

MECHANICAL PROPERTIES OF A SOLID OXIDE FUEL CELL ELECTROLYTE

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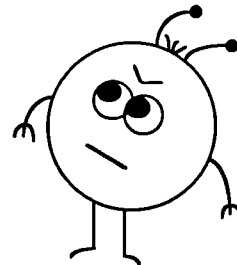
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"Consider it pure joy, my brothers, whenever you face trials of many kinds, because you know that the testing of your faith develops perseverance."

James; chapter 1, vs. 2 - 4.

"Amen to that!"
exclaims Seigfried



ABSTRACT

The aim of this thesis was to establish the mechanical properties and failure processes of the electrolyte used in the solid oxide fuel cell, both at room temperature and 950°C, the operating temperature of the cell.

The electrolyte material investigated was 8 mol% yttria stabilised zirconia. The majority of samples were provided in the form of tape-cast discs, 150µm thick, but bulk samples were also manufactured, to supplement the work on the electrolyte samples; sets of both tape-cast and bulk material were aged for 1000 hours at 950°C.

The basis of several of the mechanical testing techniques was a biaxial flexure test. Young's modulus (E) of bulk and tape-cast samples was determined at room temperature using a dynamic resonance technique, and of tape-cast samples at elevated temperatures using static tests, with a finite element analysis solution. The flexural strength of the tape-cast material was determined over a temperature range up to 1050°C, and SEM used to examine the fracture processes. Toughness of bulk material was found using single-edge notched beam tests, and of tape-cast material using indent-based techniques. A rig was built to investigate the sub-critical crack growth (sccg) properties of the electrolyte material, and during these tests it was found that creep was occurring, and consequently this was also monitored.

E at room temperature was found to be ~ 200 GPa, regardless of the samples tested, but was shown to vary non-linearly with temperature, decreasing by 40% over an increase of 500°C. The flexural strength at room temperature was controlled by surface defects, resulting from the manufacturing methods, and ranged from 290-350 MPa. Strength decreased at elevated temperatures, more so for impure material, and it was found that above 850°C the processes by which fast fracture occurred had changed. Toughness of the bulk material was $1.29 \text{ MNm}^{-3/2}$, which doubled on ageing, whereas all the mechanical properties of the tape-cast material were unaffected by the heat treatment, and a value of $1.99 \text{ MNm}^{-3/2}$ was determined. The stress exponent of sccg for bulk material at room temperature was 10, but sccg also occurred in the tape-cast material at room temperature and 950°C, and the rate was again found to be sensitive to applied stress; at low stresses at 950°C, samples survived long enough for plastic deformation to be observed, and a stress exponent of 1, and activation energy of 320 kJ/mol were determined for this creep process. These values, in addition with the evidence from the microscopic examination, indicated that creep was occurring by a grain boundary diffusion process over the stress and temperature ranges employed.

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TABLE OF CONTENTS

ABSTRACT	3
ACKNOWLEDGEMENTS	4
TABLE OF CONTENTS	5
LIST OF FIGURES	10
LIST OF TABLES	15
1.0 INTRODUCTION	19
1.1 Background to Solid Oxide Fuel Cells (SOFC)	19
1.1.1 Operation of the Solid Oxide Fuel Cell	20
1.1.2 Design of the Solid Oxide Fuel Cell	21
1.2 Basis of Thesis	22
2.0 LITERATURE REVIEW	24
2.1 Structure of Zirconia	24
2.1.1 Addition of Stabiliser	24
2.1.2 Electrical Properties	26
2.1 Foil Processing	28
2.2.1 Tape-casting	28
2.2.1. (i) <i>Properties of Tape-cast 8 mol% YSZ</i>	29
2.2.2 Tape-calendering	30
2.2.3 Sintering	30
2.3 Young's Modulus	31
2.3.1 Basic Theory	31
2.3.2 Measurement of Young's Modulus	32
2.3.2. (i) <i>Static Technique</i>	32
2.3.2. (ii) <i>Dynamic Technique</i>	33
2.3.2. (iii) <i>'Velocity of Sound' Technique</i>	33
2.3.3 Review of Young's Modulus Data for Zirconia	34
2.4 Strength	38
2.4.1 Failure Stress	38
2.4.2 Flexure Test	39
2.4.2. (i) <i>Uniaxial Flexure</i>	40
2.4.2. (ii) <i>Biaxial Flexure</i>	41

2.4.3 Fast Fracture at Room and High Temperatures	45
2.4.4 Review of Strength Data for Zirconia	46
2.5 Analysis of Data	47
2.5.1 Weibull Analysis	47
2.5.2 Student's T-test	50
2.5.3 F-test	51
2.6 Fracture Toughness	51
2.6.1 Strain Energy Release Rate	51
2.6.2 Stress Intensity Factor	51
2.6.2.(i) <i>SENB Test</i>	53
2.6.2.(ii) <i>DT Test</i>	54
2.6.2.(iii) <i>Indentation Test</i>	55
2.6.2.(iv) <i>ISB Test</i>	56
2.6.3 Review of Toughness Data for FSZ	59
2.7 Sub-Critical Crack Growth	59
2.7.1 Predicting Lifetime to Failure	61
2.7.1.(i) <i>Static Fatigue Tests</i>	62
2.7.1.(ii) <i>Dynamic Fatigue Tests</i>	62
2.7.1.(iii) <i>Strength-Probability-Time (SPT) Diagrams</i>	64
2.7.2 Effect of Temperature	65
2.8 Creep	66
2.8.1 General Creep Behaviour	66
2.8.2 Creep Processes in Ceramics	68
2.8.2.(i) <i>Dislocation Creep Processes</i>	68
2.8.2.(ii) <i>Diffusional Creep Processes</i>	68
2.8.2.(iii) <i>Grain Boundary Sliding and Cavitation</i>	69
2.8.2.(iv) <i>Effect of Grain Size</i>	69
2.8.2.(v) <i>Eventual Fracture</i>	69
(a) <i>Effect of Defects and Impurities</i>	69
(b) <i>Fracture Mechanism Maps</i>	70
2.8.3 Types of Creep Test	71
2.8.4 Review of Creep Data for YSZ	72
2.8.4.(i) <i>Fully Stabilised Zirconia</i>	72
(a) <i>Single Crystal Material</i>	72
(b) <i>Polycrystalline Material</i>	73
2.8.4.(ii) <i>Partially Stabilised Zirconia</i>	74
 3.0 EXPERIMENTAL PROCEEDURE	 78
3.1 Sample Analysis	78
3.1.1 Thin-film Samples	78
3.1.1.(i) <i>Sample Preparation</i>	78
3.1.1.(ii) <i>Microstructural Analysis</i>	79
3.1.1.(iii) <i>Physical Properties</i>	79
3.1.1.(iv) <i>Phase Analysis</i>	79
3.1.1.(v) <i>Chemical Analysis</i>	80

3.1.1.(vi) <i>Topography and Profile Measurements</i>	80
3.1.2 Bulk Samples	81
3.1.2.(i) <i>Sample Preparation</i>	81
3.1.2.(ii) <i>Analysis</i>	81
3.2 Young's Modulus	81
3.2.1 Dynamic Techniques	81
3.2.1.(i) <i>GrindoSonic</i>	81
(a) <i>Bulk Samples</i>	81
(b) <i>Tape-cast Samples</i>	83
3.2.1.(ii) <i>Velocity of Sound</i>	84
3.2.2 Static Techniques	86
3.2.2.(i) <i>Uniaxial Flexure</i>	86
3.2.2.(ii) <i>Biaxial Flexure</i>	86
3.3 Strength	86
3.3.1 Uniaxial Flexure	86
3.3.2 Biaxial Flexure	86
3.3.2.(i) <i>Ball-on-ring Geometry</i>	86
3.3.2.(ii) <i>Ring-on-ring Geometry</i>	89
3.3.2.(iii) <i>SEM Analysis</i>	91
3.4 Fracture Toughness	91
3.4.1 Single-edge Notched Beam (SENB) Tests	91
3.4.2 Double Torsion (D.T.) Tests	92
3.4.3 Indentation Tests	92
3.4.4 Indentation Strength Bend (ISB) Tests	93
3.5 Static Fatigue	94
3.5.1 Apparatus	94
3.5.2 Static Fatigue Preparations / S-P-T Diagram	95
3.5.3 Creep	96
3.5.4 SEM / TEM Examination	98
 4.0 RESULTS	 101
 4.1 Sample Analysis	 101
4.1.1 Thin Film Samples	101
4.1.1.(i) <i>Microstructure</i>	101
4.1.1.(ii) <i>Physical Properties</i>	101
4.1.1.(iii) <i>Phase Analysis</i>	101
4.1.1.(iv) <i>Compositional Analysis</i>	101
4.1.1.(v) <i>Topography and Profile</i>	102
4.1.2 Bulk Samples	104
4.2 Young' Modulus	105
4.2.1 Dynamic Techniques	105
4.2.1.(i) <i>GrindoSonic</i>	105
(a) <i>Bulk Samples</i>	105
(b) <i>Tape-cast Samples</i>	105
4.2.1.(ii) <i>Velocity of Sound Technique</i>	106

4.2.2 Static Techniques	106
4.2.2.(i) <i>Uniaxial Flexure</i>	106
4.2.2.(ii) <i>Biaxial Flexure</i>	107
4.3 Strength	108
4.3.1 Uniaxial Flexure	108
4.3.2 Biaxial Flexure	109
4.3.2.(i) <i>Ball-on-ring</i>	109
4.3.2.(ii) <i>Ring-on-ring</i>	110
4.4 Fracture Toughness	122
4.4.1 Single-edge Notched Beam (SENB)	122
4.4.2 Double Torsion (DT)	123
4.4.3 Indentation and ISB	123
4.5 Static Fatigue	128
4.5.1 Sub-critical Crack Growth / SPT diagrams	128
4.5.2 Static Fatigue Tests	130
4.5.3 Creep	132
 5.0 DISCUSSION	 139
 5.1 Sample Microstructure and Composition	 139
5.1.1 Thin Film Samples	139
5.1.2 Bulk Samples	143
5.1.3 Summary of Main Points	143
5.2 Young's Modulus	144
5.2.1 Dynamic Techniques	144
5.2.2 Static Techniques	145
5.2.2.(i) <i>Problems With Test Techniques</i>	145
5.2.2.(ii) <i>Performance of the Different Samples</i>	146
5.2.3 Summary of Main Points	149
5.3 Strength	150
5.3.1 Uniaxial Flexure	150
5.3.2 Biaxial Flexure	150
5.3.2.(i) <i>Effect of Friction in Ring-on-ring Test</i>	150
5.3.2.(ii) <i>Performance of the Different Materials</i>	151
5.3.3 Summary of Main Points	154
5.4 Fracture Toughness	155
5.4.1 Bulk Samples - Single-edge Notched Beam Tests	155
5.4.2 Tape-cast Samples	157
5.4.2.(i) <i>Sources of Error in Indentation and ISB Tests</i>	157
5.4.2.(ii) <i>Double Torsion Tests</i>	158
5.4.2.(iii) <i>Toughness of Tape-cast Samples</i>	159
5.4.3 Summary of Main Points	161
5.5 Static Fatigue Tests	162
5.5.1 Sub-critical Crack Growth and Strength-Probability-Time Diagram	162
5.5.2 Creep	165
5.5.3 Summary of Main Points	170

6.0 CONCLUSIONS	173
6.1 Conclusions of Work Performed	173
6.2 Significance for the SOFC	174
7.0 FURTHER WORK	177
7.1 Short-term Research	177
7.2 Long-term Research	178
APPENDIX	180
LIST OF REFERENCES	183

LIST OF FIGURES

CHAPTER 1

Figure 1.1 - diagram illustrating the electrochemical reaction across a cell in the SOFC 20

Figure 1.2 - diagram illustrating the configuration of the planar SOFC 21

CHAPTER 2

Figure 2.1 - diagram illustrating the crystal structure of cubic zirconia 24

Figure 2.2 - showing the zirconia rich section of the yttria stabilised zirconia phase diagram 26

Figure 2.3 - showing the variation in ionic conductivity with stabiliser addition for YSZ 27

Figure 2.4 - diagram illustrating the tape-casting process 29

Figure 2.5 - comparing the change in E with temperature for various polycrystalline ceramics 32

Figure 2.6 - diagram illustrating the uniaxial flexure test geometries and resulting stress distribution through sample thickness and along the tensile face of the sample; (a) - change in stress through thickness; (b) - 3-point-bend; (c) - 4-point-bend 40

Figure 2.7 - diagram illustrating the radial and tangential stresses produced during biaxial flexure 41

Figure 2.8 - diagram illustrating the stress distribution along the tensile face of a sample during biaxial flexure 42

Figure 2.9 - diagram illustrating the biaxial flexure test geometries; (a) - ball-on-ring; (b) - ring-on-ring 42

Figure 2.10 - diagram illustrating the non-linear relationship which develops between applied load and maximum stress due to increasing membrane stresses 44

Figure 2.11 - diagram illustrating the effect of test-rig geometry on the magnitude of the stress concentration below the loading ring	44
Figure 2.12 - diagram of the Weibull distribution function, illustrating the effect of m	48
Figure 2.13 - diagram illustrating the comparison of two sets of data to a pre-existing standard set	50
Figure 2.14 - diagram illustrating mode 1 crack propagation	52
Figure 2.15 - diagram showing the SENB test and sample dimensions	53
Figure 2.16 - diagram showing the DT test and sample dimensions	54
Figure 2.17 - diagram illustrating the crack systems which may be produced during an indentation test	55
Figure 2.18 - typical v - K_I curve	60
Figure 2.19 - diagram showing plot of $\log(\sigma_f)$ versus $\log(t_f)$	62
Figure 2.20 - diagram showing a typical SPT plot	64
Figure 2.21 - illustrating the general creep curves found in metals; (a) - class A metal; (b) - class B metal	66
Figure 2.22 - fracture mechanism map for the CaF_2 structure	71
CHAPTER 3	
Figure 3.1 - diagram illustrating the sample and apparatus positioning required to detect the flexural vibration of bars	82
Figure 3.2 - diagram illustrating the set-up required to detect the vibration of tape-cast discs; (a) - flexural mode; (b) - torsional mode	83
Figure 3.3 - basic apparatus used to measure the velocity of sound through a sample at room temperature	85
Figure 3.4 - the apparatus used to measure the velocity of sound through a sample at room temperature	85

Figure 3.5 - diagram of uniaxial tests used to calculate E; (a) - 3-point-bend; (b) - 4-point-bend	86
Figure 3.6 - diagram of the ball-on-ring biaxial flexure apparatus	88
Figure 3.7 - diagram of the steel ring-on-ring biaxial flexure apparatus used at Erlangen	89
Figure 3.8 - diagram showing the cross-sectional preparation of SENB samples	92
Figure 3.9 - diagram of the static fatigue rig constructed at Imperial College	95
Figure 3.10 - diagram illustrating the measurement of the length of deformed samples, using the 'triangle' technique	98
CHAPTER 4	
Figure 4.1 - DIGIMAPS showing the Y3+ distribution in tape-cast material; (a) - set C aged; (b) - set D	102
Figure 4.2 - Talysurf profile of a tape-cast disc from set C	103
Figure 4.3 - graph showing the variation in E with temperature for bulk and tape-cast FSZ, and alumina samples, tested using GrindoSonic, uniaxial and biaxial flexure techniques	108
Figure 4.4 - typical fracture initiation site for set A: featureless. Also shows fine porosity distribution	110
Figure 4.5 - fracture face for set A, showing the transgranular crack path and crack-like defects	110
Figure 4.6 - comparison of Weibull plots for set B tested using a solid steel support ring (ss), a support ring made of ball-bearings (bb), and tested at Imperial College using the Si ₃ N ₄ rig (IC)	111
Figure 4.7 - comparison of Weibull plots for sets B, C, and D, tested at room temperature	112
Figure 4.8 - comparison of Weibull plots for sets C and D, tested at room temperature and 950°C	112

Figure 4.9 - typical fracture initiating defect for set B; porous defect	115
Figure 4.10 - transgranular fracture path and porosity distribution throughout fracture face of set B, and sometimes in clusters	115
Figure 4.11 - intergranular fracture path seen in set C away from the initiation site, at room temperature	116
Figure 4.12 - overview of fracture face of set C, broken at 950°C; transgranular crack path around the initiation site and approaching the compression face	116
Figure 4.13 - grain sliding as the failure initiation site for set D broken at 950°C	117
Figure 4.14 - failure initiation site for set D broken at 950°C; clearly defined grains shown at the side of the cavity	117
Figure 4.15 - overview of fracture face of set D broken at 1050°C; mixture of transgranular and intergranular crack path	118
Figure 4.16 - change in initiation sites with increasing temperature; (a) room temperature; (b) 850°C; (c) 950°C; (d) 1050°C	119
Figure 4.17 - change in crack paths with increasing temperature; (a) room temperature; (b) 850°C; (c) 950°C; (d) 1050°C	120 - 121
Figure 4.18 - comparison of failure at notch, shown in cross-section; (a) aged; (b) unaged	122
Figure 4.19 - comparison of the WYKO images taken of indents in set D, showing indent and surrounding deformation; (a) P = 100g; (b) P = 300g	124
Figure 4.20 - fracture face of set D indented with load of 200g, showing plastic deformation immediately around indent, and median crack extending into sample	126
Figure 4.21 - graph of $\log \sigma_f$ versus $\log P$ for sets C and D; gradient of -1/3 also fitted	127
Figure 4.22 - graph of $1/\sigma_f^3$ versus P for sets C and D	127
Figure 4.23 - plot of $\log (\sigma_f)$ versus $\log$ (stress rate) for bulk samples	129

Figure 4.24 - SPT diagram constructed using data obtained from figure (4.23)	129
Figure 4.25 - showing the typical initiation site of fracture for samples used to construct SPT diagram - a bevelled corner. (This sample tested at 100 N/min.)	130
Figure 4.26 - plot of $\log t_f$ versus $\log \sigma$ for sets B and C	132
Figure 4.27 - typical Talysurf profile of a plastically deformed sample; this sample held under 90 Mpa (35% σ_o) at 950°C for 1200 hours	133
Figure 4.28 - graph of $\log$ strain rate versus $\log$ stress; (a) including all data points; (b) omitting 'wayward' 35% data point	134
Figure 4.29 - graph of $\ln$ strain rate versus $1/T$	134
Figure 4.30 - graph showing corrected deflection versus time obtained from LVDT for a sample held at 950°C under a load of 25% σ_o	136
Figure 4.31 - showing pore coalescence in the central region of samples; (a) - 50% σ_o , 950°C; (b) - 50% σ_o , 950°C; (c) - 40% σ_o , 1000°C	137

CHAPTER 5

Figure 5.1 - diagram illustrating the difference in crack paths through heat treated SENB samples; (a) - unaged; (b) - aged	156
Figure 5.2 - showing the plot of $\log$ (normalised time to failure) versus $\log$ (applied static stress) for sets B and C tested at room temperature and 950°C; values for set C from the 45 and 50 % load not shown, due to misalignment of rig	164
Figure 5.3 - showing the change in stress experienced with time along the tensile face, due to the large displacement, for a sample held under an initial load of 129 Mpa at 950°C for 1200 hours	167
Figure 5.4 - shows the change in maximum tensile stress for the initial loads over a period of 1200 hours	168

LIST OF TABLES

CHAPTER 2

Table 2.1 - comparison of the conductivity of FSZ at 1000°C, using different dopants as stabiliser	25
Table 2.2 - comparison of the activation energies and coefficients for self-diffusion of the ionic species in YSZ	25
Table 2.3 - summary of mechanical data of tape-cast 8 mol% YSZ	29
Table 2.4 - summary of the literature of E for single and polycrystalline zirconia, over a range of compositions and temperatures	37
Table 2.5 - summary of strength data for tape-cast and calendered FSZ	46
Table 2.6 - summary of the creep data available in literature	76

CHAPTER 3

Table 3.1 - summary of the manufacturer and nominal dimensions of the sets of samples used in project	78
Table 3.2 - summary of the sample numbers and test conditions used to determine strength of each set; ss - solid support ring; bb - support ring of ball-bearings; IC - silicon nitride rig	90
Table 3.3 - summary of test conditions used to analyse the stress exponent and activation energy for creep. σ_0 - Weibull strength for set C at 950°C	96

CHAPTER 4

Table 4.1 - summary of the structural, physical, and chemical analysis of tape-cast material, $\pm$ one standard deviation	102
Table 4.2 - mean surface roughness values of tape-cast material, $\pm$ one standard deviation	103
Table 4.3 - summary of the warpage of the tape-cast material, $\pm$ one standard deviation	104

Table 4.4 - showing the variation of E with temperature for bulk samples, tested using the GrindoSonic	105
Table 4.5 - mean E, $\pm$ one standard deviation, for tape-cast FSZ and ground alumina discs, tested using the GrindoSonic	106
Table 4.6 - showing the variation of E with temperature calculated using the 'velocity of sound' technique	106
Table 4.7 - showing the variation in normalised E values with temperature for tape-cast bars, tested using 3-point-bend flexure test	107
Table 4.8 - summary of the mean strength, $\pm$ one standard deviation, for heat treated bulk samples tested using 3-point-bend flexure	108
Table 4.9 - summary of the mean strength, $\pm$ one standard deviation, and Weibull data for set A tested at room temperature and 950°C using the ball-on-ring flexure test. () give the number of samples tested	109
Table 4.10 - summary of Weibull data for sets B, C, and D, tested using the ring-on-ring biaxial flexure rig at room temperature and 950°C; ss - solid support ring; bb - support ring of ball-bearings; IC - Si ₃ N ₄ rig; () gives number of samples tested	113
Table 4.11 - summary of mean strength, $\pm$ one standard deviation, for sets B, C, and D tested using the ring-on-ring biaxial flexure rig at room temperature and 950°C; ss - solid support ring; bb - support ring of ball-bearings; IC - Si ₃ N ₄ rig; () gives number of samples tested	114
Table 4.12 - summary of the variation in mean strength with temperature of set D, $\pm$ one standard deviation; () gives the number of samples tested	114
Table 4.13 - mean toughness values, $\pm$ one standard deviation, calculated for heat treated SENB samples	122
Table 4.14 - summary of the mean toughness, $\pm$ one standard deviation, calculated for set D using DT	123
Table 4.15 - summary of mean toughness values, $\pm$ one standard deviation calculated from crack length measurements for sets C and D, using the post-indent and ISB tests, over a range of indent sizes	125
Table 4.16 - summary of toughness values, $\pm$ one standard deviation, calculated	128

for bulk and tape-cast samples using different techniques

- Table 4.17** - summary of the static fatigue data obtained for set C. n_f - number of samples which failed; n_t - number of samples tested; extraordinarily long t_f for 45% σ_o and 50% σ_o due to rig misalignment 131
- Table 4.18** - summary of creep data for set C using two different methods to measure strain 133
- Table 4.19** - summary of the stress exponent and activation energy calculated for creep using two methods for measuring strain, and comparing the effect of including an 'errant' data point 135

CHAPTER 1
INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 Background to Solid Oxide Fuel Cells (SOFC)

At present, ~ two thirds of the world's electricity generation is based on fossil fuel (coal, oil, gas) technology (IEA, 1993). However, there are serious problems arising from this source of power, mainly associated with the efficiency and pollution of the production systems. There is not a limitless supply of readily available fuels, so the systems must be made to operate as efficiently as possible. However, the demand for smaller plants, ~ 10 MW size, is increasing, as power generation becomes more localised; these plants operate less efficiently than the larger ones, and so ways of improving the present technology must be found. In addition, the pollution which accompanies the present technology, especially the emission of NO_x and SO_x , is causing increasing world-wide concern, and adding to the demand that alternative processes need to be adapted or developed now ready for future employment (Blomen, 1996).

Fuel cells are one type of renewable energy systems being developed, and of these the solid oxide fuel cell (SOFC) has the potential of being one of the best sources of electrical energy in the future, both for industrial and vehicle usage. The pollution output is very low and its efficiency of ~ 60-65% exceeds that of all the technology currently in operation. In addition, it is also more adaptable in terms of fuel consumption and site positioning, and more acceptable to the public, than other alternative power sources. However, at present the SOFC is far more expensive to produce, costing between \$500-1000/kW compared with less than \$300/kW for a gas turbine, and these high manufacturing costs mean it is unlikely to actually replace the present systems in the foreseeable future. It is believed that the entrance of the SOFC into the commercial market will be in combination with present technology; a 3MW plant is planned, consisting of a gas turbine and three SOFCs, with the ultimate aim of achieving 85% efficiency (Blomen, 1996; Steele, 1996).

1.1.1 Operation of the Solid Oxide Fuel Cell

All fuel cells are electrochemical devices, converting chemical energy from the reaction between a fuel and an oxidant to electrical energy. Their basic structure is the same as a battery - anode / electrolyte / cathode - but the fuel and oxidant are supplied continuously from an external source, so that the power from the fuel cell may also be drawn continuously (Christie, 1993). The solid oxide fuel cell is a high temperature cell, and its components are made of solid oxides. The basic unit consists of a dense electrolyte capable of conducting oxygen ions, coated on either side with porous, electrically conducting, electrodes. Many of these units, or cells, are stacked together and held in place by an interconnection material, to produce the stack system. The electrochemical reaction which occurs across the cell is shown in figure (1.1).

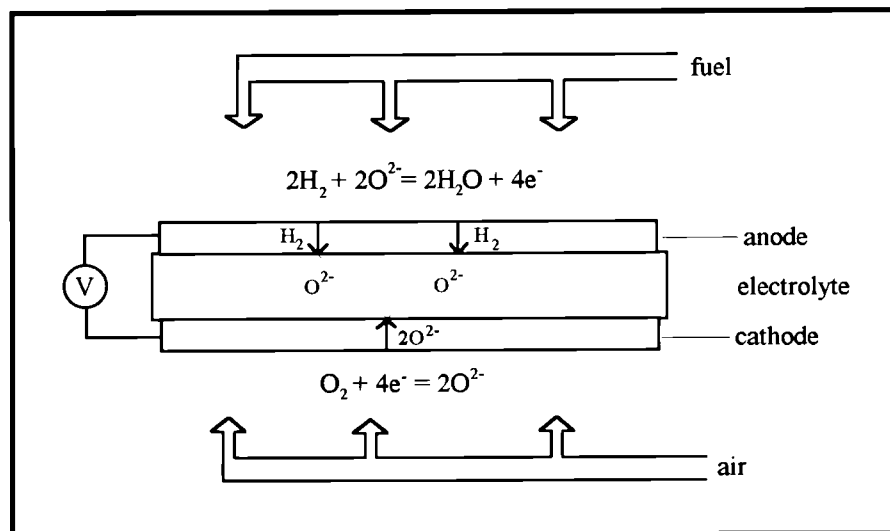


Figure (1.1) - diagram illustrating the electrochemical reaction across a cell in the SOFC (Stevens, 1986).

Fuel, such as hydrogen in the case of figure (1.1), is supplied to the anode, and oxygen or air to the cathode. At the cathode electrons are supplied from an external circuit, so that the oxygen is reduced to form oxygen ions. These diffuse through the electrolyte, under the influence of the oxygen pressure gradient across it, to the anode where they oxidise the fuel, producing water and releasing electrons. These electrons flow through the external circuit back to the cathode - and it is this electron flow through the external circuit that provides the DC electricity.

The maximum voltage which can be achieved is given by the Nernst equation, and depends on operating conditions of oxygen partial pressure and temperature. At present the operating temperature is at 950°C, which limits the materials selection, but does offer some advantages. First it means that internal reforming of hydrocarbons to hydrogen can

take place, which is cheaper than having to add an external reformer as is necessary for the low temperature fuel cells. Also the 'waste' heat can be channelled and used either to continue the reaction or for additional applications, improving the efficiency up to $\sim 70\%$ (Christie, 1993).

1.1.2 Design of the Solid Oxide Fuel Cell

There are two main designs for the SOFC, tubular and planar. The impetus behind the planar design is the reduction in manufacturing costs of the SOFC; it makes use of comparatively low cost production processes (e.g. tape-casting, screen-printing), and involves fewer fabrication steps. It also gives a higher power density, but the major drawback is that it needs seals at the edges of the plates, to prevent the gases mixing; finding a material with the necessary physical and chemical properties required for the sealant is proving to be rather challenging (Kleinlein, 1993; Christie, 1993).

It is the electrolyte in the planar design that is the subject of this thesis, and a diagram showing the planar geometry adopted by Siemens is given in figure (1.2) (Wersing, 1992). In this case the electrolyte has two functions, both to separate, and support, the electrodes on either side of it. The unit cells are held together in a stack by a bi-polar plate, which also allows the gases to pass at 90° to each other.

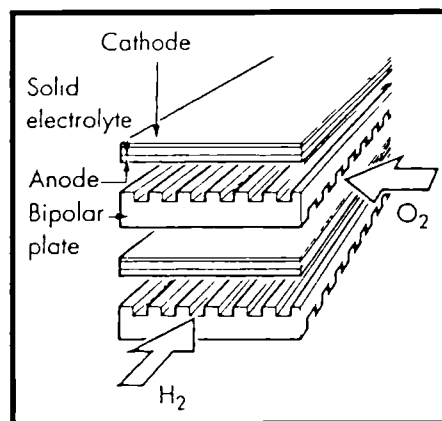


Figure (1.2) - diagram illustrating the configuration of the planar SOFC.

The electrodes need to be porous and have a high electrical conductivity, in order for the gases to infiltrate them. The electrolyte, on the other hand, needs to be dense so that the gases do not leak across it and so react directly. In addition, it must have a high ionic conductivity, that is independent of the oxygen partial pressure over several orders of magnitude; it needs to be mechanically and chemically stable for long periods at high temperatures in reducing and oxidising atmospheres, and it must be compatible with the other components used in the stack (Kleinlein, 1993; Minh, 1993).

1.2 Basis of Thesis

The electrolyte which Siemens use at present is made of cubic yttria stabilised zirconia, approximately 150 μ m thick. Small stacks have been able to run for over a year (Schafer, 1993), so it is known that this material operates successfully as a conductor. However, there is a dearth of information on its mechanical properties under SOFC operating conditions, and hence this is the subject of investigation for this thesis.

The work was in partnership with KWU, Siemens, in Erlangen, where computer models of the entire SOFC operation were set up. Mechanical data were required for part of the programmes, in particular values of failure strength, Young's modulus, fracture toughness, and some indication of the expected lifetime of the electrolyte, all at the operating temperature of the cell; determining these values formed the initial aim of the project.

In order for the data to be industrially relevant, the material tested had to be the same as that actually used for the electrolyte - hence tape-cast samples, $\sim 150\ \mu\text{m}$ thick, were supplied. The size of these samples, and the test temperatures involved, complicated the testing techniques; a silicon nitride biaxial flexure test rig was made, which formed the basis of several of the tests employed.

The strength was determined using biaxial fast fracture, with finite element analysis calculations supplied by KWU, and the data analysed using standard statistical techniques (Weibull plots and Student's t-test). Different techniques were used to determine Young's modulus, of which biaxial flexure was successful at elevated temperatures, and this flexure test was also used as one way of calculating the toughness. A strength-probability-time diagram was constructed using data from 3-point-bend samples, from which lifetime predictions at room temperature could be made, but in order to determine electrolyte lifetime at 950°C a static fatigue rig, based on the biaxial flexure geometry, was constructed. During the static fatigue tests it was found that creep was occurring, so the rig was modified to characterise this.

The thesis is presented in four main sections: a literature review, where the background to the electrolyte material's behaviour and the test techniques used in the project are described; experimental procedure, detailing the work performed in the project; presentation of the results obtained from the experimental work, and subsequent discussion of these results. The main points are summarised in the final conclusion.

CHAPTER 2
LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

2.1 Structure of Zirconia

The electrolyte is fully stabilised zirconia (FSZ), doped with yttria. The reasons for using this material, and the type and amount of stabiliser added, are due to its good electrical properties and phase stability, rather than the structural requirements of the cell.

2.1.1 Addition of Stabiliser

Pure zirconia is polymorphic; as a solid it exists in three phases, each with a different crystal structure, depending on temperature. From its melting point at 2680°C down to 2370°C, it adopts a cubic structure; from 2370°C to 1170°C it is tetragonal; and below 1170°C it is monoclinic (Stevens, 1986). The cubic phase has the calcium fluorite crystal structure, shown in figure (2.1), which may be considered as a cubic array of large oxygen ions, with the smaller zirconium ions filling alternate cubic interstitial holes (Wyatt, 1974). As the temperature is lowered, this structure distorts to form the tetragonal and ultimately the monoclinic phase.

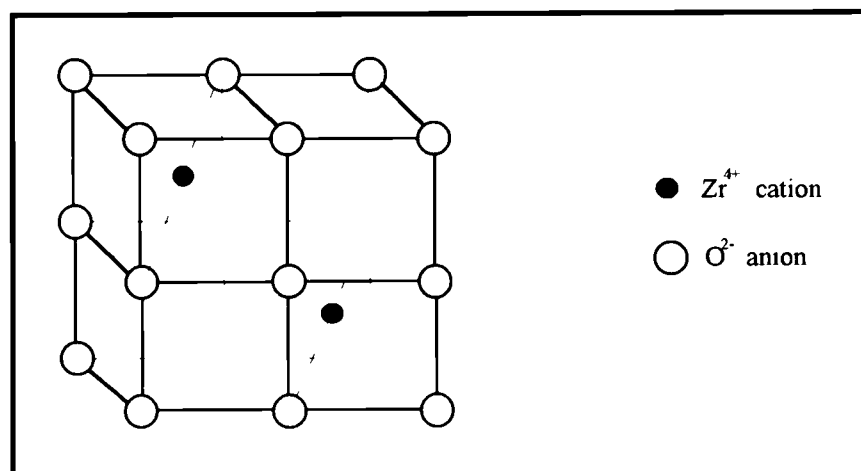


Figure (2.1) - diagram illustrating the crystal structure of cubic zirconia.

On non-equilibrium cooling from the tetragonal to the monoclinic phase a martensitic transformation occurs, with an increase in volume of 3-5%. The matrix is unable to accommodate this expansion elastically, and so it cracks. This effect means that pure zirconia has a limited use for most applications (Green, 1989).

However, the addition of certain oxides can stabilise the cubic structure down to room temperature, thus avoiding the damaging phase transformation. Examples of such oxides, which are termed stabilisers, are Y_2O_3 , MgO , CaO , and other rare-earth oxides. They are selected for their good solid solubility in zirconia and for having a cation radius no more than 40% different to that of Zr^{4+} ; of these, the rare-earth oxides improve the conductivity of zirconia the most, but Y_2O_3 is the most frequently used stabiliser in the SOFC electrolyte, because of its greater availability and lower cost (Minh, 1993). Siemens use yttria stabilised zirconia (YSZ) as their electrolyte material, and so only this material will be considered further. The conductivity of zirconia stabilised with various dopants is compared in table (2.1), and the activation energy and coefficients for diffusion of the ionic species in YSZ at the operating temperature of the electrolyte are given in table (2.2).

Table (2.1) - comparison of the conductivity of FSZ at 1000 °C, using different dopants as stabiliser (Minh, 1993; Appleby, 1993).

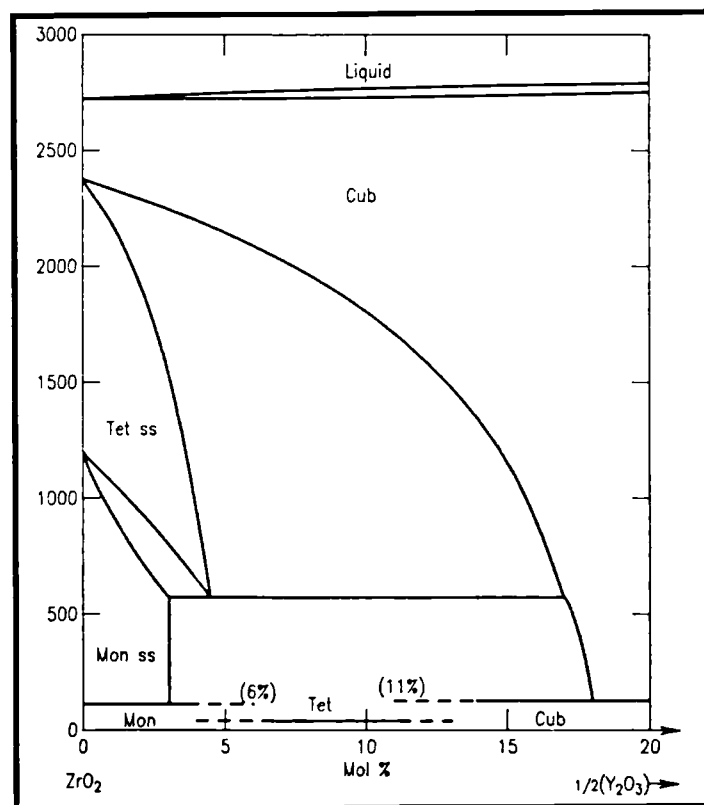
Stabiliser	Conductivity, $\Omega^{-1}\text{cm}^{-1}$
Sc_2O_3	0.25
Y_2O_3	0.1
CaO	0.025

Table (2.2) - comparison of the activation energies and coefficients for self-diffusion of the ionic species in YSZ. () denotes values determined using a 9.5 mol% YSZ single crystal (Strickler, 1964; Solmon, 1991).*

Ionic species	Ionic radius, $\text{\AA}$	Activation energy, kJ/mol (*)	S - D coefficient at 950°C , $\text{cm}^2/\text{s (*)}$
Zr^{4+}	0.84	461	1.13×10^{-20}
Y^{3+}	1.01	462	2.73×10^{-20}
O^{2-}	1.40	86	2.96×10^{-7}

The zirconia-rich portion of the YSZ phase diagram is shown in figure (2.2), where the yttria addition is shown on an $\text{YO}_{1.5}$ axis (Scott, 1975). In order to obtain a suitably dense final product the green body must be sintered at a temperature of at least 1500°C . Thus the phases which form during sintering, and hence which will be present at room temperature, will depend on the amount of stabiliser added. With additions from about 3 up to 6.5 mol% Y_2O_3 , sintering will take place in the tetragonal/cubic field, so both these phases are retained in various quantities at room temperature, producing partially stabilised zirconia (PSZ). Above 6.5 mol% Y_2O_3 , the sintering occurs in the cubic field, and this structure is retained on cooling to room temperature - the material is described as being fully stabilised. The electrolyte used in the SOFC contains 8 mol% Y_2O_3 , and so exists in the cubic form, with a lattice parameter $a_c = 5.139\text{\AA}$.

Figure (2.2) - showing the zirconia rich section of the yttria stabilised zirconia phase diagram (Scott, 1975).

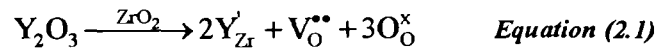


The mechanical properties of FSZ (especially strength and toughness) are inferior to those of PSZ (Green, 1989), but it is used as the electrolyte because of its superior ionic conductivity.

2.1.2 Electrical Properties

When Y_2O_3 is added to the ZrO_2 , it dissolves to form a solid solution, with the Y^{3+} ions replacing some of the Zr^{4+} ions in the fluorite lattice. However, because yttrium has a lower valency than zirconium, oxygen vacancies are produced in order to preserve

electrical neutrality, with one vacancy generated for each pair of dopant cations. This is illustrated using Kroger-Vink notation in equation (2.1) (Weller, 1986)):



It is these vacancies that enable the motion of the oxygen ions through the electrolyte. From table (2.2) it can be seen that the diffusion coefficient for anions in YSZ is much greater than that for the cations. Hence the ionic conduction across the electrolyte is due to the rapid movement of oxygen ions, under the influence of an oxygen pressure gradient.

The conductivity will be dependent on dopant concentration, since this determines the number of vacancies produced. From figure (2.3) it can be seen that conductivity increases with dopant concentration up to a point, but begins to decrease after about 9 mol% (as the Y^{3+} ions tend to cluster rather than be uniformly dispersed). Thus usually no more than 9 mol % of yttria is added when YSZ is to be used as an ionic conductor (Strickler, 1964; Minh, 1993).

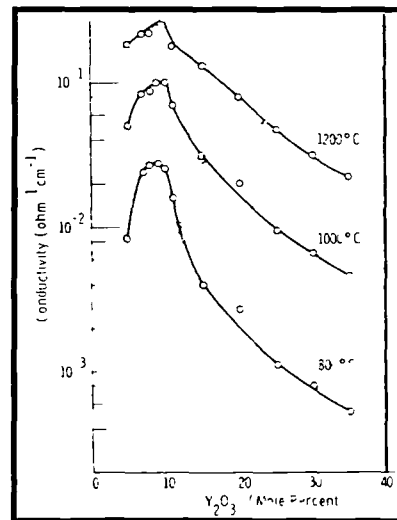


Figure (2.3) - showing the variation in ionic conductivity with stabiliser addition for YSZ (Strickler, 1964).

It has been proposed that PSZ could be used instead of FSZ, because the superior mechanical properties would compensate for the lower conductivity. However, ageing experiments on PSZ have shown that it tends to decompose to tetragonal and tetragonal', an yttria rich phase, which impairs the conductivity, and so PSZ is not stable enough to be used at 950°C (Moghadam, 1982). With FSZ no such effects have been observed, and trials using FSZ electrolytes have run successfully for several thousand hours (Minh, 1993).

2.2 Foil Processing

The mechanical failure of ceramics is almost always initiated from defects. These failure defects can be introduced during fabrication (intrinsic microstructural flaws such as voids, inclusions, abnormally large grains) and/or surface preparation of the component (extrinsic flaws such as surface cracks from machining), and can also develop whilst using the component in an aggressive environment (e.g. cavitation at high temperature). The microstructure of a ceramic, and hence its mechanical properties, are very dependent on the processing route used (Evans, 1982).

