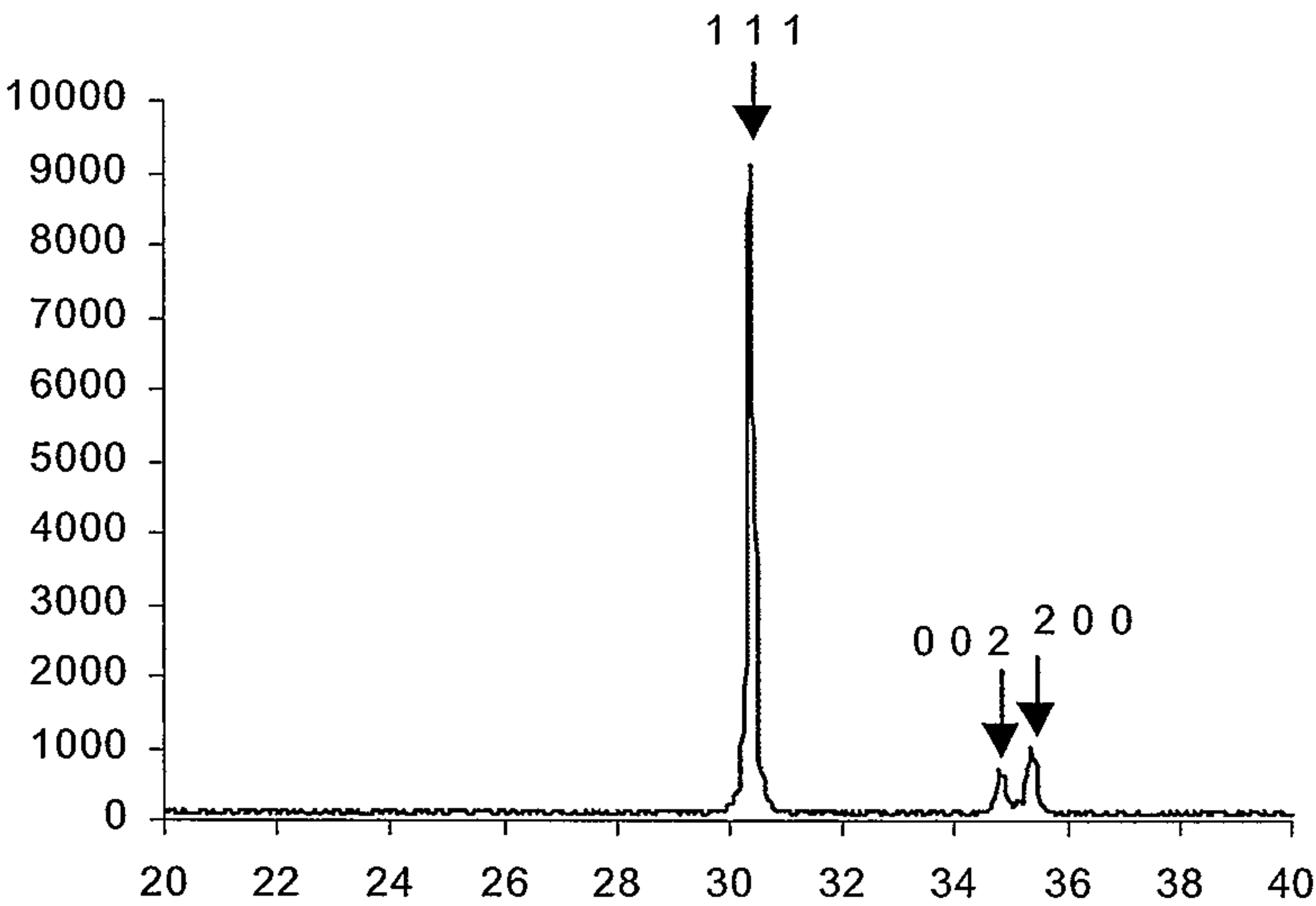


Figure 8.6 X-ray diffraction pattern of the as-sintered experimental zirconia.

The calculation of the relative amount of monoclinic phase shows that a significant quantity is already present in the as-sintered surfaces of DC-Zircon (14%) and In-Ceram Zirconia dry-pressed (23%). A smaller amount is present in the In-Ceram Zirconia slip (10%) and finally the experimental zirconia material (0.5%). This amount has noticeably increased on the fracture surfaces of DC-Zircon (46%), In-Ceram Zirconia slip (29%) and In-Ceram Zirconia dry-pressed (32%), whereas it is limited to only 6% in the case of the experimental zirconia material (Figures 8.7 to 8.10)

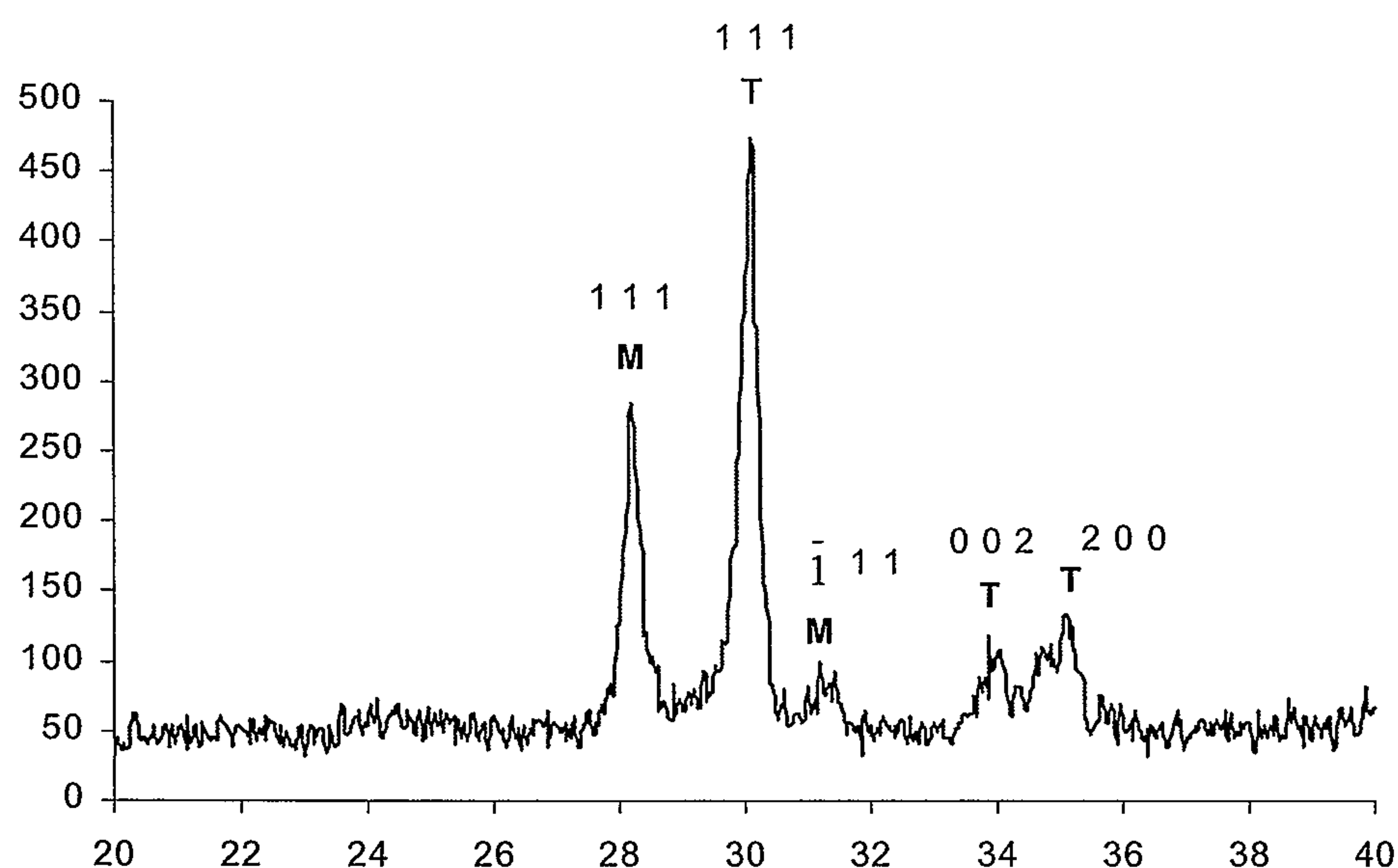


Figure 8.7 X-ray diffraction pattern of a fractured surface of DC-Zircon.

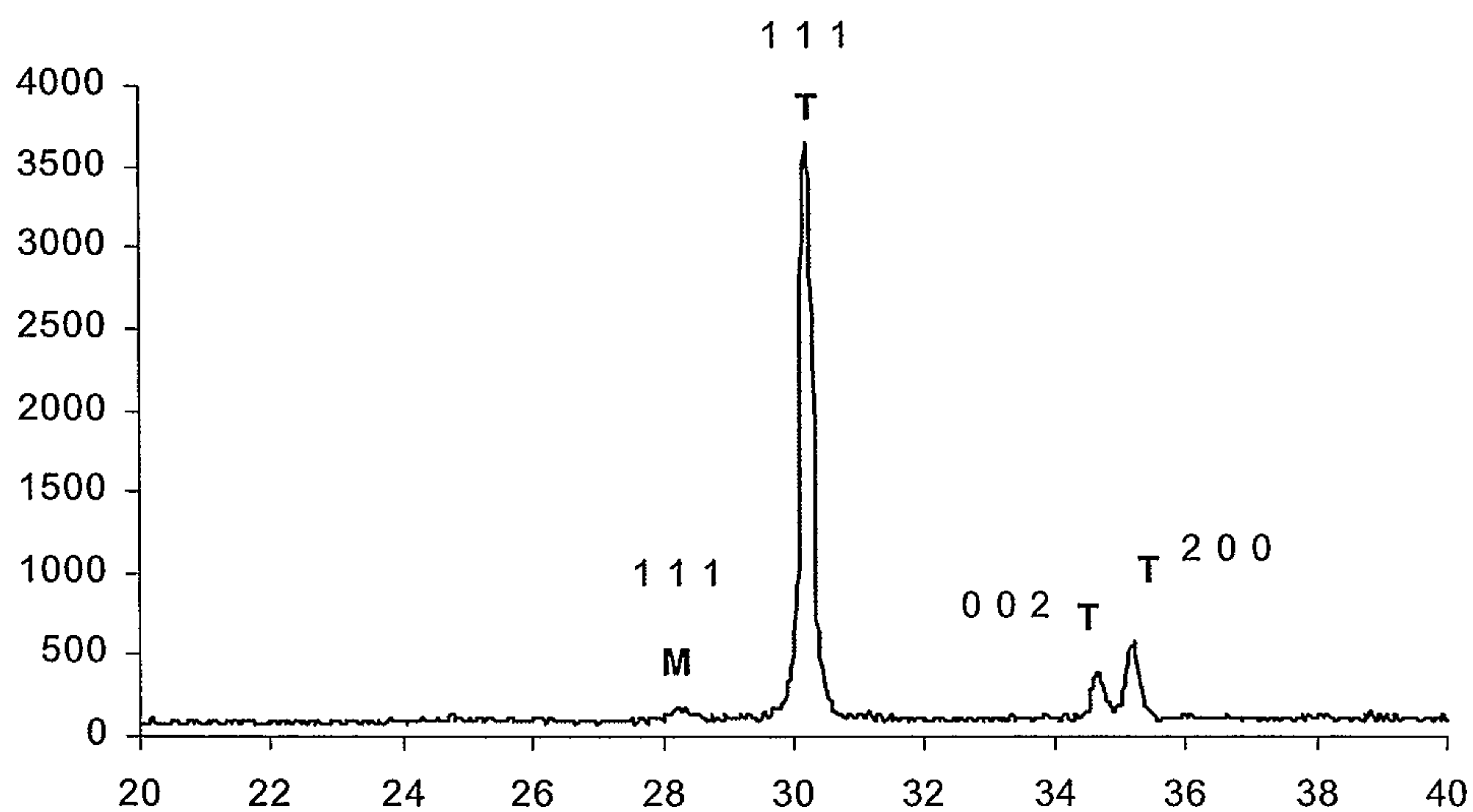


Figure 8.8 X-ray diffraction pattern of a fractured surface of the experimental zirconia.

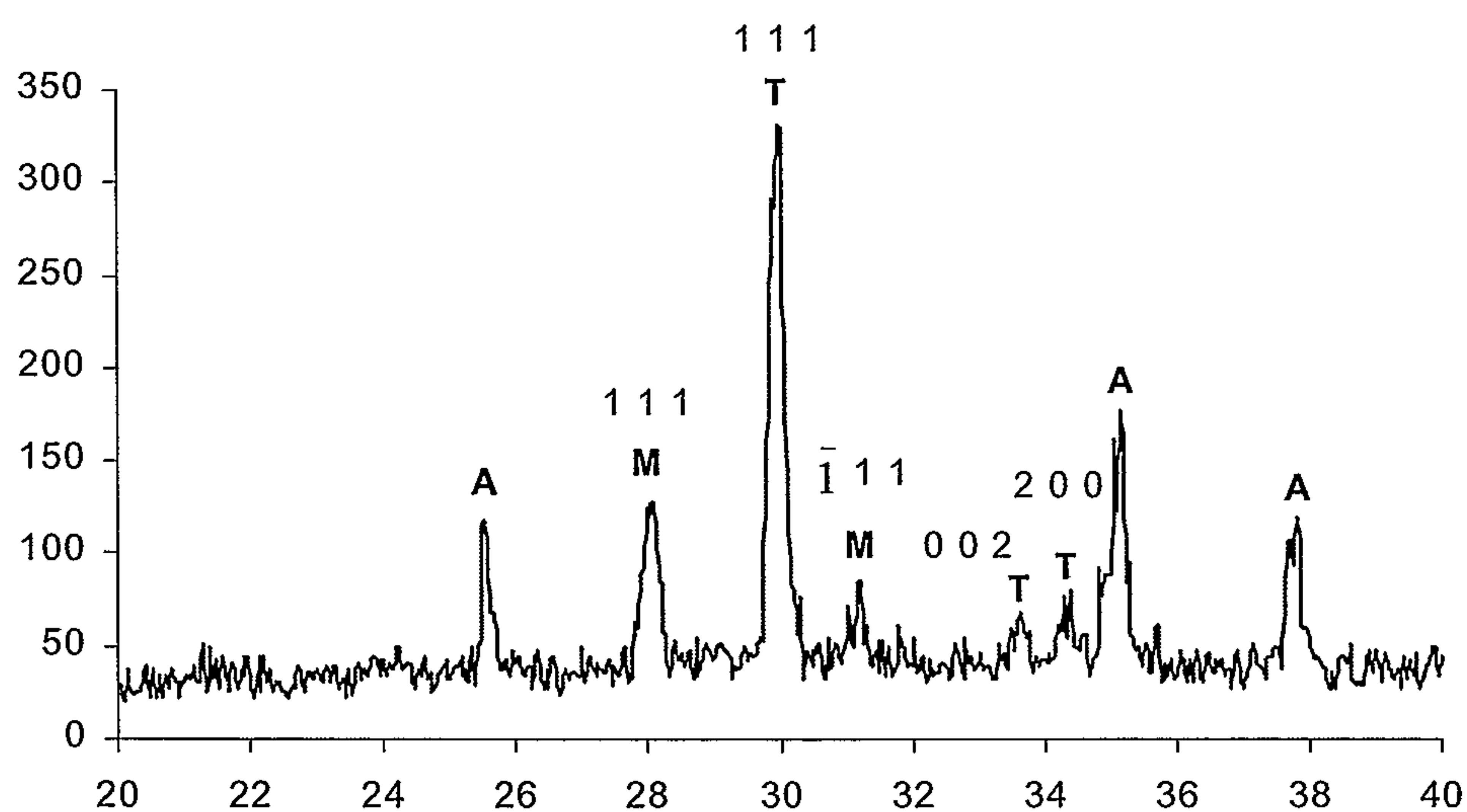


Figure 8.9 X-ray diffraction pattern of a fractured surface of In-Ceram zirconia dry-pressed.

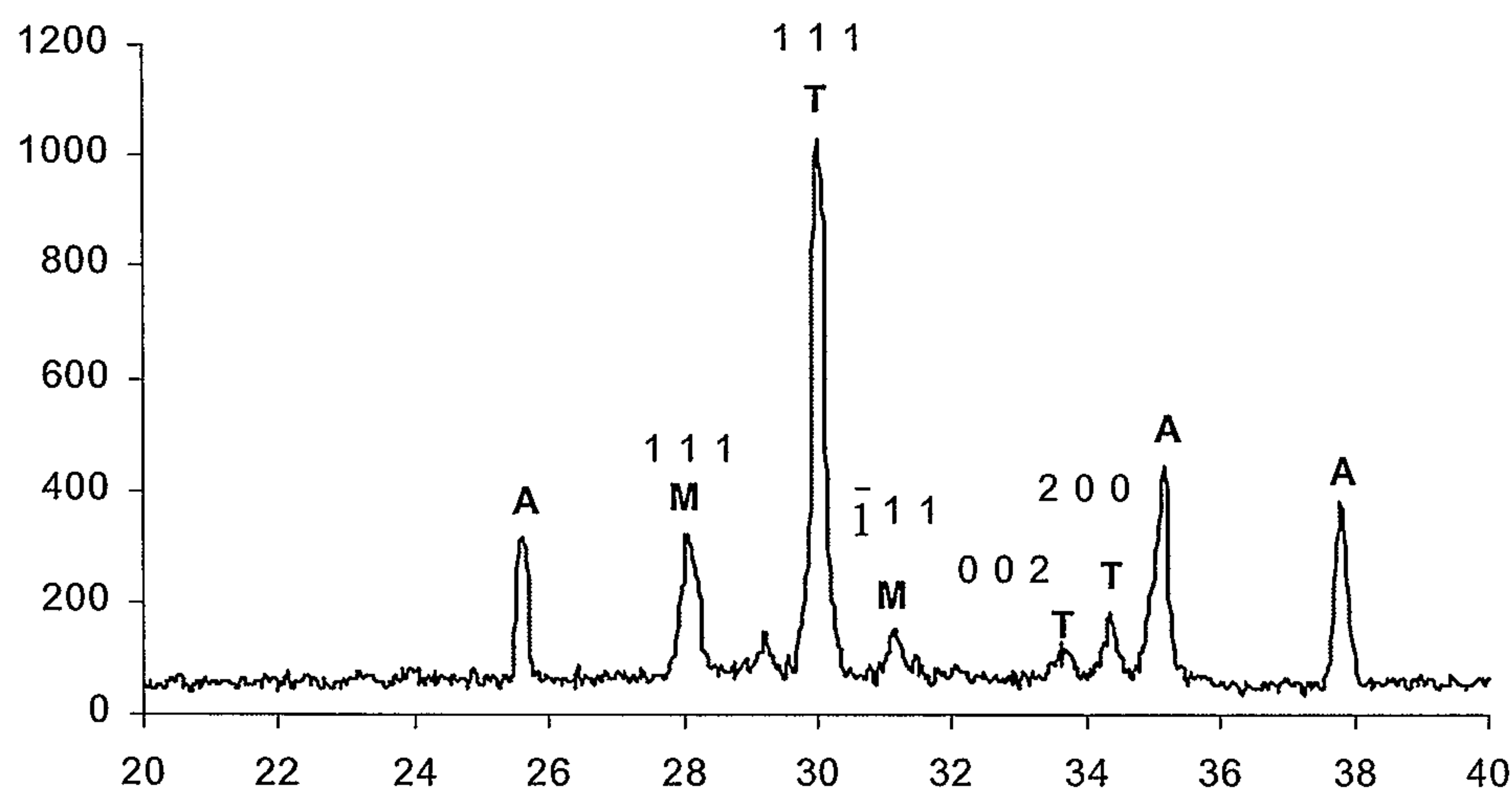


Figure 8.10 X-ray diffraction pattern of a fractured surface of In-Ceram zirconia slip.