Also, the resistance of the electrolyte is proportional to its thickness. Hence the electrolyte needs to be as thin as structurally possible, between 100-200 μm . Both the mechanical and structural requirements influence the mode of manufacture of the electrolyte.

Samples used as electrolyte material in this project were produced by two techniques, tape-casting and tape-calendering, both of which are well known thin-film production processes.

2.2.1 Tape-casting

The electrolyte used by Siemens is produced by tape-casting, a form of colloidal processing, which enables a very homogeneous green body to be produced. In addition, the flaws present in the final body are smaller and less in number than in those made by other techniques; for these reasons tape-casting leads to superior mechanical properties compared with dry pressing techniques for thin films (Plucknett, 1994; Schafer, 1993; Boch, 1991; Ham-Su, 1995).

A flow chart for the tape-casting procedure is shown in figure (2.4). The powders are mixed together with a dispersant in a solvent, and the agglomerates in the slurry broken down by milling. At this stage impurities can be introduced, depending on the milling media used (e.g. alumina impurities come from using alumina balls). A plasticiser and organic binder are added, with further milling.

Then the slurry is de-aerated to eliminate pores, pumped into a reservoir, and cast onto a glass or polymer carrier foil by being passed through a slit in the bottom of the reservoir. The sheet is then dried, punched into the required shapes, and sintered (Wersing, 1992; Plucknett, 1994; Schafer, 1993).

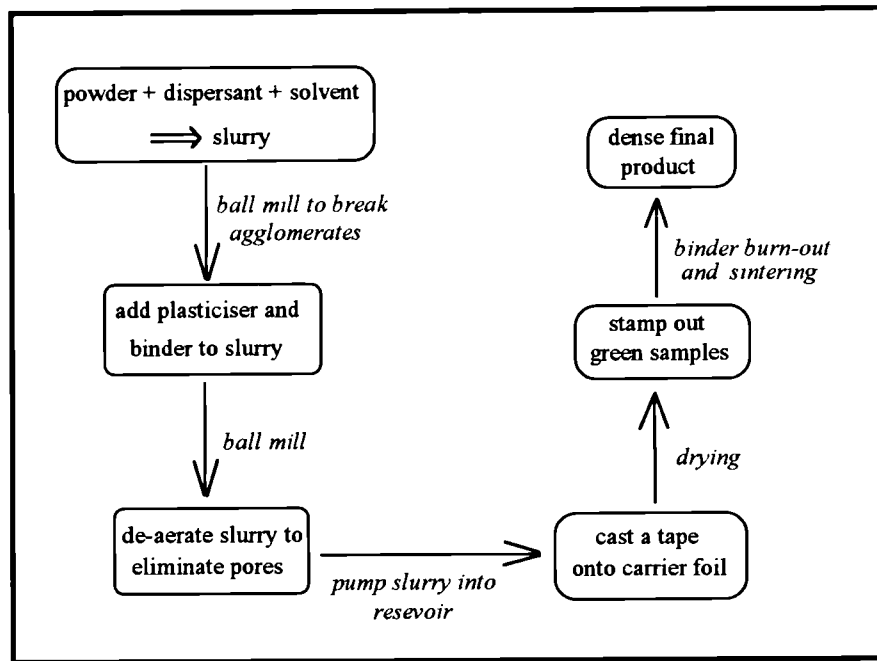


Figure (2.4) - diagram illustrating the tape-casting procedure.

The drying and sintering stages must be controlled carefully. During drying, the solvents evaporate from the slurry, to leave the sheet in the green state. If it is dried too fast, a density gradient may be set up through the material, that can lead to warpage (Plucknett, 1994). Also, it is important to ensure that all the binder is burnt out of the samples before sintering starts, or an organic residue will be left inside the samples. This involves heating them very slowly up to about 500°C and holding at this temperature for several hours. After this the samples can be sintered (Boch, 1991; Wersing, 1992).

2.2.1.(i) Properties of Tape-cast 8 mol % YSZ

There is a limited amount of data available concerning the mechanical properties of tape-cast 8 mol% YSZ produced by Kerafol for use as an electrolyte; the data are described in more detail in the relevant sections, but are summarised below in table (2.3). In addition, no data is available concerning the sccg or creep properties of this material.

Table (2.3) - summary of mechanical data of tape-cast 8 mol% YSZ (Scafe, 1994; Basu, 1993; Brocco, 1994).

Property	Value
Density	5.80 gcm ⁻³
Young's modulus	200 - 204 GPa
Flexure strength	156 - 248 MPa
Hardness	13 GPa
Fracture toughness	1.2 - 1.6 MNm ^{-3/2}

2.2.2 Tape-calendering

Another method of producing thin-films is by tape-calendering. The powder and organic binders are mixed together in a two-roll mill, which breaks down agglomerates and de-aerates the mixture, producing a plastic dough. This is then passed between two rollers, to produce the thin sheet from which samples are cut, dried, and sintered.

ICI developed a viscous processing route (British patent application number 5709598), which involves applying shear forces to the dough, via extrusion; this was shown to break down agglomerates much more successfully than only using the two-roll mill, with a consequent increase in fracture strength. Work performed on alumina showed that the strength doubled when using this route, from $\sim 300\text{MPa}$ to 760MPa , and the fracture initiating defects were reduced from $100\mu\text{m}$ to $\sim 40\mu\text{m}$ (Alford, 1987).

Although the intrinsic microstructural defects within tape-calendered material will be reduced by this technique, extrinsic defects can be introduced from the surface finish of the rollers, as the dough is passed through them. To minimise this, it is important that these rollers are kept clean and highly polished.

2.2.3 Sintering

During sintering the material densifies, as the powder particles are bonded together and the space between them is reduced by diffusion. Because diffusion follows the Arrhenius equation, the temperature at which sintering takes place will have a significant effect on the rate of densification. The time for which sintering occurs also affects the extent to which diffusion will proceed, and hence the quality of the final properties. Generally the sintering conditions are selected to compromise between residual porosity and grain growth (Kingery, 1976).

If any impurities are present in the powder they tend to segregate at the grain boundaries during sintering, forming a glassy phase. Such phases usually soften at lower temperatures than the rest of the material, and so are detrimental to the component's high temperature mechanical performance. Grain boundaries also tend to have a higher electrical resistivity than the bulk, especially if they contain impurities. Thus to optimise ionic conduction, the electrolyte should have fairly large, uniform grains, with as little impurity as possible at the grain boundaries.

2.3 Young's Modulus

2.3.1 Basic Theory

The elastic moduli measure the strain produced in a material by a given stress, in the absence of any non-elastic effects (Lee, 1994). The most important for this project is the Young's modulus, E , or stiffness, which is defined as the uniaxial stress, σ , required to produce unit strain, ϵ , in the same direction as the imposed stress, in the absence of any orthogonal constraints, i.e. it is a measure of a material's resistance to change in length when loaded in uniaxial tension. On a macroscale it is represented as:

$$E = \frac{\sigma}{\epsilon} \quad \text{Equation (2.2)}$$

The extension of the body is due to the extension of the atomic separations. The stronger the atomic bond, the higher the stress required to increase the spacing, leading to a higher E . On a microscale this is represented as:

$$E \propto \frac{d^2F}{ds^2} \quad \text{Equation (2.3)}$$

where F = interatomic force
 s = atomic separation

Thus materials with the highest Young's modulus values tend to be ceramics with strong covalent bonding. Also, because the bond strength varies with crystallographic direction, E will vary with crystallographic direction too. This effect is important when dealing with single crystals, but for polycrystals the grains are usually randomly oriented, and so the overall E is isotropic (Richerson, 1982; Lee, 1994).

A factor which affects E in polycrystals is porosity, since pores can be considered as a phase with zero E , and so will reduce the modulus. Usually 100% densification of a ceramic body is not achieved on sintering, so the final product will contain some porosity. Several equations have been proposed to show the effect of porosity on E , which take the general form shown in equation (2.4) (Morrell, 1985):

$$E = E_0 e^{-bV} \quad \text{Equation (2.4)}$$

where E_0 = E of fully dense material
 b = constant; function of Poisson's ratio, pore shape and distribution
 V = volume fraction of porosity

The dependence of E on grain size is only an indirect one, through the effect grain size and shape has on porosity (Lee, 1994).

E is also affected by temperature. As the temperature is increased the material expands, i.e. the atomic separation increases, so that the force required to separate the atoms further is reduced, and so E decreases. However, this has a small effect on the modulus of pure, single-phase materials, until additional high temperature processes begin to operate. Larger decreases in E are seen in impure materials at high temperatures, due to the softening of the impurity phases (Lee, 1994). Figure (2.5) illustrates the variation in E with temperature of several ceramic materials.

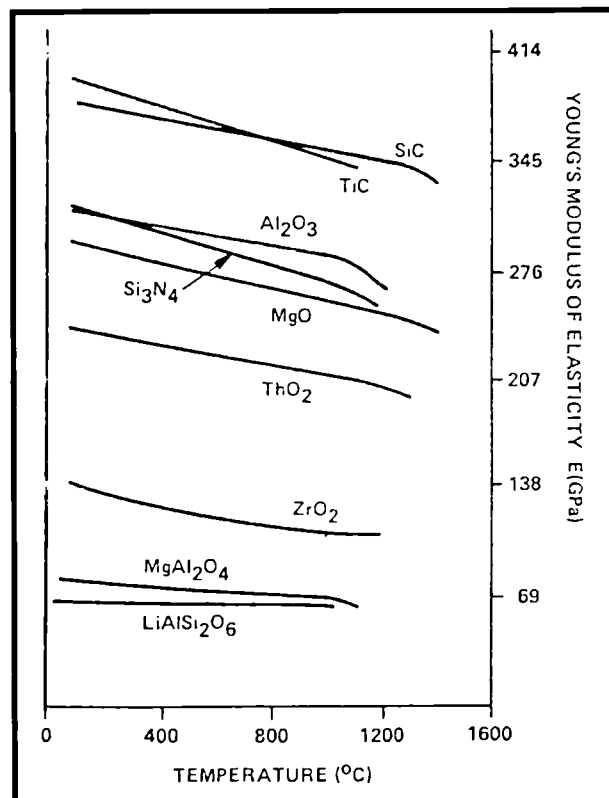


Figure (2.5) - comparing the change in E with temperature for various polycrystalline ceramics, including unstabilised zirconia (Richerson, 1982).

2.3.2 Measurement of Young's Modulus

Three well established techniques were used in the project to measure E .

2.3.2.(i) Static Technique

The static methods involve deforming the sample and measuring the induced strain, e.g. by using strain gauges on a specimen in pure tension or compression, or by measuring the force versus deflection plot of a flexure test. However there are several problems associated with these techniques:

- often large specimens are required
- there is a risk of permanent damage to the sample
- difficult to adapt to high temperatures
- if using the force versus deflection (F/δ) data from a flexure test, unless the compliance of the apparatus is known, the deformation of the fixtures will be incorporated into the F/δ curve, thus introducing errors in the measurement of sample deflection.

In addition, internal friction, which measures the absorption of energy within the structure, hence indicating which deformation processes are occurring, cannot be measured using this technique (Ponton, 1987; Richerson, 1982).

2.3.2.(ii) *Dynamic Technique*

The dynamic method measures the resonance of the material. The sample is supported at its nodal points and made to vibrate at its fundamental frequency, or at overtones of this. The frequency is measured and used to calculate E , since the resonant frequency is a function of the sample dimensions, mass, and E . The vibration is induced in different ways.

The technique developed by Forster, 1937, directs sound waves of a given frequency at a suspended sample, and detects the resultant forced vibration. The frequency of the waves is adjusted until the fundamental resonant frequency of the sample is found - shown by the increase in the detected amplitude - and this used to calculate E .

The 'GrindoSonic' technique uses a mechanical impulse to cause the sample to vibrate at its natural frequency. The frequency of vibration is detected using a piezoelectric transducer in contact with the sample, or a microphone, and E calculated from the natural frequency, sample dimensions and mass using equations developed by Spinner and Tefft, 1961.

2.3.2.(iii) *'Velocity of Sound' Technique*

The velocity at which sound passes through a material is dependent on the material's density, Poisson's ratio, and Young's modulus. By attaching two piezoelectric transducers to either side of a sample, a pulse of sound can be sent through the sample from one face, and detected at the opposite face. By measuring the time taken for the pulse to pass through the sample, the velocity at which the sound travelled in the material can be calculated. E can then be found from equation (2.5) (Sailor, 1982).

$$E = \rho v^2 \quad \text{Equation (2.5)}$$

where ρ = material density
 v = longitudinal velocity of sound in material

The main difficulty with this method is due to loss in the sound energy, either because of poor contact between the sample and transducers, or attenuation. This effect is due to the sound energy being absorbed by the material, and scattered at defects; the amplitude and intensity of the received pulse decreases with sample length, so attenuation can be reduced by using smaller samples. Additional complications can arise through a mixture of waves being transmitted and detected, e.g. if sound travels as a surface wave along the edge of the sample, as well as a longitudinal wave through the bulk of the sample (Bhardwaj, 1986; Leatherland, 1995).

2.3.3 Review of Young's Modulus Data for Zirconia

The E behaviour of a range of zirconia compositions, and over a range of temperatures, is presented below, and summarised in table (2.4).

The room temperature modulus of single and polycrystals has been shown to vary only slightly with yttria content, with the value for polycrystals increasing by ~5% within a composition range of 2 - 25 mol% yttria stabiliser (Ingel, 1988). E for a single crystal of 13 mol% YSZ (cubic) is given by Green, 1989, as 233GPa.

Scafe, 1994, improved Forster's technique to test thin samples, using laser to detect the amplitude of vibration. The modulus of 8 mol% material produced by Kerafol, of thickness 150 μ m and 280 μ m, was tested at room temperature with this apparatus, and a value of 204GPa obtained. This is in good agreement with the E value for 8 mol% Kerafol material quoted by Basu, 1993, of 200GPa.

The effect of temperature on Young's modulus of unstabilised zirconia is shown in figure (2.5), where it can be seen that E decreases gradually from ~ 140 to ~ 108GPa over a temperature increase of 1000°C. The variation with temperature of the modulus of yttria, which has a cubic structure, was studied using Forster's technique by Marlowe, 1965, who found that E decreased linearly by ~ 16% over the temperature range of room temperature to 1400°C, but above this temperature dropped quite sharply, which was attributed to the presence of impurities. Marlowe (1965) also measured the internal friction (IF) of yttria, and observed small peaks at ~ 200°C and at 850°C; there was no

other response until 1350°C, when the IF response rose sharply, which corresponds to the sharp drop in modulus.

Chan, 1991, obtained the elastic constants of a single crystal of monoclinic zirconia at elevated temperatures using the 'velocity of sound' technique; E can be calculated from these constants using equation (2.6), (Nye, 1964), and is found to decrease gradually by ~ 15% over a temperature range of 1000°C.

$$E = \frac{(2C_{12} + C_{11})(C_{11} - C_{12})}{C_{12} + C_{11}} \quad \text{Equation (2.6)}$$

where C_{11}, C_{12} = elastic constants of the material

Wachtman, 1959, studied several materials using Forster's technique, including polycrystalline PSZ stabilised with 10 mol% CaO. For this material he found that the modulus decreased by ~ 20% over 1000°C, but that two thirds of this decrease took place within the first 500°C rise, and after this the drop in E was more gradual. Above 1000°C, the modulus began to decrease rapidly again - this is believed to be the result of impurity phases softening and the onset of grains sliding. Shimada, 1984, also studied PSZ, stabilised with 3 mol% yttria, using the same technique up to 650°C, and found a rapid decrease in E, ~ 14%, over the initial 250°C rise in temperature, which also coincided with a peak in internal friction at 200°C. From 250°C - 650°C, the decrease was more gradual, ~ 6%, and linear. The same curve was followed upon heating and cooling.

The presence of impurities does not explain the relatively large, non-linear decrease at the lower temperatures. In Wachtman's work (1959), using Ca-PSZ, the composition should correspond to a stable structure up to 900°C (Duwez, 1952), so the changes can not be due to a transformation occurring. Shimada attributed the internal friction peak at 200°C to dislocation movement, induced by the high frequency being used, but gave no suggestions as to the non-linear response of E with temperature found. As yet, there has been no realistic explanation for this phenomenon.

Buckley, 1967, measured the modulus of fully (8.8 mol%) and partially (4.7 and 3.5 mol%) stabilised YSZ between room temperature and 950°C using a resonance technique. As the temperature increased, the modulus of all the compositions decreased, dropping 14% in a linear fashion for the 8.8 mol% composition and 22% for the 4.7 mol%, although this dropped by 17% over the initial 565°C. The behaviour of the 3.5 mol% was different, decreasing linearly by 18% up to 620°C, but then more than doubling as the temperature rose to 950°C. On cooling, the material showed a hysteresis,

before returning to a value 9% below the original room temperature value. The author also tested Ca-PSZ (6.4 and 4.3 mol%), which mirrored the YSZ behaviour. E of both materials decreased as temperature increased up to 565°C, but whereas the 6.4 mol% composition continued to drop up to 925°C (with an overall decrease of 22%) and on cooling followed the same curve back to the room temperature value, E of the 3.5 sample almost doubled by 925°C, and again showed a hysteresis on cooling, with the final value being about 25% lower than the initial room temperature value.

The author stated the behaviour of the compositions with less stabiliser was due to a transformation - presumably the author refers to the monoclinic / tetragonal transformation, although from the phase diagram this seems implausible; the border between the monoclinic/tetragonal and cubic/tetragonal phase fields occurs at $\sim 500^\circ\text{C}$ for YSZ, and 900°C for CaSZ, at which temperatures no abnormalities in the E versus temperature curves were detected. Also, if this were the reason, the PSZ materials which contained more stabiliser would also be expected to display similar behaviour. The E values presented for YSZ at room temperature ranged from 76GPa to 155GPa, which is a large spread for material of similar compositions, and are much lower than generally accepted data; this was attributed to differences in density, but does cast doubts on the reliability of the data.

Kandil, 1984, used the 'velocity of sound' technique to measure the elastic constants of single crystals of FSZ, with yttria compositions ranging from 8.1 - 17.9 mol%. Using equation (2.6), E was calculated from these constants, and shown to decrease linearly with temperature in all cases ($\sim 10\%$ over the range of room temperature up to 700°C) except for the sample with the lowest yttria content. This initially showed a drop in E of 15% up to $\sim 450^\circ\text{C}$, but then rose by 24% as the temperature increased to 700°C . Subsequent runs over the same temperature range no longer gave reproducible results and this material was believed to be structurally unstable - but no XRD analysis was performed to confirm whether a change in the structure had occurred.

The results from Kandil (1984) on a single crystal of 8.1 mol% YSZ, and from Buckley (1967) on 3.5 mol% YSZ do follow the same pattern, but do not fit with the additional results of Buckley (1967) on material with higher yttria contents, which showed only a decrease in E , of 14 - 22%, over a temperature increase of 950°C . Buckley's (1967) results on 3.5 mol% YSZ also do not agree with those of Shimada (1984) using 3 mol% YSZ, who found only a decrease in modulus between room temperature and 650°C , and no hysteresis.

Young's modulus and internal friction of Y-TZP were monitored by Weller, 1986, and Lekki, 1992, at temperatures up to 1200°C . Both found a peak in internal friction at

around 200°C, and also that the modulus decreased rapidly, by ~ 10% at low temperatures, e.g. between room temperature and 150°C for Lakki (1993). After this region the modulus decreased linearly until higher temperatures, ~1100°C, where the softening of impurities caused it to drop more rapidly. Weller (1986) proposed that the effect around 200°C was due to dipoles (of $(Y_z V_o^{**})$) reorienting, under the influence of a mechanical and / or electric field; at higher temperatures these dipoles are able to dissociate.

Table (2.4) - summary of the literature of E for single and polycrystalline zirconia, over a range of compositions and temperatures.

Author	Composition	Temperature range	E behaviour
Scafe, 1994; Basu, 1993	8 mol% YSZ; tape-cast	RT	200-204 GPa
Green, 1989	13 mol% YSZ single crystal	RT	233 GPa
Ingel, 1988	2-25 mol% YSZ	RT	varies by ~ 5%
Chan, 1991	monoclinic single crystal	RT - 1000°C	decreases gradually by 15%
Richerson, 1982	monoclinic polycrystalline	RT - 1000°C	decreases gradually by 22%
Weller, 1986; Lakki, 1993	2-3 mol% Y-TZP	RT - 1300°C	decreases by 10% up to 150°C, more gradually above this temperature
Wachtman, 1959	Ca-PSZ	RT - 1000°C	decreases by 14% up to 500°C, more gradually above this temperature
Shimada, 1984	3 mol% Y-PSZ	RT - 650°C	decreases by 14% up to 250°C, more gradually above this temperature
Buckley, 1967	3.5 mol% Y-PSZ	RT - 950°C	- hysteresis behaviour
	4.7 mol% Y-PSZ	RT - 950°C	- 17% decrease up to 565°C
	8.8 mol% Y-FSZ	RT - 950°C	- 14% gradual decrease
Kandil, 1984	8.1 mol% YSZ single crystal	RT - 700°C	- hysteresis behaviour
	11-18 mol% YSZ single crystal	RT - 700°C	- linear decrease by 10%

Thus the conclusions which can be drawn from the literature are follows:

- the room temperature E of Kerafol samples, 8 mol% YSZ, ~ 200GPa
- E of pure zirconia and pure yttria decreases linearly with temperature
- the modulus of impure PSZ drops rapidly at temperatures above 1000°C

- E of TZP and PSZ shows a change in slope with temperature at around 200 - 400°C, accompanied by a sudden rise in IF. Proposals to explain this include a phase transformation, dislocation motion, dipole activity
- modulus of FSZ polycrystals decreases linearly with temperature, as does that for single crystals of FSZ at high (>11 mol%) yttria content. Reports differ as to whether this decrease is followed by a dramatic increase.

2.4 Strength

2.4.1 Failure Stress

Strength is a measure of the stress necessary to plastically deform or break a sample, with the latter usually being the most relevant for ceramics. The maximum theoretical strength of a body (that of separating rows of atoms) is scarcely ever achieved in practice, which is attributed to the presence of defects within the body. In a ceramic failure usually occurs as a crack propagates through the sample, and the body falls apart. Griffith determined an energy criterion for fracture to take place (crack propagation can occur if the energy required to form an additional crack of size da can just be delivered by the system), and from this calculated the applied stress required to cause fracture in a body. This was termed the Griffith stress, σ_{Gr} , and is given in equation (2.7) (Broek, 1986):

$$\sigma_{Gr} = \sqrt{\frac{2\gamma E}{\pi a}} \quad \text{Equation (2.7)}$$

where γ = surface energy
 E = Young's modulus
 $2a$ = crack length

Ceramics tend to fail catastrophically, which means that as soon as the crack starts to propagate it continues rapidly through the sample, even though the applied stress may only be at σ_{Gr} . This is because stress is concentrated at crack tips; the actual stress experienced at the tip of a crack was calculated by Inglis, 1913, as shown in equation (2.8):

$$\sigma_{tip} = 2\sigma_{app} \sqrt{\frac{c}{\rho}} \quad \text{Equation (2.8)}$$

where ρ = the radius of curvature at crack tip
 c = crack length

In ceramics, unless some form of crack blunting process is in operation, crack tips are usually so sharp due to the strong directional bonding that ρ is taken at its minimum value of $a_o/2$, where a_o is the mean interatomic distance. This means that σ_{tip} is always greater than σ_{app} , and so the crack propagation will always lead to catastrophic failure when σ_{Gr} is applied (Broek, 1986).

Because of this stress concentration the strength of ceramics is strongly dependent on the defects present, and also on their orientation to the applied stress, which means that the test technique will affect the strength value obtained. Under compression, defects tend to close up. Under tension they are opened up and experience stress at their tips; this provides much more severe testing conditions than the compression test. However, it is difficult to prepare ceramic samples for a pure tensile test; a more convenient technique is the flexure test (Fessler, 1984).

2.4.2 Flexure test

In this test the sample is bent/flexed, so that the top half is put in compression, and the bottom half in tension. This by-passes the need for gripping and complicated sample preparation. There is a stress gradient through the sample thickness, from maximum compression on the upper surface to maximum tension on the lower surface, as shown in figure (2.6(a)). Thus the flaws which are subjected to the greatest tensile stress will be those at or close to the lower surface - hence the flexure strength reflects the surface flaw population (Evans, 1982; Ashby, 1991; Fessler, 1984).

With all flexure tests, problems arise due to friction and misalignment, which can introduce errors in the calculated strength of up to 10%. Friction is minimised by using rollers or balls to support the samples rather than fixed supports, and misalignment can be corrected for by suitable design of the rig (Shetty, 1981, 1983; de With, 1989; Scholten, 1992).

Two types of flexure test were used in this project, uniaxial and biaxial.

2.4.2. (i) Uniaxial Flexure

The uniaxial test flexes bars in a 3 or 4-point loading configuration, shown in figure (2.6 (b) and (c)). Because the force is applied uniaxially, the orientation of the flaws in the sample (with respect to the applied load) will affect the breaking stress - the 'worst' flaw may not be subjected to the maximum stress, and the strength be overestimated as a result. In the 3-point configuration, only the line of material that is directly underneath the applied roller will experience the maximum stress, whereas in the 4-point configuration it is the area between the inner rollers that is under the maximum tensile stress. Thus the 4-point bend test gives a more accurate strength value, because there is a higher probability of stressing worse flaws in this larger region (Godfrey, 1986; Shetty, 1983). The standard equations used to calculate strength from these flexure geometries are given in equation (2.9 (a) and (b)) for 3 and 4-point-bend respectively.

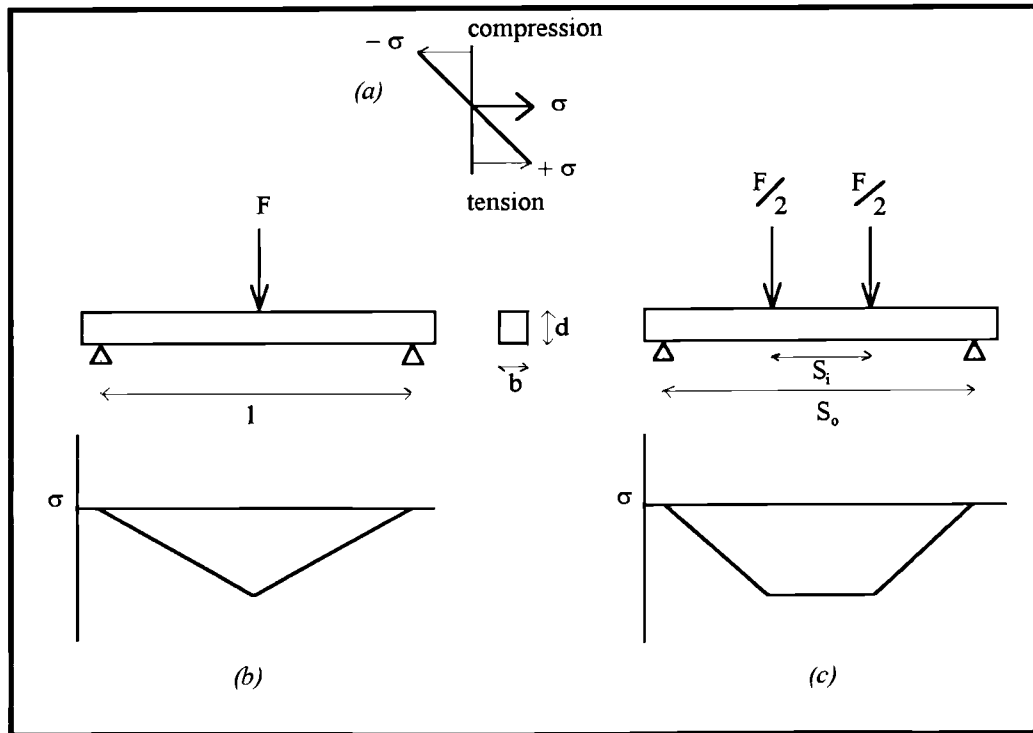


Figure (2.6) - diagram illustrating the uniaxial flexure test geometries and resulting stress distribution through sample thickness and along the tensile face of the sample. (a) - change in stress through thickness; (b) - 3-point-bend; (c) - 4-point-bend (Metals Handbook, 1985).

$$\sigma = \frac{3Fl}{2bd^2} \quad \text{Equation (2.9(a))}$$

$$\sigma = \frac{3(S_o - S_i)F}{2bd^2} \quad \text{Equation (2.9(b))}$$

where F = applied load

all other dimensions are given in figure (2.6).

2.4.2.(ii) Biaxial Flexure

Biaxial flexure was chosen to determine the strength of the electrolyte for two reasons; it was considered to reflect service conditions more accurately than other flexure tests, and it was also the most convenient test to use with samples as thin as those which were provided.

In biaxial flexure all the flaws within the loaded region are under the same stress, and so the worst defect within this area will cause failure. These loading conditions are more severe than with the uniaxial flexure tests, but are more similar to those experienced by the component in service; hence the failure strength is lower, but more relevant, than the uniaxial values (Godfrey, 1986; Shetty, 1983).

The tests involves supporting a specimen on a circular ring, and applying a load in the centre, so that the specimen is flexed in two directions, rather than just one. Radial and tangential stresses are produced, which are illustrated in figure (2.7) (Greiner, 1991):

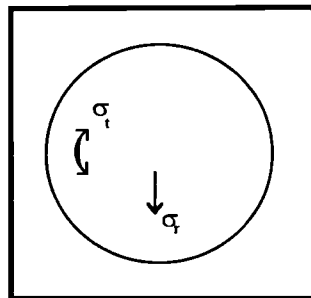


Figure (2.7) - diagram illustrating the radial, σ_r , and tangential, σ_t , stresses produced during biaxial flexure.

The stress distribution produced in a biaxial test can be considered in two parts, shown in figure (2.8). There is a central zone where the stress is constant and maximum in all directions - this is the condition of true biaxial flexure. Outside this region the radial and tangential stresses decrease, but non-linearly, so true biaxial flexure is no longer observed (Shetty, 1982; Greiner, 1991).

From figure (2.8) it can be seen that the stress is almost zero at the outer region of the sample. Hence the flaws produced at the sample edges during manufacture will experience a much lower stress than those at the centre, and so will not contribute to failure; fracture is always expected to originate from the central zone, from a micro structural defect. This means that no special edge preparation of the 150 μ m thick disc samples used in the project is required (Shetty, 1983; Kleinlein, 1993).

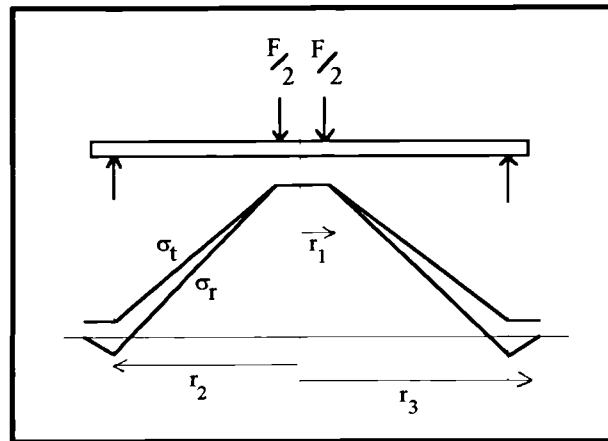


Figure (2.8) - diagram illustrating the stress distribution along the tensile face of a sample during biaxial flexure (DIN 52 292, 1984).

Two biaxial flexure geometries were used in the project, ball-on-ring and ring-on-ring, which are shown in figure (2.9). The standard equations used to calculate the fracture strength from them are given in equation (2.10(a) and (b)) for ball-on-ring and ring-on-ring respectively (de With, 1989; DIN 52 292, 1984).

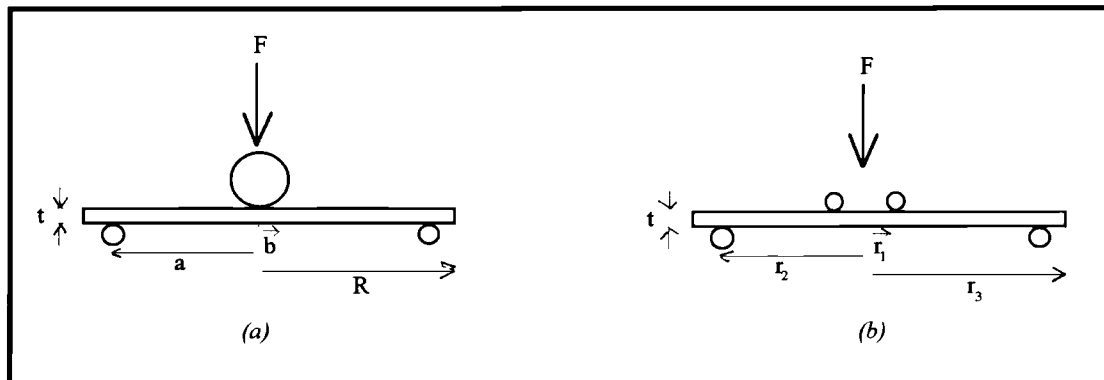


Figure (2.9) - diagram illustrating the biaxial flexure test geometries. (a) - ball-on-ring; (b) - ring-on-ring.

$$\sigma_r = \sigma_t = \sigma_f = \frac{3F(1+\nu)}{4\pi t^2} \left\{ 1 + 2 \ln \frac{a}{b} \left[\frac{(1-\nu)a^2}{(1+\nu)R^2} \right] \left[1 - \frac{b^2}{2a^2} \right] \right\} \quad \text{Equation (2.10(a))}$$

$$\sigma_r = \sigma_t = \sigma_f = \frac{3F(1+\nu)}{2\pi t^2} \left\{ \ln \frac{r_2}{r_1} + \frac{(1-\nu)(r_2^2 - r_1^2)}{(1+\nu)2r_3^2} \right\} \quad \text{Equation (2.10(b))}$$

where F = applied force

ν = Poisson's ratio

all other dimensions are given in figure (2.9)

The ball-on-ring test consists of pushing a ball into the centre of the sample which is supported on a ring. It is a simpler set-up than the ring-on-ring test, and friction between the sample and rig is less (Shetty, 1981, 1983). However, there is confusion over what value to use for the loading radius, since point contact with the sample is lost as soon as the specimen starts to bend, and the area of contact will increase as the test proceeds (Ritter, 1980). The accepted value for b is one third of the sample thickness (Shetty, 1981; de With, 1989); however, these authors were using samples which were 2mm or more in thickness, in order to ensure that the deflection was not so large that this b value would be exceeded. With the thin electrolyte material the deflection will be much greater, so this b may not be applicable.

However, using $b = t/3$ for samples 2mm thick may not even be acceptable; Shetty (1981, 1983) compared results from uniaxial and biaxial tests, on samples with comparable areas of maximum stress, and found the biaxially tested samples were stronger. This result is surprising, since the biaxial flexure values would be expected to be lower, and suggests that the value taken for b was too small (Godfrey, 1986; Ritter, 1980).

Even if there were no doubts concerning the radius, the area subjected to the maximum stress would be fairly small - for a sample 150 μ m thick then only an area of radius 50 μ m will be subjected to the maximum stress. This small region would contain a statistically small number of flaws compared with other geometries, and so the ball-on-ring test was not used for the majority of the electrolyte strength tests in this project.

The ring-on-ring test consists of pushing two concentric rings into each other, and is accepted as the DIN standard for biaxial flexure (DIN 52 292, 1984). The advantages of using this geometry compared to the ball-on-ring are that the loading dimensions are all known, and the maximum stress acts over a much larger area.

A problem specific to the biaxial flexure of very thin samples arises due to the extent of the deflection. When the sample bends to over half its thickness, the stretching of the middle surface starts to become significant and must be included in the stress analysis (Hearn, 1985). (The stresses at the middle surface are termed 'membrane stresses'.) The DIN standard (1984) specifies sample and rig dimensions that ensure the deflection will not exceed half the sample thickness; the specified sample thickness is 3mm, but the samples to be used in this project were of the same thickness as the actual electrolyte, 150 μ m, and so the membrane stresses need to be accounted for.

With the introduction of the membrane stresses the neutral axis moves towards the upper surface, so that more of the sample is put in tension; since more of the sample is now 'carrying' the load, the sample stiffness appears to increase. Thus the relationship between applied load and resulting maximum stress becomes non-linear, as shown in figure (2.10), and the simple stress formula can no longer be applied. The deviation from linearity increases as the applied load is increased. The stress within the central zone is no longer constant, but the radial stresses are magnified under the load ring, leading to a stress concentration directly beneath the loading ring. Kao, 1971, showed that the magnitude of this concentration depended on the rig geometry, and was least when the ratio of the inner to outer rings, $r_1/r_2 = 0.2$, as shown in figure (2.11).

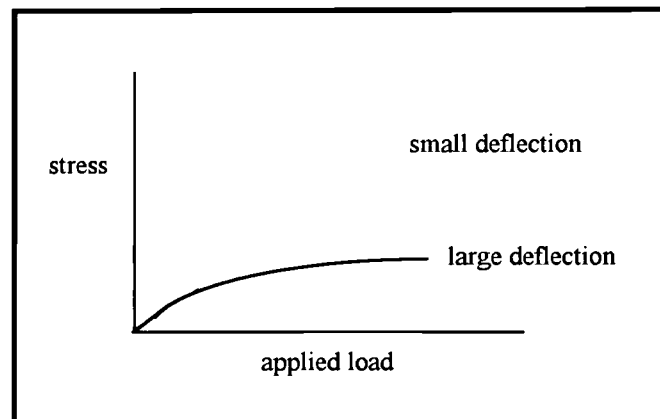


Figure (2.10) - diagram illustrating the non-linear relationship which develops between applied load and maximum stress due to increasing membrane stresses (Greiner, 1991).

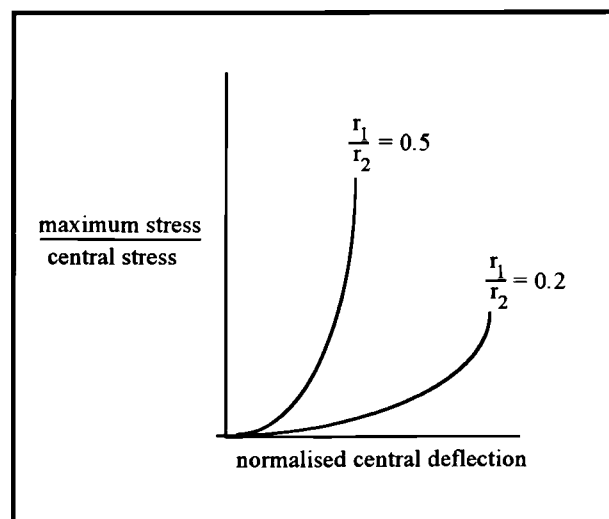


Figure (2.11) - diagram illustrating the effect of test-rig geometry on the magnitude of the stress concentration below the loading ring (Kao, 1971).

This stress concentration led to doubt being expressed as to whether the ring-on-ring test could be used as a strength test for thin specimens, because it meant that there was uncertainty in the load being taken to break the sample (de With, 1989; Ritter, 1980; Shetty, 1980). Shetty (1980) performed tests that revealed a magnification of up to 21% when comparing experimental to theoretical stress values, and claimed that the breaking stress could not be quantified accurately.

However, the work by Shetty (1980) was performed with an r_1/r_2 value of 0.5, which Kao (1971) had proved to be the geometry that would produce the greatest deviation, predicting errors of this proportion. Also, work by Keim, 1990, showed that it is possible to predict the extent of the deviation, and hence calculate the true breaking stress. Using finite element analysis (FEA), Keim (1990) plotted the predicted stress versus load and strain versus load curves for a test rig geometry of $r_1/r_2 = 0.2$, incorporating the membrane stress effect, and these curves were found to agree very well with experimental results obtained using strain gauges.

Using this stress analysis to provide accurate fracture stress values, the ring-on-ring test was considered the most stringent flexure test, and so used for the majority of the strength tests of the electrolyte material.

2.4.3 Fast fracture at room and high temperatures

When ceramics are tested under fast fracture at room temperature, they usually fail catastrophically. Grain boundaries and porosity can inhibit crack growth, but once the Griffith stress is attained, the crack propagates rapidly, in either a transgranular or intergranular fashion. Some ceramics have particularly effective strengthening mechanisms, e.g. the transformation toughening in tetragonal zirconia polycrystals, which has a strength up to 1200MPa, but this is not the case with FSZ, where a strength up to ~ 350MPa has been recorded (Green, 1989).

Ceramics tend to retain their strength up to higher temperatures than other materials (e.g. metals, polymers), making them suitable for high temperature applications. Processes such as slip, grain boundary sliding, and creep do occur, but these usually do not start to operate until $\sim 0.5T_m$ (where T_m is the melting point), which is above 1000°C for most ceramics (Morrell, 1985).

At these temperatures the defects which control strength at room temperature (fabrication and surface flaws) may no longer dominate the fracture processes, as other defects are introduced (such as cavities), or defects which have no effect at room

temperature become more significant. Probably the most significant defect for fast fracture at high temperature is the presence of impurities. Their effect can be quite damaging because they segregate at grain boundaries, creating a secondary phase which has a melting point that is often much lower than the bulk material. When this phase starts to soften, it may initially blunt crack tips, leading to a strength increase, but eventually its viscosity is reduced so much that the grains slide over each other and the component can no longer support any load. Obviously this form of failure will only be significant in polycrystals; in single crystals dislocations and slip manifest themselves at higher temperatures (Morrell, 1985; Brennan, 1982).