8.4.2 Microstructure

8.4.2.1 In-Ceram Alumina materials

Examining the microstructure of In-Ceram Alumina materials (dry-pressed and slip) showed that alumina particles (Al_2O_3) represent the main crystalline content for both materials. In-Ceram Alumina dry-pressed consists of equiaxed (faceted and spherical particles), embedded into a glassy phase (Figure 8.11). The faceted particles measured from 1 to 4 μm in diameter, and the spherical grains measured less than 1 μm diameter. The crack behaviour of this material after indentation was found to be symmetric (similar length in X and Y directions). At the microstructure level, cracking was found to propagate around the alumina particles (intergranular pattern) (Figure 8.12). The toughening mechanisms observed were crack bridging, crack deflection and contact shielding (Figure 8.13).

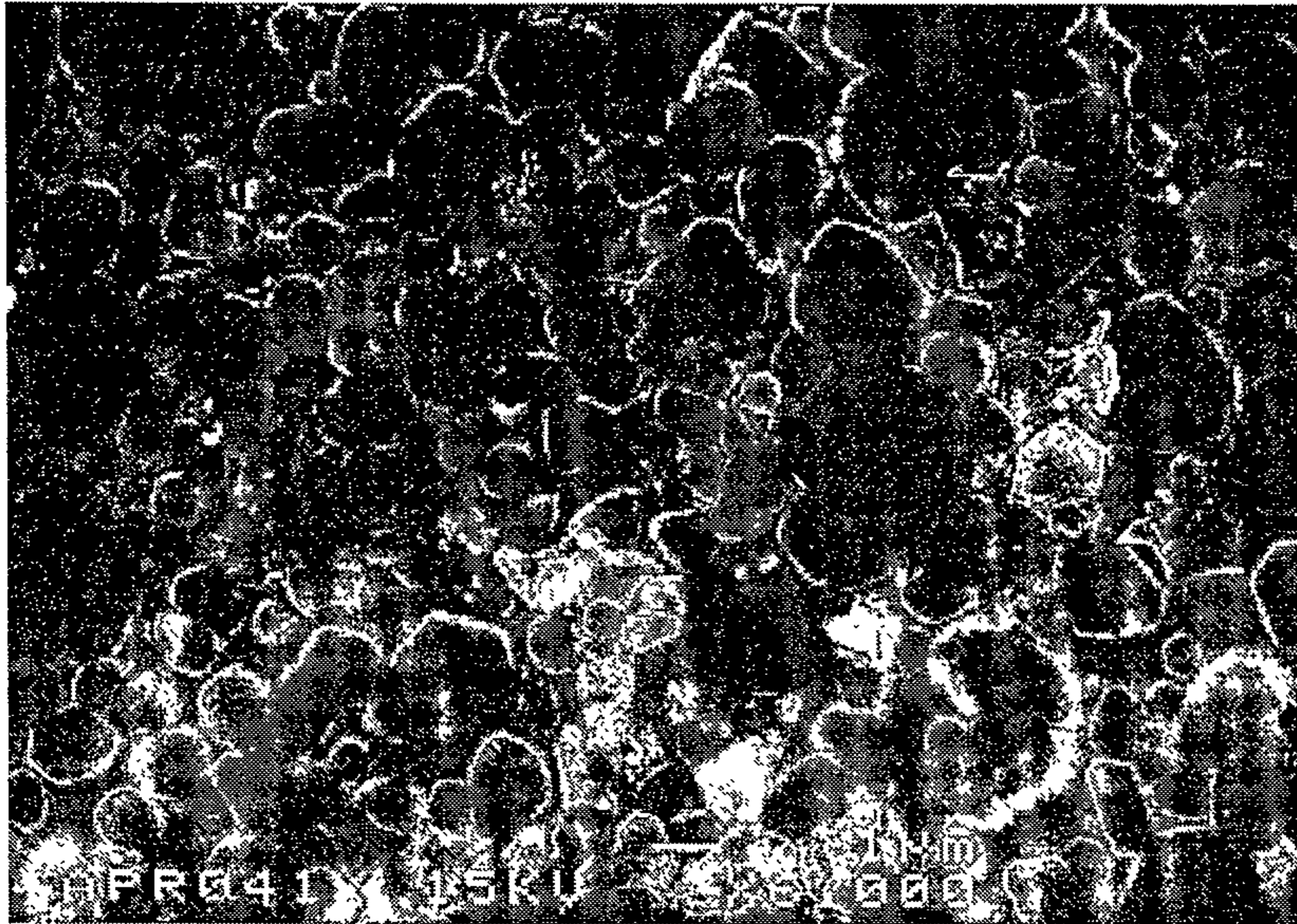


Figure 8.11 SEM of the microstructure of In-Ceram Alumina dry-pressed, showing equi-axed alumina particles (faceted and spherical).



Figure 8.12 SEM of In-Ceram Alumina dry pressed, showing the crack propagation through the microstructure, where the crack is deflected by the faceted and spherical particles of alumina (intergranular crack pattern).

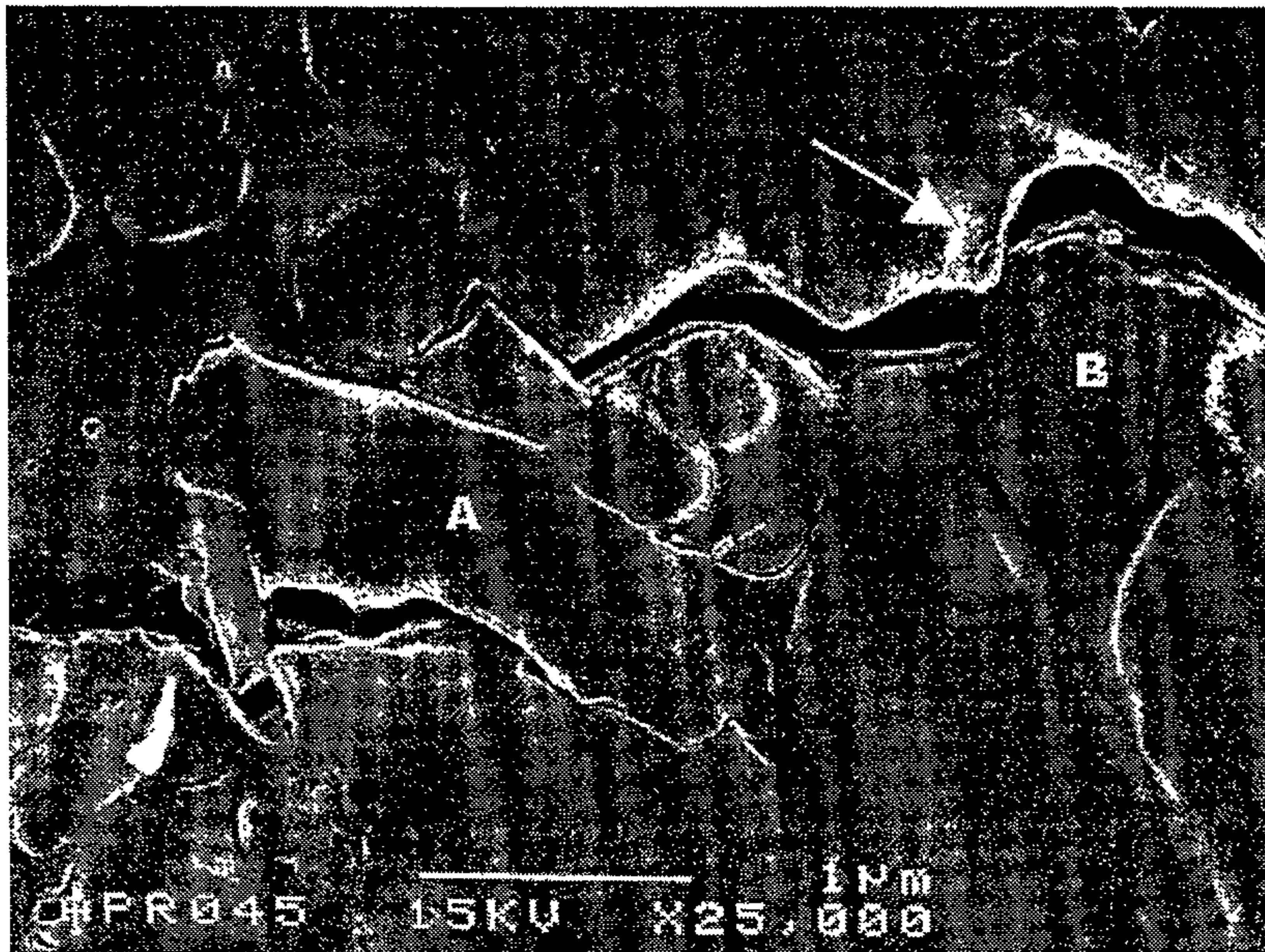


Figure 8.13 SEM of In-Ceram Alumina dry-pressed at higher magnification, where toughening mechanisms such as bridging (A) and contact shielding (B), and crack deflection, can be seen. The arrow indicates a chipping of one of the two crystals and also friction between crystals.

In-Ceram Alumina slip mainly consists of many elongated alumina particles (10-12 μm long and 2.5-4 μm wide). However, the faceted and spherical crystals, found in the In-Ceram Alumina dry pressed, can also be seen (Figure 8.14). During the preparation of the slip, the elongated alumina crystals may have become oriented. This was assumed as a result of the crack behaviour following the indentation. Similar to the crack behaviour found in Empress 2 material, the crack propagated through these elongated alumina crystals (transgranular pattern) and/or around (intergranular pattern), according to their orientation. This generated asymmetric cracks and dissipated a greater amount of energy (Figure 8.15). As with In-Ceram Alumina dry-pressed, there were several toughening mechanisms involved such as crack deflection, contact shielding and bridging (Figure 8.16).