2.4.4 Review of Strength Data for Zirconia

Gut, 1994, compared the strength of tape-cast and calendered FSZ at room temperature using three different flexure techniques, and the results are summarised in table (2.5). The trend in the strengths is as would be expected, with the ring-on-ring flexure being the most severe test, and the 3-point-bend being the least. The tape-casting method is also shown to produce better mechanical properties than the calendering, although no microstructural data was presented to compare the two manufacturing techniques.

Table (2.5) - summary of strength data for tape-cast and calendered FSZ.

Processing route	Sample thickness	Strength, MPa		
		3-point-bend	4-point-bend	ring-on-ring
calendered	210 μ m	250	211	171
tape-cast	250 μ m	400	330	211

Basu, 1993, tested 130 μ m thick, 8 mol% YSZ samples made by Kerafol, using the ring-on-ring flexure test at room temperature and 1000°C. The strength at room temperature ranged from 156 - 248 MPa, whereas at 1000°C the strength was found to be 156 MPa. However, the high temperature value was calculated assuming that there was very little change in the Young's modulus; if this is not correct, the actual strength at high temperature could be lower than 156MPa.

The effect of defects and impurities on strength was demonstrated by Govila, 1991, who performed fast fracture tests on MgO-PSZ from room temperature up to 1300°C. The strength dropped from 680 MPa to 400 MPa over the temperature region where the amount of transformation toughening declined (between room temperature and $\sim$ 600°C), but then was constant up to 1000°C; above this temperature the strength dropped again, which was attributed to the softening of impurities. SEM examination of

the fracture faces showed that from room temperature up to 600°C the source of failure was surface defects, but above this temperature the fracture origin could not always be identified.

The other temperature effect will be the function of time at temperature, i.e. ageing. Data showing the effect of ageing on the mechanical properties of FSZ are limited, although from conductivity measurements no other phases have been seen to develop on holding FSZ at 1000°C for over a year (Schafer, 1993), and the self-diffusion is too slow for segregation of the Y^{3+} and Zr^{4+} to occur on a significant level. Gut (1994) also aged batches of tape-cast samples at 950°C for various times up to 1500 hours, and then broke them under fast fracture at room temperature; the Weibull strength remained constant, although the Weibull modulus dropped from 9 to 7 after the heat treatment.

2.5 Analysis of Data

The strength data was presented using a Weibull analysis, and so the strength of the sets under different testing conditions could be compared. In order to compare the significance of any differences in data, the student's t-test was used.

2.5.1 Weibull Analysis

When ceramic bodies are produced they contain a number of different types of flaws, each type ranging in size and shape, and this leads to a variation in strength within a batch of supposedly identical samples. Thus for ceramics there is no fixed failure strength, but the strength must be defined in terms of the probability that a sample will fail at a certain stress (Godfrey, 1986; Bergman, 1984).

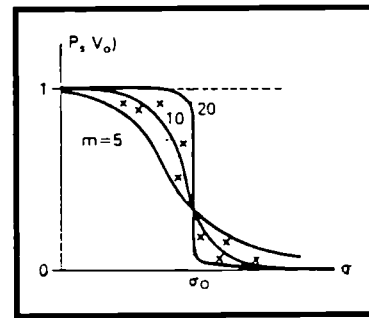
The most commonly used method of calculating this probability is by a Weibull analysis. This is based on the 'weakest-link' theory - that strength is controlled by the most serious flaw. The flaw which causes failure is not necessarily the largest, but the one which has the highest value of K_I at its tip; this depends on the position and orientation of the flaw with regards to the applied stress, as well as its dimensions (Bergman, 1994).

The survival probability, P_s , of a component of volume V under an applied tensile stress σ is given in equation (2.11) (Ashby, 1986):

$$P_s(V) = \exp \left[- \frac{V}{V_o} \left(\frac{\sigma - \sigma_u}{\sigma_o} \right)^m \right] \quad \text{Equation (2.11)}$$

where V_o = volume of each sample in test batch
 σ_u = threshold stress below which probability of failure is zero; for ceramics it is usually taken as 0
 σ_o = stress at which 37% of the batch survive
 m = Weibull modulus, which gives an indication of the scatter in strengths within the batch around the value σ_o ; a low value for m , as is the case in many ceramics, means the scatter is large - as illustrated in figure (2.12)

Figure (2.12) - diagram of the Weibull distribution function, illustrating the effect of m (Ashby, 1986).



Weibull data from different batches are compared using σ_o and m , which are obtained by rewriting equation (2.11) as

$$\ln \ln \frac{1}{P_s} = m \ln \sigma - m \ln \sigma_o \quad \text{Equation (2.12)}$$

and plotting $\ln \ln(1/P_s)$ against $\ln(\sigma)$, to give a Weibull plot. A straight line is fitted to the data, and m obtained from the gradient, and σ_o calculated from the point of intersection with the $\ln(\sigma)$ axis.

To plot equation (2.12), a probability function must be fitted to the strength data provided from the flexure tests. The data are arranged in ascending order of strength, and the j 'th result is assigned a cumulative probability of failure P_j . The functions used to calculate these probabilities are called 'estimators', and several have been proposed. Their accuracy depends on the number of samples, n , tested in the batch, with there being more consistency as n increases. However, testing vast quantities of samples is impractical; Sullivan, 1986, found that by using the estimator given in equation (2.13), consistent and accurate Weibull data could be obtained from 20 samples. With less than 20 samples, m tended to be underestimated.

$$P_j = \frac{j - 0.5}{n} \quad \text{Equation (2.13)}$$

Survival probability, P_s , is used in quality control, and is given by

$$P_s = 1 - P_f \quad \text{Equation (2.14)}$$

where P_f = failure probability

P_f is set at a fixed level, and the material produced must reach this standard. For the electrolyte, during operation, Siemens have set a probability of failure value of 10^{-6} , which means that a failure rate of 1 electrolyte per 10^6 is acceptable (Kleinlein, 1993).

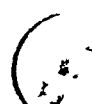
In order for the Weibull analysis to be applicable, several conditions concerning the failure of the samples must be fulfilled:

- the material must be homogeneous throughout its structure
- the type of defects within each sample must be the same; the defect population must be random, and there has to be a statistically significant number of defects in the stressed region
- only one failure mechanism must be in operation throughout the batch (Quinn, 1991).

These conditions mean that it is not really possible to predict high temperature behaviour from data found at room temperature, or to predict failure behaviour under compression from tensile data. It is also apparent that care must be exercised in using data from flexure tests for design purposes, for two reasons.

Firstly, the defect population within the test samples is often different to that in the component. It must be ensured that the samples are manufactured and prepared in the same way as the component, so that the microstructure, intrinsic, and extrinsic defects are the same. SEM analysis is essential to compare the flaws and failure modes of test samples and actual components in service.

Secondly, the stress distribution in a flexure test is not uniform throughout the sample; only a thin layer along one surface is subjected to the peak stress, and the stress distribution will also vary with position relative to the applied load. When calculating the design stress for a component, equation (2.11) needs to be integrated over the sample volume (Quinn, 1991; Ashby, 1986).

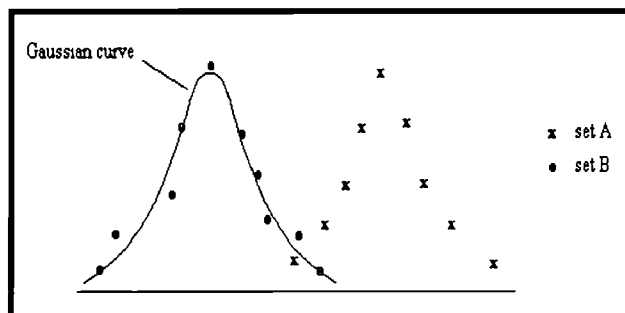


2.5.2 Student's T-test

This is a statistical method of stating how similar two sets of data are, and hence whether they can be considered as belonging to the same set.

The test assumes that both sets follow a normal, Gaussian, distribution, and compares their mean and standard deviation (S.D.) values, also taking into account the number of specimens tested, to see whether they lie (within the experimental scatter) on the same distribution curve. This is illustrated in figure (2.13), where two sets of data, A and B, are compared to a pre-existing Gaussian curve; set A has a similar S.D. value, but a greater mean value, than the standard set, and so cannot be considered the same, whereas set B has a similar S.D. and mean, and so is taken as being the same as the pre-existing set.

Figure (2.13) - diagram illustrating the comparison of two sets of data to a pre-existing standard set.



The test assumes that the Null-Hypothesis is applicable, i.e. that the two sets of data lie on the same distribution curve, and hence the specimens are actually from the same batch, and then calculates the probability that this assumption is true, using equation (2.15):

$$t = \frac{\bar{X} - \mu}{\frac{s}{\sqrt{n}}} \quad \text{Equation (2.15)}$$

where $\bar{X}$ = mean of tested batch
 μ = mean of standard batch
 s = standard deviation of tested batch
 n = number of samples in tested batch

The value of t obtained, along with the value for n , can be looked up in tables to give the probability of the assumption being true. A value $\leq 5\%$ is taken as being statistically significant, i.e. if the probability of the Null-Hypothesis being true is less than 5%, then the data came from different sets (Clarke, 1983).

2.5.3 F-test

This works on the same principle as the t-test, but can be used to compare several batches of data, rather than just two (Miller, 1988). The equations are more complicated than with the t-test, and are given in the appendix.

2.6 Fracture Toughness

The fracture toughness of a material is given as its resistance to the rapid propagation of a crack under stress through the material - i.e. the material's resistance to fracture. It can be quantified by the critical stress intensity factor, K_{IC} , or by the critical strain energy release rate, G_c .

2.6.1 Strain Energy Release Rate

In terms of energy, crack extension occurs when $G > R$, where R is crack resistance. This is expressed, in equation (2.16) (Broek, 1986), as:

$$-\frac{\partial G}{\partial a} = \frac{\partial F - U}{\partial a} > \frac{\partial W}{\partial a} \quad \text{Equation (2.16)}$$

where δF = work done by external force in creating crack extension δa
 U = elastic energy stored in plate of unit thickness
 δW = energy for crack formation

2.6.2 Stress Intensity Factor

As mentioned in section (2.4.1), the energy for fracture can be supplied by the application of a stress, which is concentrated at the crack tips. During a fracture test, the concentration of the stress will depend on its angle of application to the crack tip, and the crack shape, and also the type of test being used; these factors can be expressed in terms of K , the stress intensity factor. An example of the stress intensity factor at the tip of a sharp crack is given in equation (2.17):

$$K = \sigma Y \sqrt{c} \quad \text{Equation (2.17)}$$

where σ = far-field tensile stress applied perpendicular to the plane of the crack
 Y = geometrical factor for specimen and crack geometry
 c = crack length

There is some discrepancy in values given for K , since crack propagation can occur without causing immediate failure to the material. This is termed sub-critical, or slow, crack-growth, and will be dealt with in section (2.7). The critical stress intensity factor, K_{Ic} , is the stress intensity value at which catastrophic (rapid) crack propagation occurs, and is a material property. This is the value which should be quoted for fracture toughness (Morrell, 1985).

There are three different modes in which a crack can be propagated, termed 1, 2, and 3. K_{Ic} designates the stress intensity factor for mode 1, which concerns crack opening, as shown in figure (2.14), and it is this parameter which will be dealt with in this section.

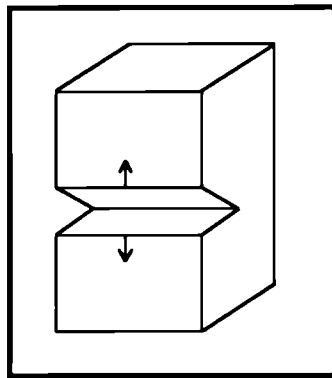


Figure (2.14) - diagram illustrating mode 1 crack propagation (Broek, 1986).

Although K_{Ic} is a material parameter, it is found that the value obtained during a test does vary, depending on which test technique is being used. Each technique uses a different sample and loading geometry and so generates a different stress field at the crack tip; this field may alter with the change in ratio of crack length to sample thickness (Morrell, 1985).

Four techniques were used to study the toughness of FSZ in this project - single edge notched beam (SENB), double torsion (DT), measurement of post-indent crack lengths, and indentation strength in bending (ISB). Each method involves inserting an artificial crack into the sample, in order that the conditions at the source of fracture can be controlled - in terms of its position in relation to the applied stress, and to the flaw size and shape.

2.6.2.(i) SENB Test

This technique is probably the simplest in terms of sample preparation and technique. The artificial crack is a notch cut into one edge of a bar, which is then fractured under 3- or 4-point-bend loading and K_{Ic} is calculated from the fracture load and sample dimensions; the 3-point-bend apparatus is shown in figure (2.15), and K_{Ic} is found using equation (2.18) (Anderson, 1990):

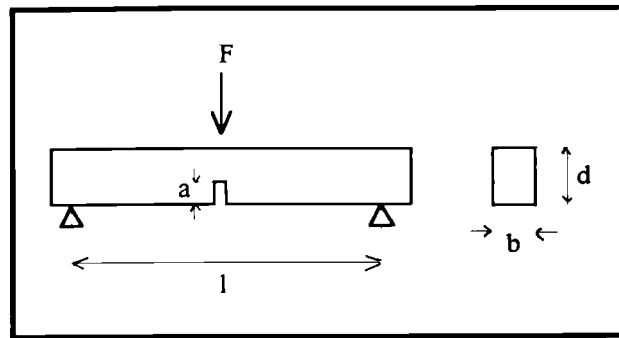


Figure (2.15) - diagram showing the SENB test and sample dimensions.

$$K_{Ic} = \frac{3P_f l Y \sqrt{a}}{2bd^2} \quad \text{Equation (2.18)}$$

where P_f = fracture load
 Y = calibration factor, which is function of geometry
 and all other terms are defined in figure (2.15)

The insertion of the notch can affect the results. Since ceramics in service tend to contain and fail from atomically sharp cracks, the notch also needs to be this sharp if this test is to give a realistic K_{Ic} value. However, Ponton, 1987, showed that if the notch-root width was less than 0.1mm, the resultant K_{Ic} could be considered as if found from using an atomically sharp crack. Dagleish, 1980, found that inserting a notch with a 0.3mm wide saw blade actually produced damage, with sharp cracks propagating into the sample from the notch; this meant that the notch was sharp but that 'a' was underestimated in the calculation, resulting in a lower value for K_{Ic} . Annealing samples prior to testing helped to reduce the damage, and consequently also the sharpness of the crack.

Dagleish (1980) also found, using acoustic emission and dye penetrants, that a limited amount of sub-critical crack growth (sccg) often occurs prior to failure during testing, which again means that the calculated K_{Ic} is too low. The true value of 'a' was ascertained from SEM examination and when this value was used, K_{Ic} was found to rise

by 3-12%. However, sccg can be minimised by using a fast loading rate, and if the force versus deflection graph is linear the effect of sccg is usually considered negligible.

2.6.2.(ii) DT Test

This geometry tests samples in the form of plates, and is shown in figure (2.16). The sample is supported on parallel rollers and loaded using a point contact on a notch at one edge; the crack propagates from this notch through the material. Often the sample is grooved down the centre, to guide the propagating crack in a straight direction; without this groove the sample must be aligned extremely carefully, otherwise the crack deviates towards the side of the specimen.

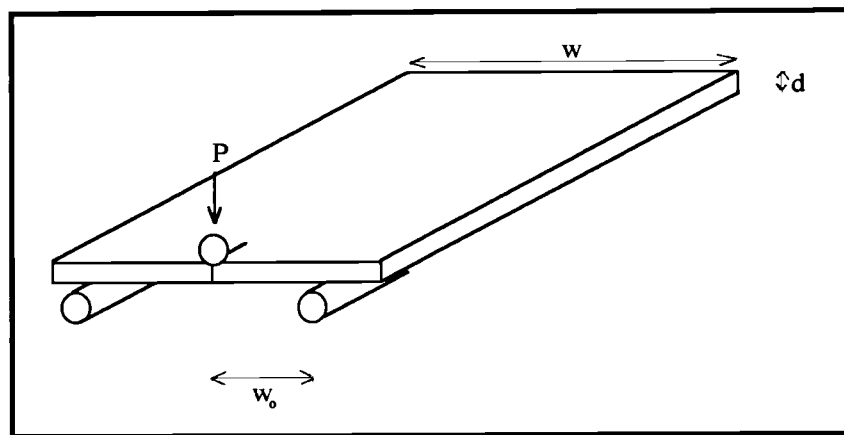


Figure (2.16) - diagram showing the DT test and sample dimensions.

K_I is calculated using equation (2.19) (Davidge, 1979), where the terms are defined as shown in figure (2.16).

$$K_I = \sqrt{12(1+\nu)} \frac{Pw}{\sqrt{wd^2}} \quad \text{Equation (2.19)}$$

From equation (2.19) it can be seen that K is independent of the crack length; this means that K is constant over the region of sample in front of the crack, so the crack propagates through the material in a stable manner (Lawn, 1975). Because the crack growth is stable, the DT test is particularly useful for obtaining crack velocity versus K_I curves.

The SENB and DT tests use macroscopic cracks ($>100\mu\text{m}$), which can yield a K_{Ic} result that is greater than that found using much smaller cracks (Bleise, 1994; Dransmann, 1994). Cracks of this size are not typical of the type of flaw present in the electrolyte material (it would fail), so the K_{Ic} found from these tests may not be applicable to the actual electrolyte. Thus another technique was needed, where K_{Ic} from 'natural' sized

flaws could be found and that could be used on samples 150µm thick. The indentation-based tests are two such techniques.

6.2.2.(iii) Indentation Test

The indentation test is a very simple technique, which requires only a small amount of material, and is used to determine hardness. The Vickers hardness test involves pushing a diamond pyramid into the sample surface, which on removal leaves an impression of itself - the indent. The size of the indent is varied by using different loads to push the diamond into the surface, and the material hardness is calculated from this load and the indent dimensions.

Often cracks are produced from the corners of the indent. As the diamond is pushed into the surface both elastic and plastic stresses are generated. When the diamond is removed, the compressive, elastic stresses are also removed, and the cracks, which had been constrained, are able to grow under the influence of the residual tensile stresses (Anstis, 1981).

Different crack systems can be induced from the indentation, which are shown in figure (2.17). They comprise of radial cracks, which grow along the sample surface; median or Palmquist cracks, which grow vertically below the surface; and lateral cracks, which spread horizontally below the surface, away from the indent (Ponton, 1989(a)).

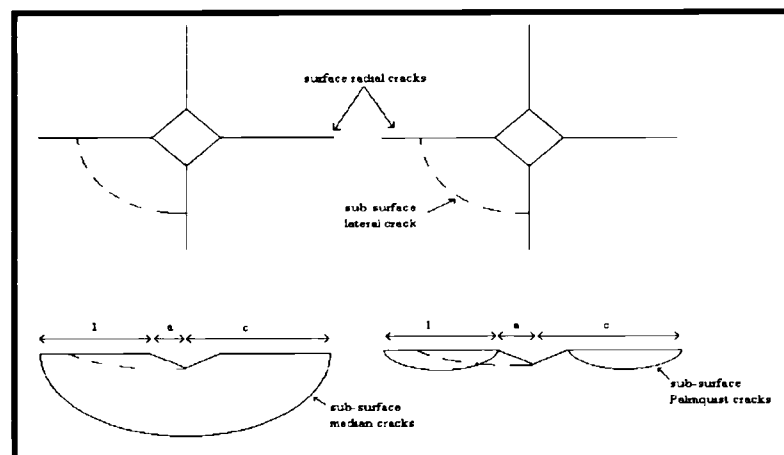


Figure (2.17) - diagram illustrating the crack systems which may be produced during an indentation test.

The K_{Ic} is an inverse function of the crack lengths, and many equations are available in the literature to calculate it from measurements of the indent size and radial crack lengths; some of these equations are based on a particular crack system, such as the

Palmquist cracks. Most of the equations can be used to rank the toughness of different materials successfully, although they do not always give the same values. These equations have been reviewed by Ponton, 1989(b), who suggested that one of the most generally applicable is equation (2.20):

$$K = 0.0363 \left(\frac{E}{H_v} \right)^{0.4} \left(\frac{P}{a^{1.5}} \right) \left(\frac{a}{c} \right)^{1.56} \quad \text{Equation (2.20)}$$

where E = Young's modulus of sample
 H_v = hardness of sample
 P = indent load
 $2a$ = length of indent diagonal
 $2c$ = length of crack produced from indent

However, it has generally been concluded that large errors can be associated with K_{Ic} measured by this method, mostly due to inaccuracies in measuring the correct crack lengths within the microstructure. Also it is only possible to be sure of the crack system in operation, and hence which set of equations to apply, by sectioning the samples (rather than assuming the crack system from the indent load used or the a/c ratio produced); often if lateral cracking is present it will affect the stress field, and sometimes actually break through the sample surface, disfiguring the crack patterns (Ponton, 1989(b); Jones, 1987). Any stresses already present in the sample surface prior to indenting will also affect the crack extension (Chantikul, 1981; Antis, 1981), and in addition, Ponton (1989(b)) recommended that the sample thickness should be at least 10 times greater than $2c$, to avoid any interaction of the stress field from the indentation with the lower surface of the sample. All these factors conspire to there being the potential for an error in the toughness of up to 30% (Morrell, 1985).

2.6.2.(iv) ISB Test

A way to overcome the inaccuracies of the post-indent crack data is by using the ISB test. This uses the radial crack from an indent as the dominant flaw in a sample, which is then fractured in a strength test. The stress intensity factor for crack extension, K_{ext} , is given by K_{app} from the applied stress and K_{res} from the residual indentation stress field, whereas resistance to crack extension from the microstructure is given by K_{mic} , as illustrated in equation (2.21) (Cook, 1985; Chen, 1996):

$$K_{ext} = \frac{\chi P}{c^{3/2}} + \psi \sigma_f \sqrt{c} \quad \text{Equation (2.21(a))}$$

$$K_{mic} = K_c^\infty - \frac{Q}{c^{3/2}} \quad \text{Equation (2.21(b))}$$

where χ = an elastic parameter which relates the elastic and plastic processes that occur during indentation
 P = indent load
 c = crack length at point of fracture
 ψ = crack geometrical term
 σ_f = fracture stress
 K_c^∞ = K at infinite crack length (K_{lc})
 Q = microstructural effect

Unstable crack propagation occurs when $K_{ext} \geq K_{mic}$, i.e. the critical stress intensity factor is given by equation (2.22):

$$K_c^\infty = K_{app} + K_{res} + \frac{Q}{c^{3/2}} \quad \text{Equation (2.22)}$$

The unstable crack propagation occurs at a certain crack length, c_m , which Marshall, 1979, found to be:

$$c_m = \left[\frac{4\chi(P + P^*)}{K_c^\infty} \right]^{2/3} \quad \text{Equation (2.23)}$$

where $P^* = \frac{Q}{\chi}$

Using this value of c_m , Cook (1985) rearranged equation (2.22) to express fracture stress in terms of indent load, as shown in equation (2.24):

$$\sigma_f = \frac{3K_{lc}^{4/3}}{4^{1/3} \psi \chi^{1/3} (P + P^*)^{1/3}} \quad \text{Equation (2.24)}$$

It is found that two regimes are described. For small cracks, less than c_m , χP^* is much greater than χP , and the strength no longer varies in a linear manner with indent load, but is controlled by the microstructure. For cracks larger than c_m , χP^* is insignificant, and there is a linear dependence between σ_f and P . A graph of log (stress) versus log

(indent load) should give a straight line, of gradient $-1/3$, if the crack system is in this regime.

Chen (1996) rearranged equation (2.24) to show that if a graph of $1/\sigma_f^3$ versus P was plotted, it would give a straight line; K_{Ic} could be obtained from the gradient and the intercept with the y-axis would give the value of P^* .

Values for χ and ψ need to be known. χ is a material property, measuring the intensity of the residual stress field, whereas ψ relates to the shape of the crack and specimen geometry, and so is independent of the material being tested. The values most commonly used in ISB tests for these constants so far are (Chantikal, 1981; Antis, 1981; Cook, 1987; Bleise, 1994):

$$\begin{aligned}\psi &= 1.24 \\ \chi &= 0.004 \sqrt{\frac{E}{H_v}}\end{aligned}$$

Newman, 1981, used FEA models to develop equations that enabled ψ to be calculated for different crack and specimen geometries, which Chen (1996) used in calculating K_{Ic} for several materials by a miniature disc bend test. Chen (1996) concluded that taking a value of $\psi = 1.2$ was accurate enough, and ψ would be constant over a wide range of indent sizes, as long as the crack size was small with respect to the sample dimensions.

Work has been performed concerning the toughness of several ceramics determined using the ISB method, e.g. in alumina, tested over the range of 0.5 - 300N (Cook, 1987; Bleise 1994), where a deviation away from $-1/3$ was found for the gradient of the $\log(\sigma_f)$ versus $\log(P)$ plot, and which was taken as evidence of R-curve behaviour. However, Bleise (1994) suggested it could also be attributed to a transition from Palmquist to median crack systems, or that the shape of the crack front is changing from semi-circular to semi-elliptical (and hence ψ is varying), and cautioned against using this technique. It is expected that such issues can be resolved from SEM examination, but these results do highlight the potential for error in assuming a toughness value for very small flaws by merely extrapolating from high load (i.e. large flaw) regions.

Several papers, (Zhang, 1991, 1993; Chen, 1995, 1996) have been published in which ISB tests were performed using biaxial flexure to fracture disc samples. This has an advantage over uniaxial flexure tests in that no special alignment of the cracks is required. The majority of samples tested were ZnS, and the data was found to agree well with K_{Ic} of this material determined by other techniques. It was also specified (Zhang, 1991) that the sample thickness must be at least 10 times greater than the indent crack, in

order to ensure that the stress field generated from the indent was not affected by the lower surface of the sample; this limits the range of indent loads that can be used.

2.6.3 Review of Toughness Data for FSZ

The toughness of bulk FSZ has been given in the range of 2-3MNm^{-3/2} (Minh, 1993), whereas the limited data published concerning samples of the electrolyte thickness is lower. Basu, 1993, tested 8 mol% YSZ samples produced by Kerafol, of grain size 20µm and thickness 130µm, using the indentation technique, and calculated a room temperature value of 1.2 MNm^{-3/2} from equation (2.25):

$$K_I = \chi \frac{P}{c^{3/2}} \quad \text{Equation (2.25)}$$

where $\chi = 0.016 \sqrt{\frac{E}{H_v}}$

Brocco, 1994, also tested FSZ samples supplied by Kerafol, ranging in thickness from 150µm - 300µm, using the same indentation equation as Basu (1993), and found a room temperature value of 1.62MPam^{1/2}; this is higher than that determined by Basu (1993), although no data concerning the microstructure for these samples was disclosed

No evidence for R-curve behaviour of FSZ has been found.

2.7 Sub-Critical Crack Growth

The stress intensity factor, which characterises the stress conditions at a crack tip, is given by:

$$K = \sigma Y \sqrt{c} \quad \text{Equation (2.17)}$$

where σ = far-field tensile stress applied perpendicular to the plane of the crack
 Y = geometrical factor, taking into account both specimen and crack shape
 c = length of crack

A component placed under a stress fails when K reaches a critical value, K_c ; for every applied stress there will be a critical flaw size, a_c , at which failure occurs. When a stress is applied to a sample, failure occurs immediately if the worst flaw in the material, a_o , is

greater than a_c , whereas if a_0 is less than a_c the lifetime of the component under this load should be unlimited (Fett, 1984).

However, it has been found that ceramics and glasses actually have a finite lifetime when left under a load which is less than the expected failure load. This is because the worst crack can grow from its initial length a_0 to the critical length a_c despite $K < K_c$; this is known as sub-critical crack growth (sccg), and there is a timelag to failure of the sample whilst this occurs (Morrell, 1985).

The lifetime of the component depends on how quickly the crack grows to the critical length. It has been found that the rate of crack extension depends on factors such as the environment, temperature, and applied load; the usual way of expressing the crack rate is in a velocity (v) - K_I diagram, and a typical diagram is shown in figure (2.18):

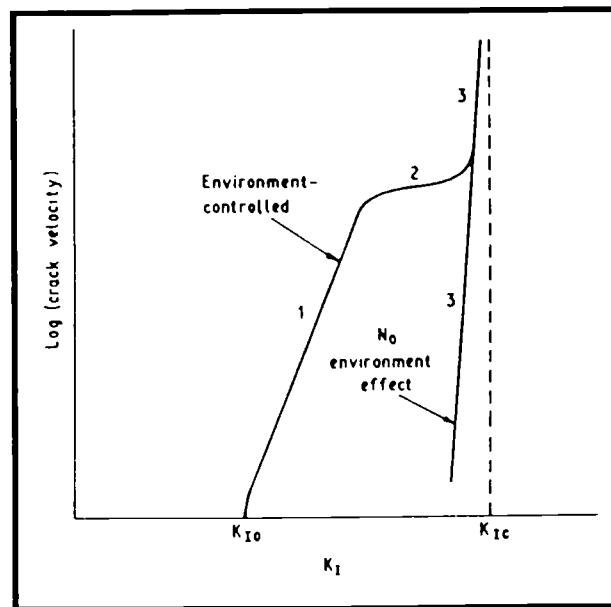


Figure (2.18) - typical v - K_I diagram.

From figure (2.18) it can be seen that there is a threshold K_I value, below which crack extension will not occur, and that above this value the plot can be divided into three regions. Regions 1 and 2 are affected by the environment around the crack, whilst region 3 is the inherent material behaviour (and only region 3 would be seen if the material were tested in a vacuum, or an inert environment).

The environment can cause crack growth in two ways - by actually dissolving the material at the crack tip, or by lowering the fracture surface energy inside the crack so that fracturing the atomic bonds is easier. The rate of propagation in region 1 depends on the reaction rate between the material and corrosive species, but in region 2 it depends on how quickly the species can diffuse to the tip, and is independent of K . Oxides are

particularly susceptible to attack from water, so it is possible that FSZ would show a $v - K_I$ plot similar to that in figure (2.18) if tested in air (Morrell, 1985; Liniger, 1993; Davidge, 1973).

2.7.1 Predicting Lifetime to Failure

The rate of crack propagation is much slower in region 1 than in regions 2 and 3, so this is the region which will dominate the component lifetime if it occurs. The rate in region 1 follows a power law, given in equation (2.26):

$$v = AK_I^n \quad \text{Equation (2.26)}$$

and time to failure, t_f , is calculated from equation (2.27):

$$t_f = B\sigma^{-n} \quad \text{Equation (2.27)}$$

where A, B = constants which take into consideration the surface treatment and history of the samples.

n = material constant

σ = applied stress

When predicting the lifetime of a component that will undergo scg, it is assumed that most of the sample life is spent with the crack growing in region 1, following equation (2.26); thus it is necessary to obtain values for n in order to calculate t_f . Typical values for n are quite large, e.g. 10 - 200, so the effect of stress will be important (Morrell, 1985; Rockar, 1978).

$V-K_I$ curves can be obtained directly using the double torsion (DT) test, measuring the compliance of the sample as the crack propagates, and obtaining n from the gradient in region 1 of the $v-K_I$ plot. Velocities down to 10^{-9} m/s can be followed with this method. However, one problem is that the DT test uses large, artificial cracks, which may not behave in the same way as the smaller, natural defects present in the material, and if a guiding groove is used, it may introduce damage ahead of the growing crack, so the material actually tested is not typical of the rest of the sample. Also, the DT focuses on only one failure mechanism - that of the growth of a pre-existing flaw - whereas this may not actually be the mechanism by which the component fails under its service conditions (Davidge, 1973; Seshadri, 1982; Quinn, 1987). Another method of obtaining n is from static or dynamic fatigue tests.

2.7.1.(i) Static Fatigue Tests

The static test is based on equation (2.26), namely:

$$t_f \propto \sigma^{-n} \quad \text{Equation (2.27(a))}$$

By applying different constant stresses, different failure times will ensue. A graph of log (fracture stress) versus log (time to failure) gives three regions, as shown in figure (2.19), which correspond to those in the $v - K_I$ plot, and n can be obtained from the gradient in region 1.

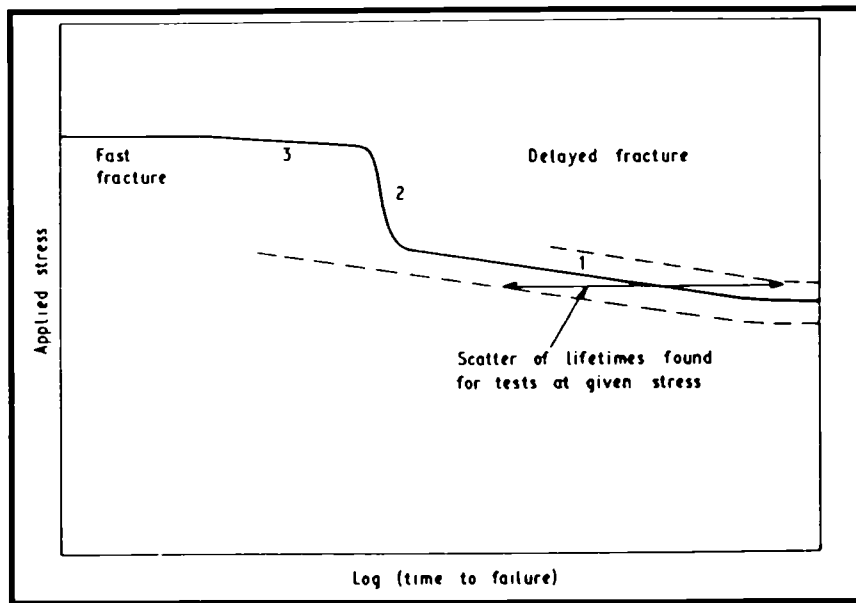


Figure (2.19) - diagram showing plot of $\log(\sigma_f)$ versus $\log(t_f)$.

This is probably the best method for obtaining n , since it uses natural flaws, and is relatively easy to perform under the operating conditions of the component, so that the failure mechanism is actually that which would occur in service. However, the drawbacks of this method are that the tests can take a long time to complete, and also that there is a large amount of scatter in the data, due to the scatter of the natural flaw population in the samples, so that many samples need to be tested (Quinn, 1987; Morrell, 1985).

2.7.1.(ii) Dynamic Fatigue Tests

The dynamic technique is based on equation (2.28):

$$\sigma = B \sigma^{\frac{1}{n+1}} \quad \text{Equation (2.28)}$$

which leads to equation (2.29):

$$\log \sigma = \log B + \frac{1}{n+1} \log \dot{\sigma} \quad \text{Equation (2.29)}$$

where σ = failure stress of a sample broken under a constant stressing rate $\dot{\sigma}$.

Thus by testing several batches of samples under varying stress rates, it is possible to obtain different median failure stresses. A graph of log (fracture stress) versus log (stress rate) gives a straight line of gradient $1/(n+1)$, from which n can be calculated (Morrell, 1985; Rockar, 1978).

This technique also uses natural flaws, and is more economical with regards to time and material, but assumptions have to be made. The first is that the crack velocity is in region 1, and that the same crack growth mechanism is operating over the stressing rate range employed. Secondly, it must be assumed that the specimens broken under each stress rate have the same flaw distributions, so that it can be assumed that the median strength values which are used have equal failure probabilities. In addition, although n is supposed to be a material parameter, Rockar (1978) did find that different surface treatments did affect the scatter in flaws, leading to statistical uncertainty in n .

Fett, 1985, devised a way of obtaining the v - K_I plot from static and dynamic tests without having to obtain n , meaning that the assumption of $vel = AK_I^n$ does not have to be made. Fett (1985) also claimed that the technique will actually measure velocities below that which is possible using the DT technique, so that data does not have to be extrapolated down to these low rates.

The method relates the inert strengths, σ_c , of N samples to the strengths of N samples tested under static fatigue, σ . The strengths are converted to stress intensity factors by equation (2.30):

$$\frac{K_I}{K_{Ic}} = \frac{\sigma}{\sigma_c} \quad \text{Equation (2.30)}$$

and a graph of K_I/K_{Ic} versus t_f plotted. From taking the gradient at each K_I/K_{Ic} value a graph of vel - K_I/K_{Ic} can be produced. Initial results on alumina seemed to work well, with a straight line dependency (i.e. following the power law in region 1). This method has the advantages of using natural flaws, the actual service conditions of the component, and measuring low velocities, but once again assumptions do have to be made - that the flaw populations are the same, and also that the variations in t_f are due

only to variations in inert strength, and not different failure mechanisms operating (Gupta, 1994).

2.7.1.(iii) Strength - Probability - Time (SPT) Diagrams

For design purposes it is necessary to be able to predict the lifetime of a material under particular service conditions. There are two aspects to the strength behaviour that must be considered. First, the statistical variation in strength due to the scatter in flaw size; this is characterised by Weibull plots. Secondly, the sccg effects, which ideally would be characterised using natural flaws growing under the operating conditions of the component (Seshadri, 1982).

One way of estimating the survival probability is to combine the time dependent and statistical strength features on the same diagram, called an SPT diagram, an example of which is shown in figure (2.20). This enables the probability of survival for a component needing to be held for a specific time under a specific stress to be estimated.

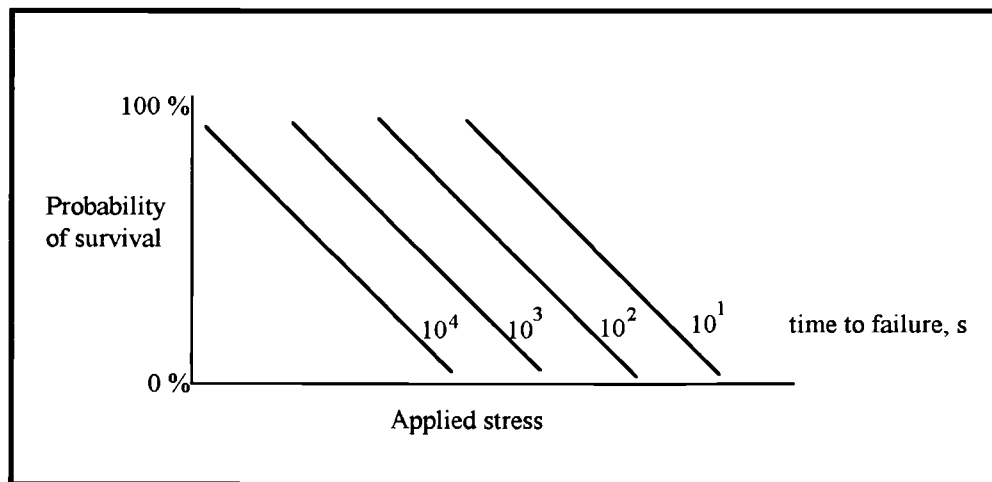


Figure (2.20) - diagram showing a typical SPT diagram.

SPT diagrams are produced by breaking a batch of samples under a constant stress rate, from which the median fracture stress, σ_{med} , and the median time to failure, t_{med} , are calculated. The equivalent time, t_{eq} , for a sample to break if placed under this load as a static load is calculated from equation (2.31) using the known value for n :

$$t_{eq} = \frac{t_{med}}{n+1} \quad \text{Equation (2.31)}$$

Each individual fracture stress within the batch is then adjusted to the equivalent static stress, σ_{eq} , which would cause failure in this equivalent time using equation (2.32):

$$\sigma_{eq} = \sigma_{med} \left(\frac{t_{med}}{t_{eq}} \right)^{1/n} \quad \text{Equation (2.32)}$$

so that the natural range in strength within a batch is expressed for the failure time. These equivalent strengths are then plotted as a Weibull probability plot. This process is repeated for several t_{eq} values, so that a series of probability lines can be constructed, corresponding to a series of failure times (Morrell, 1985).

It must always be borne in mind that SPT diagrams will only predict the probability of failure under certain conditions. The only guarantee of survival is to use a proof test, whereby samples which fail below a designated cut-off stress are eliminated from the batch (Morrell, 1985; Davidge, 1973).

2.7.2 Effect of Temperature

Oxides are more stable in air at high temperatures than non-oxide materials, but the long-term decrease in strength at high temperature may be greater than expected from the degradation in the short-term fracture strength. This is because sccg is enhanced by a rise in temperature, but also there may be more than one failure mechanism in operation. In addition, the effect of impurities on short-term strength is unlikely to be the same for longer times, because different processes, such as creep, may occur over the longer time. Hence it is necessary to use appropriate high temperature stress rupture tests, which allows the material to fail in the failure mode relevant to its service conditions (Morrell, 1985; Quinn, 1987).

Flexure tests are a common form of stress rupture test, yet they can be complicated if non-linear creep deformation occurs, which can cause the stresses to redistribute and hence rupture to occur at unexpectedly low stresses.

Another effect of enhanced sccg at high temperatures can manifest itself in samples which did not fail, since the residual strength of samples tested at room temperature after being held under stress at high temperature often decreases. As a consequence, residual strength measurements are sometimes used as a measure of high temperature degradation (Morrell, 1985; Quinn, 1987).

2.8 Creep

This is defined as the increase in strain with time, which a material subjected to a constant load and certain temperature conditions will undergo (Ashby, 1980). i.e., it is the permanent deformation resulting from holding a material under load over a particular temperature. Creep is well known in metals, and more recently has been shown to occur in ceramics too, although the mechanisms by which it occurs are not identical to those in metals under the same conditions.

2.8.1 General Creep Behaviour

The mechanism by which creep occurs, and hence the shape of creep curve, is dependent on the applied stress, temperature, and also the microstructure of material. Significant creep ($\epsilon > 1\%$) in a metal starts to occur at temperatures around $0.4T_m$, where T_m is the melting temperature. For ceramics this temperature is higher, at $0.5 - 0.6T_m$ of the major phase, or if impurities are present, within 50°C of T_m of their glassy phase (Morrell, 1985). It has been found that pure oxide ceramics tend to behave in a similar way to pure metals, with the same creep processes in operation (Evans, 1993).