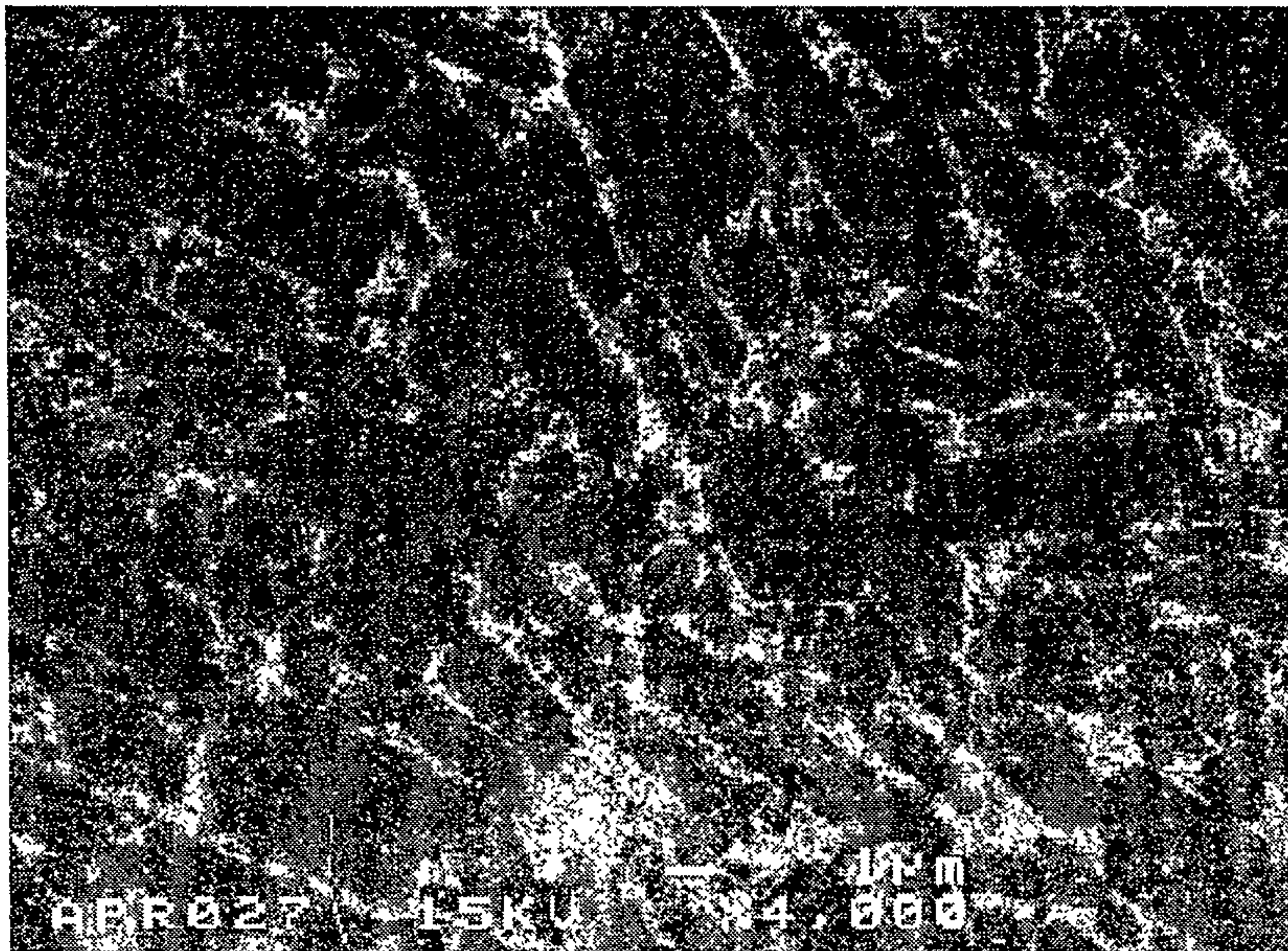


Figure 8.14 SEM of In-Ceram Alumina slip microstructure, showing the three different types of alumina crystals: elongated, faceted and spherical.

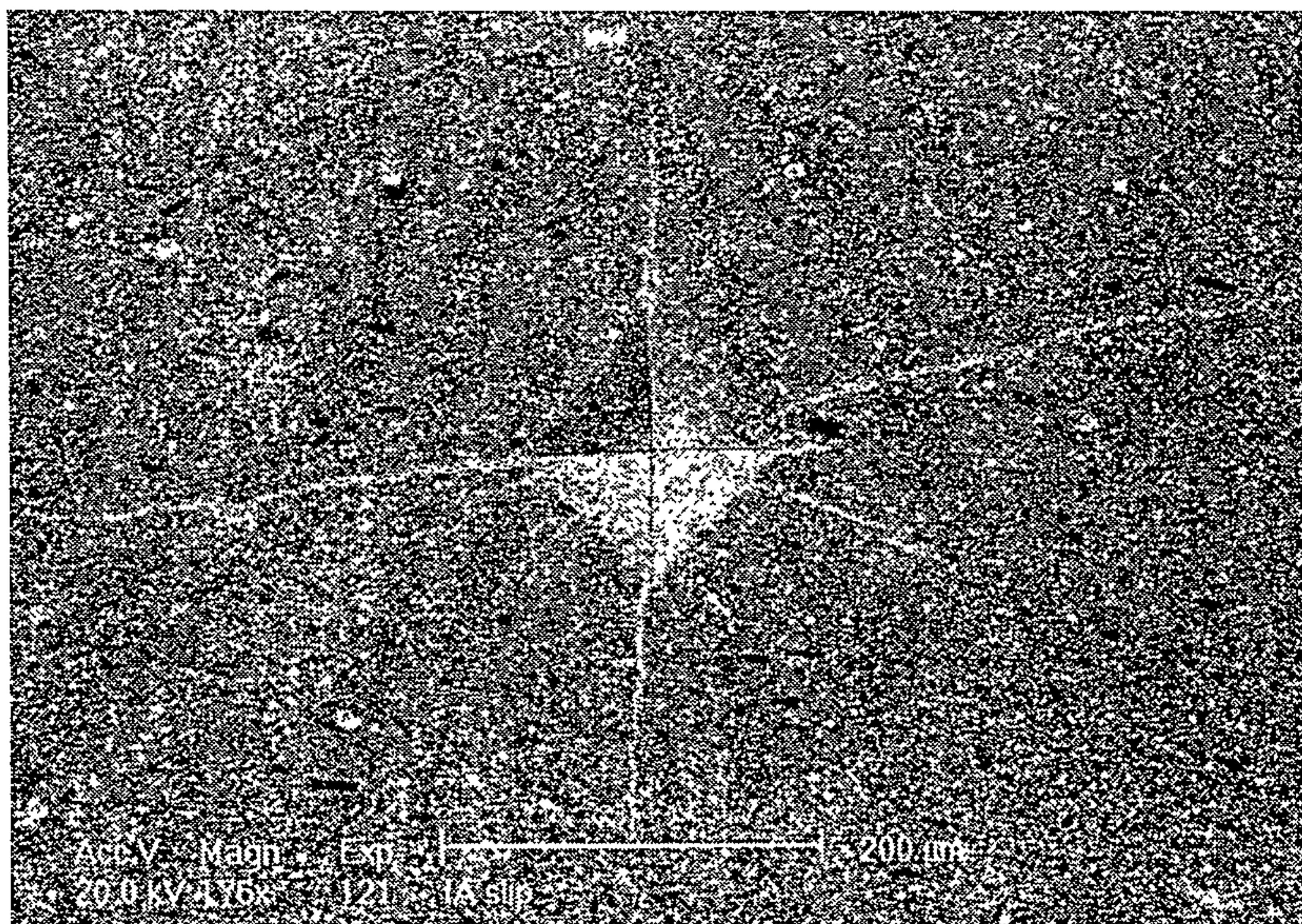


Figure 8.15 SEM of a residual impression of In-Ceram Alumina slip after indentation, showing non-symmetric cracks. Shorter cracks were observed propagating perpendicular to the elongated grains, whereas the longer ones are propagating parallel to the length of the elongated crystals.