There are two general forms of the creep curve, which are shown in figure (2.21).

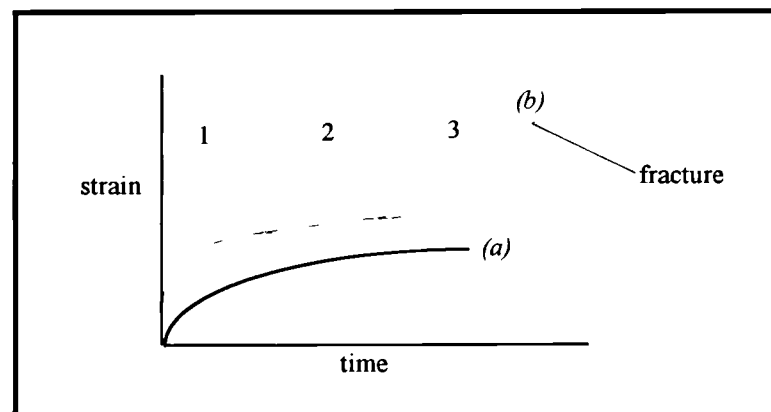


Figure (2.21) - illustrating the general creep curves found in metals; (a) - class A metal; (b) - class M metal.

Most metals follow the form of line (b), that for class M, as do many oxides, and so the details of this curve will briefly be explained. The curve can be divided into three regions, and the deformation mechanisms and equations governing each region are different. In region 2 an equilibrium has been attained; the creep rate is constant, and there is no change in stress at any point across the sample. This is where it is assumed that most of

the deformation usually takes place, and so is often the most significant region when predicting the lifetime of a material. (It must be acknowledged that for accurate lifetime predictions all the creep curve needs to be taken into account, but the equipment required for this was beyond the scope of this project.)

In region 2 the strain rate has an Arrhenius dependence on temperature, as shown in equation (2.33):

$$\dot{\varepsilon} = A \exp \left[-\frac{Q}{RT} \right] \quad \text{Equation (2.33)}$$

where A = a constant
 Q = activation energy for creep
 T = temperature, K

The relationship between strain rate and stress has a power dependence, following Norton's law, equation (2.34):

$$\dot{\varepsilon} = A \sigma^n \quad \text{Equation (2.34)}$$

where A = a constant
 σ = applied stress
 n = stress exponent

The values of Q and n may vary with the stress and temperature range applied, and both must be determined for a constant microstructure. Any microstructural change can lead to a different creep rate, because strain rate is also affected by grain size, according to equation (2.35):

$$\dot{\varepsilon} \propto d^{-P} \quad \text{Equation (2.35)}$$

where d = mean grain diameter
 P = factor for grain size dependence

2.8.2 Creep Processes in Ceramics

Creep can occur by several different processes, or a combination of them; these are described briefly below.

2.8.2.(i) Dislocation Creep Processes

Creep in metals is often due to dislocation activity within the grains - intragranular deformation. For dislocation activity to occur without cavitation requires 5 independent slip systems to be operational - this is possible in most metals at relatively low temperatures, but does not occur in most ceramics because of their more complex structure, and hence more limited slip systems. Also, grain boundaries oppose dislocation motion, and since the grain size of ceramics tends to be smaller than that of metals, this also limits dislocation activity in ceramics. Hence the intragranular processes make a limited contribution to plasticity; deformation and failure is mostly connected with the grain boundaries (Morrell, 1985; Wilkinson, 1992).

2.8.2.(ii) Diffusional Creep Processes

Diffusion is possible due to the presence and movement of vacancies; atoms can only move through the material if they have sufficient energy, and if there is an adjacent vacant site to move into. Diffusion can take place more easily along certain routes, such as where there are fewer bonds (surfaces), or where the atomic arrangement is less regular and more open than in the crystal lattice (grain boundaries, dislocations); the importance of these preferred paths depends on the creep conditions, most notably on temperature, since diffusion is an Arrhenius process.

At low stresses but high temperatures, diffusion through the crystal lattice is rapid, so the 'easy' paths make little contribution to diffusion. In this situation the rate controlling step is lattice diffusion, and this is termed Herring-Nabarro creep. The vacancies move from regions under low to high stress; the stress exponent, n , = 1; the activation energy for creep is the same as that for self-diffusion, Q_{SD} . As the temperature decreases, the self-diffusion coefficient decreases exponentially, so stress directed diffusion along the 'easy' paths makes an increasingly more significant contribution to creep deformation. This is termed Coble creep; $n = 1$; $Q < Q_{SD}$, and the usual 'easy' paths are the grain boundaries (Evans, 1993).

A potential danger which can emerge from diffusion processes, and hence also during creep, is that of demixing. Cation diffusion in oxygen ion conductors is much slower than that of the anions, and so the rate-determining-step in diffusional processes will be

controlled by the cations; when there is more than one cation, and if there is a significant difference in their diffusion coefficients, segregation may occur, leading to the precipitation of new, unstable, phases. However, such an effect has not been detected over the past 30 years of investigation into the electrolyte behaviour (Kilner, 1981).

2.8.2.(iii) Grain Boundary Sliding and Cavitation

At low stresses and strain rates the strain can be accommodated by diffusion. However, when higher stresses are applied, diffusion by itself will not occur fast enough to allow continuous deformation; at high temperatures the grains are able to move relative to each other, and so creep occurs by grain boundary sliding.

The movement of the grains causes the formation of cavities at their points of intersection (triple points) and also along their boundaries. The intergranular growth of these cavities contributes to the creep deformation, but also tends to be the main cause of creep fracture (section 2.8.2.(v)). The presence of impure phases at the grain boundaries can greatly increase the grain sliding process; these phases tend to have low melting points compared to the bulk material, and so soften and become viscous, unable to support a load, before the bulk. Thus, although the grains themselves are not deformed, they slide or can be pulled apart at temperatures where the pure material would maintain mechanical integrity (Evans, 1993; Morrell, 1985; Porter, 1981)

2.8.2.(iv) Effect of Grain Size

The effects of grain size on creep become more significant as the grains become smaller. For diffusional creep processes the grain size will influence the creep rate according to d^{-p} (equation (2.35)), where p varies with the diffusional process taking place. For Herring-Nabarro creep, $p = 2$; for Coble creep, $p = 3$. For dislocation creep there is a small effect from the grain size, and a value of $p = 0$ is assumed.

Grain sliding due to impurities at the grain boundaries will also cause more damage as the grain size decreases.

2.8.2.(v) Eventual Fracture

a) Effect of Defects and Impurities

The mode of failure depends on applied stress and temperature range, but also on the microstructure - the defects introduced during processing can dictate to a certain extent the lifetime of component. Wilkinson, 1992, performed flexure and tensile creep tests

using alumina samples, and found that in all stress regimes the failure was linked to flaws in the samples.

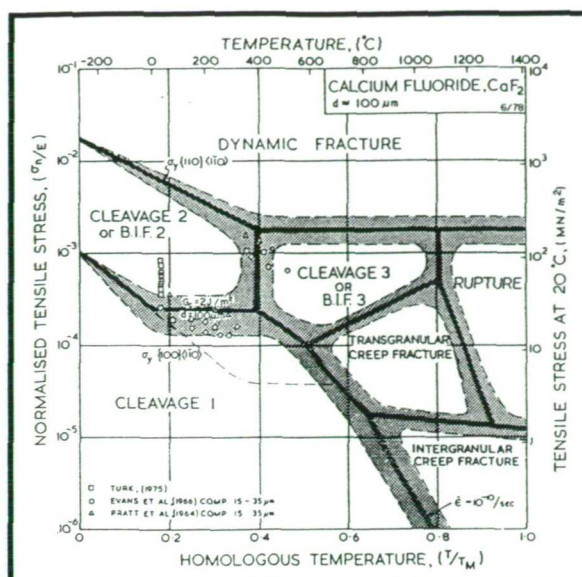
At very high stresses (e.g. $\sigma = 200\text{MPa}$), creep failure occurs by slow crack growth from a single flaw until the crack reaches critical size, and catastrophic growth occurs. The type of flaw involved in this failure can be a processing defect, large grain, glassy deposit - any inhomogeneity in the microstructure can produce a stress concentration. (This is similar to the sources of failure in material tested under fast fracture.)

As the stress is decreased, it seems that in ceramics cavitation is the source for some plastic deformation, but almost always the origin of failure. At high temperatures and stresses, wedge-shaped cavities form at the triple points, where the grains pull apart; as the grains continue to slide the cavities form a crack which propagates between the grains. At lower stresses the wedge-shaped cavities are unable to form, but cavities which are more spherical in shape form along the grain boundaries; these link to form microcracks, which grow and coalesce throughout the sample, eventually forming a critical sized defect from which failure ensues. Both the wedge and spherical-shaped cavities are nucleated from regions of stress, which arise either from the applied shear stress or from points of stress concentration. However, this nucleation stress is reduced if there are already voids in the material, and porosity is an example of such pre-existing voids. Hence the failure crack will often originate from pores at the grain boundaries - which are a product of the processing technique - and propagate in an intergranular manner (Wilkinson 1992; Porter, 1981; Evans, 1993).

b) Fracture Mechanism Maps

These summarise the fracture behaviour of materials with regards to the normalised stress and temperature ranges applied (Evans, 1993). They show the type of creep fracture processes which have been found to operate within each region, and the map for the CaF_2 structure, which is the structure for cubic zirconia, is shown in figure (2.22).

Figure (2.22) - fracture mechanism map for the CaF_2 structure (Gandhi, 1979).



2.8.3 Types of Creep Test

A tensile test is considered the ideal, because the same stress conditions are experienced throughout the sample (Fett, 1988). However, there are problems with gripping brittle materials in tensile tests, so compression tests are usually used instead, although these are not totally suitable because buckling can occur (Hollenberg, 1971). A flexure test would appear to be an easy solution to performing creep tests on brittle materials under tension, but, despite the simple geometry, the analysis is not straightforward.

One problem arises from uncertainty in the applied stress. In a fast fracture flexure test, the stress distribution is linear through the sample thickness, so stress and strain are linear. In a creep flexure test the stress and strain will only be linear if the creep exponent $n = 1$. When $n \neq 1$, and a dead weight load is applied, the stresses relax and redistribute in the sample as the test proceeds. The stress on the tensile face is reduced, whilst that on the compression face is increased, and as a consequence, the applied stress tends to be overestimated.

Additional problems arise if the strain is calculated from the profiles of deformed test samples. During creep, the neutral axis tends to move from the middle plane of the sample towards the compression face, so that more of the sample is in tension, and it is also found that samples undergoing creep do not deflect in the same way as in elastic deflection. Thus if the equations used to calculate strain are based on geometry or on elastic deflections, the resultant value will contain some degree of inaccuracy. Work performed using vitreous-bonded alumina samples in 4-point-bend tests showed that strain could be quantified by measuring the final deflection of creep bars, but only if it was assumed that the same amount of creep occurred in the compression and tension

regions of the samples, and that secondary stage creep was attained; these assumptions were found not to apply in these particular examples (Hollenberg, 1971; Jakus, 1988; Fett, 1988).

So many assumptions need to be made concerning the applied stress, and which portion of the creep curve the system is actually operating in, that the 'dead weight' flexure test has been largely discarded as a means of obtaining quantitative creep data; however, it is useful for indicating that creep deformation is actually occurring, since the deformation is very obvious (Morrell, 1985; Quinn, 1991).

2.8.4 Review of Creep Data for YSZ

Data on the creep of single crystals and polycrystals of FSZ are available, although for samples of different yttria content and often under higher temperature conditions than will be experienced in the SOFC. (8mol% YSZ melts at around 2750°C (Scott, 1975), so using the general guide of $0.5T_m$, one would expect creep processes to start operating around 1240°C for the pure material.) Further data are available for PSZ, in the temperature range where the tetragonal phase is stable; however, there will be differences in behaviour between this and cubic material, due to the differences in grain size. All the data quoted were obtained from compression tests, and are summarised in table (2.6).

2.8.4.(i) Fully Stabilised Zirconia

a) Single Crystal Material

Martinez-Fernandez, 1990, investigated the deformation of 9.4 mol% single crystals, in the temperature range 1300-1550°C, under stresses ranging from 50-160 MPa and strain rates from 10^{-7} to 10^{-4} s⁻¹, and oxygen partial pressures of 0.21 and 10^{-5} atm. The values of Q and n varied, depending on temperature; below 1400°C, Q was 714 kJ/mol, and n was 7.3, whereas above 1450°C both Q and n decreased, to 589 kJ/mol and 4.5 respectively. TEM examination showed dislocation activity occurred under all conditions, but the dislocation density was lower at the higher temperatures. This, along with the decrease in Q and n , suggests that at the higher temperatures diffusion is rapid enough to cause recovery. The change in oxygen pressure was found to have no effect on creep rate.

Baufeld, 1995, investigated the creep of 11 mol% single crystals, under stresses up to 500 MPa and a strain rate of 10^{-6} s⁻¹, and in the lower temperature range of 700 -

1150°C. Creep was shown to occur at all temperatures, although the stress at which it commenced decreased as the temperature increased (e.g. from 460 MPa at 700°C to 220 MPa at 1150°C). Q at 700°C and an applied stress of 460 MPa was quoted as 318 kJ/mol, which is lower than that found by Martinez-Fernandez (1990) and TEM examination revealed the presence of dislocations in slip-bands.

The shapes of the stress-strain plots at 700°C and 1150°C were different, with the curve at the lower temperature being jagged whilst at 1150°C the plot was more smooth. Thus it could be that as the temperature was raised the creep processes did alter, and hence the discrepancy in the values of Q for dislocation creep quoted by Baufeld (1995) and Martinez-Fernandez (1990) could be due to the different temperature range employed.

b) Polycrystalline Material

Dimos, 1987, performed tests on 25 mol% YSZ polycrystals, of grain size varying from $\sim 3 - 15 \mu\text{m}$, under stresses ranging from 8 - 60 MPa, and temperatures 1400-1600°C. On comparing with the single crystal data found by Martinez-Fernandez (1990) the results showed that at applied stresses less than 100 MPa the resultant strain rate was always greater for the polycrystalline material. Despite no data being disclosed concerning the purity of the polycrystalline samples, this does show that the main deformation mode in polycrystalline YSZ will be associated with grain boundaries, e.g. grain boundary sliding or diffusion creep. A grain size exponent of 2.2 was determined.

Dimos (1987) also examined the microstructure of deformed samples; the grains were still equiaxed (undeformed), and no microcracking or cavitation was detected by SEM, nor were any dislocations observed by TEM examination. This lack of deformation of the grains, along with linear relationship between creep rate and applied stress, and $Q_{\text{creep}} \sim Q_{\text{SD}}$, indicated Herring-Nabarro creep was occurring.

Dimos (1987) also analysed for the demixing of Zr^{4+} and Y^{3+} ions, by holding samples under a stress of 30 MPa at 1600°C for 75 hours, and afterwards chemically analysing them in the SEM, but no concentration gradient was detected. They suggested that the lack of gradient was either because the grains were rotating during the test (hence no concentration gradient was formed, and so no demixing was able to occur), or that the demixing process itself would not occur to any significant degree. The authors claimed that the grains would need to rotate about 30° in order to prevent the formation of a concentration gradient, but the very small cation diffusion coefficients given in table (2.2) make the first suggestion a very unlikely option. Since the diffusion coefficients of Zr^{4+} and Y^{3+} are fairly similar, it is probably safe to assume demixing did not occur to any

significant degree during their experiment using 25 mol% YSZ, and so will not occur during the operation of the 8 mol% electrolyte, as already mentioned by Kilner (1981).

2.8.4.(ii) Partially Stabilised Zirconia

Evans, 1970, tested 6 mol% polycrystalline YSZ under stresses ranging from 8 - 71 MPa, and temperatures from 1317-1535°C, and observed two values for n , of 1 and 6. Following from SEM examination he proposed that the region where $n = 1$, at lower stresses, is controlled by cation diffusion, and pores form at the grain boundaries which grow and coalesce. At higher stresses these pores propagate locally to produce longer cracks, which is the region where $n = 6$. The activation energy value, 361 kJ/mol, was lower than that found by Dimos (1987) for the polycrystalline FSZ.

Seltzer, 1975, tested compositions between 6-8 mol% YSZ, under stresses ranging from 1-69 MPa, and temperatures between 1500°C and 2000°C. A value of 1.5 was obtained for n at the lower stresses, and Q was found to be 538 kJ/mol. above 1500°C. The microstructural observations showed that below 1550°C, creep by grain boundary sliding occurred. The value of n is in reasonable agreement with that found by Evans, 1970, although the activation energies are not - this is probably due to the different test conditions used.

Bravo-Leon, 1992, tested 6 mol% samples, of grain sizes 1.8, 3.4, and 6.3 μm , over the stress range 5 - 90 MPa and temperature range 1350 - 1450°C. It was found that the stress exponent remained the same, at 1.5, for the small grained material over all the temperature and stress ranges, but this was true for the large grained material only when the applied stress was less than 10MPa; above this stress the material began to degrade, as described below, and Q and n were not calculated. A grain size exponent of 2.2 was determined.

From SEM and TEM examination of samples from each batch it was found that there was no plastic deformation of the grains; they maintained their equiaxed shape and no dislocations were observed. For the large grained material at high stresses and strain rates, a lot of cavitation was also seen between the grains. It was concluded that the deformation occurred by grain boundary sliding, via bulk diffusion. With the small grains, extensive deformation can occur because the grains can slide over each other; the material is termed 'superplastic'. With the larger grains, bulk diffusion cannot accommodate such large deformations and so cavitation also occurs.

There is reasonably good agreement between the stress exponents found under low stresses for all the 6 mol% PSZ material ($n \sim 1.5$), although the activation energies were

not so consistent, with that found by Evans (1970) being lower. The agreement with the polycrystalline FSZ, where bulk diffusion was also in operation, is also reasonably good.

Nauer, 1990, tested materials of different compositions and purities, with a yttria content varying from 2 - 4 mol%, but all with very fine grain sizes ($<1\mu\text{m}$), under the stress range of 5-80 MPa and at 1350°C . The value of Q for all the samples, and n for the large-grained samples, was found to decrease, from 590 - 500 kJ/mol, as the applied stress was increased; this is in contradiction to Bravo-Leon (1992) who found that n and Q of their smallest grained ($1.8\mu\text{m}$) material remained constant with temperature and stress.

At lower stresses, the strain rate of the impure samples was always greater than for pure ones of equivalent composition and grain size, whereas at high stresses this was not so apparent. The work with impure samples was continued, and in 1993 Lakki used internal friction measurements to shed light on the deformation mechanisms operating; pure and impure samples of 2 mol% YSZ were used, the impure ones containing additions of alumina and silica, under stress and temperature ranges of 2.5-300 MPa and $1100 - 1400^{\circ}\text{C}$. As with the samples previously tested, Q was found to decrease as stress increased. The strain rate for the impure material was five times faster than for the pure, quoted at a temperature of 1350°C and stress 10MPa, although it was believed that in under all the test conditions for both types of sample, grain boundary sliding was the mechanism by which creep occurred.

In summary, creep of YSZ has been observed across a wide range of compositions and microstructures, and under a range of creep conditions. Deformation in single crystals of FSZ occurs by dislocations (even at temperatures as low as $0.3T_m$), but the strain rate of polycrystalline material is higher, indicating that creep by grain boundary processes is more significant. There is some inconsistency in the values obtained for the creep stress exponent, which does seem to vary with grain size and stress regime; it is difficult to compare the values, since the authors used different materials and conditions, but a value of $n = 1-1.5$ was found for FSZ and PSZ polycrystalline material with a grain size above $2\mu\text{m}$. Likewise, the activation energy varied with test conditions, but in the main was in the range of 500 - 600 kJ/mol for the polycrystalline materials.

The effect of impure grain boundary phases, and grain size, on the amount of plasticity displayed was more pronounced at lower stresses. The mode of failure of the material is dependent on strain rate or stress range being applied, but was also affected by the grain size. In general, creep of a polycrystal was found to occur by grain boundary sliding and bulk diffusion, with cavitation also occurring for larger grained material tested at higher stresses.

Table (2.6) - summary of the creep data available in literature.

Authors	Y ₂ O ₃ content, mol%	Temperature range, °C	Stress range, MPa	Grain size, μm	Q, kJ/mol	n	P	Comments
Martinez-Fernandez, 1990	9.4 single xtl	1300 - 1550	50 - 160	-	714 ($T < 1400$) 589 ($T > 1450$)	7.3 4.5	-	dislocations recovery by cation diffusion
Baufeld, 1995	11 single xtl	700 - 1150	< 500	-	318		-	dislocations
Dimos, 1987	25	1400 - 1600	8 - 60	2.6 - 14.5	550	1	2.2	HN creep
Evans, 1970	6	1317 - 1535	8.3 - 71	17	361	1.5 (low σ) 6 (high σ)		failure by cavitation
Seltzer, 1975	6	1500 - 2000	0.7 - 69		538	1.5 (low σ)		
Bravo-Leon, 1993	6	1350 - 1450	5 - 90	1.8 - 6.3	560	1.5	2.2	bulk (HN) diff, cavit. for larger grains
Nauer, 1990	2, 3, 4	1350	5 - 80	0.4 - 0.8	590 (5MPa) 500 (80MPa)	2.4 1.4 - 2		Q, n vary with stress, but always gb sliding
Nauer, 1993	2, impure	1100 - 1400	2.5 - 300					g.b. sliding, due to impurities

CHAPTER 3

EXPERIMENTAL PROCEEDURE

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3.1 Sample Analysis

Two types of samples were used in the project; those made by thin-film processes (tape-casting and tape-calendering), following the same manufacturing process as that used to produce the actual electrolytes, and bulk samples in the form of bars which were prepared at Imperial College. All samples were nominally 8 mol% YSZ.

3.1.1 Thin-film Samples

3.1.1.(i) Sample preparation

The majority of these samples were in the form of discs, which were provided by three different manufactures, ICI, Kerafol, and Siemens. ICI used a viscous processing technique, followed by tape-calendering, to produce their material, whilst the samples from Kerafol and Siemens were tape-cast. Full details of the manufacturing processes can not be revealed for reasons of industrial sensitivity, but Siemens used a longer binder burn-out time than Kerafol before sintering their tape-cast samples, and the final sintering temperature was 1550°C in both cases. Nominal dimensions of each batch are given in table (3.1). Specimens from set C (provided by Kerafol) were also aged at 950°C for 1000 hours, to compare with the properties of the unaged material.

Table (3.1) - summary of the manufacturer and nominal dimensions of the sets of samples used in project.

Manufacturer	Project name	Diameter, (mm)	Thickness, (mm)
ICI	set A	29.0	0.23
Kerafol	set B	21.9	0.16
	set C	22.0	0.16
Siemens	set D	22.4	0.15

Material from Siemens was also provided in the form of square plates, 50mm x 50mm, x 0.15mm, which is the actual size of the electrolyte, made by the same process as set D. These samples were used in double torsion tests, and some were cut into bar samples for Young's modulus measurements.

3.1.1.(ii) Microstructural Analysis

To measure the mean grain size, the tensile face of samples from each batch were covered with a thin layer of gold and examined in the JOEL T-220 SEM. The grain size was calculated from photographs taken of these surfaces using the linear intercept method (Metals Handbook, 1985). The mean was taken of four samples per batch, covering areas ranging from 355 - 3064 μm^2 .

X-ray texture goniometry was performed on one sample from set B to ascertain whether the tape-casting process caused an anisotropic microstructure to develop (i.e. texture). This involves setting the x-ray detector at an angle so that it will only pick up diffracted x-rays from a particular set of planes. The sample is both spun and tilted, so that it is completely scanned, and the positions of the detected x-rays displayed on a stereographic projection. If there is preferred orientation then peaks from the selected planes will occur only at specific positions, whereas if the orientation is random, then x-rays will be detected continuously as the sample rotates.

X-ray texture goniometry was performed using a Philips PW1078 Texture Goniometer, set to detect the (111) peaks.

3.1.1.(iii) Physical Properties

Sample densities were measured by Archimedes' technique, using distilled water.

The thermal expansion was measured using a Netzsch dilatometer (402E). A bar sample from set D was cut to a length of 17.6 mm, and its expansion measured over a temperature range of room temperature to 1000°C, at a heating rate of 10°C/min. From this the thermal expansion coefficient could be calculated.

3.1.1.(iv) Phase Analysis

X-ray diffraction (XRD) was performed on one specimen from each batch to identify the phases present, using a Philips PW1710 diffractometer. Cu_α radiation was used, at a scan rate of 0.04°(2 θ)/sec., over the range 5 - 100 °(2 θ).

Siemens also performed XRD on the original powder used to manufacture their samples, and on a sintered specimen from set D, over a temperature range of room temperature up to 1100°C.

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) were also performed to see whether a phase transformation, or any microstructural change, occurred as the temperature was raised. Such structural changes are accompanied by the absorption or emission of energy, in the form of heat, and these techniques monitor the temperature of the sample with respect to a reference as the system is heated; any additional variation in temperature of the sample indicate a structural change. Specimens of diameter 3 mm were cored out from unaged and aged samples of set C, and analysed using a Stanton Redcroft differential scanning calorimeter and a Stanton Redcroft STA thermal analyser over a temperature range of room temperature to 1200°C, and at a heating rate of 20°C/min.

3.1.1.(v) Chemical analysis

Chemical analysis was carried out in order to identify and quantify the constituents and any impurities that were present, using the energy dispersive analysis of x-rays (EDAX) facility fitted to the JSM 35 SEM. For this technique, two samples from each batch were polished to a 6µm diamond finish, and coated with a layer of carbon, before being examined.

3.1.1.(vi) Topography and profile measurements

Surface roughness and sample profiles were both obtained using the Taylor-Hobson Talysurf 10; this involves drawing a diamond tipped stylus across the sample surface, producing an electrical signal which is converted and displayed on a meter as average roughness, R_a , or on a chart as the profile. R_a is the average of the height variation of the surface about a reference level, and was measured using five samples from each batch. Five scans, of length 12.5 mm, were taken for each sample surface, and the mean calculated for both faces. The profiles of five samples from each batch were measured using a scan length of ~ 21mm, traversing the diameter of the discs; two scans were taken of the surface of each face, at 90° to each other. The vertical magnification was set at x1000, and the horizontal at x10.

In addition, the profiles of the smooth surface of three samples from set C were measured. Then the rough surfaces were polished flat, and the profiles of the smooth surfaces re-measured.

3.1.2 Bulk Samples

3.1.2.(i) Sample preparation

The bars produced were approximately 37mm long, 4.5mm wide, and of variable heights, ranging from 0.5-5.0 mm. They were made in the green state by uniaxially pressing the YSZ powder, grade TZ-8Y supplied by TOSOH, in a die, followed by cold isostatic pressing at 300MPa. The second pressing process had been shown to produce stronger and more dense samples than if just the uniaxial process was used. These bodies were then sintered at 1500°C for 2 hours, and the top and bottom surfaces of the sintered samples were ground parallel using a SiC wheel. Samples for strength tests also had their edges bevelled.

Bars for strength and toughness experiments were also aged at 950°C for 1000 hours.

3.1.2.(ii) Analysis

XRD was used to determine the phase composition of the bars, and the mean grain size and density measured in the same way as for the tape-cast samples. The thermal expansion coefficient was measured with the dilatometer, using a sample 15.7mm long.

3.2 Young's Modulus

The Young's modulus of tape-cast and bulk samples was measured at room and high temperatures using static and dynamic techniques.

3.2.1 Dynamic Techniques

3.2.1.(i) GrindoSonic (MK5 'Industrial')

a) Bulk Samples

A value of E could be obtained from causing the bar to vibrate in just the flexural mode; the positions of the supports, mechanical impulse and detector necessary for this mode are shown in fig (3.1).

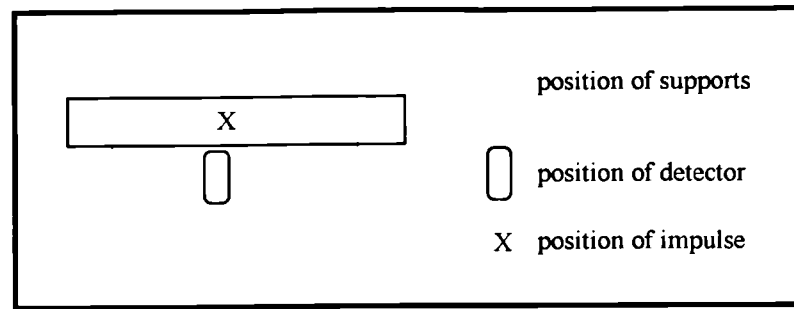


Figure (3.1) - diagram illustrating the sample and apparatus positioning required to detect the flexural vibration of bars.

Different materials were used as the supports, e.g. soft foam, alumina slats and rollers, rubber, and both the transducer and microphone were used as detectors. There was no difference in the frequency value obtained using these different support materials, so for the sake of convenience, rubber supports and the microphone detector were used at room temperature. E was calculated from the frequency of vibration, and sample mass and dimensions, according to equation (3.1) (Spinner and Tefft, 1961):

$$E_F = 0.94642 \left(\frac{\rho_B l^4 f^2}{t^2} \right) T \quad \text{Equation (3.1)}$$

where E_F = elastic modulus calculated from the flexural vibration
 ρ_B = bulk density
 l = sample length
 f = fundamental resonance frequency
 t = cross-sectional dimension
 T = correction factor, incorporating Poisson's ratio

In order to see whether E would be affected by thickness bars were ground to different thicknesses, ranging from 0.5mm - 5.0mm. Five bars were tested in each set, all at room temperature

Samples from the 5mm thick set were aged at 950°C for 50, 100, 150, 200 hours and the modulus re-measured, to investigate whether ageing would affect the modulus.

In order to measure E at high temperatures bars were supported on 1.5mm wide alumina slats inside a furnace, and caused to vibrate by dropping 3mm diameter steel ball-bearings onto them through a hole in the furnace roof. The frequency could only be detected up to a temperature of 201°C.

b) Tape-cast Samples

This material was tested in the form of discs, which needed to be excited in both flexural and torsional mode to obtain a value for E , calculated using equation (3.2) (Glandus, 1981); the support, impulse and detection positions are shown in fig (3.2). It was found that in order to obtain consistent readings rubber supports and the microphone detector had to be used, and small ball-bearings, of diameter 1mm, dropped onto the discs from a height of $\sim 15\text{cm}$, to create the impulse.

Five samples from each of sets B, C (unaged and aged), and D were tested at room temperature. In addition, the polished discs from sets C and D, as well as the ground alumina discs, which were prepared in order to determine E by the static technique (see section (3.2.2.(ii))), had their modulus measured by the GrindoSonic.

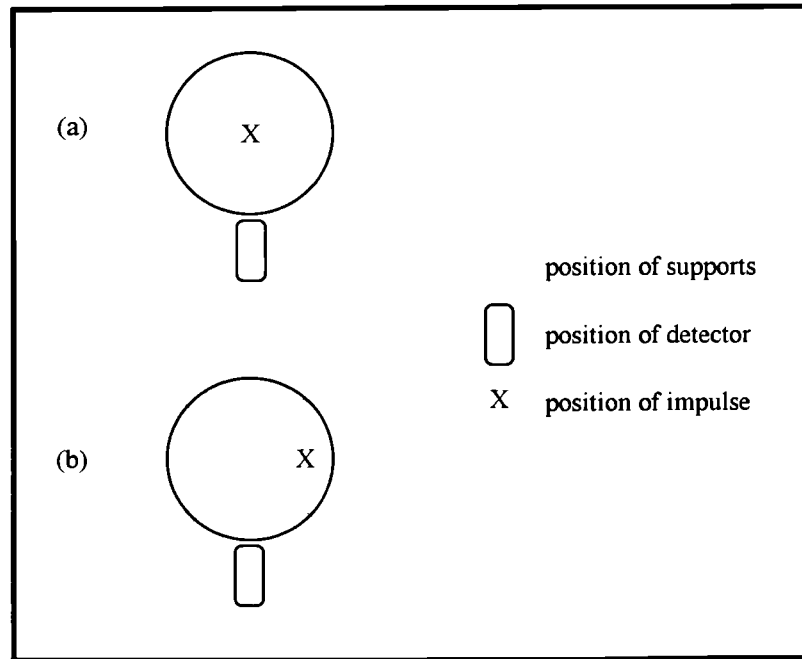


Figure (3.2) - diagram illustrating the set-up required to detect the vibration of tape-cast discs; (a) - flexural mode; (b) - torsional mode.

$$E = \frac{E_1 + E_2}{2} \quad \text{Equation (3.2)}$$

$$E_1 = 37.6991 \frac{f_I^2 D^2 m (1 - \nu^2)}{K_1^2 t^3} \quad \text{Equation (3.2a)}$$

$$E_2 = 37.6991 \frac{f_F^2 D^2 m (1 - \nu^2)}{K_2^2 t^3} \quad \text{Equation (3.2b)}$$

where	E	=	Young's modulus
	E_1	=	torsional contribution to Young's modulus
	E_2	=	flexural contribution to Young's modulus
	f_T	=	fundamental resonant frequency of the disc in torsion
	f_F	=	fundamental resonant frequency of the disc in flexure
	D	=	diameter of disc
	m	=	mass of disc
	ν	=	Poisson's ratio
	K_1, K_2	=	correction factors
	t	=	thickness of disc
	r	=	radius of disc

3.2.1.(ii) *Velocity of sound*

A 2.24mm thick slice was cut from a bar, and the sides ground parallel. This was clamped tightly between the two piezoelectric transducers, with silicone gel being used to ensure good acoustic coupling between the sample and transducer surfaces. Repeated pulses of amplitude 50 dB were sent through the sample and detected using the Dunegan/Endevco 3000 series acoustic equipment, with type B piezoelectric transducers, and the signal was processed using a Sonotek programme. The apparatus is shown in figure (3.3). An aluminium sample of similar dimensions was used before each run as a control. The longitudinal elastic modulus, E_L , was calculated using the ultrasonic pulse velocity measurement from equation (3.3) (Szilard, 1982).

$$E_L = \rho v^2 \quad \text{Equation (3.3)}$$

where	v	=	ultrasonic longitudinal pulse velocity
	ρ	=	density of sample

To perform the test at elevated temperatures, waveguides were needed to connect the sample to the transducers. Fakhr, 1979, showed that stainless steel transmits an acoustic signal adequately, so was used as the waveguide material. The waveguides were 195mm long, and of diameter 4.5mm, widening out to 10mm at one end in order to fit properly with the transducer faces. The transducers were coupled onto the external ends of the waveguides by gluing and the sample clamped between the tips using silicone gel as before, and then a small furnace was pulled over the sample, as shown in figure (3.4). The system was allowed to reach equilibrium at each temperature, before sound waves were passed through the sample. The test temperatures were 20°C, 100°C, 200°C, 300°C, and 350°C.

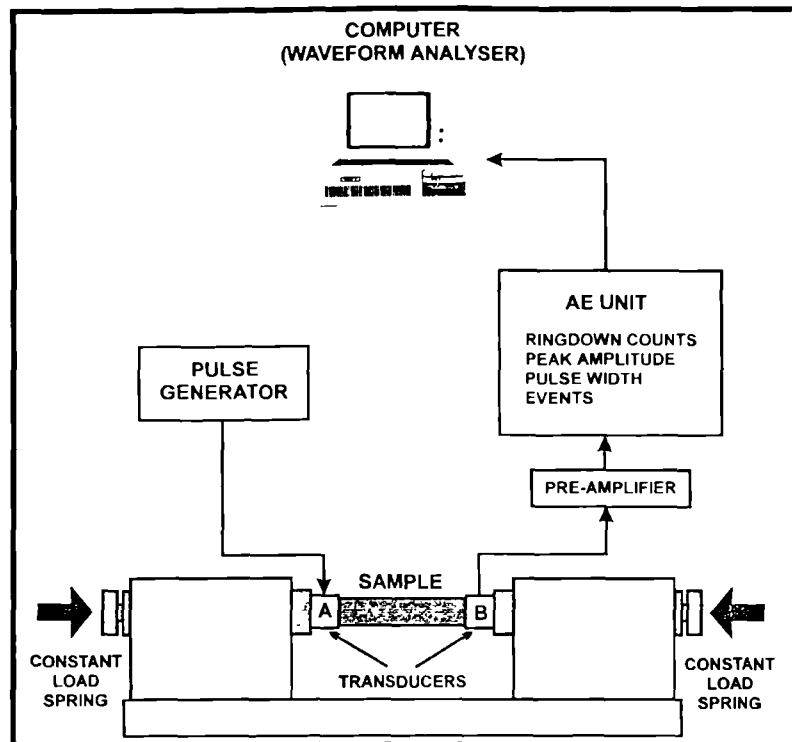


Figure (3.3) - basic apparatus used to measure the velocity of sound through a sample at room temperature.

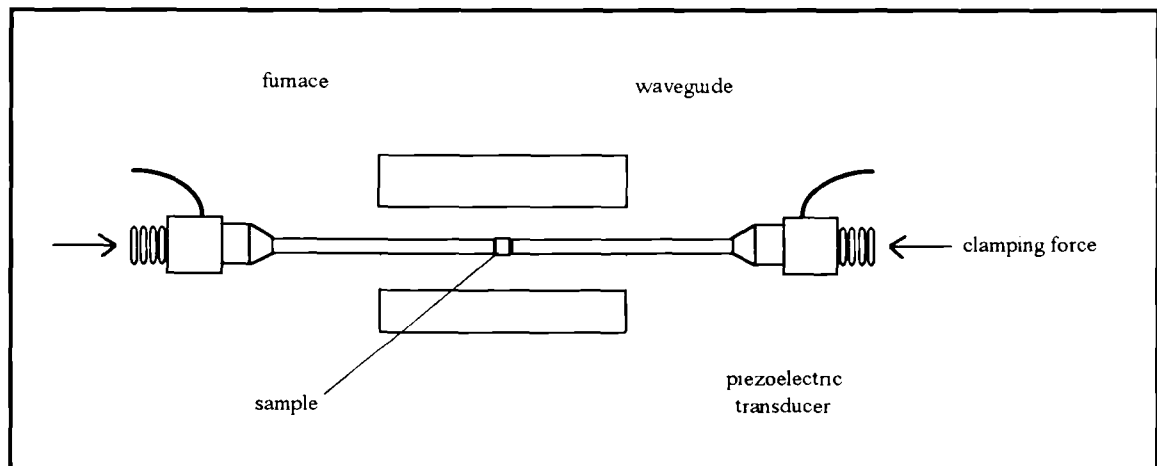


Figure (3.4) - the apparatus used to measure the velocity of sound through a sample at elevated temperatures

3.2.2 Static Techniques

Attempts to determine E at temperatures higher than 350°C using dynamic methods proved to be unsuccessful. Thus static techniques were also employed.

3.2.2.(i) Uniaxial Flexure

Bars approximately $40\text{mm} \times 10\text{mm} \times 0.15\text{mm}$ in size were cut from the tape-cast plates of set D, and tested in both 3 and 4-point-bend flexure, as shown in figure (3.5), using an alumina testing rig.

The bars were flexed by applying a set load, which was lower than the estimated failure load, and the force versus deflection plot was obtained up to this point; then the bars were unloaded, and the temperature increased. This process was repeated at each temperature, so that force / deflection plots of the same sample in the same position were obtained over a range of temperatures, up to 600°C . (The deflection values were the cross-head displacement values, since it had been found previously that placing a LVDT in contact with these thin samples caused them to misalign.) E was calculated using the gradients of these plots, from equations (3.4 (a) and (b)) (Metals Handbook, 1985).

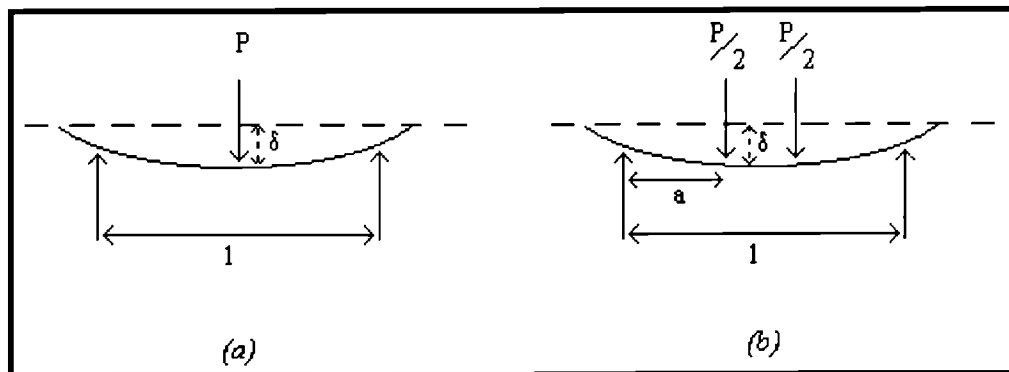


Figure (3.5) - diagram of uniaxial flexure geometries used to calculate E ; (a) - 3-point-bend; (b) - 4-point-bend.

$$E = \frac{Pl^3}{4\delta bd^3} \text{ Equation (3.4a)}$$

$$E = (3l - 4a) \frac{2Pa^2}{\delta bd^3} \text{ Equation (3.4b)}$$

where P = applied load

b = width of bar

d = depth of bar

all other dimensions given in figure (3.5)

3.2.2.(ii) Biaxial Flexure

A programme was developed in Mechanical Engineering department (Adamson, 1995), which could calculate E from the entire force versus deflection (F/δ) biaxial flexure plots. Using an assumed E value, the programme would produce the F/δ curve that would be obtained during biaxial flexure. This curve was then compared to the experimental F/δ data, and the assumed E value adjusted until the curves overlapped. This value was taken as the modulus.

Using this technique E was calculated at room temperature and 950°C for sets C and D, using 15 samples at each temperature. From problems noticed when testing these samples, 2 extra samples from each set were polished so that they were completely flat on both surfaces, and then tested at temperatures ranging from room temperature to 1050°C. Also, two alumina discs were cut and ground flat to thicknesses of 140µm and 270µm and tested in the same manner, in order to check the validity of this technique for such thin specimens.

3.3 Strength

3.3.1 Uniaxial Flexure

The strength of unaged and aged bars, and the effect that the ground surface finish might have, was investigated using a 3-point-bend apparatus. Three batches of samples were tested, which had been prepared differently: the faces of 12 unaged samples were ground parallel using a SiC wheel and these samples tested, the faces of 12 bars were ground parallel prior to ageing and then tested, and 11 bars were aged and then the faces ground parallel before being tested. The tests were all performed at room temperature using a Nene testing machine with a 1kN load cell, at a loading rate of 1mm/min., and the strength was calculated from equation (2.9(a)) using dimensions measured at the position of fracture.

3.3.2 Biaxial Flexure

3.3.2.(i) Ball-on-ring Geometry

The ball-on-ring apparatus was made of silicon nitride and is shown in figure (3.6). The support ring consisted of 23 polished sapphire balls, and was of diameter 25mm. The

plunger, by which the load was transferred, was aligned concentrically with the support ring. The apparatus was fitted onto a MAYES (ESH 100D) servo-hydraulic testing machine, with a 10 kN load cell.

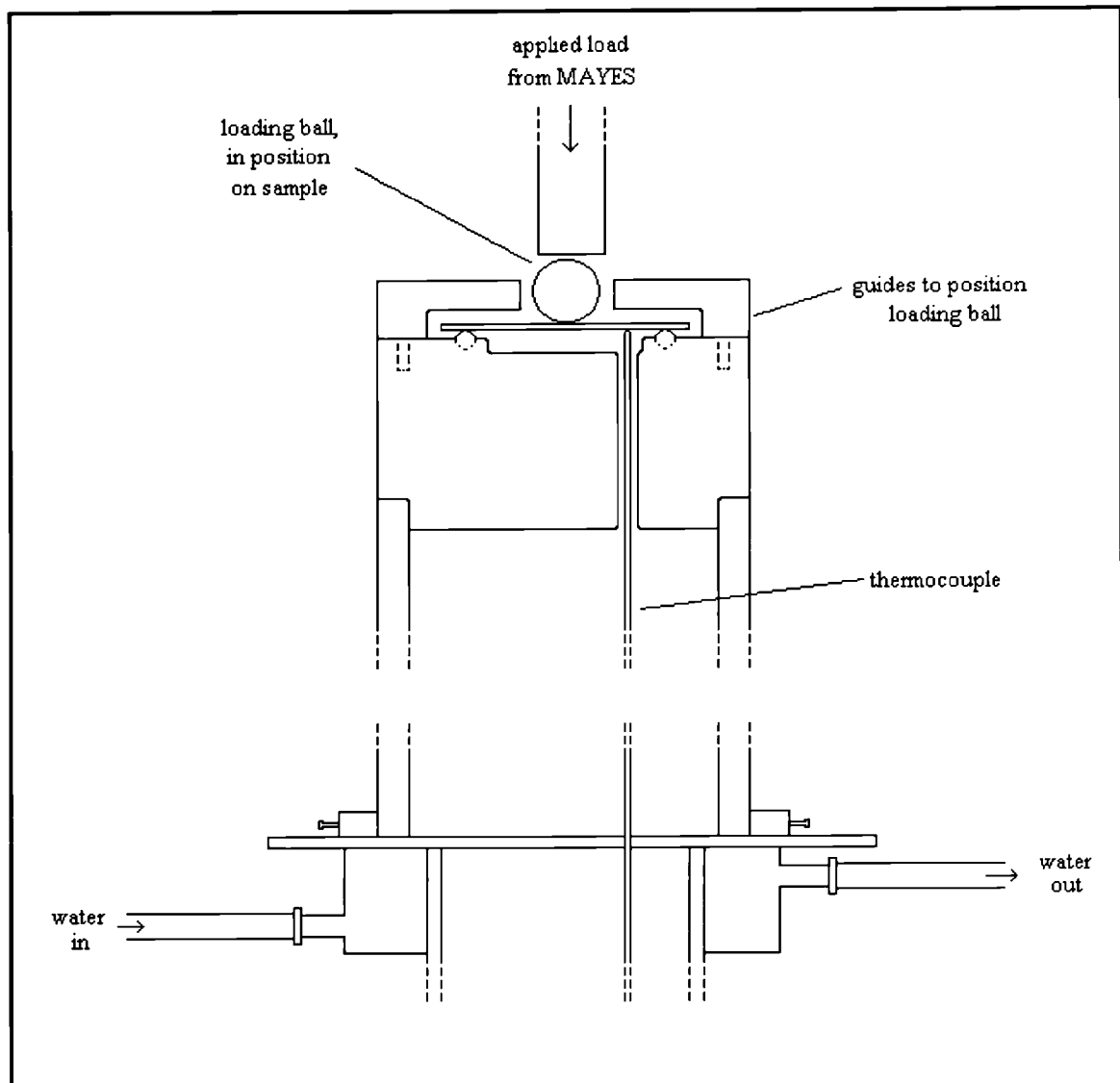


Figure (3.6) - diagram of the ball-on-ring biaxial flexure apparatus.

Samples were loaded by an alumina ball being pushed into their centre, at a rate of 0.5 mm/min. Force versus deflection plots were recorded as each test proceeded, until the sample fractured; the strength was calculated from equation (2.10(a)) using the load at this point, and taking the dimensions of the specimens at the origin of fracture. This position was estimated by re-assembling the fractured samples; the origin was taken as the point at which the fragments met. The loading radius, b , was taken as a third of sample thickness. (The samples were thick enough that the small displacement equation was applicable.)

The samples tested using this apparatus were the discs of set A, supplied by ICI. 9 discs were tested at room temperature, and 7 at 950°C.

3.3.2. (ii) *Ring-on-ring Geometry*

The initial ring-on-ring flexure tests were performed at Erlangen, using a steel apparatus, which is shown in figure (3.7). The 'cap' that is placed over the support ring ensured that the loading and support rings would be concentric, and that the sample would be centrally aligned to within 0.2mm. The diameters of the loading and support rings were 3.4mm and 17.0mm respectively, giving a ratio of 0.2.

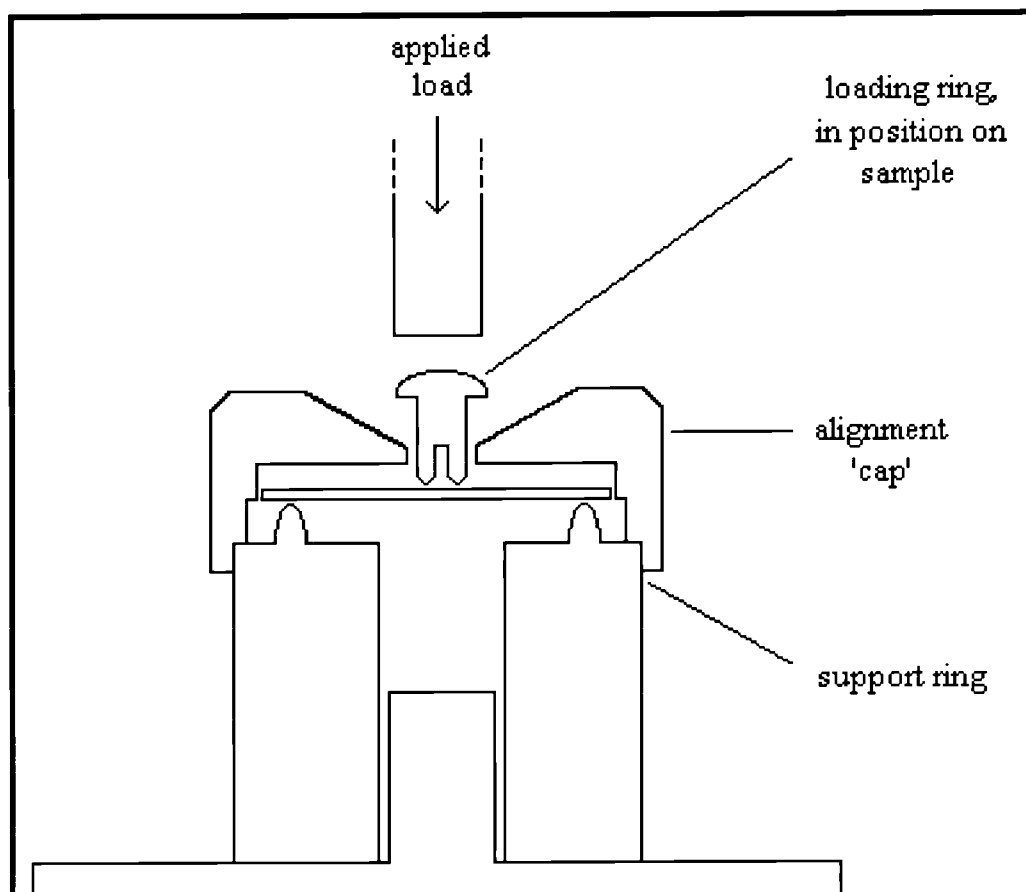


Figure (3.7) - diagram of the steel ring-on-ring biaxial flexure apparatus used at Erlangen.

60 samples from set B were tested at room temperature on this rig, 30 using a solid support ring, and 30 using a support ring made of ten polished ball bearings which were free to rotate. It was noticed that the samples had different textures on either side, with one surface being grooved and the other dimpled. Each sample was tested so that the dimpled surface was placed in tension, since it was assumed that this side would contain the most severe flaws. The samples were loaded at a rate of 0.6mm/min. until failure, using a 10kN load cell, and the failure stress of each sample calculated using an equation

derived from the Siemens FEA programme (Keim, 1990). These results were used to determine the mean strength and produce Weibull plots.

At Imperial College a silicon nitride ring-on-ring rig was built, based on the Erlangen design. The support ring consisted of 23 polished sapphire balls, and the loading ring had been ground and polished where it would contact the sample. 20 more samples of set B were tested at room temperature using this rig on the MAYES, now fitted with a 2.5kN load cell, at a rate of 0.5 mm/min, and the resulting Weibull parameters compared with those found using the Siemens' apparatus.

The Si_3N_4 rig was then used to test discs from sets C and D at room temperature and elevated temperatures. The conditions that these were tested under are given in table (3.2), along with a summary of the preceding samples. All the results were analysed and displayed in Weibull plots as before.

Table (3.2) - summary of the sample numbers and test conditions used to determine strength of each set. ss - solid support ring; bb - support ring of ball-bearings; IC - silicon nitride rig.

Set	Number of samples	Temperature, °C
A	9	RT
	7	950
B		
ss	30	RT
bb	30	RT
IC	20	RT
C		
unaged	15	RT
unaged	20	950
aged	20	RT
D		
	15	RT
	5	850
	15	950
	5	1050

3.3.2.(iii) SEM analysis

The fracture faces of some of the samples broken under each test condition from each set were gold coated and examined in the JSM 840 and T-220 SEM, to investigate the cause of failure and to study the microstructures.

EDAX was used to monitor the short and long-term effects of temperature on the yttria and impurity distribution, with digimaps being made of the tensile surfaces to reveal whether any segregation had resulted from the temperature treatments.

3.4 Fracture Toughness

3.4.1 Single-edge Notched Beam (SENB) Tests

Bars 4.73 - 4.78 mm thick were produced (section 3.1.2), and notched to a depth of 0.80 mm, using a diamond blade 0.3mm wide. These dimensions were used in order to give a minimum a/w ratio of 0.17 (Davidge, 1979; Dalglish, 1980). The effect of ageing on toughness was investigated by holding some samples at 950°C for 1000 hours. 5 bars were notched before aging, and 5 after aging, and 7 bars were notched and tested without any heat treatment.

All the bars were broken under 3-point-bend at room temperature, using a Nene testing machine at a loading rate of 1 mm/min. The toughness was calculated from equation (2.18), using the failure load and dimensions measured at the origin of fracture.

The fracture faces of samples from each batch were examined in the SEM, to obtain information on the sources of failure and crack propagation from the notch. The region behind the crack front, and damage at the notch tip, were analysed by cutting cross-sections of a sample from each batch, which were polished down to 3µm, as shown in figure (3.8). These were then thermally etched at 1300°C for 2 hours before being examined in the SEM.

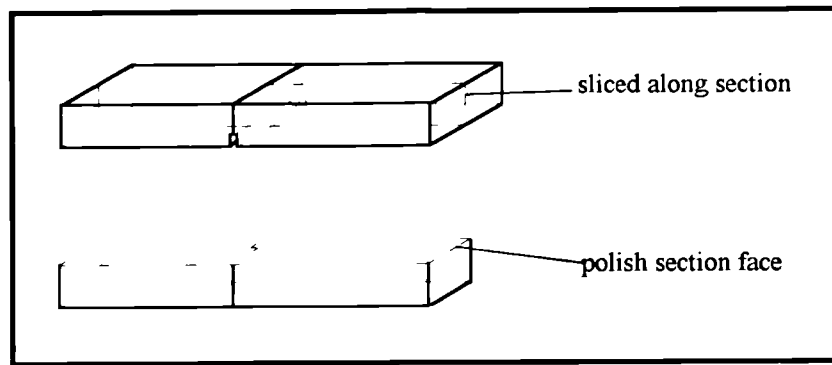


Figure (3.8) - diagram showing the cross-sectional preparation of SENB samples.

3.4.2 Double Torsion (D.T.) Tests

The samples tested were the tape-cast plates of set D material. A crack was introduced by scoring a notch about 5mm long in the centre of one side (with a diamond tip), and tapping the edge gently until a fine crack had propagated a few mm from this notch. A guiding groove was not used with these samples. The testing apparatus was a simplified version of a DT rig, using a 3-point-bend test set-up. The sample was supported at the notched edge, and the load applied directly onto the notch, away from the crack tip, as illustrated in figure (2.16).

The samples were loaded at a rate of 0.01mm/min, using an Instron (model no. 4200) with a 10N load-cell. A force versus displacement curve was plotted as the test proceeded; the load increased steadily as the sample was loaded, and then dropped slightly - this is the point at which the crack began to propagate. The load then remained constant until the sample failed catastrophically, and this is the load that was used in the toughness calculations, to give K_{Ic} .

5 samples were tested, and K_{Ic} calculated from equation (2.19). The fracture face of one sample was examined in the SEM.

3.4.3 Indentation Tests

For this technique tape-cast samples from sets C and D were polished down to a 3 μ m diamond finish. Initial tests using a Vickers indenter, at loads ranging from 2.5 kg down to the lowest possible of 1.0 kg, caused the samples to shatter, so the indents were inserted with a Leitz microindenter, which enabled lower indent loads to be used.

Indents were inserted into set D using loads ranging from 100 - 500g, and the resultant indent size and crack lengths measured optically immediately after indenting, and one day later for some samples, to see whether any crack growth had occurred with time. Some indented samples from set D were also examined in the SEM and the indent and crack dimensions were measured and compared with those obtained optically.

Unaged and aged samples from set C were indented using loads ranging from 100 - 350g, and the dimensions 2a and 2c measured optically. The toughness was calculated in all cases using equation (2.20).

In addition to SEM examination, a 3-D image of the indents and damage produced in the surrounding area from the indentation process was produced using the 'WYKO' interferometer. This technique used a Mirau objective lens to produce white light fringes, and a CCD camera in place of an eyepiece to collect the data. By moving the microscope head up and down very precisely, the fringes could be monitored over a height range, to give the 3-D image. Indented samples from set D were analysed.

3.4.4 Indentation Strength Bend (ISB) Tests

Since the indent sizes were fairly small in comparison with the intrinsic defects in the tape-cast material all the ISB samples were polished down to 3 μ m, in order to remove the surface flaws which could be greater than the indent crack. Indents were put into the centre of the samples, to an accuracy of 10 μ m, and the hardness, H_v , calculated from the optically measured indent sizes. The samples were then loaded until failure in biaxial flexure, using an Instron (model no. 1185) at a rate of 1mm/min, within 30 minutes of being indented.

The fracture face of each sample was examined in the SEM to ensure that fracture had initiated from the indent, and the size of the radial crack at the onset of catastrophic failure measured from the photographs. Samples which did not fail from the indent were not used to calculate toughness for that batch.

5 discs were tested from set D at each of the following indent loads, P; 0g, 100g, 200g, 300g, 350g. From set C the ISB test was used to compare the toughness for unaged and aged material. 4 unaged and 4 aged discs were each tested at indent loads of 100g and 200g. All tests were performed at room temperature.

The fracture strength, σ_f , was calculated from the failure load and sample dimensions, in the same way as for the strength samples, and graphs of $\log(\sigma_f)$ versus $\log(P)$ and $1/\sigma_f^3$

versus P were plotted for each set, from which the toughness was calculated. In order to compare the results from the ISB and indentation techniques, the size of the radial crack at the onset of catastrophic failure was measured from the SEM photographs and the toughness calculated using equation (2.21(a)), employing the E values determined from the natural frequency (*GrindoSonic*) technique.

3.5 Static Fatigue

3.5.1 Apparatus

The static fatigue rig was constructed as shown in figure (3.9), built to fit on an AWF 12/5 Lenton furnace, in which ten samples could be tested at one time. In order to be comparable with the biaxial fast fracture data the geometry of the static fatigue rig should be the same as that of the fast fracture rig; however minor adaptations had to be made, so the two rigs were not identical. The support rings were made of alumina tubes which were ground at one end to a knife-edge and then rounded off to give a solid support ring of diameter 17mm. The same was done for the loading rings, which were also tubes of alumina with one end rounded to give a contact diameter of 3.4mm. The samples, support rings, and loading rings were aligned concentrically by means of an alignment 'box'.

The lifetime of each sample was recorded individually by hour timers. Each timer was connected in series with a miniature roller switch, and power was maintained to the timer as long as this switch was closed. Steel loads of varying masses were made to fit on top of the loading rods, and these loads were designed so that they would keep the switches closed as long as the sample below remained intact. Once the sample broke, the loading ring and hence the load would drop down, opening the switch, and so stopping the timer. In this way the sample lifetimes were measured individually, to an accuracy of 0.01 hours.

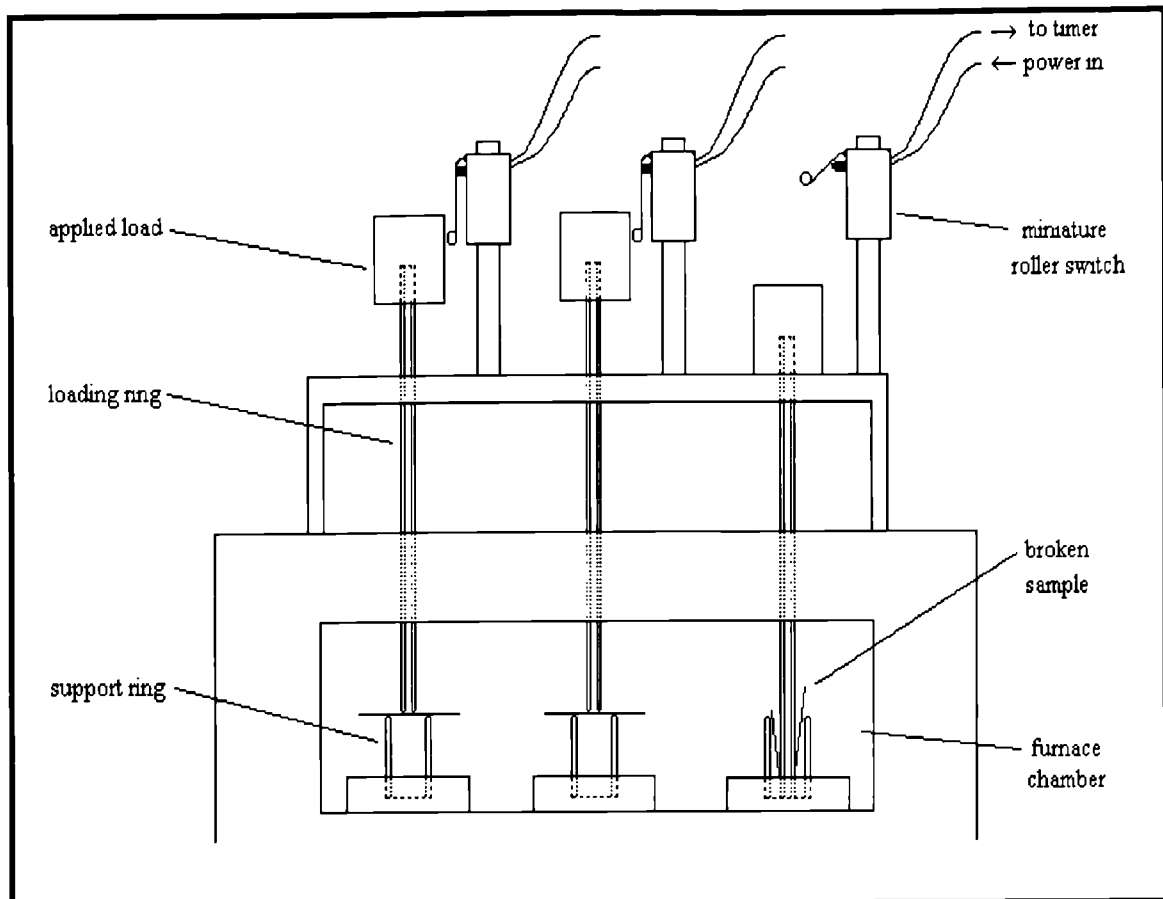


Figure (3.9) - diagram of the static fatigue rig constructed at Imperial College.

3.5.2 Static Fatigue Preparations / S-P-T Diagram

It was necessary to estimate the loads that would be required to cause failure of the tape-cast material within 1000 hours. To do this 5 batches of bevelled bars were broken in 3-point-bend tests on the Nene testing machine, each set at a different loading rate. The loading rates used were 1, 5, 40, 100, 1000 N/min., and there were ten samples in each batch. The median strength at each rate was calculated and used in a plot of $\log(\sigma_{med})$ versus $\log(\text{loading rate})$, from which the parameter n_f was obtained; this was then used in producing an SPT plot, and from this plot the load to cause failure of the discs within 1000 hours at 950°C was estimated to be 1N. The fracture faces of bars from each batch were examined in the SEM, in order to compare their cause of failure with those of the discs.

It was anticipated that the samples tested in static fatigue would fail over a range of times, and so the fracture faces of those which failed earlier would be exposed inside the furnace to a temperature of 950°C for a number of hours. In order to see whether this would affect the fractography, eight bars were broken under fast fracture, and one half of

the fractured sample heat treated. The treatments consisted of holding two pieces for 50, 100, 150, and 200 hours each at 950°C. Then the fracture faces of these samples were compared to those of the untreated halves using the SEM.

3.5.3 Creep

Samples from set C were used for the static fatigue experiments, but it was found that instead of fracturing after a certain time, as had been expected, the samples were deforming plastically. Thus it was decided to try and characterise the creep that was occurring, by measuring the stress exponent n_c , and the activation energy Q .

To calculate n_c , different loads were made, and five samples held under each load at the same temperature of 950°C, for approximately the same length of time, 1200 hours. The loads used, with the corresponding stresses, and the time each test was run for, are given in table (3.3).

To calculate Q , the load was kept constant but the temperature altered over a range of 75°C. Again, five samples were tested at each temperature, for times varying from 203 - 1200 hours, as detailed in table (3.3).

5 samples from set B were also tested, at 950°C and under a load of 40% σ_o , to observe the effect that a larger grain size would make on the creep rate.

Table (3.3) - summary of test conditions used to analyse the stress exponent and activation energy for creep. σ_o - Weibull strength for set C at 950°C.

load, (N)	σ_{app} , MPa	% σ_o	Temperature, °C	Time, (hrs)
1.0	46	18	950	1000
1.61	65	25	950	1200
2.53	90	35	950	1200
2.92	103	40	950	1200
3.12	116	45	950	1200
3.65	129	50	950	1200
4.30	145	56	RT/950	all failed < 0.5
5.87	181	70	RT/950	all failed < 0.5
2.92	103	40	1000	203
2.92	103	40	975	837
2.92	103	40	925	1000

An LVDT was also fitted to one sample, in order to monitor the deflection occurring with time. The LVDT replaced part of the applied load, making up the applied stress of 25%, at a temperature of 950°C.

The permanent deflection of each surviving sample was measured by scanning the profile of the tensile surface with a Taylor-Hobson Talysurf, which operated to an accuracy of 0.1µm. This Talysurf was computer controlled, and stored the profile as 1460 separate (x, y) points; these were transferred to an excel file, from where the data could be manipulated. Two scans were taken of each sample, at 90° to each other, and the strain for each scan calculated separately, in order to give a mean strain for each sample.

Two techniques were used to calculate strain from the deflection data. The first, termed the 'Fett' technique, only used data from the central region of the samples. It is based on the assumption that the shape of the deflected sample within the equibiaxial stress region (i.e. inside the loading ring) can be taken as a part of a spherical surface. Strain is determined geometrically from equation (3.5) (Fett, 1988):

$$\varepsilon = \frac{4t\delta}{r^2} \quad \text{Equation (3.5)}$$

where ε = strain
 t = sample thickness
 δ = deflection
 r = radius of region under consideration

In each case the radius was taken as ~ 1.5 mm from the maximum point of deflection. A smooth curve was fitted to this selected region using an excel least-squares-regression-programme, which eliminated spurious deflections due to surface roughness, and the deflection measured from this plot. Hence strain was calculated using equation (3.5).

The second technique measures the extension of the deformed sample, and strain is calculated from equation (3.6):

$$\varepsilon = \frac{l_{ext} - l_o}{l_o} \quad \text{Equation (3.6)}$$

where l_{ext} = deformed length
 l_o = original length

This technique used the Talysurf data across the whole surface, by forming right-angled triangles between each set of x and y points and calculating the hypotenuse, as illustrated in figure (3.10) and equation (3.7). The sum of these hypotenuse gave the deformed length of the samples. This technique was termed the 'triangle' technique.

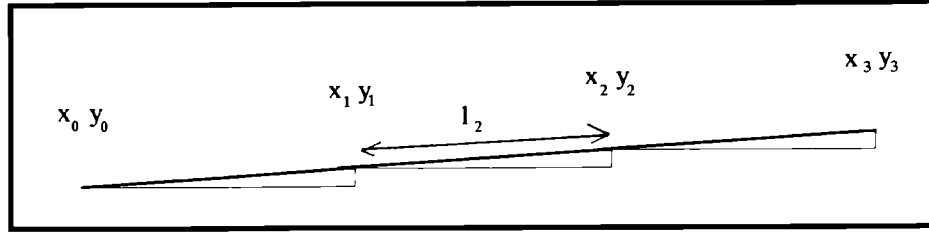


Figure (3.10) - diagram illustrating the measurement of the length of deformed samples, using the 'triangle' technique.

$$l_2 = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2} \quad \text{Equation (3.7)}$$

The strain values calculated by both methods were converted to the strain rate via the known time of the test.

(Another technique to measure the strain was to paint Fe₂O₃ grids, consisting of a regular array of 1mm diameter circles, onto the tensile surface of samples before testing, and to measure the deformation of the circles after the test. However, attempts at producing consistent grids proved unsuccessful, so this method was abandoned.)

3.5.4 SEM / TEM Examination

The fracture faces of samples which had failed at various times during the tests were examined in the SEM, as were the tensile surfaces of samples which had deformed but not fractured. Also, some samples which had survived the creep tests were fractured under biaxial flexure at room temperature; these fracture faces were compared using the SEM with those which had failed during the creep tests.

TEM specimens were prepared from the central region of a deformed sample that had been loaded at 50% σ , which had displayed the most deformation, and also from unaged and aged samples, to elucidate the deformation processes by which creep had occurred, and to check whether any new phases had developed during the heat treatments.

Specimens 3 mm in diameter were cored out from the samples, and these were then levelled, dimpled, and ion-beam thinned until a tiny hole had been worn through the centre. The surrounding area was up to $\sim 0.2\mu\text{m}$ thick, and suitable for examination in the TEM. Two microscopes were used - the JOEL 2000 FX Mark 1, which was fitted with EDAX analysis facilities, and the high resolution JOEL 2010. This work was carried out with the assistance of Mr. Y. Li.

CHAPTER 4

RESULTS

CHAPTER 4

RESULTS

4.1 Sample Analysis

4.1.1 Thin Film Samples

4.1.1.(i) Microstructure

The average grain size for each set is given in table (4.1), where it can be seen that the mean grain size of sets A and C was smaller than that of sets B and D.

The texture goniometry showed that the grains were oriented in a completely random manner, with no preferred grain orientation resulting from the tape-casting process.

4.1.1.(ii) Physical Properties

The density values for each set are given in table (4.1), where it can be seen that the density of set C was lower than both sets B and D.

The thermal expansion coefficient of set D determined from the dilatometry run was $1.05 \times 10^{-5} / ^\circ\text{C}$, with there being no sudden gradient changes in the expansion plot.

4.1.1.(iii) Phase Analysis

XRD revealed that the structure of each set was completely cubic, as listed in table (4.1), from room temperature up to 1100°C . Neither the DSC nor the DTA analysis revealed any phase transformations, or gave any indication that structural changes were occurring, over the temperature range of room temperature up to 1200°C .

4.1.1.(iv) Compositional Analysis

The EDAX results showed that there was a variation in the yttria content between the sets from the quoted nominal 8 mol%; the yttria content varied from 7.0 mol% in set D to 8.7 mol% in set A (see table (4.1)). The only significant amount of impurity detected

was alumina, and this was only in the set A material, supplied by ICI. DIGIMAPS plotted for samples from each set showed the yttria distribution was not completely random, but lay more heavily in the form of rings, as shown in figure (4.1). These rings appear to be the outline of grains, but if so would correspond to a grain size of 10 - 20 μm , irrespective of the material being analysed. This is actually greater than any of the measured grain sizes, and the same distribution was found for samples with different grain sizes. Thus the yttria does not lie simply along all the grain boundaries.

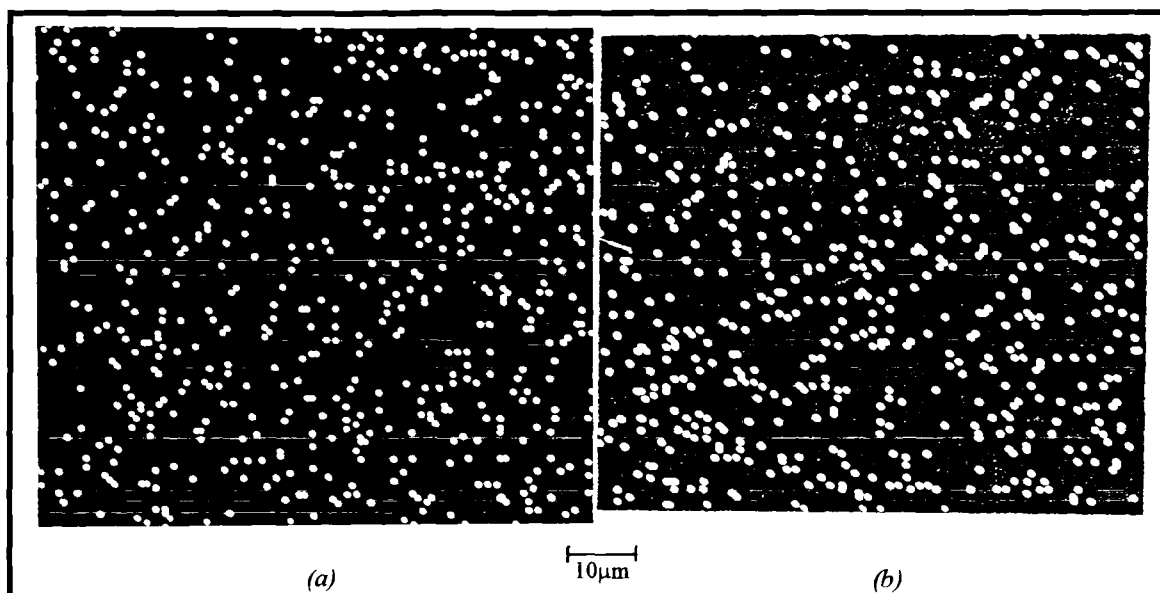


Figure (4.1) - DIGIMAPS showing the Y^{3+} distribution in tape-cast material; (a) set C aged; (b) set D.

Table (4.1) - summary of the structural, physical, and chemical analysis of tape-cast material, $\pm$ one standard deviation.

Set	Phase	mol% Y ₂ O ₃	mol% Al ₂ O ₃	mean d, μm	mean ρ, g/cm ³
A	cubic	8.7	0.7	3.2 ± 0.29	-
B	cubic	7.7	negligible	8.8 ± 0.70	6.02 ± 0.15
C					
unaged	cubic	7.7	negligible	3.6 ± 0.59	5.81 ± 0.10
aged	cubic	7.7	negligible	3.2 ± 0.35	5.83 ± 0.06
D	cubic	7.0	negligible	5.9 ± 0.22	6.08 ± 0.01

4.1.1.(v) Topography and Profile

It could be seen by eye that the surface finish of the samples were different. The ICI material (set A) was smooth on both surfaces, whereas the samples from Kerafol and Siemens were 'rough' on one side and 'smooth' on the other. The rough surfaces

appeared dimpled, and tiny 'burst blisters' were observed on some; the smooth surfaces of samples from Kerafol (sets B and C) were covered in parallel grooves, measured as 200 μ m apart, but were flat on the material from Siemens (set D), although scratches could be seen across many of these surfaces. The roughness values determined from the Talysurf are given in table (4.2).

Table (4.2) - mean surface roughness values of tape-cast material, $\pm$ one standard deviation.

Set	R _a values, μ m	
	Smooth surface	Rough surface
A	0.11 ± 0.05	-
B parallel to grooves across grooves	0.08 ± 0.01	0.29 ± 0.05
	0.15 ± 0.02	-
C - unaged parallel to grooves across grooves	0.11 ± 0.02	0.31 ± 0.06
	0.16 ± 0.02	-
C - aged parallel to grooves across grooves	0.12 ± 0.02	0.29 ± 0.04
	0.15 ± 0.03	-
D	0.09 ± 0.04	0.21 ± 0.04

The surface profiles measured by the Talysurf showed that the samples were quite warped, as illustrated in figure (4.2). The profiles were reasonably symmetrical around the centre, and the warpage was measured as a peak-to-trough value, which is given in table (4.3); the smooth surface virtually always contained the 'trough'. The extent of the warpage varied within the sets, but in general was less severe in set D, and had decreased in the aged samples from set C.

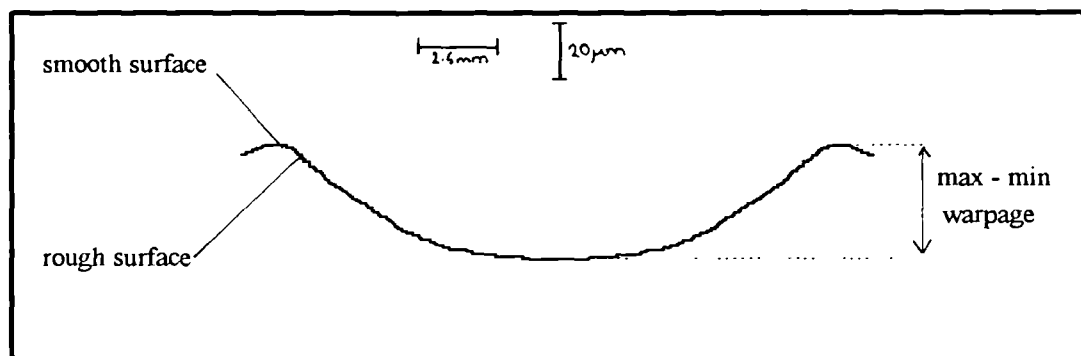


Figure (4.2) - Talysurf profile of a tape-cast disc sample from set C.

The profiles of the three samples from set C, measured before and after polishing away the rough surface, altered in just one case, where the peak-to-trough value doubled, from 34 μm to 69 μm .

The warpage measured across the plates of set D material was much less than that found in the discs, table (4.3).

Table (4.3) - summary of the warpage of the tape-cast material, $\pm$ one standard deviation.

Batch	peak-to-trough, μm
A	43 ± 5
B	44 ± 16
C	
unaged	39 ± 26
aged	26 ± 9
D	
discs	26 ± 15
plates	8 ± 2

There was often a slight variation in thickness, approximately 1-3 μm , across the diameters of the discs.

4.1.2 Bulk Samples

XRD of the bars revealed that the structure consisted of cubic phase. The average grain size was $6.9 \pm 0.1\mu\text{m}$, and density was found to be $5.99 \pm 0.005\text{ g/cm}^3$.

The value for the coefficient of thermal expansion was found to be the same as for the tape-cast material, $1.05 \times 10^{-5}/^\circ\text{C}$.

4.2 Young's Modulus

4.2.1 Dynamic Techniques

4.2.1.(i) GrindoSonic

a) Bulk Samples

There was no systematic variation in Young's modulus with thickness of the bulk samples over the thickness range of 0.5 - 5.0 mm. The average value obtained for all the bars was 201 GPa, with a standard deviation of 3. Using different materials as the supports, and changing the detector, made no difference to the modulus value calculated. There was no change, within the experimental scatter, in the modulus value for the aged bulk material, which is as would be expected for this property.

As the temperature was raised it became difficult to detect the frequency of vibration. A consistent frequency could only be obtained up to $\sim 200^{\circ}\text{C}$; the modulus decreased with increasing temperature (see table (4.4) and figure (4.3)).

Table (4.4) - showing the variation of E with temperature for bulk samples, tested using the GrindoSonic.

Temperature, $^{\circ}\text{C}$	Young's modulus, GPa	Normalised E values
20	198	1.0
102	195	0.98
201	148	0.75

b) Tape-cast Samples

The average room temperature values determined for the tape-cast samples from sets B, C and D, and also for the alumina samples prepared at IC, are given in table (4.5). The values for set C are slightly lower than for sets B and D, but the general agreement with E of FSZ given in the literature is good, as is that found for the alumina samples.

Table (4.5) - mean E , $\pm$ one standard deviation, for tape-cast FSZ and ground alumina discs, tested using the GrindoSonic.

Set	Young's modulus, GPa	
	as-fired surface	polished surface
B	202 ± 6	-
C unaged aged	195 ± 5	213 ± 9
	193 ± 2	-
D	203 ± 8	236 ± 2
Al₂O₃	352 ± 4	-

4.2.1.(ii) 'Velocity of Sound' Technique

No accuracy or consistency in the detected signal could be obtained at room temperature using either the aluminium or FSZ samples. When the wave guides were used, a signal could be detected using both Al and FSZ samples, but there was still no consistency in the values obtained. The results obtained for the FSZ over the temperature range of 350°C are displayed in table (4.6), where the erratic nature of the readings obtained can be seen.

Table (4.6) - showing the variation of E with temperature calculated using the 'velocity of sound' technique.

Temperature, °C	1st attempt, GPa	2nd attempt, GPa	3rd attempt, GPa
20	74	24	21
100	96	58	21
200	96	47	24
300	28	24	41
350	24	24	33

4.2.2 Static Techniques

4.2.2.(i) Uniaxial Flexure

The tape-cast samples used in the 4-point-bend geometry failed at such low loads that the force versus deflection plots could not be readily obtained with the equipment available. However, force versus deflection plots from the 3-point-bend geometry could

be used, and values of E were calculated up to 600°C. Since the deflections were measured using cross-head displacements, and the sample dimensions were outside the limits set for the test, the actual values did not agree well with literature (at RT); however, the values were normalised with regards to the room temperature value, and included in figure (4.3). These values are given in table (4.7), where E is shown to decrease with temperature.

Table (4.7) - showing the variation in normalised E values with temperature for tape-cast bars, tested using 3-point-bend flexure test.

Temperature, °C	Normalised E
20	1.0
200	0.83
400	0.60
600	0.58

4.2.2.(ii) Biaxial Flexure

It was found that the force versus deflection plots of the discs tested in the 'as-fired' state were not sufficiently smooth to obtain accurate enough deflection values from, but this problem was improved considerably by using polished discs. The compliance of the rig was deducted from the overall deflection readings, and the corrected readings used to calculate E in the FEA model; the mean room temperature values were 199, 247, 303 GPa for sets C, D, and alumina respectively. The values for set C and alumina are slightly less than would be expected.

Although the values obtained from the different tests on the bulk and tape-cast samples differed considerably, when the results from each test (except the velocity test) were normalised to their room temperature value, good agreement for the temperature dependence of E was found (see figure (4.3)). Figure (4.3) demonstrates that whereas E for alumina was approximately constant over the temperature range of room temperature up to 800°C, the modulus of FSZ fell significantly with increasing temperature up to 600°C, and then rose less rapidly on further increasing the temperature up to 1050°C. Such a large change in modulus with temperature is unusual.