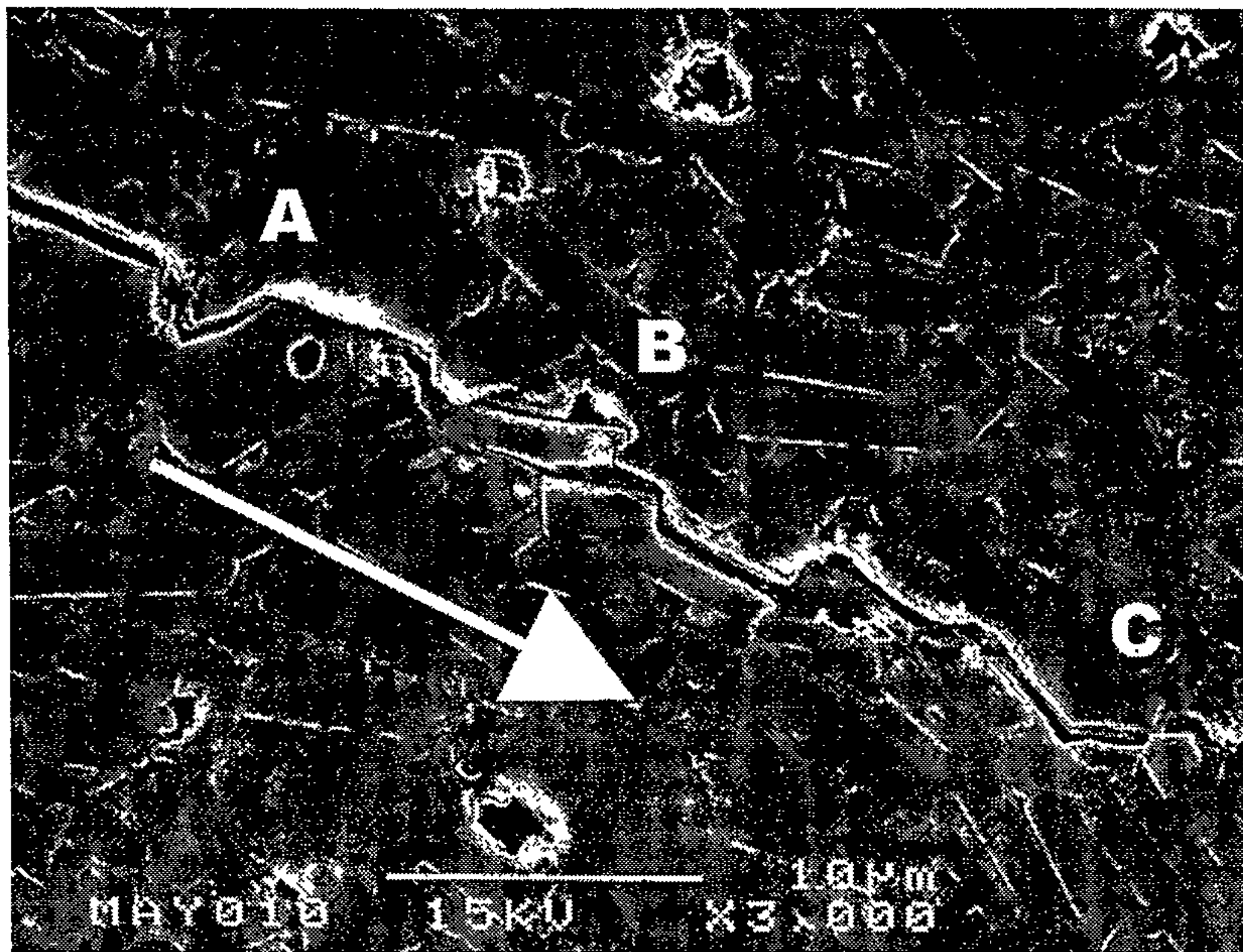


Figure 8.16 SEM of In-Ceram Alumina slip showing three different toughening mechanisms: pull-out of crystals (A), bridging (B), and crack deflection (C). The arrow indicates the crack propagation direction after indentation.

8.4.2.2 In-Ceram Zirconia materials

The microstructures of In-Ceram Zirconia dry-pressed (Figure 8.17) and slip (Figure 8.18) are very similar. The alumina crystals in both materials were almost identical to those found in the In-Ceram Alumina slip. However, the elongated alumina crystals were smaller (6 μm long and 2 μm wide) than those of In-Ceram Alumina slip (Figures 8.19 and 8.20). Zirconia (ZrO_2) crystals were found in both materials, faceted crystals (2 μm) and fine spherical crystals (< 1 μm). The crack pattern was found to be transgranular for the zirconia crystals (Figures 8.19 and 8.20), whereas it is intergranular for alumina crystals, except when the crack tip propagates perpendicularly to the elongated grains. Toughening mechanisms observed were crack deflection, crack shielding (bridging and pull-out of elongated grains) and microcrack toughening (Figures 8.19 and 8.20). Apart from the porosity difference

found between the two materials, being greater in In-Ceram Zirconia dry pressed, the two materials are very similar.

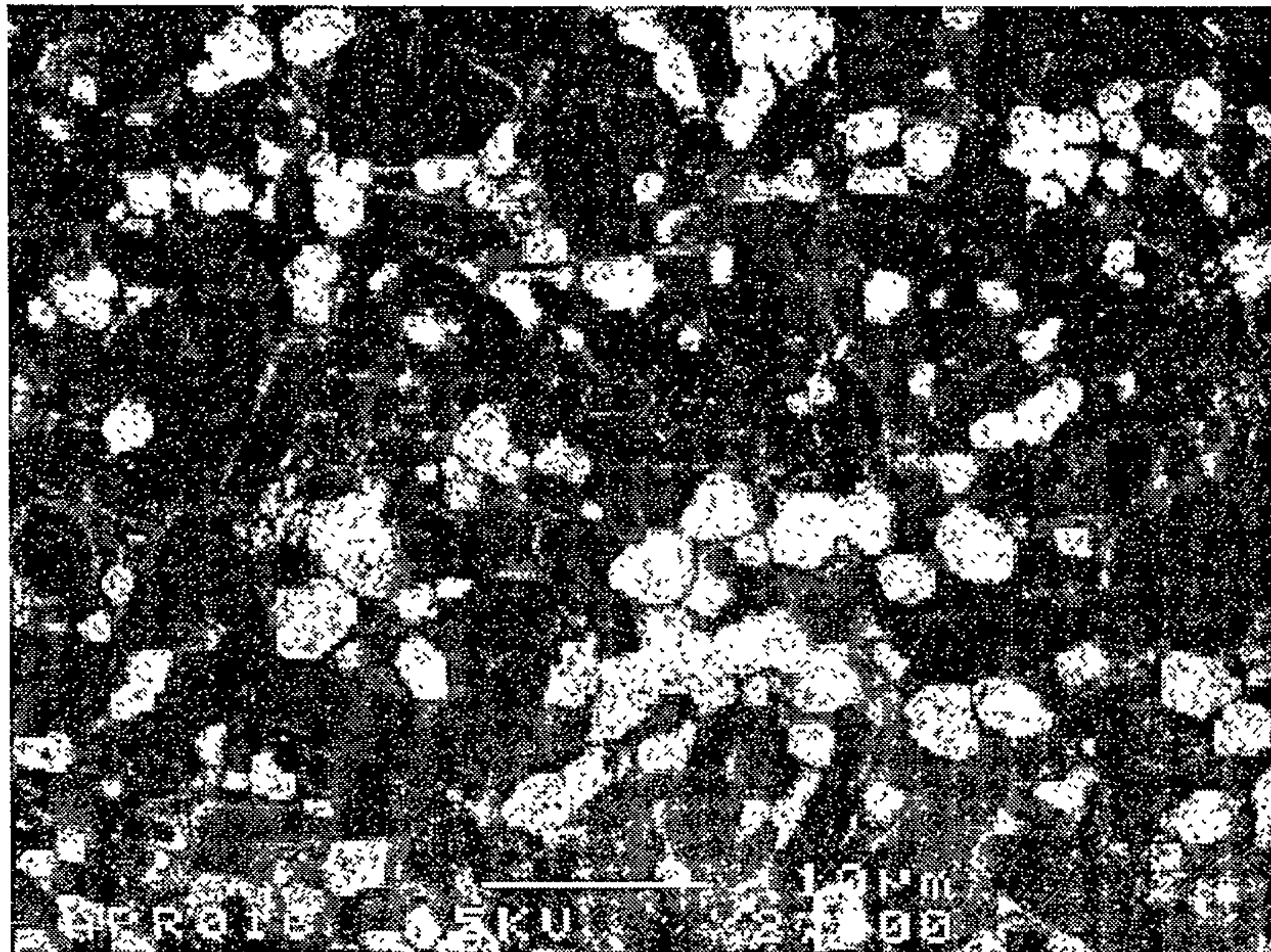


Figure 8.17 SEM of In-Ceram Zirconia dry-pressed, showing the white crystals (zirconia crystals) are agglomerated, and black crystals (alumina crystals) are embedded in a glass matrix. The atomic number of the different phases highlights them in the back-scattered mode of the SEM.