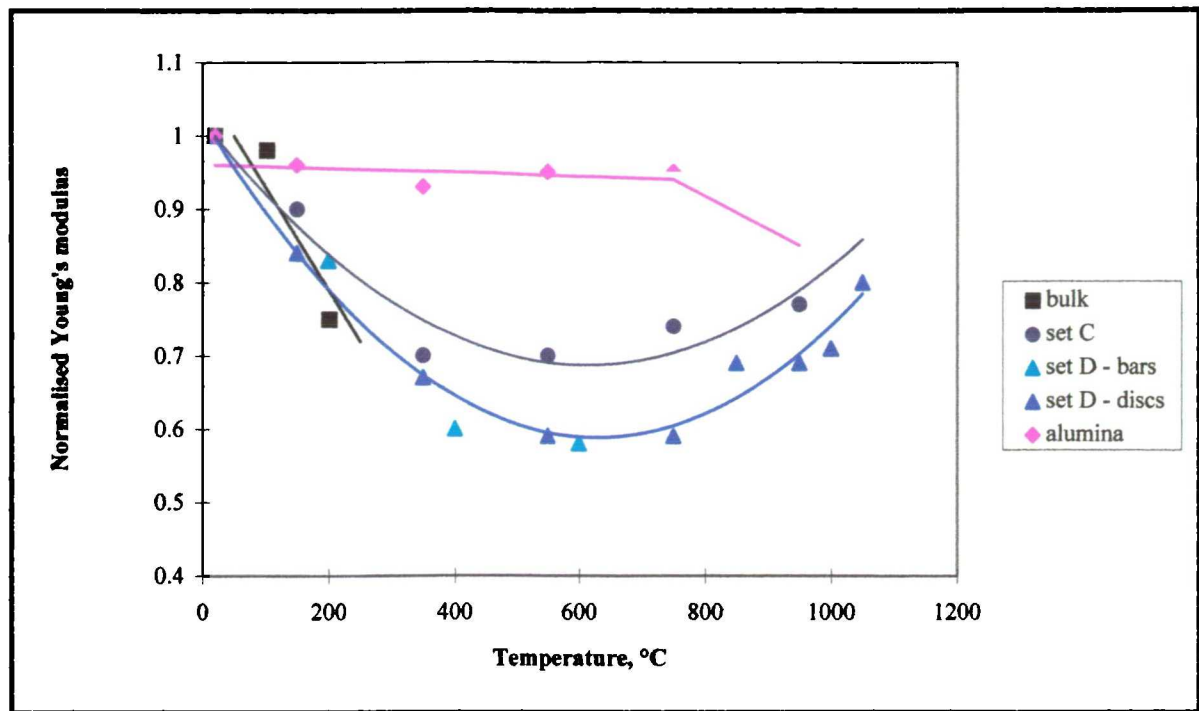


Figure (4.3) - graph showing the variation in E with temperature for bulk and tape-cast FSZ, and alumina samples, tested using GrindoSonic, uniaxial and biaxial flexure techniques.

4.3 Strength

4.3.1 Uniaxial Flexure

The mean strengths and standard deviations of the three sets of bars broken under 3-point-bend are given in table (4.8). The values for the unaged and aged / ground batches were virtually identical, and the t-test showed that the differences between all three batches were statistically insignificant.

Table (4.8) - summary of the mean strength, $\pm$ one standard deviation, for heat treated bulk samples tested using 3-point-bend flexure.

Set	Strength, MPa
unaged	232 ± 21
ground/aged	219 ± 41
aged/ground	231 ± 20

4.3.2 Biaxial Flexure

4.3.2.(i) Ball-on-ring

The mean strength and standard deviation of set A broken at room temperature and 950°C is given in table (4.9); the strength was found to have decreased by 57%, and the S.D. by 45% at the elevated temperature, which was confirmed as a significant difference. At both temperatures the samples failed into 3-6 fragments, emanating from the disc centre. The Weibull strength and modulus is also given in table (4.9), which confirm the strength drop, but show the scatter increases at the higher temperature.

Table (4.9) - summary of the mean strength $\pm$ one standard deviation, and Weibull data for set A tested at RT and 950°C using the ball-on-ring flexure test. () gives the number of samples tested.

Strength data	Test temperature	
	RT (9)	950°C (7)
mean strength	276 $\pm$ 38	119 $\pm$ 21
Weibull strength	293	128
Weibull modulus	7.9	6.4

Fracture faces of specimens tested at room temperature and 950°C were examined using the SEM. This showed that in all cases the site of crack initiation could be located at the tensile surface, but in only one sample was there an obvious defect - a porous cavity approximately 20µm in length, which opened onto the surface. In all the other samples examined, the area of initiation was of a similar size, but did not contain such a defect, as shown in figure (4.4). Although it is acknowledged that preferential scattering of the X-rays may occur from an uneven surface, EDAX was used to examine the area around the initiation sites in the fracture faces of specimens tested at 950°C; no additional segregation of yttria or alumina was detected, compared with the analysis from the polished samples broken at room temperature. The crack propagated in a transgranular fashion through every sample, as shown by the relatively flat fracture surface - see figure (4.5).

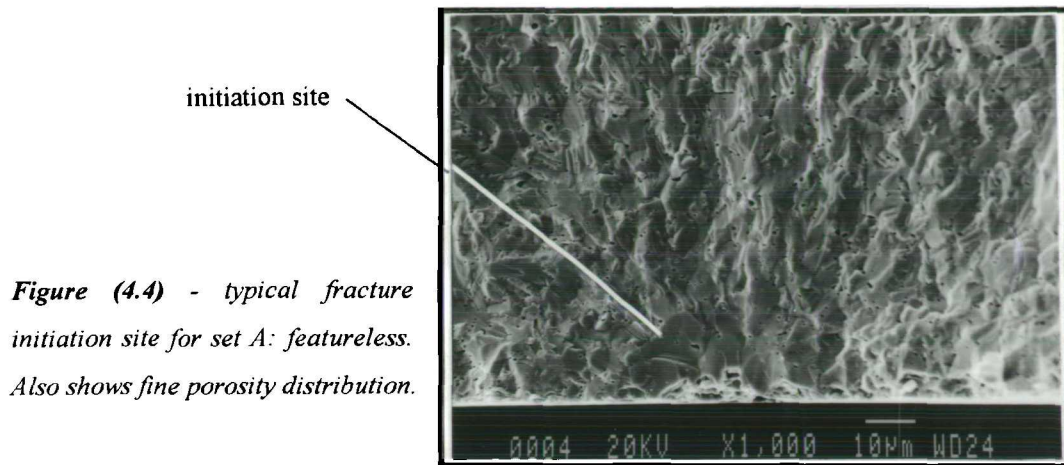


Figure (4.4) - typical fracture initiation site for set A: featureless. Also shows fine porosity distribution.

The microstructure seemed homogeneous in that there were no abnormally large grains, or inclusions, but defects were present in the form of cracks lying parallel to the sample surface, between 20 to 40µm long and 1µm thick, and distributed throughout the fracture faces (see figure (4.5)). Fine pores, most of which were spherical, were distributed throughout the structure, shown in figure (4.4).

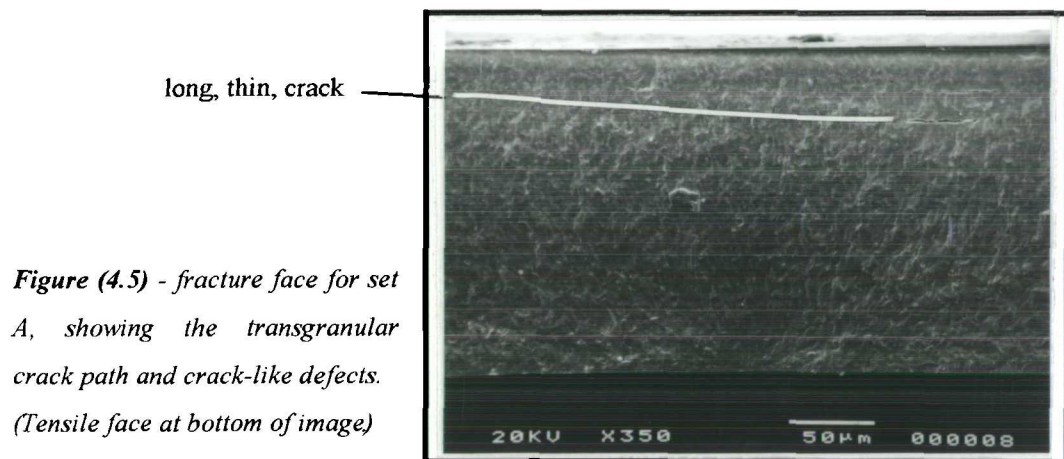


Figure (4.5) - fracture face for set A, showing the transgranular crack path and crack-like defects. (Tensile face at bottom of image)

4.3.2.(ii) Ring-on-ring

For every sample failure was found to have initiated from the tensile face, which was the rough surface for sets B, C, and D, and in the region of the loading ring, either directly underneath it, or slightly to one side. The number of fragments produced usually ranged from 2-11 pieces for set C, although the aged samples shattered into more, and set D never into more than 9 - and for those broken at 850°C, only into 2 pieces.

Young's modulus values were required to calculate strength from the FEA. At room temperature the GrindoSonic values for unpolished samples from each set were used; at high temperatures, the reduction from the room temperature values for sets C and D

were calculated using the individual curves shown in figure (4.3), and these values used in the calculations.

The Weibull plots for samples of set B tested at Erlangen, using the solid steel support ring (ss) and the steel support ring made of ball-bearings (bb), and tested at Imperial using the silicon nitride rig (IC) are compared in figure (4.6), where very good agreement between the three sets is shown. The Weibull strength and modulus were determined from the best-fit line, fitted to the data using a least-squares analysis, and the data summarised below in table (4.10).

The Weibull plots comparing the room temperature fracture behaviour of sets B, C, and D are shown in figure (4.7), and the plots of sets C and D tested at room temperature and 950°C are given in figure (4.8). These plots were all obtained using the silicon nitride rig at Imperial, and the Weibull data from them are summarised in table (4.10).

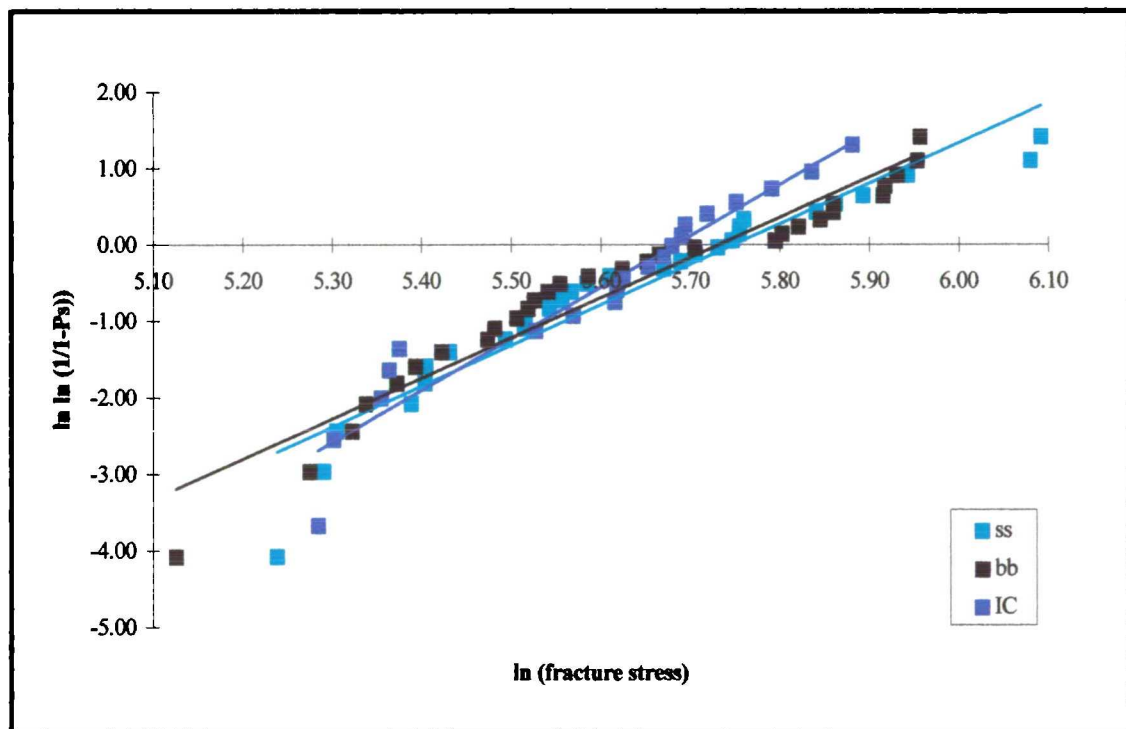


Figure (4.6) - comparison of Weibull plots for set B tested using a solid steel support ring (ss), a support ring made of ball-bearings (bb), and tested at Imperial College using the Si_3N_4 rig (IC).

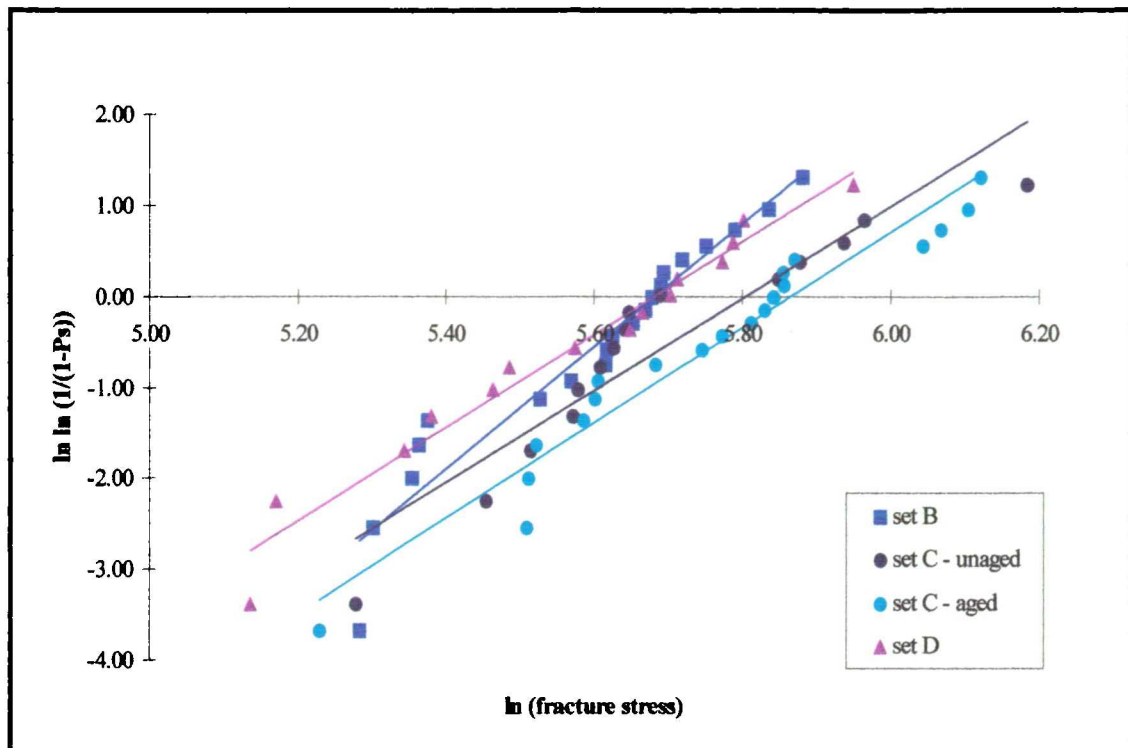


Figure (4.7) - comparison of Weibull plots for sets B, C, and D, tested at room temperature.

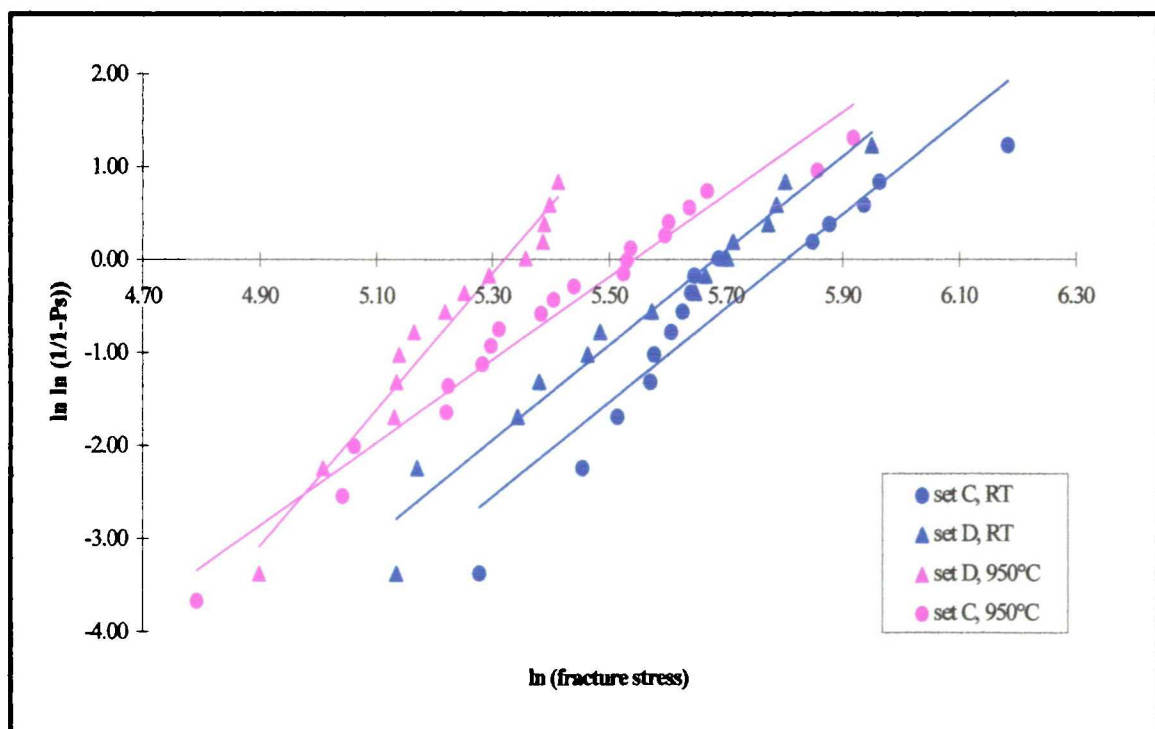


Figure (4.8) - comparison of Weibull plots for sets C and D tested at room temperature and 950°C.

Table (4.10) - summary of Weibull data for sets B, C, and D, tested using the ring-on-ring biaxial flexure rig at room temperature and 950°C. *ss* - solid support ring; *bb* - support ring of ball-bearings; *IC* - Si_3N_4 rig; () gives number of samples tested.

Set	Weibull data at RT		Weibull data at 950°C	
	σ_w , MPa	m	σ_w , MPa	m
B				
ss	314 (30)	5.3	-	-
bb	309 (30)	5.3	-	-
IC	294 (20)	6.8	-	-
C				
unaged	332 (15)	5.1	256 (20)	4.5
aged	353 (20)	5.2	-	-
D	294 (15)	5.1	205 (14)	7.3

The Weibull strengths at room temperature were of the same order, although set C was stronger than the others, and in reasonable agreement with the strength of FSZ given in literature. With the exception of the samples from set B tested at IC, the Weibull modulus was fairly constant between the different materials and rigs, despite the variation in the number of samples tested. A value of ~ 5 is reasonable for a ceramic tested in the as-fired condition. At 950°C, the Weibull strength of both sets C and D was found to decrease, by 23% for set C and 30% for set D. The Weibull modulus also changed in each case, but there did not seem to be any consistency in this, with it decreasing slightly for set C and increasing for set D.

The mean strength and standard deviation values were also calculated for each set and are given in table (4.11) (the mean strength was always $\sim 8\%$ less than the Weibull strength). The t-test was used to compare the sets and showed that there was no statistical difference between the samples from set B tested using the slightly different rigs, which was also the case for the data from sets B and D tested at room temperature using the Imperial apparatus. However, there was a statistical difference between unaged set C and sets B and D, where set C was stronger in each case. As with the bulk samples, the difference between the unaged and aged strength values of set C was shown as being statistically insignificant.

The t-test also confirmed that the decrement in strength for sets C and D at the elevated temperature was significant. The % decrease was the same using mean strengths as with Weibull.

Table (4.11) - summary of mean strength $\pm$ one standard deviation for sets B, C, and D tested using the ring-on-ring biaxial flexure rig at room temperature and 950°C. ss- solid support ring; bb - support ring made of ball-bearings; IC - Si_3N_4 rig; () gives number of samples tested.

Set	Mean strength, σ , MPa	
	RT	950°C
B		
ss	290 $\pm$ 67 (30)	-
bb	284 $\pm$ 64 (30)	-
IC	275 $\pm$ 47 (20)	-
C		
unaged	305 $\pm$ 74 (15)	233 $\pm$ 63 (20)
aged	325 $\pm$ 74 (20)	-
D	270 $\pm$ 61 (15)	189 $\pm$ 29 (14)

The mean strength data for set D over the temperature range RT to 1050°C are summarised in table (4.12), where the strength is shown to have decreased between room temperature and 850°C, but was beginning to rise between the temperatures of 850°C and 1050°C. The f-test confirmed that the difference in strength at each test temperature was significant, despite the small sample numbers tested at 850°C and 1050°C.

Table (4.12) - summary of the variation in mean strength with temperature of set D, $\pm$ one standard deviation; () gives the number of samples tested.

Temperature, °C	Mean strength, MPa
RT	270 $\pm$ 61 (15)
850	178 $\pm$ 39 (5)
950	189 $\pm$ 29 (14)
1050	214 $\pm$ 56 (5)

Set B was only tested at room temperature and most of the samples which were examined in the SEM were those weaker than the Weibull strength value, since these fractured into less fragments and so were easier to examine. The source of failure in these samples was usually found to be porous cavities, in the range 30-50 μm long, extending 10-20 μm inside those samples examined, and which were lying either on or

close to the tensile face, although occasionally the failure region was completely flat or featureless. A typical fracture initiating defect is shown in figure (4.9). A few samples which were stronger than σ_0 were examined, but a single source of failure could not be identified. The crack path was transgranular across the fracture face of the samples, and as with set A, small pores were seen everywhere across the face, although in set B they were sometimes found in clusters too (figure (4.10)).

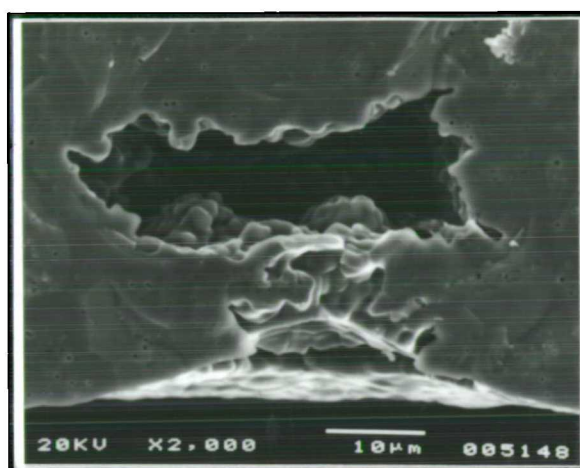


Figure (4.9) - typical fracture initiating defect for set B; porous defect.

pore cluster



Figure (4.10) - transgranular fracture path and porosity distributed throughout fracture face of set B, and sometimes in clusters.

The samples from set C tested at room temperature failed from porous cavities, ranging from 20 to 60 μm long, and extending about 20 μm from the surface into the disc; thus the initiation sites were similar to those in set B. The fracture face was transgranular around the defect area, but further away, in contrast to set B, was slightly intergranular,

merging into transgranular as the compression face was approached. As with set B, small pores and pore clusters could be seen throughout the microstructure.

Since the aged samples (set C) usually fractured into more fragments than the unaged (for similar strengths), only the weaker samples were examined, and the source of failure was found to be porous cavities in all cases. As with the unaged samples, the crack path was transgranular around the defect, but intergranular further away, figure (4.11).

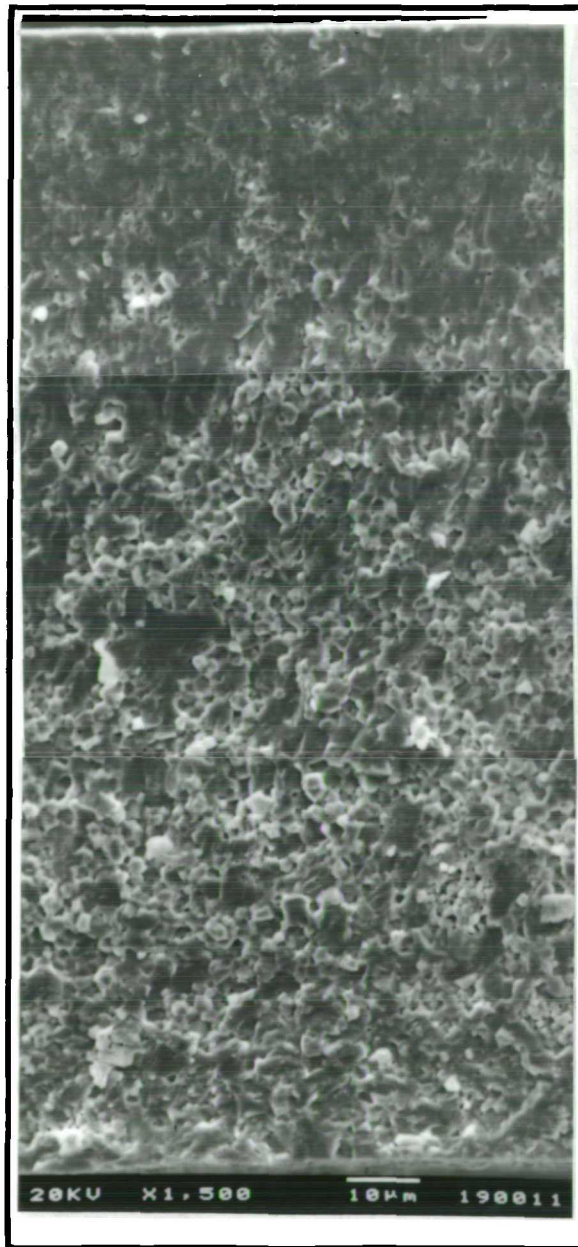


Figure (4.11) - intergranular fracture path seen in set C away from the initiation site, at RT.

For the samples broken at 950°C, the source of failure was porous cavities in some cases, for both strong and weak samples, but in others no obvious defect in the microstructure could be seen at the initiation site. The grain structure around the initiation region and approaching the compression face was always transgranular, and figure (4.12) shows a typical example of this, but the majority of the fracture face was intergranular.

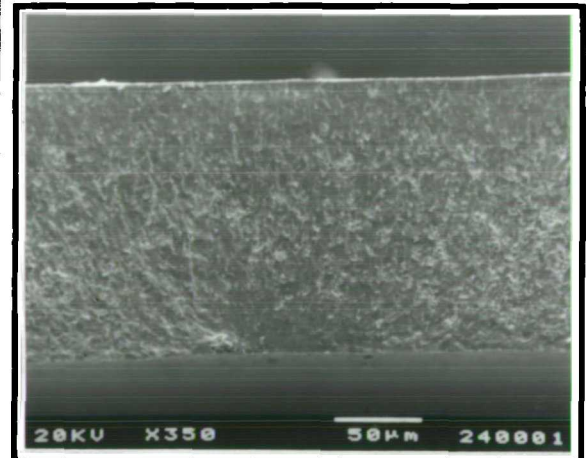


Figure (4.12) - overview of fracture face of set C, broken at 950°C; transgranular crack path around the initiation site and approaching the compression face,

The fractography of set D (supplied by Siemens) also changed as the temperature was raised. Both weak and strong samples which had been broken at room temperature were examined, and failure found to have initiated at cavities at or near to the tensile surface. These cavities tended to be long and narrow, 25 - 60 μ m in length, and 15 - 20 μ m deep. The crack path was transgranular across the faces, and there were less pore clusters than in the samples made by Kerafol (sets B and C).

At 850°C, cavities were still the source of failure, and the path was transgranular around the region and approaching the compression face, but further away it was starting to show intergranular tendencies.

At 950°C, the failure source was not always a cavity; sometimes there were two or three grains clearly defined, as in intergranular failure, surrounded by a completely flat, featureless region, shown in figure (4.13); the failure would seem to be initiated by a grain sliding process. For samples which did fail from cavities, there were small regions at the sides of the cavities where individual grains were clearly defined, as shown in figure (4.14). This was not observed in the samples which had been broken at the lower temperatures. In the vicinity around the initiation area the grain structure was transgranular, but became more intergranular further away.

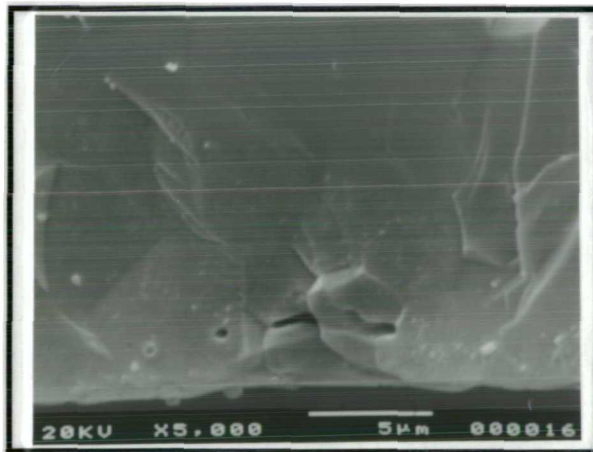


Figure (4.13) - grain sliding as the failure initiation site for set D broken at 950°C.

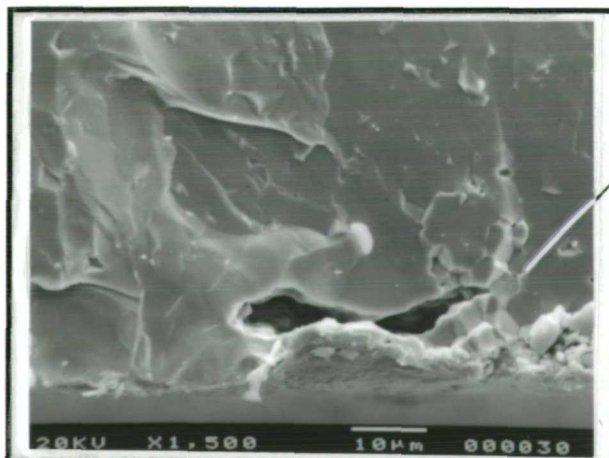


Figure (4.14) - failure initiation site for set D broken at 950°C; clearly defined grains shown at the side of the cavity.

This change in initiation site was revealed most obviously in the samples which had been broken at 1050°C; at this temperature only the two weaker samples failed from cavities at the tensile face, and around the sides of these porous defects was an intergranular structure, as seen in the samples tested at 950°C. The failure source in the other samples was from a few grains, with the immediate surrounding region being completely flat. The fracture faces now were very different to the room temperature ones. Close to the initiation region the structure was transgranular, interspersed with intergranular patches, but away from this region the path was completely intergranular, apart from a transgranular band at the compression face; an example of the fracture in the region of the defect is given in figure (4.15).

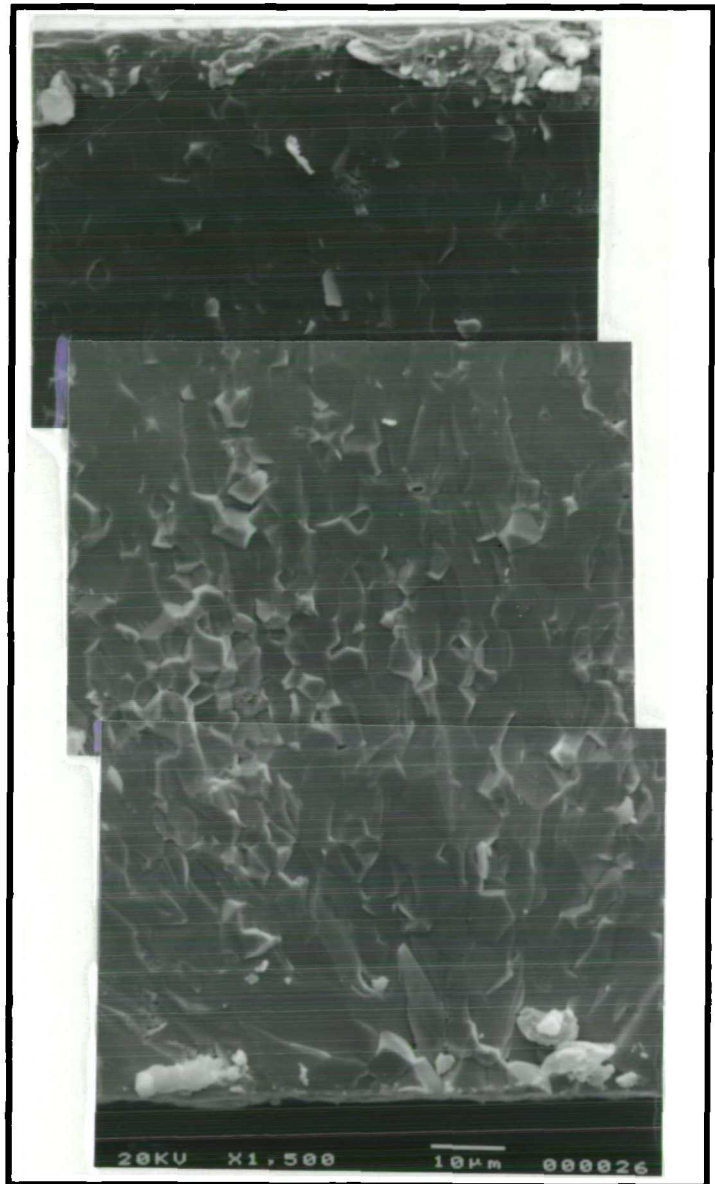


Figure (4.15) - overview of fracture face of set D broken at 1050°C; mixture of transgranular and intergranular crack path.

The difference in initiation sites and crack paths across the fracture face as the temperature was raised from room temperature to 1050°C is illustrated in figures (4.16) and (4.17).

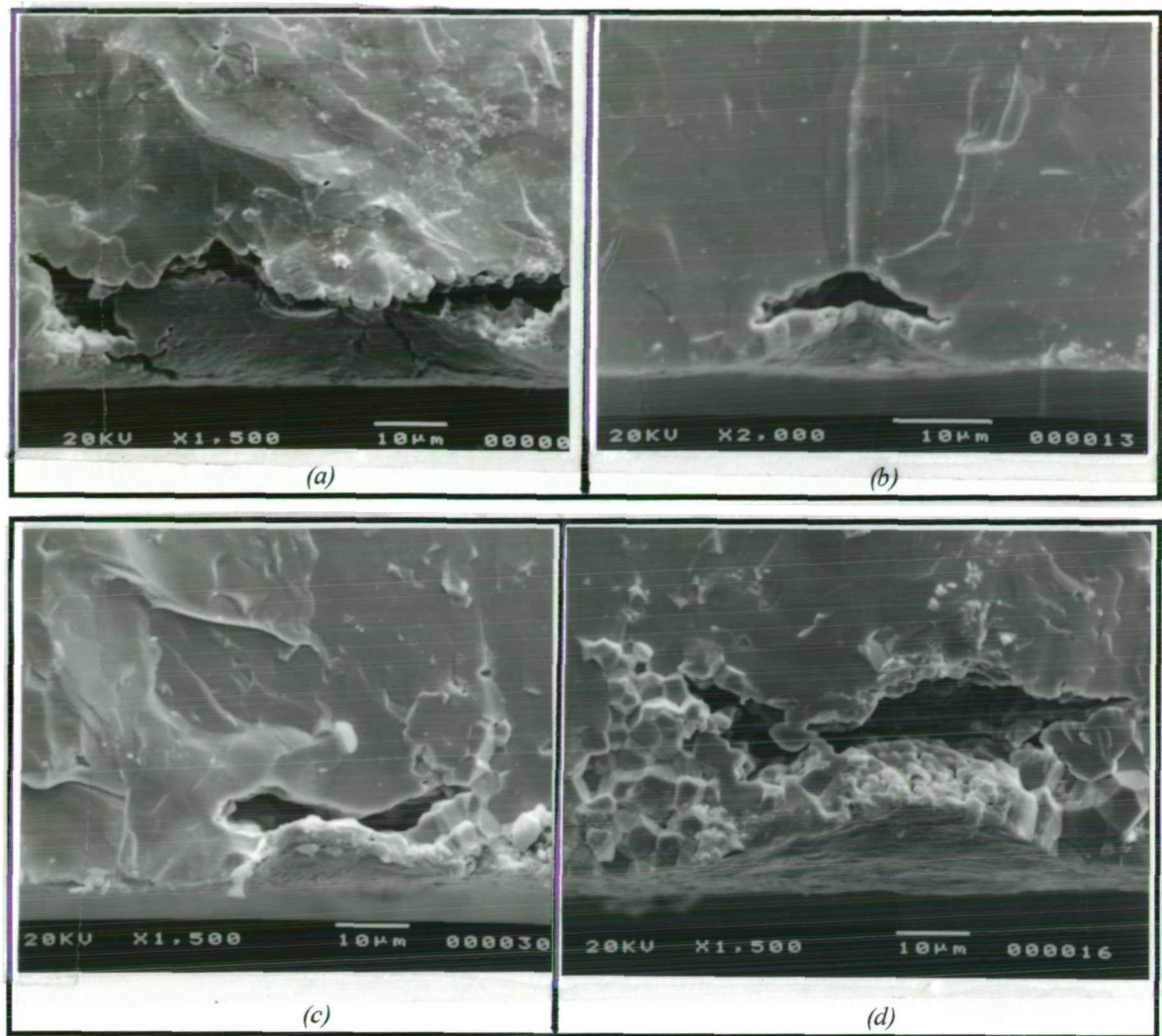


Figure (4.16) - change in initiation sites with increasing temperature; (a) RT; (b) 850°C; (c) 950°C, (d) 1050°C.

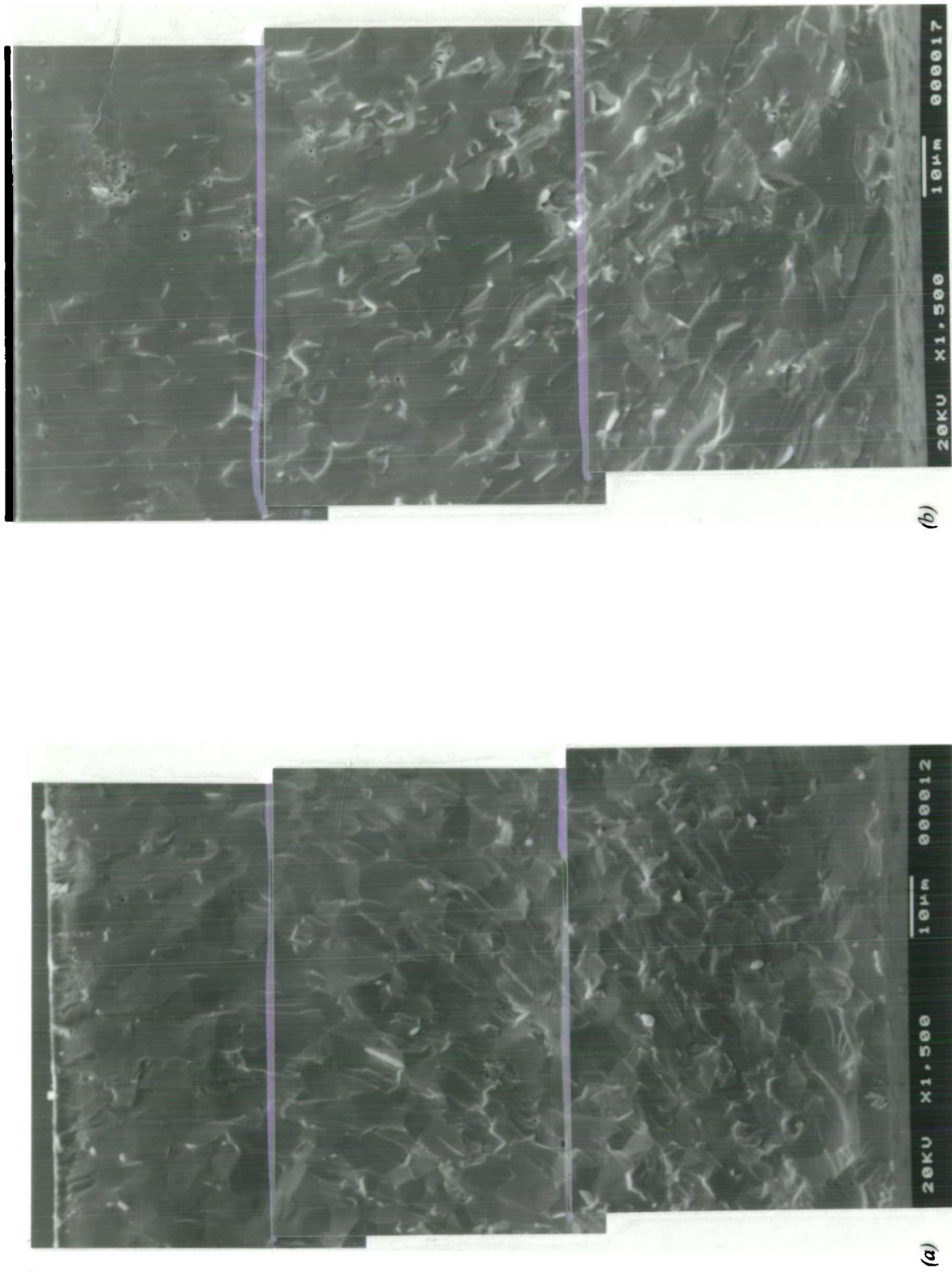


Figure (4.17) - change in crack paths with increasing temperature; (a) room temperature; (b) 850°C

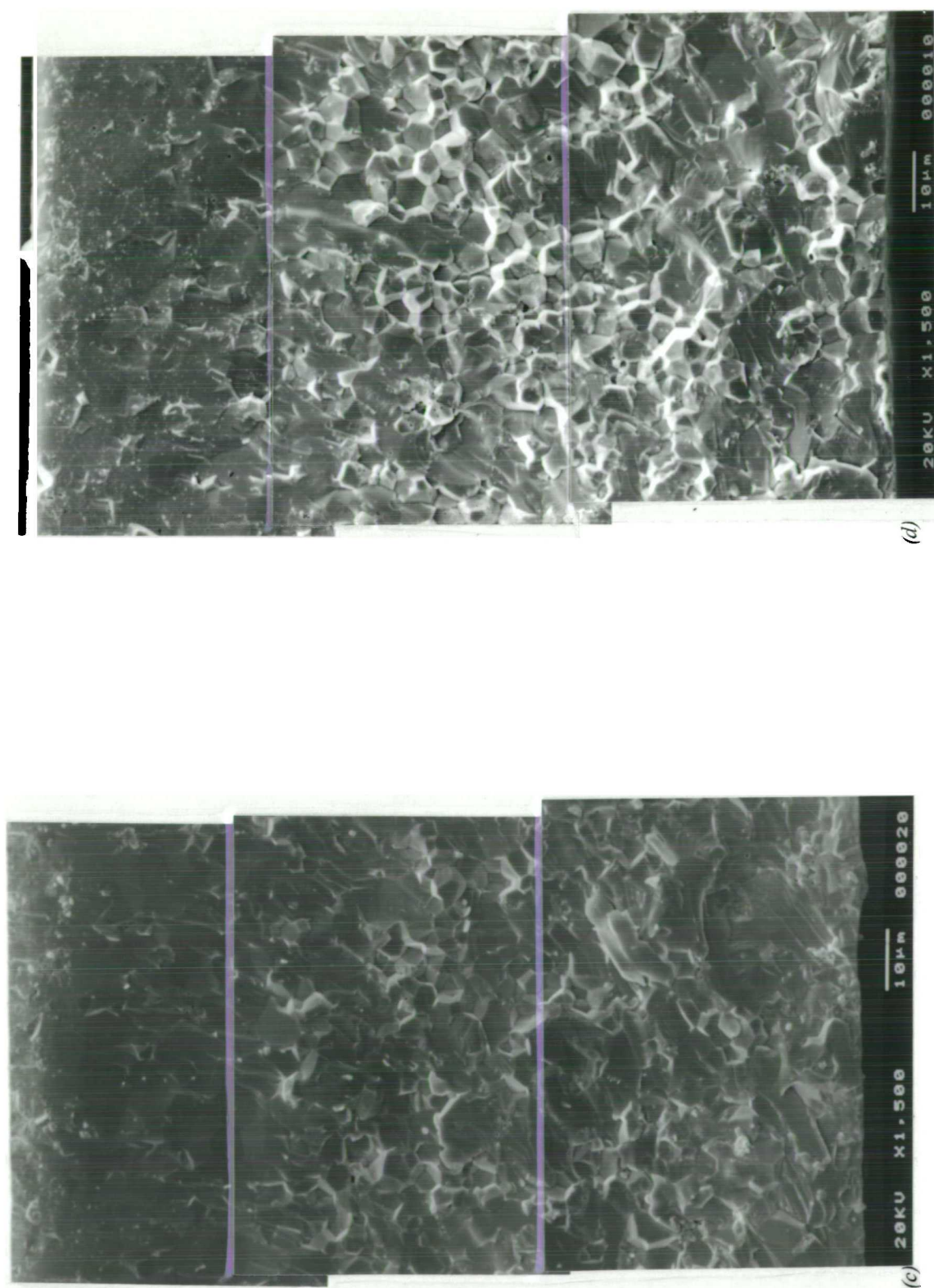


Figure (4.17) - change in crack paths with increasing temperature; (c) 950°C; (d) 1050°C

4.4 Fracture Toughness

4.4.1 Single-edge Notched Beam (SENB)

The values of K_{Ic} for the differently prepared bulk samples are given in table (4.13), and use of the t-test showed that there was a statistically significant difference between each of the three sets.