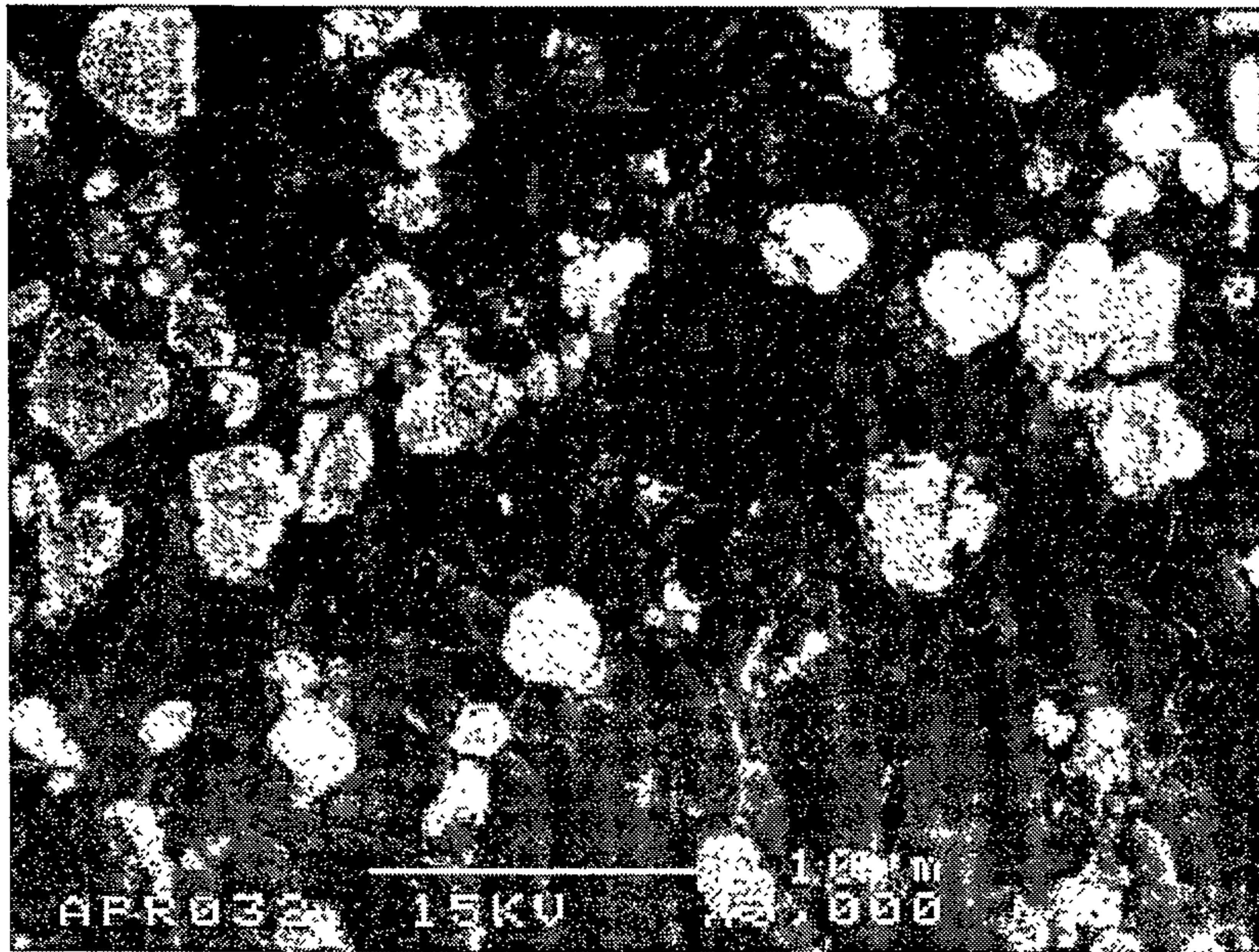


Figure 8.18 SEM of the microstructure of In-Ceram Zirconia slip, showing a very similar microstructure to that of In-Ceram Zirconia dry-pressed.

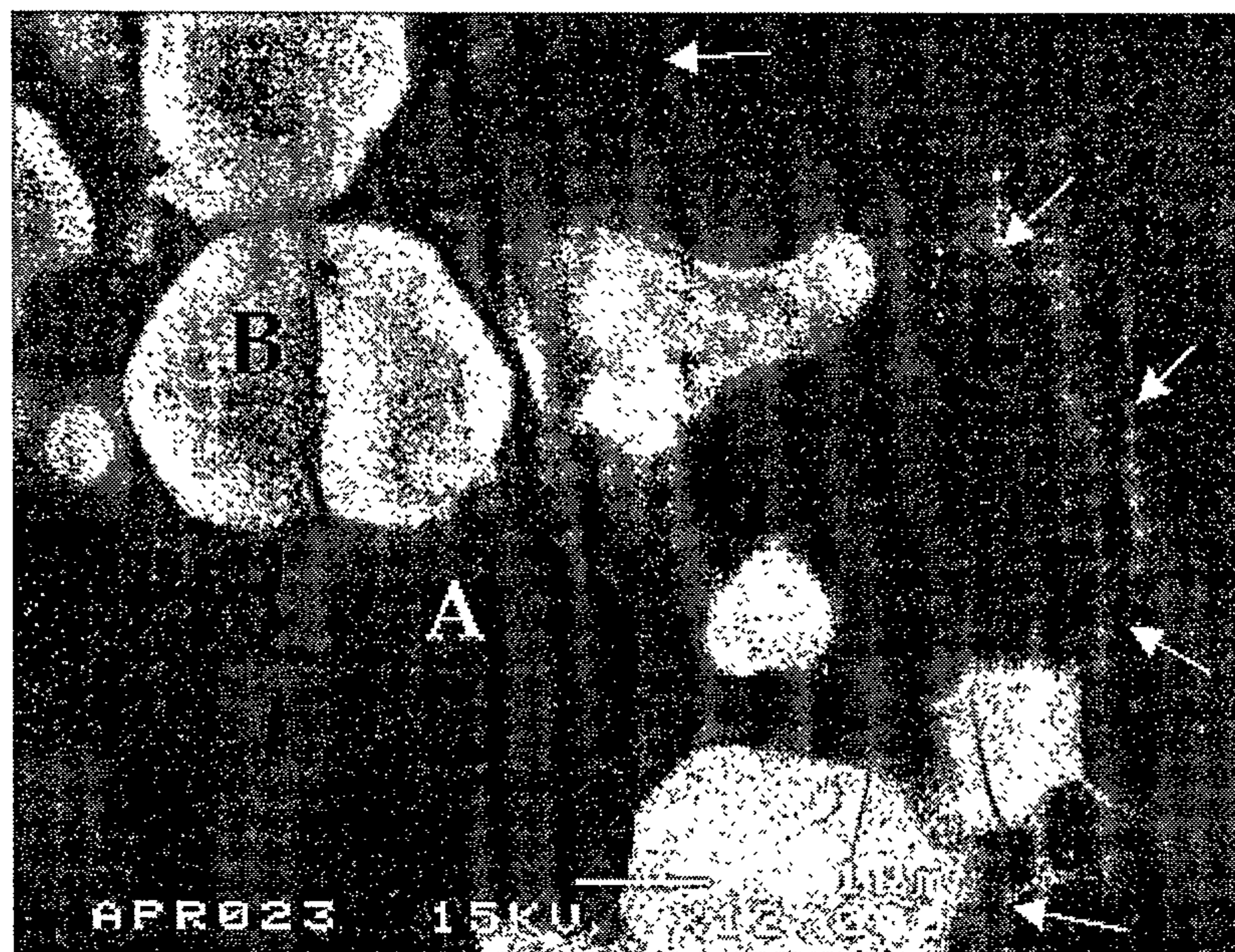


Figure 8.19 SEM of In-Ceram Zirconia dry-pressed at higher magnification, showing a transgranular crack pattern for zirconia crystal (B). The arrows indicate location of microcracks in the glass matrix and at the boundary between particles and glass.



Figure 8.20 SEM of In-Ceram Zirconia slip. The crack propagates through zirconia crystals, transgranular crack pattern (A and B) and around alumina crystals, resulting in an intergranular crack pattern (C).

8.4.2.3 DC-Zircon and the experimental zirconia materials

The experimental zirconia and DC-Zircon materials were found to have very fine microstructures (mean zirconia crystal size $0.21\ \mu\text{m}$ and $0.28\ \mu\text{m}$ respectively) (Figures 8.21 and 8.22). However, scanning electron microscope images showed discernible differences between the two materials. DC-Zircon is a dense material and has less than 1% of porosity. Moreover, the pores found were spherical with a small diameter ($< 0.3\ \mu\text{m}$), and located at the interboundary regions. The experimental zirconia, in contrast, has a greater porosity (9%) (Table 8.2). Furthermore, some pores have elongated shape and a size of up to $5\ \mu\text{m}$.

The crack behaviour of the two materials was also significantly different. In DC-Zircon, the crack demonstrated a straight crack trajectory and propagated through the transformed crystals and into the interboundary regions (Figure 8.23). In the

experimental Zirconia the crack pattern showed a more tortuous and mainly intergranular trajectory (Figure 8.22).



Figure 8.21 SEM of DC-Zircon, showing dense and very fine crystals of zirconia.



Figure 8.22 SEM of the experimental zirconia material, showing very fine crystals of zirconia and an intergranular crack pattern.

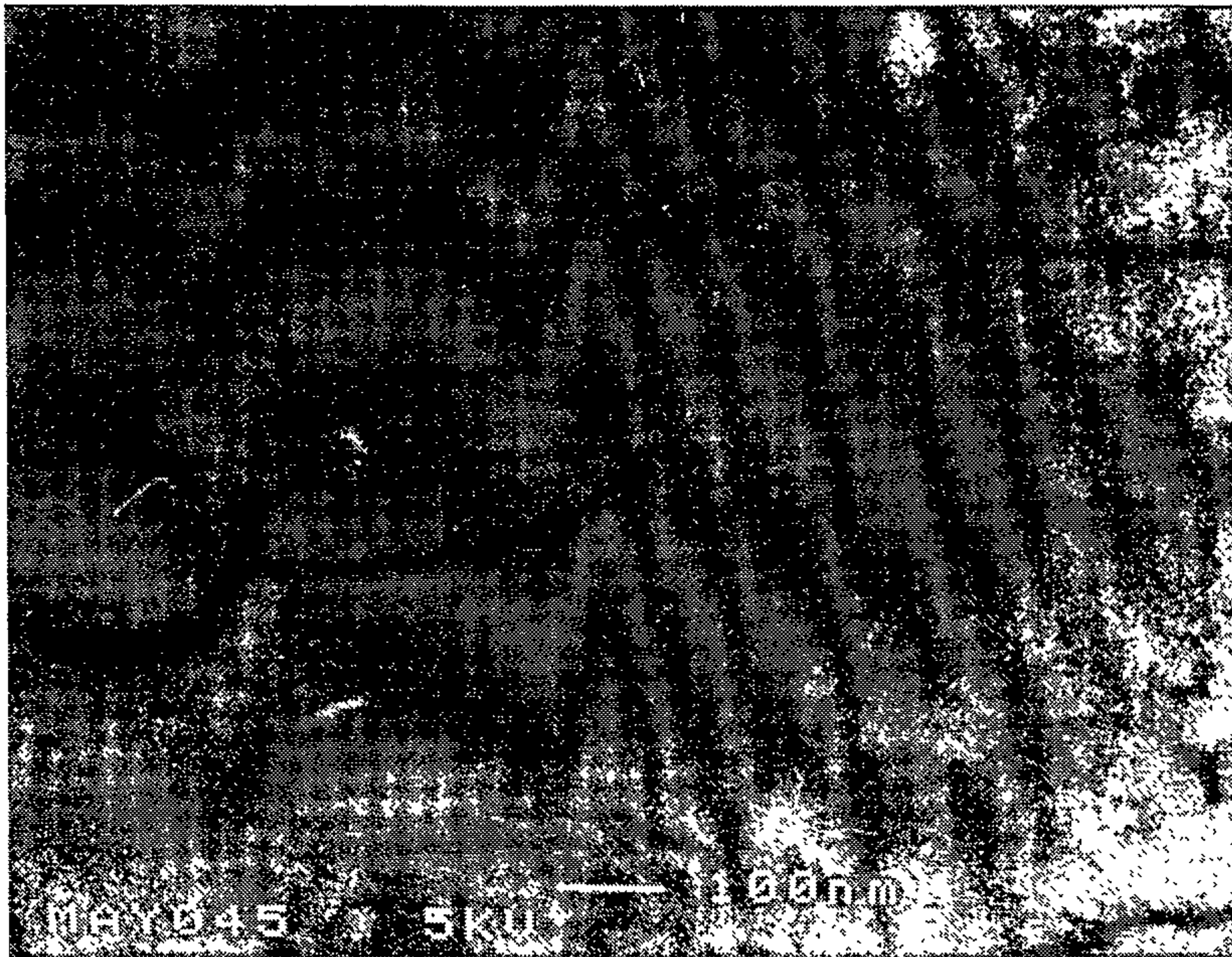


Figure 8.23 SEM of DC-Zircon, showing crack propagation through the particles of zirconia as well as interboundary regions.