Table (4.13) - mean toughness values, $\pm$ one standard deviation, calculated for heat treated SENB samples.

Sample	K_{Ic} , $\text{MNm}^{-3/2}$
unaged	1.29 ± 0.29
aged/notched	2.36 ± 0.12
notched/aged	2.94 ± 0.41

The manner in which the crack propagated through the samples was also different for each set, most notably between the aged and unaged samples. From the SEM examination of the cross-sections, failure in the aged samples was shown to always originate at the notch tip, and the crack propagated in a straight line through the sample, at 90° to the longitudinal axis; thus the fracture faces were flat. In the unaged samples, however, failure often originated from the edge or corner of the notch tip, and the crack followed a convoluted path through the sample.

The difference in fracture is illustrated in figure (4.18).

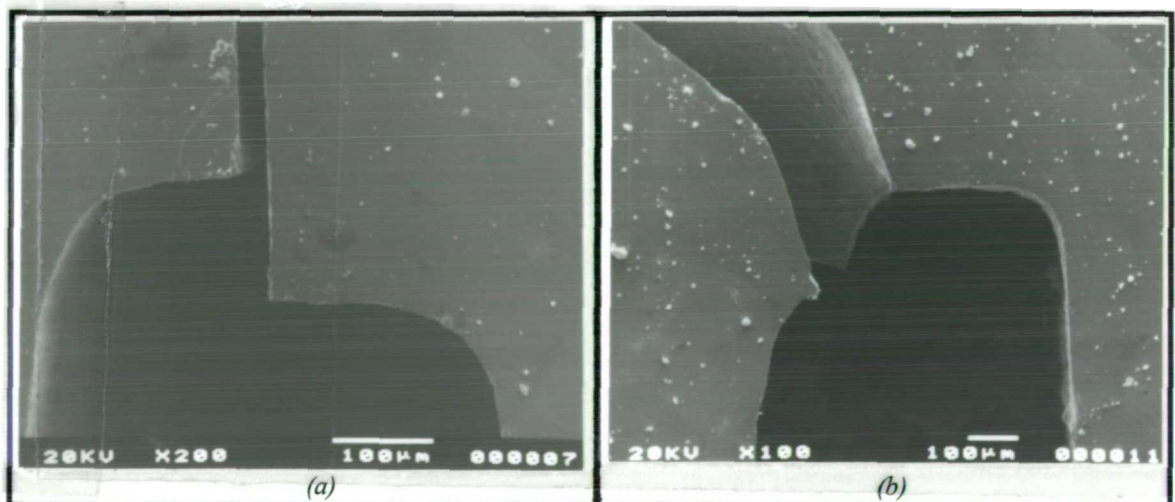


Figure (4.18) - comparison of failure at notch, shown in cross-section; (a) aged; (b) unaged.

There was a slight difference in the fracture faces of the samples which had been notched before and after ageing, with there being a few cracks and chips along the edge of the notch tips of the aged/notched samples which were not present in the notched/aged samples.

SEM examination behind the crack front, on the polished cross-sections, did not reveal evidence of extensive micro cracking in any of the sets, although there was a limited amount in the aged/notched samples.

4.4.2 Double Torsion (D.T.)

Toughness values for the plate samples of set D were calculated from the forces required to initiate and propagate the crack, and the average results shown in table (4.14). The cracks could be seen by eye propagating in a stable manner through the plates, but the rate increased rapidly as the crack tip approached the end of the sample, leading to catastrophic failure.

Table (4.14) - summary of the mean toughness, $\pm$ one standard deviation, calculated for set D using D.T.

Toughness, $\text{MNm}^{-3/2}$	
Initiation	Propagation
3.78 ± 0.38	3.03 ± 0.2

SEM examination of the fracture face showed that the crack had propagated steadily from the notch through the length of the sample.

4.4.3 Indentation and ISB

Young's modulus values were required to calculate toughness from the indentation techniques; the values used were those found by GrindoSonic for the unpolished material for each set.

Cracks were produced in tape-cast samples by indentation; the cracks initiated from the indent corners, and tended to be straight rather than follow a convoluted path. All samples indented at 500g spalled, so that the crack lengths could not be measured. For lower indent loads, the discrepancy in crack lengths measured by the optical microscope

and SEM increased as the indenting load decreased, with the values measured optically being underestimated. However, the toughness values were calculated using the optical measurements, in order that the readings from the ISB samples, which were fractured immediately after indenting, could also be incorporated. The estimated error in the toughness would be $\sim 26\%$ at the lowest load, dropping to $\sim 7\%$ with the 300g. The change in crack length after 1 day in a laboratory atmosphere was less than $1\mu\text{m}$ and therefore insignificant as far as the calculation of fracture toughness was concerned.

The plastic deformation that occurred on indenting the ceramic could be seen in the SEM, with material pushed up around the edges of the indent, but this was shown much more clearly using the WYKO optical interferometer. Images comparing the plastic deformation immediately around the indent, and the area it extended over, produced using loads of 100g and 300g are shown in figure (4.19); the radial cracking is not shown up well in this mode, but the surface displacement is well defined. Material was piled up to a height of $1.5\mu\text{m}$ around the indents, and the indents were also measured by the optical interferometer as $\sim 2\mu\text{m}$ deep.

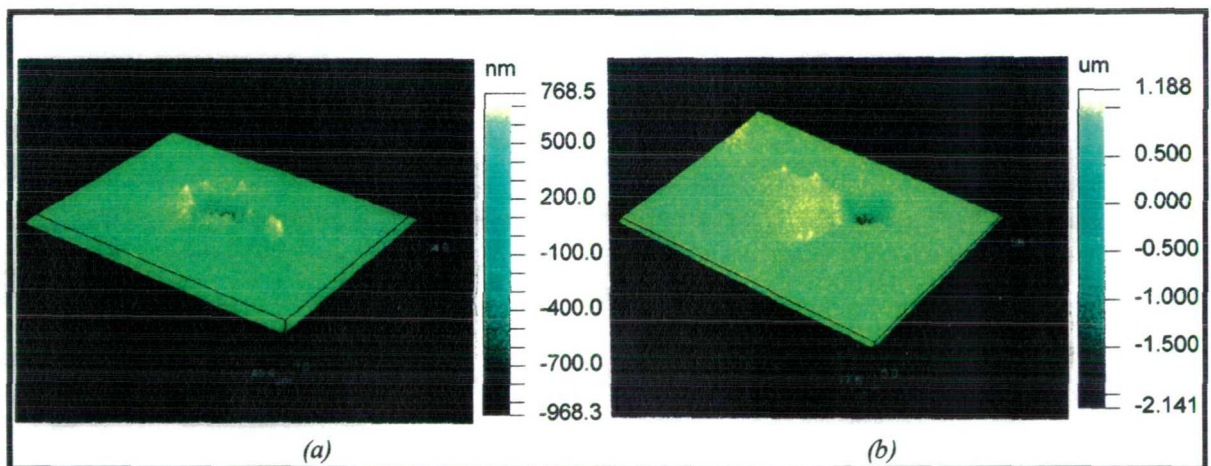


Figure (4.19) - comparison of the WYKO images taken of indents in set D, showing indent and surrounding deformation; (a) $P = 100\text{g}$, (b) $P = 300\text{g}$

The average K_{Ic} results from the post-indent technique (found using equation (2.20)) for sets C and D are given in table (4.15), where they are compared with K_{Ic} from the ISB technique (found using equation (2.21(a))), and shown to be much higher. The post-indent data shows that the size of the indent load did affect the toughness values, with K_{Ic} of set C being significantly higher when 100g and 200g were used, and of set D with 100g, than when the higher indent loads were used. There was very little difference between the unaged and aged toughness of set C at equivalent loads, nor was there a difference between the toughness of sets C and D at loads of 300g and 350g

Table (4.15) - summary of mean toughness values $\pm$ one standard deviation calculated from crack length measurements for sets C and D, using the post-indent and ISB tests, over a range of indent loads.

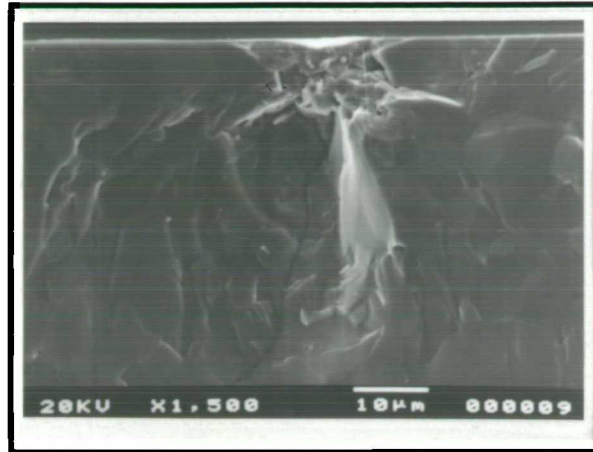
Set	Hardness GPa	Indent load, g	K_{IC} , MNm ^{-3/2}	
			Post-indent	ISB
C unaged	16.5 $\pm$ 0.2	100	4.33 $\pm$ 0.56	1.19 $\pm$ 0.15
		200	4.04 $\pm$ 0.50	0.80 $\pm$ 0.03
		300	3.24 $\pm$ 0.31	-
		350	2.99 $\pm$ 0.30	-
C aged	15.8 $\pm$ 0.1	100	4.29 $\pm$ 0.77	1.16 $\pm$ 0.13
		200	4.15 $\pm$ 0.46	0.87 $\pm$ 0.14
		300	2.97 $\pm$ 0.35	-
		350	3.11 $\pm$ 0.32	-
D	17.2 $\pm$ 0.1	100	5.08 $\pm$ 0.57	1.57 $\pm$ 0.19
		200	3.51 $\pm$ 0.63	1.62 $\pm$ 0.14
		300	3.52 $\pm$ 0.61	1.43 $\pm$ 0.00
		350	3.38 $\pm$ 1.20	1.44 $\pm$ 0.02

With the ISB test, the samples fractured into 2 or 3 pieces. The fragments were then examined in the SEM to verify whether failure had initiated from the indent. Two samples from set D, indented at 100g, failed from porous defects and so they were not used to calculate toughness, but in all other cases the samples failed from the indents. The unindented samples from set D failed from large porous cavities near the tensile surfaces.

The values found by the ISB tests were lower than the indentation toughness (table (4.15)), and the trends found in either technique were not the same; for set C, toughness dropped considerably as the load increased from 100g to 200g (by 30% and 25% for unaged and aged material respectively), whereas for set D there was found to be no significant difference in the toughness calculated at each load; the toughness of set D by the ISB method was always greater than that of set C. However, in agreement with the post-indent method, there was no significant difference in the unaged and aged results for equivalent loads.

SEM examination of the fracture faces of broken samples also revealed the extent of damage produced inside samples from the indent. Figure (4.20) shows the plastic deformation immediately around the indent, but also the median crack extending into the sample for set D, indented with a load of 200g. The size of the median crack varied with the indent load, but was approximately $t/4$ at 200g, $t/3$ - $t/2$ for 300g, and $t/2$ for 350g, indent loads of only 100g and 200g when indenting set C for ISB testing.

Figure (4.20) - fracture face of set D indented with load of 200g, showing plastic deformation immediately around indent, and median crack extending into sample.



From figure (4.20) the shape of the indentation radial crack seems to change from a typical half-penny to a semi-elliptical shape as fast fracture proceeds. This was so for all indent sizes.

The graph of $\log(\sigma_f)$ versus $\log(P)$ for each set is shown in figure (4.21). The gradient of the best-fit line to the data of set D is -0.24, but when a line of gradient -1/3 is added, it also fits reasonably with the data, which indicates the absence of R-curve behaviour. The gradients for set C are -0.22 and -0.07 for the unaged and aged samples respectively, although with there only being two data points it is not possible to ascertain the influence of normal experimental scatter on these results.

The graph of $1/\sigma_f^3$ versus P is shown in figure (4.22). The data for set D lies on a straight line, and from the gradient and intercept of this line values of $1.99 \text{ MNm}^{-3/2}$ and 0.2 N were calculated for toughness and P^* , respectively. The toughness of unaged set C found from figure (4.22) was $1.13 \text{ MNm}^{-3/2}$ and that of the aged material was $1.42 \text{ MNm}^{-3/2}$, although again these values must be treated with caution due to the low number of data points. All the toughness values calculated from the graphical ISB technique are greater than those found using equation (2.21(a)), which are presented in table (4.16).

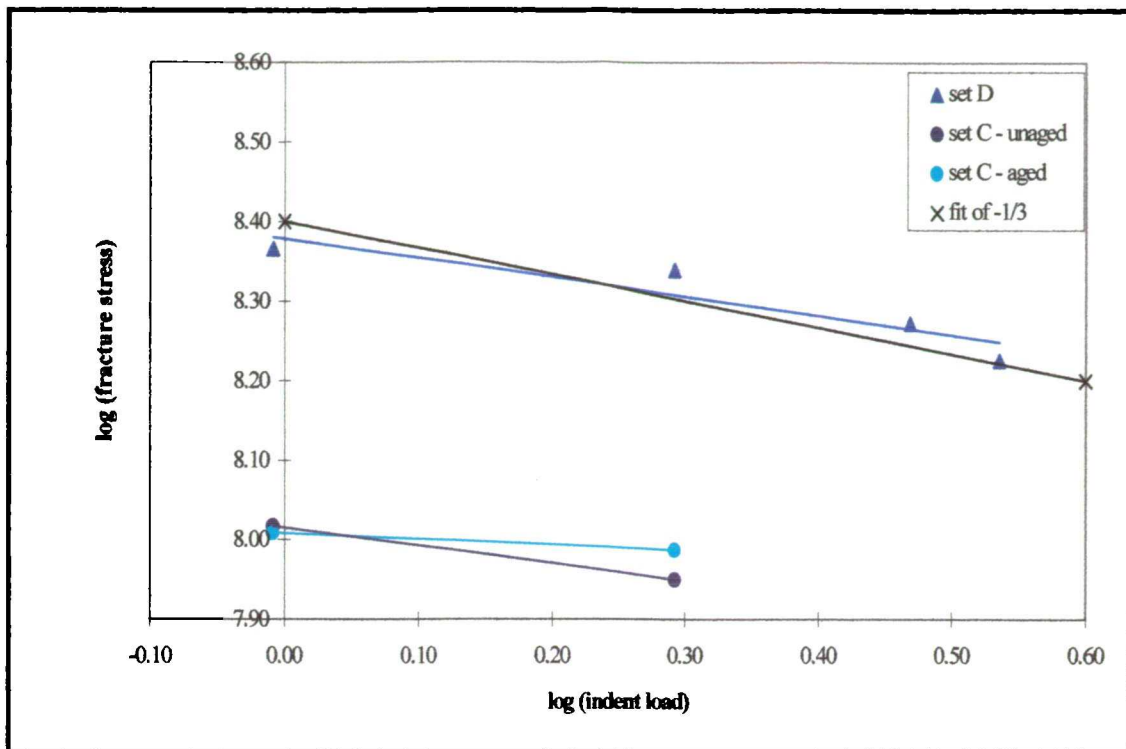


Figure (4.21) - graph of $\log \sigma_f$ versus $\log P$ for sets C and D; gradient of $-1/3$ also fitted.

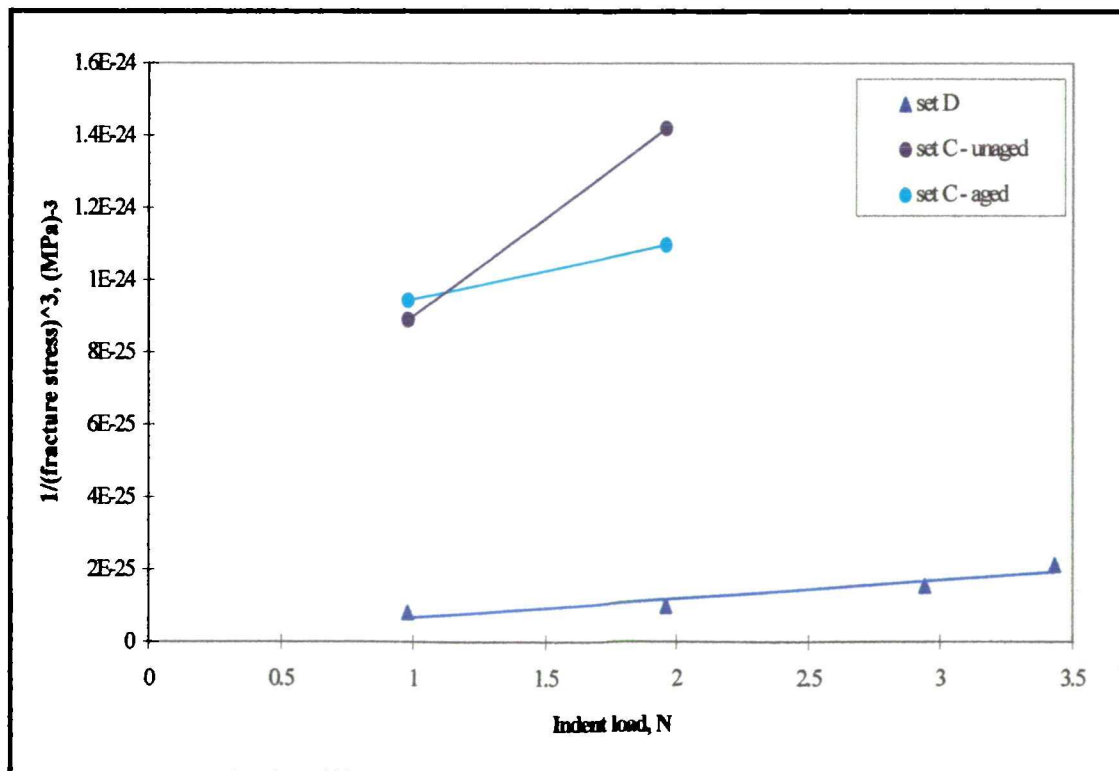


Figure (4.22) - graph of $1/\sigma_f^3$ versus P for sets C and D.

The results from each of the techniques used for the evaluation of toughness are summarised below in table (4.16). The values are all of the order expected from the literature (Brocco, 1994; Basu, 1993), but do not agree very well between techniques.

Table (4.16) - summary of toughness values $\pm$ one standard deviation calculated for bulk and tape-cast samples using different techniques.

Set	Average K_{Ic} , $\text{MNm}^{-3/2}$				
	SENB	DT	Indentation	ISB (eqn (2.21(a)))	ISB (fig (4.22))
Bulk					
unaged	1.29 ± 0.29				
aged/notched	2.36 ± 0.12				
notched/aged	2.94 ± 0.41				
C					
unaged			3.65 ± 0.64	0.94 ± 0.20	1.13
aged			3.63 ± 0.69	1.02 ± 0.21	1.42
D		3.03 ± 0.20	3.87 ± 0.81	1.52 ± 0.09	1.99

4.5 Static Fatigue

4.5.1 Sub - Critical Crack Growth / SPT Diagrams

The effect of loading rate on the fracture strength of the bars is illustrated in figure (4.23), as a plot of log (median strength) versus log (loading rate). The batches tested at rates of 5 N/min and 100 N/min clearly do not fit in with the other rates, which may be because they were manufactured at a different time; however, they still follow the same trend as the other batches, in that fracture strength increases as loading rate increases. The n_{sf} and B values determined from the gradient and intercept for the two lines are 10.2 and 51.2×10^6 for the 1, 40, 1000 N/min. rates, and 22.1 and 50.2×10^6 for the 5 and 100 N/min. rates. Thus B is fairly constant, whereas the value for n_{sf} is quite affected. The n_{sf} value of 10.2 was used to construct an SPT plot following the methodology presented in section (2.7.1.(iii)), and this plot is shown in figure (4.24).

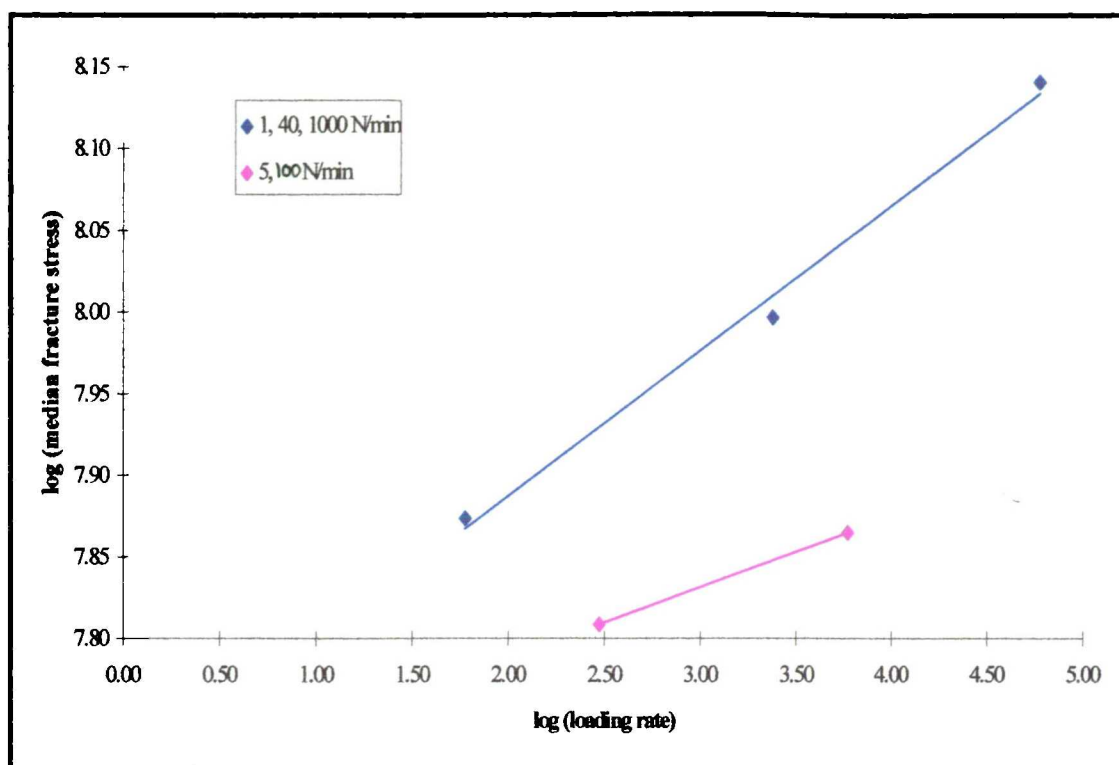


Figure (4.23) - plot of log (fracture stress) versus log (stress rate) for bulk samples.

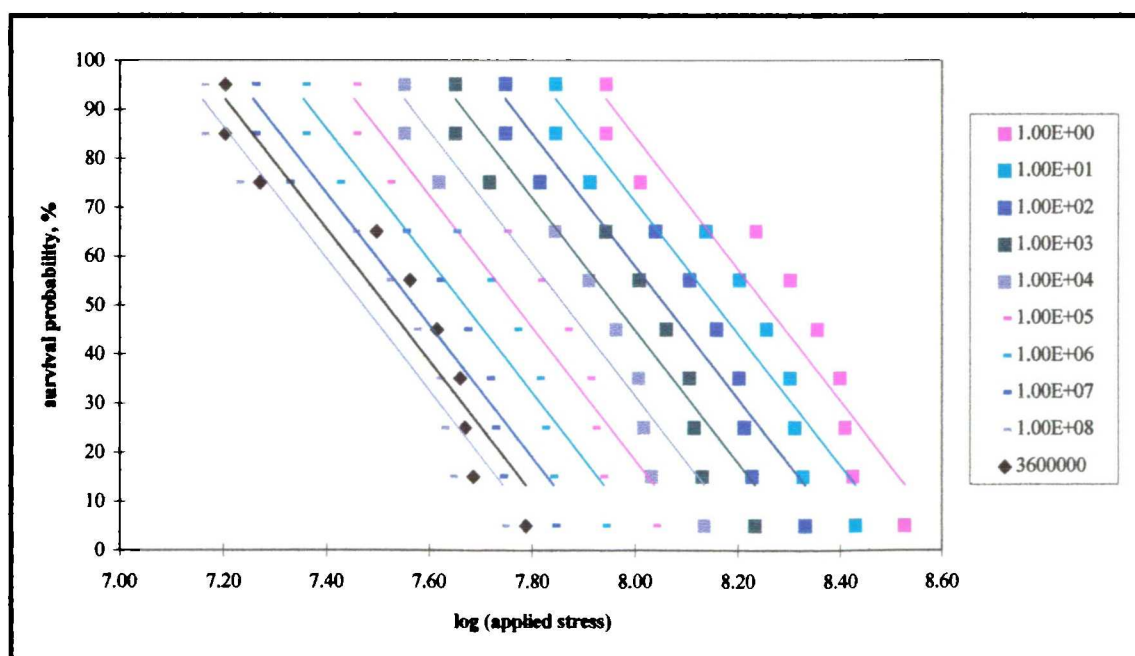
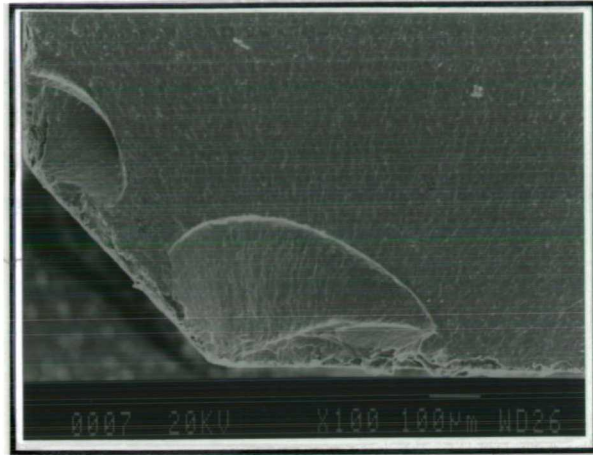


Figure (4.24) - SPT diagram constructed using data obtained from figure (4.23).

The SEM examination of the fracture faces of these bars showed that at all the stress rates used, failure initiated at the bevelled corners, i.e. from grinding damage, an example of which is shown in figure (4.25). This contrasts with the tape-cast samples, which often

failed from large pores. The crack path through the bars was transgranular in all cases. On comparing the fractography of the samples which had been aged after testing for up to 200 hours with the unaged opposite faces, no difference in microstructure was found; thus the fragments of broken samples could be left inside the furnace for at least 200 hours without the features of the fracture face being affected.

Figure (4.25) - showing the typical initiation site of fracture for samples used to construct SPT diagram - a bevelled corner. (This sample tested at 100 N min.)



Before static fatigue tests could commence, an estimate had to be made of the failure load that would give failure in the longest acceptable test time of 1000 hours. Using the SPT plot, the applied stress required for bars at room temperature was calculated as being ~ 75 MPa, which then needed to be adjusted for discs broken at 950°C . By comparing the room temperature fast fracture strength of set A with that of the bars broken under a comparable rate, the applied stress required for discs at room temperature was found, and corrected to a high temperature value by taking into account the percentage drop in strength that occurred at 950°C . Thus the stress expected to cause failure within 1000 hours of the discs loaded in static fatigue at 950°C was calculated as 46MPa (which transpired to be 18% of the Weibull strength of set C at 950°C), which corresponded to a load of 1N. (At the time of this work, the fast fracture data for set C at 950°C was not available, and the estimated stress of 46 MPa was subsequently proved to be too low; a value of ~ 75 MPa, 30% of σ_o , would have been the appropriate applied stress (1.9N).)

4.5.2 Static Fatigue Tests

Using the applied stress of 46MPa, none of the samples had failed after 1000 hours, so the test was terminated and the samples broken under fast fracture at room temperature, to compare their residual strengths with as-fired samples. The Weibull strength was 248 MPa, and the modulus value 4.8. On comparing these values with the room temperature strength of the unaged and aged samples presented in table (4.10), it can be seen that the

high temperature static fatigue has significantly reduced the strength, but has had little effect on the Weibull modulus.

When higher static loads were applied to fresh samples, it was observed that samples would usually either fail within a few minutes, or they would survive and deform plastically as the test proceeded. Exceptions to this were found for set B, where one sample survived for just over two days, and also for the samples from set C which were loaded at 45% and 50% σ_o , where only one sample failed under each load; this is believed to be due to misalignment of the system. The average time to failure, t_f , for set B was 6.75 minutes; the static fatigue data for set C is summarised in table (4.17) and shown in figure (4.26), where it can be seen that the general trend (ignoring the values at 45 and 50% σ_o , where the rig was misaligned) is for the time to failure to decrease, and for the proportion of samples that failed to increase, as applied load increases. It was also found that the time to failure under the applied stress of 56% σ_o was very similar at room temperature and 950°C.

*Table (4.17) - summary of the static fatigue data obtained for set C.
 n_f - number of samples which failed; n_t - number of samples tested;
 extraordinarily long t_f for 45% and 50 % due to rig misalignment.*

% σ_o	Temp. °C	n_f/n_t	Mean t_f mins
18	950	0/10	> 1000 hours
25	950	1/5	7.2
35	950	3/5	16.4
40	950	3/5	10
45	950	1/5	28 hrs
50	950	1/5	501 hrs
56	950	3/3	5.4
56	RT	6/6	5.8
70	RT	6/6	1.5

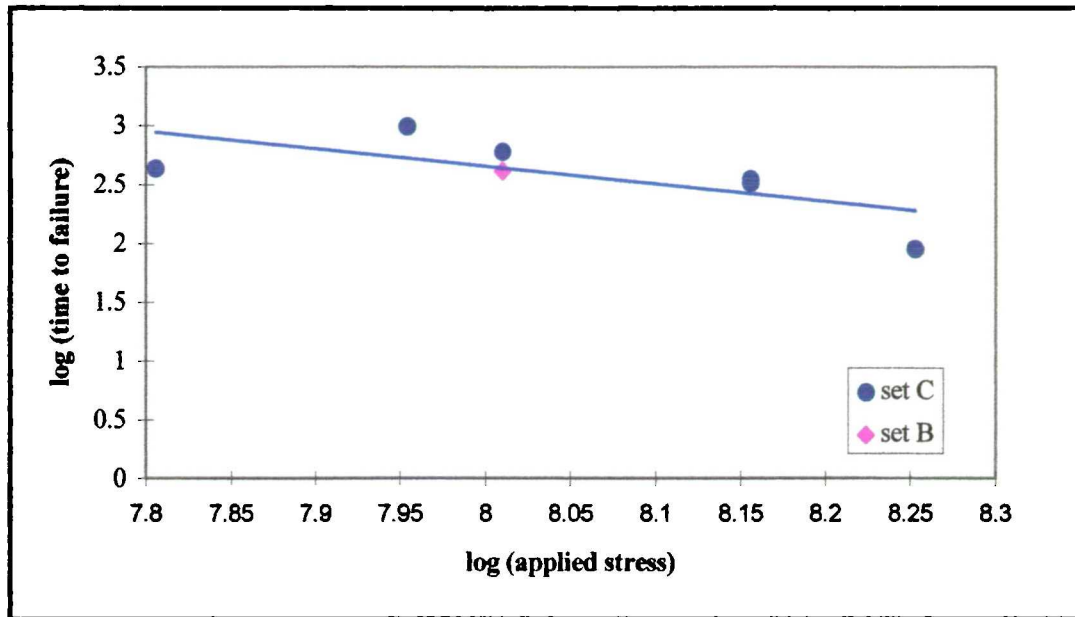


Figure (4.26) - plot of $\log(t_f)$ versus $\log(\sigma)$ for samples from sets B and C.

The SEM examination of the fracture faces showed that for all the samples which failed at room temperature, under 56% σ_0 and 70% σ_0 , fracture originated from a porous defect at or close to the tensile face. Samples which failed immediately the load was applied at 950°C also failed from porous defects, but this was not the case for samples which displayed delayed failure at 950°C, where there was no obvious defect as the source of failure, and the initiation site was flat.

Samples from the 18%, 45%, and 50% σ_0 loads which survived at 950°C and were subsequently broken at room temperature all failed from porous defects. One sample from the 45% σ_0 set was broken in a controlled manner, and the strength calculated as 271MPa, which is higher than the Weibull strength calculated for the samples held under 18% σ_0 , but less than the mean (305MPa) and Weibull (332MPa) strengths of the as-received material tested at room temperature.

4.5.3 Creep

With the exception of the misaligned samples loaded under 45 and 50% σ_0 , it was found that the two Talysurf profiles recorded for each sample agreed closely, with the difference in deflections being less than 10%. A typical profile is shown in figure (4.27). There was also good agreement in the strains calculated within each set of test

conditions, using both the 'Fett' and 'triangle' techniques, with an error range of 2-11% found within each set. The creep data from both techniques are summarised in table (4.18), and displayed in figures (4.28) and (4.29) as plots of strain rate against applied stress and $1/T$ respectively. The strain rate is shown to increase as applied load is increased, and as the temperature was raised; only the data obtained using an applied stress of 35% shown in figure (4.28(a)) does not seem to fit with this general trend, but even these data do not lie far from the best fit curves of figure (4.28(b)).

Figure (4.27) - typical Talysurf profile of a plastically deformed sample; this sample held under 90 MPa (35% σ_d) at 950°C for 1200 hours.

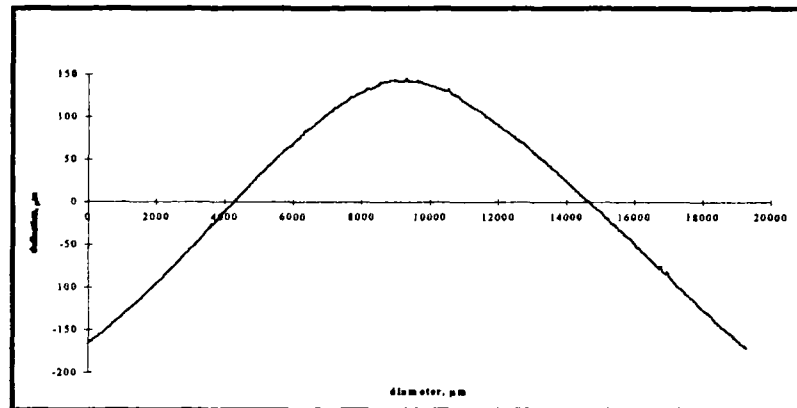


Table (4.18) - summary of creep data for set C using two different methods to measure strain.

$\sigma\%$, MPa	T, °C	ϵ_{Fett}	$\epsilon_{Triangle}$
25	950	8.51×10^{-10}	1.17×10^{-10}
35	950	1.22×10^{-9}	2.06×10^{-10}
40	950	1.09×10^{-9}	1.55×10^{-10}
45	950	1.19×10^{-9}	1.96×10^{-10}
50	950	1.23×10^{-9}	2.03×10^{-10}
40	1000	6.21×10^{-9}	6.64×10^{-10}
40	975	1.71×10^{-9}	2.64×10^{-10}
40	950	1.09×10^{-9}	1.55×10^{-10}
40	925	8.85×10^{-10}	1.44×10^{-10}

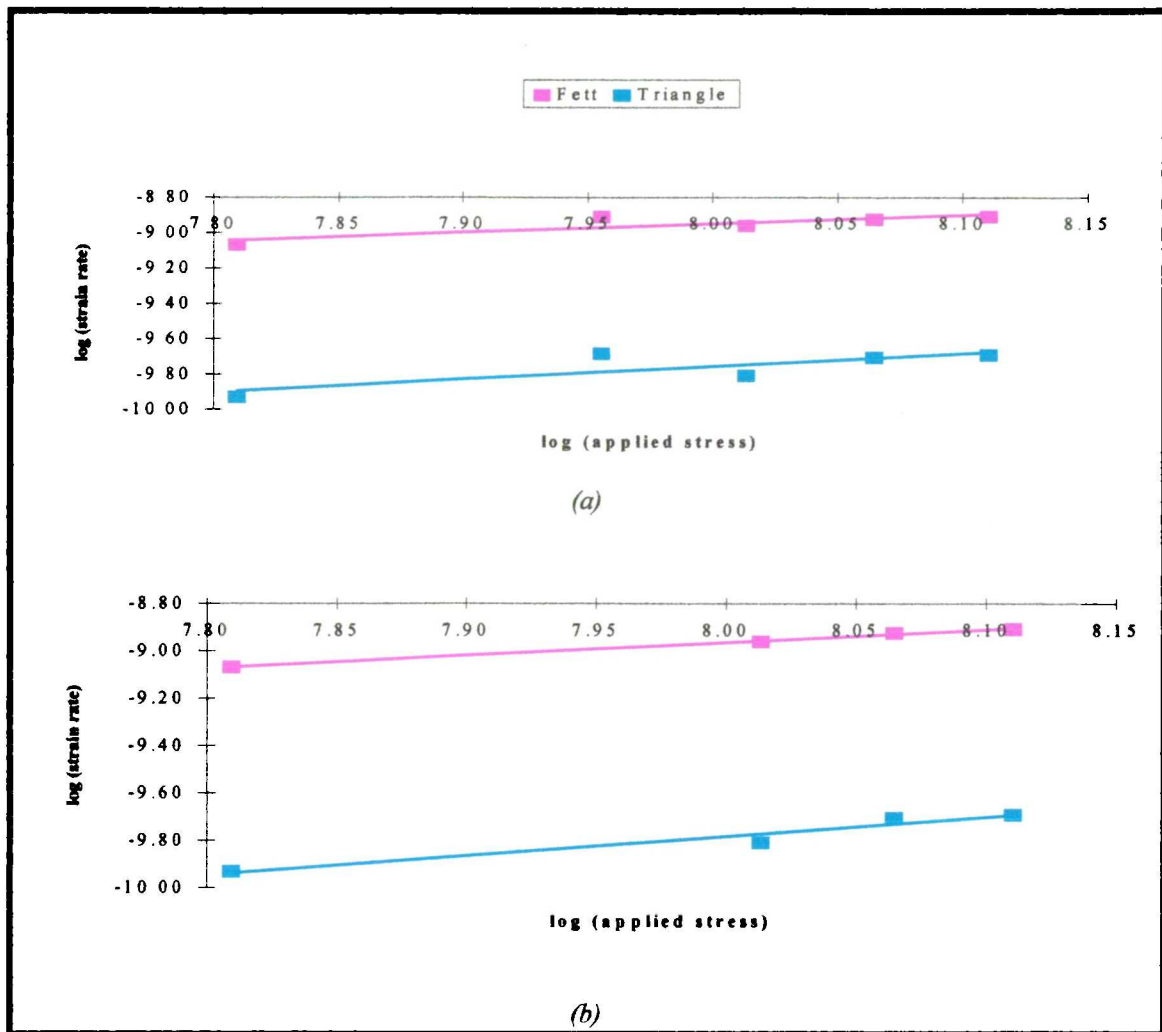


Figure (4.28) - graph of $\log \dot{\epsilon}$ versus $\log \sigma$, (a) including all data points; (b) omitting 'errant' 35% data point.