8.4.3 Mechanical properties

The flexural strength and fracture toughness of the pressable materials reported in the previous chapters have been added to the present results to allow a statistical comparison. The mechanical properties (flexural strength and fracture toughness) results of the nine materials are listed in Table 8.1.

The statistical analysis divided the investigated materials into five groups in which materials of the same group (indicated by the superscript number) do not show any statistical difference (Table 8.1). DC-Zircon demonstrated the highest flexural strength; there is no statistical difference in the flexural strength between the experimental zirconia material, In-Ceram Zirconia slip and In-Ceram Alumina slip. In-Ceram Alumina slip is statistically as strong as In-Ceram Zirconia dry-pressed and In-Ceram Alumina dry-pressed. There is no statistical difference in the flexural

strength between In-Ceram Alumina dry-pressed, Empress 2 and the experimental pressable material. Finally, Empress 1 is the weakest material.

In respect of the fracture toughness, the materials are also divided into five groups in which there is no significant difference in the fracture toughness between materials in the same group, but they are tougher than the previous group or groups. Empress 1 in Group 1 (the lowest fracture toughness); the experimental pressable material, Empress 2 and In-Ceram Alumina dry-pressed in Group 2; In-Ceram Zirconia dry-pressed, In-Ceram Alumina slip and In-Ceram Zirconia slip in Group 3; the experimental zirconia material in Group 4; and DC-Zircon in Group 5.

Other investigated features such as crystalline and glass contents, percentage of porosity are reported in Table 8.2.

Material	Flexural Strength (MPa) (SD)	Fracture Toughness (MPa · m ^{1/2}) (SD)
Empress 1	106 (17) ¹	1.39 (0.3) ¹
Experimental pressable material	303 (49) ²	3.32 (0.65) ²
Empress 2	306 (29) ²	3.14 (0.51) ²
In-Ceram Alumina dry- pressed	440 (50) ^{2, 3}	3.6 (0.26) ²
In-Ceram Zirconia dry- pressed	476 (50) ³	4.9 (0.36) ³
In-Ceram Alumina slip	594 (52) ^{3, 4}	4.4 (0.48) ³
In-Ceram Zirconia slip	630 (58) ⁴	4.8 (0.50) ³
Experimental Zirconia material	680 (130) ⁴	5.5 (0.34) ⁴
DC-Zircon	840 (140) ⁵	7.4 (0.62) ⁵

Table 8.1 Averages of flexural strength and fracture toughness of all materials. The superscript number indicates (for materials with the same number) groups with no significant statistical difference.

Materials	Phase	Volume Fraction (%)
Empress 1	Leucite	36
	Glass	55
	Porosity	9
Empress 2	Lithium Disilicate	65
	Glass	34
	Porosity	1
Experimental pressable material	Lithium Disilicate	67
	Glass	30
	Porosity	3
In-Ceram Alumina slip	Alumina	68
	Glass	27
	Porosity	5
In-Ceram Alumina dry-pressed	Alumina	67
	Glass	29
	Porosity	4
DC-Zircon	Y ₂ O ₃ - ZrO ₂	99
	Porosity	< 1
Experimental Zirconia material	Y ₂ O ₃ - ZrO ₂	91
	Porosity	9
In-Ceram Zirconia slip	Alumina	33.8
	Zirconia	34.0
	Glass	23.0
	Porosity	8.0
In-Ceram Zirconia dry-pressed	Alumina	35.5
	Zirconia	32.2
	Glass	21.5
	Porosity	11.0

Table 8.2 Volume fractions of each phase of all materials, and porosity.

8.5 Discussion

Among all investigated materials, Empress 1 was found to be the weakest material. It also demonstrated the lowest fracture toughness, which was expected and may be further explained by its chemical composition and microstructural features. As explained in Chapter 4, fine leucite crystals are the reinforcing components for this material. These crystals are distributed in a brittle glass matrix. The volume of the brittle phase (glass matrix, 55 %) is less than the amount of the reinforcing components, 36%. The porosity and toughening mechanisms of this material have been explained Chapter 4.

Comparing the fracture toughness and flexural strength of the two lithium disilicate systems, Empress 2 and the experimental pressable material, showed no significant difference. This is virtually consistent with wide similarities found between the two systems. Both materials are stronger and tougher than Empress 1, which can be ascribed to the shape, size and amount of their crystalline content.

Initially, it was expected that In-Ceram Alumina dry pressed would demonstrate better mechanical properties than In-Ceram Alumina slip. This was believed because of a more consistent processing of In-Ceram Alumina dry-pressed material carried out by the manufacturer (block sintering). However, the opposite occurred and may be explained by the microstructural features. Although there were minimal variations between the two materials, these were found to significantly affect their mechanical properties. One previous study supported such an assumption [3]. It has also been stated that greater fracture toughness can be achieved if the crack propagates perpendicular to the elongated crystals [3]. The elongated alumina

crystals may become oriented during the slip processing. In this study, it was assumed that the crystals' length was oriented parallel to the specimen's long axis (bar used for 3-point bending test) and normal to the applied tensile stress during testing, which caused an increase in the flexural strength of this material compared to that of In-Ceram Alumina dry-pressed, which had more randomly oriented smaller alumina particles. This indicates that microstructural features play a major role in determining the mechanical properties, especially the fracture toughness and flexural strength of both materials.

No comparative study was found in the literature that compared the pressable materials Empress 1 and Empress 2 with the In-Ceram Alumina materials, either slip or dry-pressed. This study showed that In-Ceram Alumina slip is stronger and tougher than the dry-pressed and also than all pressable materials. This significant difference is attributed to the microstructure, particularly the alumina particles.

The significant difference found in porosity between In-Ceram Zirconia slip and dry-pressed might be a possible explanation for the strength difference between the two materials. However, this is difficult to determine, as there was a different distribution of flaws, which may change in different batches of specimens. Also, strength values could vary if a greater number of specimens were tested.

The two In-Ceram Zirconia systems (slip and dry-pressed) recorded higher porosity percentages than the two In-Ceram Alumina systems (slip and dry-pressed). This may be attributed to the poor distribution of Al_2O_3 and ZrO_2 particles and to their poor wettability especially with the glass matrix. Kibbel et al. (1986) and Casellas et

al. (1999) suggested that the poor solubility of coarse-grain alumina-zirconia glass compounds was due to the low coefficients of diffusion of Al_2O_3 and ZrO_2 within the glassy phase [4, 5]. In addition, poor solubility is expected in coarse $\text{Al}_2\text{O}_3/\text{ZrO}_2$ glass compounds with particles of different sizes. Furthermore, the low sintering temperature, used to avoid shrinkage and achieve the accuracy required in dental application, does not result in a better distribution of the particles. These factors did not appear to cause any effect on the fracture toughness of the two materials, which recorded similar values. The addition of 33% 12 mol-% CeO_2 partially stabilised zirconia (ZrO_2) to In-Ceram Alumina (resulting in the two systems of In-Ceram Zirconia, slip and dry-pressed) to enhance the fracture toughness did not result in a significant improvement in the fracture toughness of this material. This is because only a 10% increment of the fracture toughness was achieved. For strength, it is most likely related to factors such as porosity and presence of the glassy phase. A previous study showed that In-Ceram Zirconia slip demonstrated only a minor increase in the fracture toughness over that of In-Ceram Alumina slip [6].

When the fracture behaviour of In-Ceram Zirconia slip and dry-pressed materials were examined, it was seen in both instances that the crack propagation is generally transgranular for the zirconia particles (Figures 8.19 and 8.20) and intergranular or occasionally transgranular, depending on the orientation of the crack in respect of the elongated alumina crystals. At the crack tip, the tetragonal zirconia crystals transform, which causes compressive stresses within the transformed crystals and around the glass matrix. Also, the tetragonal zirconia crystals possess a higher coefficient of thermal expansion than the aluminium oxide crystals and glass matrix, therefore, tensile stresses will develop. The circumferential tensile stresses that

develop around the zirconia crystals, after transformation and as a result of thermal expansion difference, appear to attract the crack to the zirconia crystals and could result in a higher prevalence of transgranular fracture. Therefore, the expected toughening mechanisms in both In-Ceram Zirconia systems are: crack deflection, contact shielding attributed to the alumina crystals, phase transformation, and microcracking toughening mainly, due to zirconia crystals.

Unlike In-Ceram Zirconia materials, which contain only 33% of ZrO_2 and a significant amount of glass, the experimental zirconia and DC-Zircon ceramics are fully sintered zirconia systems. This would indicate the likelihood of better mechanical properties for these materials. This study showed that the difference in the mechanical properties of the two materials (Table 8.2) were related to the difference in the amount of the stabilising oxide (yttria), size of crystals, processing method and the effect of these factors on the porosity and metastability of the tetragonal crystals.

X-ray diffraction analysis showed that the amount of monoclinic phase change from as-sintered to the fractured surface for In-Ceram Zirconia slip (19%) was higher than that of In-Ceram Zirconia dry-pressed (9%). However, no significant difference in the fracture toughness of the two materials was found. The limitation of the X-ray diffraction could be the reason for such inconsistency. Also, different toughening mechanisms and the effect of glass content might have resulted in this unexpected similarity in the fracture toughness of the two materials. Furthermore, not only the phase transformation toughening mechanism of the zirconia (ZrO_2) particles contributes to the ultimate toughness of a compound, but other factors such as

microcrack toughening, contact shielding and crack deflection could also be pertinent. There was a remarkable amount of monoclinic particles already transformed upon cooling and detected in the as-sintered surface of In-Ceram Zirconia dry-pressed. These are responsible for generating localised stresses, which together with the high tensile stresses about the crack tip can nucleate microcracks in the glass matrix (Figure 8.19). The developed microcracks might have played an important role in the fracture toughness increase of this material [7]. Therefore, microcrack toughening (Figure 8.19) is an expected toughening mechanism in In-Ceram Zirconia dry-pressed, whereas transformation toughening may be the possible mechanism in In-Ceram Zirconia slip. When these toughening mechanisms are taken into account, it is normally expected that these materials would be far tougher than the In-Ceram Alumina systems. The insignificant difference in fracture toughness between In-Ceram Zirconia slip and In-Ceram Alumina slip indicated that these mechanisms are scarcely effective and likely to be offset by the presence of the glassy phase (23%).

The relative amount of monoclinic for all zirconia-containing materials are displayed in Figure 8.24. The as-sintered material of DC-Zircon contained a considerable amount of transformed monoclinic (14%). This material showed a greater amount of monoclinic phase on the fracture surface (46%). This high magnitude of the $t \rightarrow m$ transformation, the lack of a glass phase in this system and very minor porosity (less than 1%) are considered important factors and result in a more effective transformation toughening, and consequently better mechanical properties than all other tested ceramic materials.

The X-ray diffraction analysis of the experimental zirconia material showed a very limited occurrence of monoclinic phase in both as-sintered and fractured surfaces. This indicates that the contribution of the transformation toughening must have been almost negligible and supports the lower than expected value of fracture toughness. Furthermore, the presence of 9% volume fraction of porosity (Table 8.1) is likely to be accountable for the modest strength (considering the absence of the glassy phase), which is not statistically different from In-Ceram Zirconia slip (Table 8.1), which has a similar amount of porosity.

8.6 Conclusion

This comparative study has shown that the nine dental ceramics demonstrate a wide range of values in strength and fracture toughness, and point to the affiliation offered between microstructure, toughening mechanisms, processing and mechanical properties. It was concluded that an increase of the crystalline content as seen in the pressable materials and the fully sintered zirconia generally corresponds to an improvement of the mechanical properties. However, in materials with similar crystalline content, other factors such as porosity, the crystal size, shape and orientation and the effectiveness of each toughening mechanism are important in determining the mechanical properties.

For the glass-infiltrated alumina reinforced glass ceramics (In-Ceram Alumina slip and dry-pressed), it was interesting to note that the minimal variations of the crystal size, shape and orientation significantly affected the strength and fracture toughness of the two ceramics. This might be considered during designing of similar materials based on alumina glass ceramics. The improvement of the mechanical

properties due to zirconia particles is affected by the presence of other phases and by the metastability of the $t \rightarrow m$ transformation.

The alignment of the elongated crystals, as seen on lithium disilicate systems and In-Ceram Alumina slip system, was shown to significantly affect the mechanical properties of these ceramics. For the elongated alumina crystals (in In-Ceram Alumina slip) the alignment occurred most likely due to coincidental factors. Whereas in the case of the lithium disilicate systems, heat-pressing and shape of crystals and shape of the specimens were the main reasons for such alignment. From a clinical point of view this alignment may be a very beneficial factor in fracture resistance capability, if a suitable processing method could be developed in the future so that the alignment can take place in the connector area, where a significant amount of tensile stresses are developed.

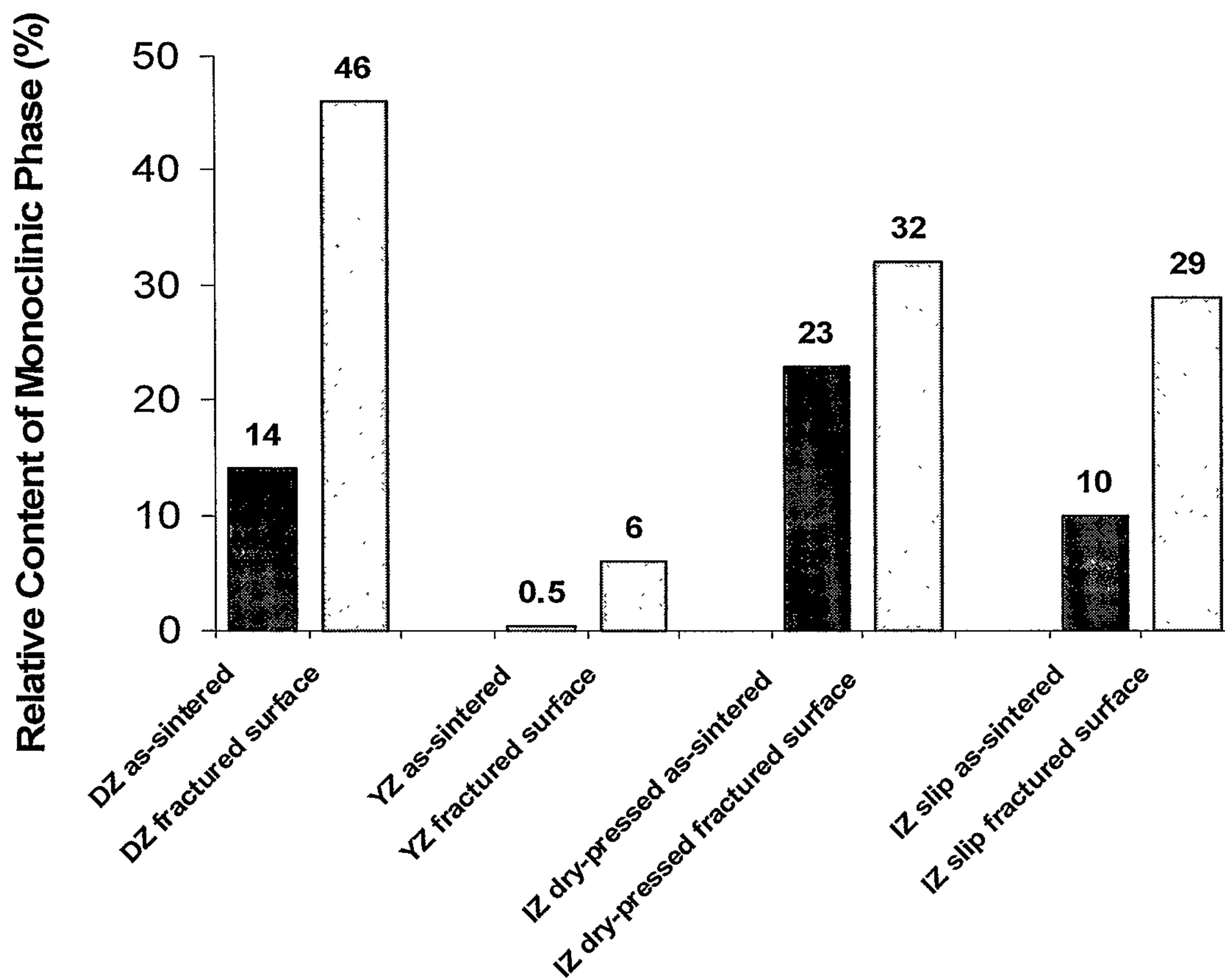


Figure 8.24 Relative amount of monoclinic of all material after sintering and after fracture.

8.7 Future directions

The main focus of the present study was the appraisal of the intrinsic mechanical properties, microstructure, and the effect of laboratory processing procedures on the mechanical properties of three pressable all-ceramic dental materials. In this chapter, the mechanical properties of the three pressable materials were compared to a number of peer all-ceramic dental materials.

This study has shown that a number of factors may affect the mechanical behaviour of these materials and subsequently their reliability. Among these factors are the processing and fabrication procedures. Factors which were not covered by the present study include aging and fatigue behaviour. In fact, dental restorations in the oral cavity are submitted to multiple daily cyclic loads of approximately 500 to 800 N in a moist environment. Also, the number of chewing cycles could reach 1400 in a single day. These forces may initiate and/or stimulate growth of pre-existing small cracks upon loading and may cause catastrophic failure. Few studies were found in the literature that appraised the effect of different media or aging on the mechanical properties of the pressable materials Empress 1 and Empress 2.

The Empress 1 material demonstrated the lowest flexural strength and fracture toughness among all materials investigated in the present study. However, previous in-vivo and in-vitro studies of this system showed excellent performance and some in-vitro reports showed that the fracture strength of this material could be compared to that of In-Ceram Alumina [8-10]. This may indicate that other factors, such as glazing, staining and adhesive cementation, may be explain the apparent remarkable reliability of the in-service restorations of Empress 1 [11-13]. To verify such an

assumption, the thermal expansion coefficient of the glazing material of Empress 1 could be measured and compared to that of the core.

In contrast to Empress 1, which has been the subject of many clinical investigations, Empress 2 has experienced very few studies that have reported on its long-term success or in-service performance. Long-term clinical studies on this system may be required to prove the reliability of this system for three-unit fixed partial denture, especially when the indentation fracture value ($1.5 \text{ MPa} \cdot \text{m}^{1/2}$) of this material is taken into account and compared to many other all-ceramic systems.

Finally, the bond strength between the core portion and the veneering material is considered to be a very important factor and may contribute to the long-term success of specific all-ceramic restorations.

8.8 References

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