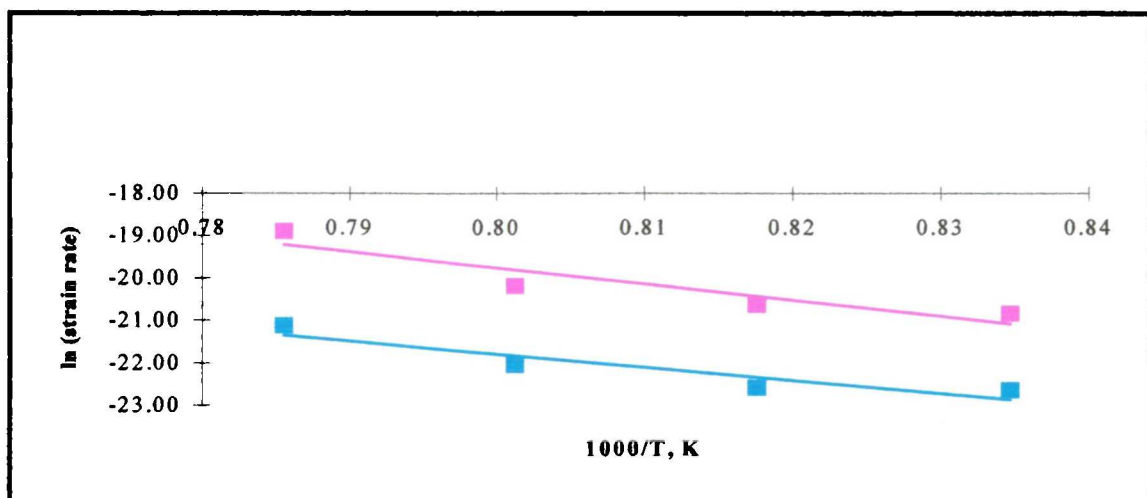


Figure (4.29) - graph of $\ln \dot{\epsilon}$ versus $1/T$.

From figures (4.28) and (4.29), it can be seen that the creep rate determined by the two techniques did not agree, with the rate found using the 'Fett' method (i.e. in the central region) always being faster. However, the discrepancy did seem to be of a constant magnitude - at 950°C the strain rate for Fett was always between $\sim 6 - 7.3$ times greater than for the triangle method; this was also true using a load of 40% at different temperatures, except at 1000°C where the factor was ~ 9.4 . i.e. constant factor with temperature as with stress.

From the graphs the creep parameters were calculated, using best-fit lines both including and omitting the 'errant' 35% data point; these are presented in table (4.19). The values using the two methods of calculating strain are of similar magnitudes.

Table (4.19) - summary of the stress exponent and activation energy calculated for creep using two methods for measuring strain, and comparing the effect of including the 'errant' 35% data point.

Technique	Stress exponent		Activation energy, kJ/mol.
	Including 35%	Excluding 35%	
Fett	0.5	0.5	320
Triangle	0.7	0.8	260

There were anomalies in the deflection measured by the LVDT, in the form of small, but abrupt (corresponding to a deflection of 5-10 μm) apparent deflections, which were attributed to temperature fluctuations, probably in the laboratory rather than the furnace. These anomalies were removed to give the plot of corrected deflection versus time shown in figure (4.30). There seem to be two regions to the graph; over the first 400 hours the deflection was relatively small, $\sim 30\mu\text{m}$, and the rate of deflection was increasing, but after this period the deflection rate becomes linear, with a gradient of $\sim 0.2\mu\text{m/hr}$ ($5.6 \times 10^{-5}\mu\text{m/s}$). The final deflection of the sample recorded by the LVDT, 178 μm , agreed well with the deflection measured from the Talysurf profile, 187 μm .

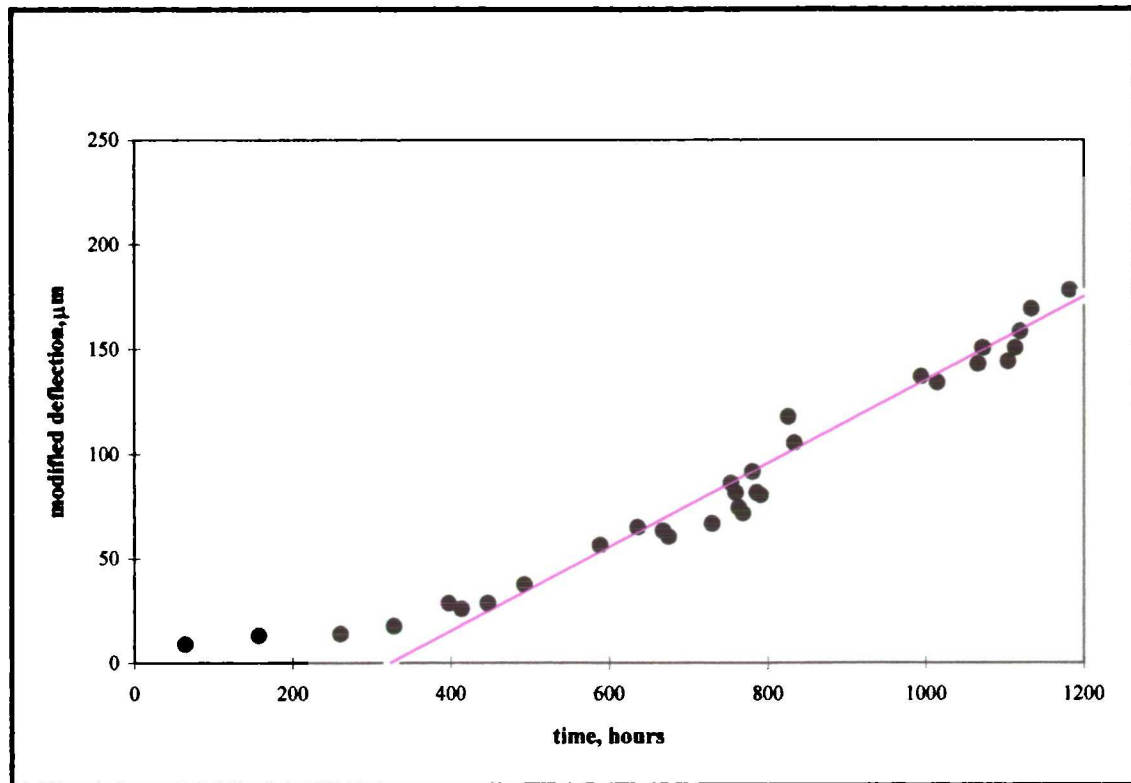


Figure (4.30) - graph showing corrected deflection versus time obtained from LVDT for a sample held at 950°C under a load of 25% σ_o .

SEM examination of the tensile surfaces of samples from set C did show some differences, according to the test conditions. The central region of all the samples under varying loads was humped and rough, whilst this was not the case towards the outer regions of the discs. In addition, for samples loaded under 50%, 45% and 35% σ_o there was evidence of cavitation: spherical pores, coalescing to form micro cracks, could be seen extending across the surface of the central region, as shown in figure (4.31), although this was more limited in the samples which had been under the load of 35% σ_o . Pores and micro cracks were also noticed in the samples which had been held under 40% σ_o at 1000°C and, to a lesser extent, 975°C, but not at 925°C. In all cases the grains were still equiaxed in shape; there was no noticeable grain elongation.

From the SEM examination of fragments of set B, material with a larger grain size which had been loaded only under 40% σ_o at 950°C, no pore coalescence or micro cracking was observed.

From the TEM examination no secondary phases were observed to have precipitated, either in the aged or creep samples of set C. No dislocations were detected, nor any grain deformation, although there was a lot of porosity distributed throughout the sample.

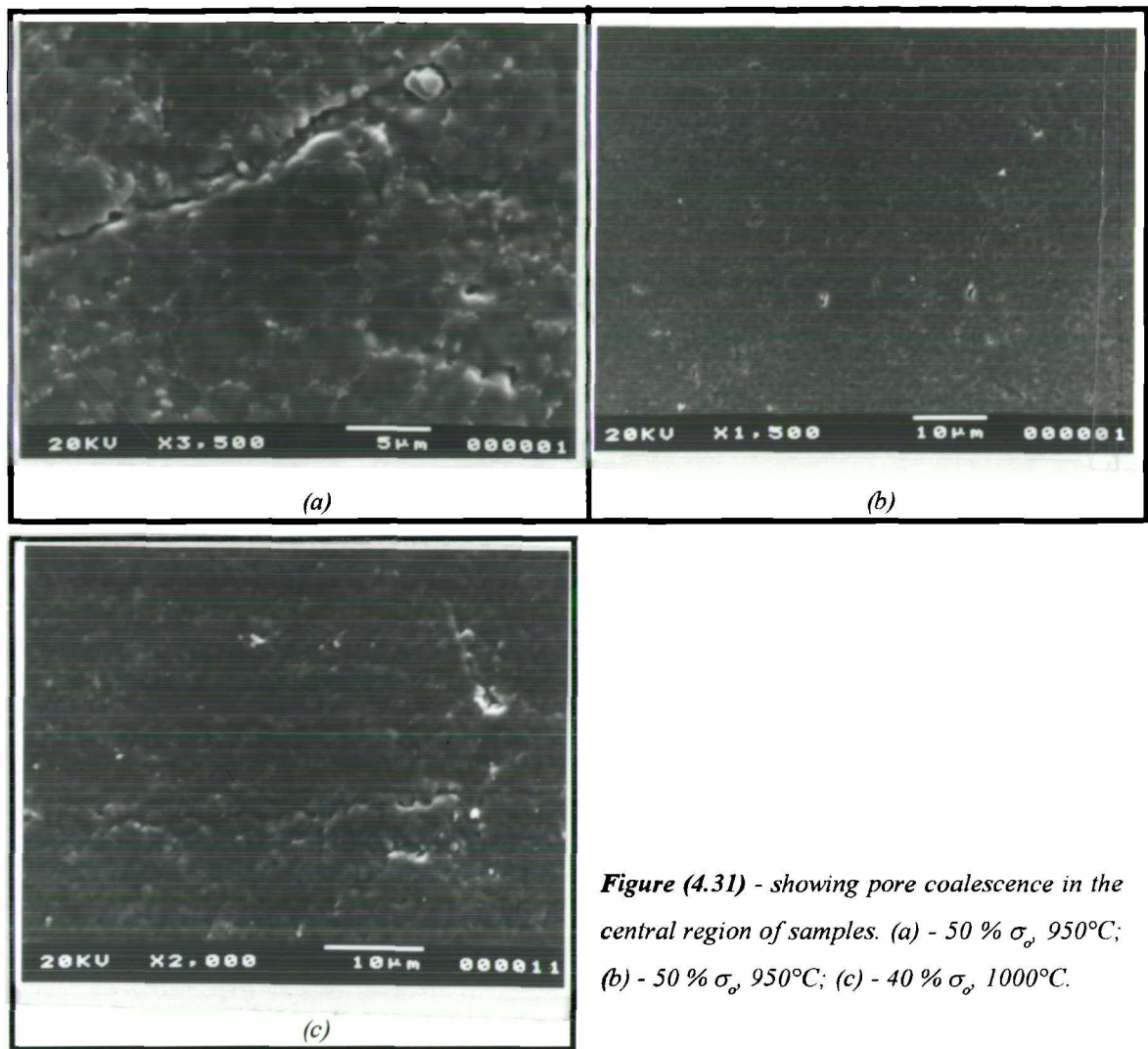


Figure (4.31) - showing pore coalescence in the central region of samples. (a) - 50 % σ_o , 950°C; (b) - 50 % σ_o , 950°C; (c) - 40 % σ_o , 1000°C.

CHAPTER 5

DISCUSSION

CHAPTER 5

DISCUSSION

5.1 Sample Microstructure and Composition

The effects of the processing routes for the tape-cast and bulk samples on the microstructure and composition are discussed in this section. The processing routes also affected the mechanical properties of the samples - most notably in the strength test results - and these are discussed in later sections.

5.1.1 Thin Film Samples

There were slight differences in the structural analysis of the sets, which would be expected for material made by different manufacturers and processing routes, but since the powder preparation and sintering specifications are limited, it is not possible to compare in detail the merits of each individual process. The mean grain sizes for sets B and D were almost triple and double respectively those for sets A and C, and the density of set B was also more similar to that of set D than set C (table (4.1)), despite sets B and C both being produced by Kerafol. Comparison of the microstructures of sets C and D (figures (4.11) and (4.17(a))) does show that set D contained less porosity, both in the form of spherical pores and pore clusters, which would explain its higher density value, but set B (figure (4.10)) seemed to contain similar amounts of porosity as set C; however, the density values from all the sets lay within the range expected for FSZ (Scafe, 1994). The changes in density and mean grain size on ageing set C were slight, and since the literature has found this material to be stable, are believed to be due to normal experimental scatter.

The chemical analysis of the batches demonstrated that, despite each batch containing nominally 8 mol% yttria, the amount of dopant varied by almost 2 mol%, with set D especially having a low yttria content (table (4.1)). However, all these compositions would lie in the cubic field on sintering, so this is the phase expected to be retained at room temperature, which was found to be the case from the XRD analysis. XRD analysis also

showed that the ageing of set C at 950°C for 1000 hours made no difference to the structure, which is as would be predicted from the phase diagram for this composition; neither were any precipitates observed after high temperature (950°C) creep of set C. The DTA and DSC results also showed that no structural changes were occurring in set C up to 1200°C. However, according to the phase diagram of Scott (1975) the composition of set D would actually lie inside the tetragonal/cubic phase field at 950°C, so of all the materials tested, this composition is the one most likely to undergo some microstructural change on ageing at this temperature. The exact position of the cubic/tetragonal border may not be shown in the diagram, so set D may still be within the cubic field, and therefore microstructurally stable, which the XRD results from the sintered and powder samples support, showing that the material remained cubic from room temperature to 1100°C. In addition, the DSC and DTA showed that there was no phase change up to 1200°C. There was also no change in grain structure observed in the SEM of samples which had been tested at temperatures up to 1050°C, and in addition, the dilatometry run using this material showed a linear expansion up to 1000°C, which would not be the case should a phase transformation occur. Thus it would seem that set D was stable, at least for all the short-term tests used in this project.

The distribution of the yttria as shown on the DIGIMAPS (figure (4.1)) was unusual, because it was apparently tied to certain regions. These regions were the same size in all the samples examined, irrespective of the grain size, and also these regions did not correspond to any feature in the samples; thus it is concluded that the DIGIMAPS are showing a random distribution and the yttria was actually distributed uniformly throughout the samples. This is supported by the TEM results, where no evidence of a grain-boundary phase was found. It is good that the yttria is not associated heavily with the grain boundaries, since this means that there will not be localised areas of the material that are structurally unstable, and also that there was no segregation occurring on ageing - although again it would have been surprising if it had, since the diffusion coefficient of Y^{3+} ions is so slow, and also similar to that of Zr^{4+} ions (table (2.2)). This, too, agrees with previous results, where the absence of decomposition was illustrated by the conductivity of the electrolyte remaining unimpaired over a year's use at temperature (Schafer, 1993).

The quality of powder used in set A is not known, so it is possible that the alumina impurities were present in the original powder, rather than introduced during the viscous processing or tape-calendering stages of production. The impurity levels in the samples from Kerafol and Siemens were so low that they would be insignificant, which should aid the retention of the room temperature mechanical properties at the operating temperature.

As expected, the tape-casting process did not produce a microstructure with a preferred orientation. However, it was responsible for the surface topography and profile of the samples, factors which were shown to affect in particular the strength and modulus from flexure tests performed using samples in their 'as-fired' condition.

The samples in batches B, C, and D all had a smooth and a rough surface (table (4.2)). The smooth surface was the side that had been in contact with the carrier foil, and so would be influenced by whatever material was used for this. The foil employed by Kerafol was metallic, and the grooves on the samples were the imprint of the foil's own surface finish. The foil used by Siemens was made of a polymer, and the scratches are possibly where the polymer had been worn down or damaged.

Although the quality and surface finish of the carrier foil is important, it was the opposite, rougher, face of the samples, exposed to air, which had a far greater influence on the strength and fracture properties of the tape-cast material. This is the surface from which the solvent must evaporate, and the binder burn out, thus producing the rough surface finish and 'blisters' observed in the present study. SEM fractography also showed that the large cavities and porous defects (figure (4.9)) from which fast fracture occurred lay along or close to this surface. These defects dominated the strength at room temperature, and were still significant at the higher temperatures, making any effects from the foil texture insignificant in comparison. The large cavities and porous defects were believed to result from bubbles trapped within the slurry, and so it is most likely that their size and frequency will be determined by the conditions chosen for the drying stage in the tape-casting process. The pore clusters (figure (4.10)) distributed throughout the structure of sets B, C, and D can probably also be attributed to the drying stage, with the observation of there being less in set D quite likely being due to the drying stage being longer, and so more controlled.

Set A was unlike the other sets in regards to the topography, and also the internal defects. The surface roughness (table (4.2)) was the same on both sides, both being smooth, and the SEM fractography did not reveal such large porous defects as the failure initiation sites - the defects were much smaller (figure (4.4)). Also, there were no pore clusters in the microstructure, but long, thin cracks, which were aligned parallel to the surface and were not seen in the other sets. The identical surface texture, and the defects illustrated in figure (4.5), are consistent with material made by the tape-calendering process.

The Talysurf profiles (table (4.3)) of the discs from each set showed varying degrees of warpage, with sets A and B being the most severe. Since samples from all the sets displayed this, it was not just a feature of a particular thin-film production process. It is known that during sintering a temperature gradient across the sample can produce warpage, as can a density gradient, but these explanations are insufficient in this case, since the samples are so thin that a temperature gradient across the thickness would be tiny, plus the warpage would occur in only one direction. Although the stacking arrangement of the samples inside the furnace is unknown, it would seem that the warpage was not produced merely by sintering - possibly the 'lip' at the perimeter is a result from the stamping process, which was used to produce discs from the green sheet.

The warpage of the plates, which are assumed to have been cut rather than stamped from the green sheet, was much less than the discs of set D; there was still the 'lip' at the edge, which was also smaller than for the discs.

It was suspected that there might be residual stresses within the discs, resulting in this warpage. Two ways of removing residual stresses are by annealing, and polishing. Both these techniques were tried, and the profiles checked to see whether they were altered. The aged samples of set C displayed less warpage than the unaged (table (4.3)), but the polishing had no overall effect. Thus it was not obvious whether any residual stresses were left in the samples from the processing stage. (If the discs do contain residual stresses, and if they were to alter with time at the operating temperature, then it makes it harder to predict the lifetime of the electrolyte, since the strength and toughness data measured with disc samples may also be affected.)

The problem of using warped samples for mechanical tests was that the discs did not sit completely flat on the support ring of the biaxial flexure rig, nor could it be guaranteed that all of the loading ring was in contact with the sample, during the initial part of flexure. This was more critical for the Young's modulus testing than for the strength results, and will be discussed in section (5.2.2.(i)).

The main problems identified from tape-casting processing are the warpage, and the cavities produced on the rough surface. The warpage complicated the mechanical tests, but could be by-passed, e.g. by polishing the samples, or using a different geometry of flexure test. However, the electrolyte will be used in the as-fired state, so will contain these processing defects. Hence its strength will be dominated by the cavities on the rough surface, and the warpage may make it difficult to fit and stack the PEN structures together, and put undue

stress in the electrolyte from the contact points. However, it is heartening that the warpage in the plates, which is the geometry that will actually be used in the stack, is so much less than in the discs used for the mechanical tests.

If these problems are to be eliminated, it must be during the processing stage, not afterwards - but not enough is known of the processing details to suggest changes.

5.1.2 Bulk Samples

The density and grain size of the bars were similar to those of sets B and D. These samples were also completely cubic, and had a low impurity content. The main difference in the two processing routes would be shown in the strength tests, since this depends on the defect populations. Both sets failed under fast fracture from surface flaws, but in the case of the bars, these were introduced during the grinding stage, and so would be more similar in size and shape within the set than in the tape-cast material; the grinding defects would also be less random than those from the tape-casting. The different flaw populations should be reflected in the actual strength values and also in the scatter of the strength data.

5.1.3 Summary of Main Points

The microstructure and composition of the samples do vary slightly from one manufacturer to another. There was a range in grain sizes, from 3.2 μm for set A to 8.8 μm for set B. The lower density of set C seems to be a consequence of the greater amount of porosity and smaller grain size.

The compositions of sets C and D were shown to be structurally stable up to 1200°C and 1100°C respectively; despite the composition of set D lying close to, or possibly within, the tetragonal/cubic phase field, there was no evidence for a structural change within the time-scale that these samples were tested in.

The surface texture and defects produced within each set did vary with the processing route. The tape-calendered material (set A) had smooth surfaces, and long, crack-like defects, aligned parallel to the surface. Porous defects at the surface were small and infrequent. The tape-cast samples (sets B, C, and D) showed the foil texture on one surface, but on the other were porous cavities, most probably resulting from the evaporation of organic compounds

during drying. The structure within the tape-cast sets also varied, with set C containing more porosity. The bulk samples had surface defects resulting from the grinding process.

The disc samples produced from the thin-film processes were also considerably warped, some of which was attributed to the stamping process used for disc production.

5.2 Young's Modulus

The Young's modulus, E , is an important parameter in that it determines the elastic tensile strain for a given service tensile stress. Also, in the present work the E value was used in calculating both the strength and toughness values, and so it was important to use as accurate an E value as possible. Not all the techniques used to determine E provided useful data, especially at elevated temperatures, and the agreement between the actual values from the static and dynamic techniques was not always very good. The dynamic calculations for E were based on sample mass, dimensions, and Poisson's ratio, whereas the static used sample and rig dimensions, applied load and resultant deflection, and compliance of the apparatus; none of these parameters change dramatically with temperature. The surprising results obtained at higher temperatures were reproducible and are believed to be a true representation of the material's behaviour.

5.2.1 Dynamic Techniques

The room temperature values determined using the GrindoSonic, both for bulk and disc samples, were consistent within each batch; the slight variations between the batches can probably be attributed to the minor differences in composition and microstructure. The values of sets B and C were in good agreement with the value given for Kerafol material in the literature (200GPa, Basu, 1993, and 204GPa, Scafe, 1994), but all the samples tested had a room temperature E value around the generally accepted value for FSZ of 200GPa.

Polishing the discs would have two effects - it removed surface porosity, and also removed the warpage and roughness, thus ensuring that the sample was sitting perfectly flat on the support. The results from the polished discs of sets C and D (table (4.5)) showed that E was affected quite considerably, rising by 8.5% and 14% respectively, with the value in one case equalling that of a perfect FSZ crystal (Green, 1989). Since there was such low scatter in the

data for the unpolished discs of sets C and D, which had different extents of warpage, it would seem that the warpage of the samples would have a minor effect on values obtained from the GrindoSonic, and the large increase in E is attributed mostly to the reduction in surface porosity.

The high temperature GrindoSonic tests (table (4.4)) were performed only on bulk samples, owing to the practicalities of the test. It was disappointing that it was not possible to detect a frequency at temperatures above 200°C, which was true whether the sample was being heated up or cooled down. The test was not attempted above ~350°C, so it is not known whether a signal would be detected at much higher temperatures - it is considered that it would not. However, the two values which were obtained at elevated temperatures do correspond with the results found from the static tests on the tape-cast material when plotted on the normalised E versus temperature graph (figure (4.3)).

The microphone detector was designed for room temperature usage, which may account for the inability to detect a consistent signal above 200°C. (A more suitable set-up for high temperature work would be to detect the signal using the PZT transducer, via a wave guide in contact with the sample; this requires a larger sample than was able to be manufactured at Imperial.)

It was hoped that the ultrasonic technique would yield high temperature data for the bulk material, but for the particular set-up used the test proved unsuccessful, even at room temperature (table (4.6)). This was attributed to misalignment of the steel wave guides, since even a small misalignment within the clamps would cause loss of good contact with the sample and some of the signal to be lost. This was emphasised as the temperature was raised and the wave guides expanded - the system could be seen to buckle. The change in temperature would also produce another inaccuracy, in that as the system expanded the contact pressure between the sample and wave guides would change, and this also would affect the resulting signal.

5.2.2 Static Techniques

5.2.2.(i) Problems With Test Techniques

The static tests were performed only on tape-cast material, but it did prove possible to monitor E up to 1050°C successfully. There was a potential source of error from the

apparatus, in that the compliance of the rig had been measured only at room temperature. In addition, it is not known how much internal damage was introduced into the samples, as they were repeatedly loaded at increasing temperatures; quite possibly there was a build-up of some damage, since several samples failed after being flexed several times to the same load.

The specimens used in the 3-point-bend flexure were so thin that the dimensions were not within the set limits for the equations used (Metals Handbook, 1985), and so the actual values obtained were not expected to be correct; however, this error was assumed to be constant, and the trend of E with temperature could be followed by normalising the values with respect to the room temperature result (table (4.7)). These specimens were not polished, but the gradients of the force/deflection plots were fairly smooth and linear, so warpage effects were considered to be insignificant.

The room temperature values of E for unpolished samples found from the biaxial flexure and FEA tests was lower than that given in the literature and found using the GrindoSonic, and the scatter within each set was greater. This scatter was reduced when the polished discs of sets C and D were tested (although only two samples from each set were used), and the values were also closer to those found by the GrindoSonic, so the original discrepancies were believed to be an effect of the surface roughness and warpage. (The initial portion of the force/deflection plots of the unpolished static tests were unsteady, which meant that the force and deflection values inputted into the FEA model were inaccurate. This was rectified using the polished discs, since the plots were smoother. Polishing was pertinent to the E tests because low loads were used, and the chart recorder amplification was set high - the loads used in the strength tests were higher, and so the effect on these data values would be negligible.) Possibly another way of by-passing the problem of warped samples would be to use a 3-ball-support biaxial flexure rig.

5.2.2.(ii) Performance of the Different Samples

The results from the static tests were normalised so that the uniaxial and biaxial trends could be compared together. The plot in figure (4.3) shows that the E of set D followed the same trend whichever geometry was used; there was a rapid drop of $\sim 40\%$ within 500°C , and then the value of E stabilised, before beginning to increase at around 800°C . The polished discs of set C also showed the same trend, although it was not identical to that of set D; set C dropped $\sim 30\%$ in 400°C , and then was stable, before increasing at $750 - 800^\circ\text{C}$. The modulus of the alumina samples remained roughly at the room temperature value until the

temperature approached $\sim 800^{\circ}\text{C}$, when it began to drop. The purity of this material was unknown, but was probably not very high, and so a drop at this temperature is not unexpected and would be attributed to the presence of a glassy phase.

The initial large drop of 30 - 40% in E , followed by the stable region, is surprising, since the decrease for both FSZ and PSZ given in the literature (Wachtman, 1959; Shimada, 1984; Buckley, 1967; Kandil, 1984) was less than this ($\sim 15\text{-}20\%$). The suggestion that the drop was due to some aberration of the rig or FEA model, or the testing of such thin samples, was dispelled by the virtually constant E values obtained for the alumina discs up to $\sim 800^{\circ}\text{C}$, tested using the same apparatus and following the same procedure. Nor could it be an effect of surface finish, or porosity, since the same trend was observed for both unpolished bars and polished discs. The impurity content of the tape-cast material was negligible, and so any effect from secondary phases softening can be discounted. E is affected by porosity, so any internal damage, such as cracking, would lower E , since this would be equivalent to increasing the porosity. However, such damage would be permanent, and so E would remain at a lower value after the test. The room temperature E of the discs was measured after the temperature runs, both by GrindoSonic and flexure techniques, and found to be the same as before the test - thus there was no significant damage induced by the tests which could account for such a drop shown in figure (4.3).

When the limited data obtained for the bulk samples from the GrindoSonic is added to the graph, it also follows the first part of this trend, with a drop of 23% between 100 and 200°C . Thus the large decrease in E at the relatively low temperatures, 100 - 400°C , must be a feature of 8 mol% YSZ material, and not just of FSZ material made by the tape-casting process.

The decrease in modulus, followed by the constant value which then began to rise again at higher temperatures found in this project is in contrast with the gradual decrease found for the polycrystalline 8.8 mol% and single crystals of 11-18 mol% YSZ, by Buckley (1967) and Kandil (1984) respectively. However, the shape of the curve agrees more with that found for the polycrystalline 3.5 mol% and single crystal of 8.1 mol%, by the same authors, although the decrease recorded by them (10-20%) is less than the 30-40% drop found in the present work. An initial large, non-linear decrease had also been observed in PSZ by other workers, but again the magnitude ($< 20\%$) was far less than that found in this case. Suggestions for this behaviour of PSZ were a phase transformation (Wachtman, 1959; Buckley, 1967), dislocations (Shimada, 1984), dipole activity (Weller, 1986). It needs to be considered

whether such factors could have influenced the modulus in this case, despite the material used being cubic.

The phase transformation can be discounted, since the results from section (4.1.1), which were discussed in section (5.1.1), clearly show that both sets C and D were stable over the temperature range used in the E tests. In addition, E obeys the law of mixtures, so that each constituent phase contributes in proportion to its volume fraction. The E of PSZ is ~ 210 GPa (Green, 1989), and so the E of the samples that had partially transformed to the tetragonal phase should still be ~ 200 GPa, and not show the decrease seen in the results of figure (4.3).

The dislocation movement mentioned by Shimada, 1984, could certainly give an internal friction peak, but would not cause E to drop, nor would it be sufficient to cause internal damage that could reduce E, by the extent shown.

Finally, the dipole re-orientation is a well established phenomenon in materials containing low dopant concentrations, and would cause an internal friction peak at low temperatures, as described by Weller (1986). But it is unlikely to occur in this case, since at dopant concentrations above ~ 3 mol% the movement of dopant ions is inhibited and the process can no longer take place (Kilner, 1996).

Although the proffered solutions can not work for this material, it is not known what does account for the E behaviour displayed in figure (4.3). However, the drop in the modulus of cubic zirconia shown in figure (4.3) may explain the relatively large, non-linear, decrease in E observed by Shimada. E obeys the law of mixtures, so that the overall modulus depends on the amount and modulus of each phase present. Using the Lever rule, the amount of cubic phase estimated to be present in the 3 mol% material was approximately 20%. At 400°C , the modulus of set C had dropped by $\sim 30\%$; from Chan's data (1991), the modulus of monoclinic phase would have dropped by $\sim 6\%$. When these decreases are applied to Shimada's (1984) room temperature value of 205 GPa, taking into account the ratio of phases present, the resultant E value at 400°C is 183 GPa; this is very close to the value of 178 GPa recorded by Shimada (1984). The same calculation was applied to the 4.6 mol% material tested by Buckley (1967), and gave a value at 400°C of 120 GPa, compared to the recorded value of 121 GPa. Whilst these values are approximate (taking into account only the presence of monoclinic and cubic phases), they do suggest that the non-linear drop in PSZ that has been documented, and for which there were no realistic explanations, could

actually be due to the large decrease in E of the cubic phase that has been observed in this project.

Whilst the rapid drop in E shown in figure (4.3) is unusual, so is the increase which was occurring in the discs of sets C and D above $\sim 700^\circ\text{C}$. Where this was noted in the literature (Buckley, 1967; Kandil, 1984), it was attributed, possibly erroneously, to an unstable structure, but this explanation was shown not to be applicable for sets C and D. No explanation can be offered for the behaviour displayed in figure (4.3).

5.2.3 Summary of Main Points

The room temperature modulus of bulk (201 GPa) and tape-cast (193-203 GPa) samples found using a dynamic technique agreed well with the literature value for FSZ.

The actual data from the static tests on tape-cast material at room temperature did not agree too well with the values found from the dynamic technique, due to the problems in testing such thin samples, and because the samples were not flat. However, the discrepancy in data for the biaxial samples was reduced by using polished discs.

The normalised E values of the bulk and tape-cast samples followed the same trend of decreasing rapidly as temperature was raised; the tape-cast samples were tested at higher temperatures than the bulk material, and showed a region where E was stable, before starting to increase at still higher temperatures. In contrast, alumina discs of similar dimensions showed a constant E as temperature increased, until $\sim 800^\circ\text{C}$, when it is likely that impurities began to soften and cause the drop in E shown in figure (4.3).

The suggestions in the literature to explain the decrease in E with temperature in PSZ are not adequate for the FSZ material; it is possible that the large drop in E found in PSZ over the initial temperature rise of $\sim 400^\circ\text{C}$ could be a consequence of the decrease in modulus of the constituent cubic phase.

5.3 Strength

5.3.1 Uniaxial Flexure

The main purpose of testing the bulk samples was to verify whether the ageing treatment affected the strength. Comparison of the strengths of the three differently treated sets (table (4.8)) showed that the ageing treatment had no effect; the intrinsic strength was unaltered, since the unaged and aged values were the same, and any surface damage was also unaffected, shown by the same strength and scatter values for the ground/aged and aged/ground sets.

5.3.2 Biaxial Flexure

The absolute strength values from set A cannot be compared directly with those of the other sets, because the test geometry used (ball-on-ring) was different. However, the fracture path and the change in behaviour which occurred on raising the temperature can be compared. Tests were carried out to directly compare the effect on strength of the other test geometries, namely a steel solid support ring (ss), support ring of ball bearings (bb), and silicon nitride (IC).

5.3.2.(i) *Effect of Friction in Ring-on-Ring Test*

The first point to be considered with the ring-on-ring rig is that of friction, which can be discussed using the room temperature data of set B. The ball-on-ring data from set A cannot be used as a comparison, since the samples of sets A and B were also different. Using two different support rings, one a solid ring (ss) and the other made of ball bearings (bb), made no significant difference (as confirmed by the t-test) to the fracture strength of set B; there was also good correlation between the Weibull data obtained using the Erlangen (ss and bb) and Imperial (IC) rigs (table (4.10)).

A difference in strength had been expected, since it was assumed that using ball bearings rather than a solid support ring would reduce the friction, and using the polished sapphire support balls and a polished loading ring would minimise it even more, resulting in a decrease in strength compared with the value for the solid support. In fact, the strength values do descend in the order $ss > bb > IC$ (tables (4.10) and (4.11)), but this is considered fortuitous, since the differences were not statistically significant. The similar values in

strength either mean that friction made a negligible contribution (at least at room temperature) to the stresses on the samples with this geometry, or that it could not be minimised any further by the adjustments that had been made in the rigs. Additional decreases would only be possible by altering the surface finish of the samples, such as by polishing. It was considered unlikely that friction would increase at high temperature, since the IC rig and samples were chemically stable at 950°C (i.e. no oxide layers would develop during a test).

5.3.2.(ii) Performance of the Different Materials

The Weibull strength at room temperature of sets B and D (tested at Imperial) were comparable (table (4.10)), and both also failed in a transgranular manner. This contrasts with set C, where the strength was higher, and the crack path was intergranular. However, the failure initiation sites in all three sets were the same - porous defects, which were of similar dimensions - and so the strength and path are not dependent solely on the type of failure initiating defect. The smaller grain size (3.6µm) of set C probably contributed to its higher strength compared with set B (8.8µm), but would not explain the intergranular fracture path, since set A (3.2µm) had a similar small grain size yet failed in a transgranular manner. The failure crack will take the path of lowest energy when propagating, and for set C this was between the grains except when nearing the compression surface, presumably because its velocity was now sufficient to allow it to pass through the grains. A grain boundary tends to be a more open structure than the bulk material, especially if there is a lot of porosity based on it, so it can be energetically more favourable for a crack to pass along the grain boundary rather than to cut through the grains (although the porosity in set C seemed to be distributed throughout the structure, and not especially at the grain boundaries (figure (4.11))).

As was found with the bars, the ageing treatment had no effect on the fast fracture behaviour of set C (table (4.11)). The strength of the aged material was statistically the same as the unaged, as were the failure sources and manner of crack propagation. The fact that the aged samples fractured into more fragments than the unaged of equivalent strengths suggests that either there is more stored elastic energy released on fracture, or the stored elastic energy remains the same and the fracture energy per unit area is reduced, so it is a little surprising that there was no difference in the strengths. There also did not seem to be any effect from the reduction in warpage on ageing; whether these two effects are related is not known, but there was no overall effect of ageing on strength. This supports the work of Gut (1994), who also found no variation in strength on ageing FSZ material.

The change in fast fracture behaviour at 950°C was not the same for each of the sets tested. At 950°C, the strength dropped for each batch, but considerably more so for set A, ~57% (table (4.9)), than for sets C and D, ~ 30% (tables (4.10) and (4.11)). For each set the S.D. decreased at 950°C, but only in set D did the Weibull modulus also increase, so the scatter was reduced significantly only in this material, produced by Siemens.

Differences between set A and sets C and D were that set A was produced by the viscous processing and tape-calendering route, rather than tape-casting; this was believed to account for the long, thin, cracks in the microstructure of set A, but these did not seem to contribute in any way to the fracture process, either by initiating failure or by impeding the crack propagation. Set A also contained a small amount of alumina, which, if present as a secondary phase at grain boundaries, can soften and weaken materials prematurely. However, the DIGIMAPS did not show that the alumina was distributed along grain boundaries, and the crack path examined in the SEM appeared to be the same at 950°C as at room temperature (transgranular), so the 57% drop in strength cannot be attributed entirely to a glassy grain boundary phase. The initiation sites also seemed to be the same at room and elevated temperature, consisting of smaller defects than found in the tape-cast samples. Thus there seems to be no explanation for such a relatively large strength decrease at 950°C for this material, unless it has yet to undergo a temperature-dependent change in failure mechanism, as discussed later in this section.

The drop in strength for sets C and D at 950°C (tables (4.10) and (4.11)) was also significant, and was slightly more for set D. The amount of scatter was also important; for set C, the S.D. and m values show that the scatter at 950°C had not really changed from that at room temperature. In contrast, the scatter of set D was shown to definitely decrease at the higher temperature. This reduction in scatter in the data could mean that the catastrophic failure from a porous defect which is found to dominate the room temperature fracture is no longer so dominant; another process, which does not rely so much on the large processing defects, is controlling failure initiation - this is consistent with the SEM observations that set D often failed from a 'transgranular' region at 950°C (discussed later).

The variation in strength with temperature for set D (table (4.12)) was unexpected; normally the strength does decrease at the higher temperatures, but in this case the strength showed a fairly sharp decrease between room temperature and 850°C, of 34%, and then actually started to increase again. This trend was confirmed statistically, despite the small sample numbers used at 850°C and 1050°C. As stated in section (5.2), Young's modulus values were used in the calculation of strength, and the variation in E of set D with temperature

(figure (4.3)) shows a similar trend as these strength results (E at 850°C was $\sim 35\%$ lower than the room temperature value, but increased as the temperature continued to increase). However, even if a constant value for E is used in the strength calculations, the strength of set D would follow the same trend shown in table (4.12), although the decrease observed between room temperature and 850°C is reduced to 28% . Thus it is concluded that the strength changes do not just reflect the changes in E . An increase in strength at elevated temperatures in brittle materials is usually associated with the onset of some form of flow which blunts cracks, e.g. the flow of a glassy phase in some aluminas and glass ceramics (Morrell, 1995; Brennan, 1982). Although set D contained negligible impurities, and so the presence of an impure glassy phase can be discounted, and the creep processes which were shown to cause deformation at 950°C are unlikely to operate within the short time-span of the fast fracture tests, the SEM results do suggest that some flow process was occurring.

As well as the changes in strength and scatter of data as the temperature was raised, the crack path across the fracture faces of sets C and D also needs to be considered. In set C (figures (4.11) and (4.12)) the crack path was the same at room and high temperatures (intergranular), but it was found that at 950°C the failure source was not always a cavity (figure (4.12)), although the initiation point was always on the tensile face and within the region of the loading ring. The crack path in set D was affected more obviously by the change in temperature, and was displayed over a wider temperature range than set C. The trend in figures (4.16) and (4.17) show that the dominance of the porous cavities, and the transgranular crack path, over the fracture mechanism decreased as the temperature increased. Large defects still contributed to failure at 1050°C , but three of the five samples tested failed from what looked to be more like a grain sliding event, and even around the cavities it seemed as if sub-critical crack growth was occurring, which was not the case at room temperature. The crack path had changed from transgranular to intergranular by 1050°C , except in the immediate region surrounding the initiation site.

It would seem that a different fracture mechanism is in operation by 950°C for set D, both in the initiation of fracture, since failure is no longer automatically initiated at a porous defect, and also in the propagation mode, since the grain boundaries are now the preferred path. Possibly the changeover in low and high temperature failure processes is demonstrated in the drop in strength before 850°C , followed by the subsequent increase. To a lesser extent this behaviour is seen in set C; although porous defects were the cause of failure in some samples at 950°C , failure in others was initiated by grain sliding, or some sub-critical crack growth. Since the scatter in data for set C at 950°C was the same as at room temperature, as well as

the mixture in initiation sites, it would seem that the changeover in fracture mechanism was still in the transition stage.

This change in mechanism may also explain the large drop in strength displayed by set A at 950°C. There was no change in fracture path through the samples seen at the higher temperature, which could mean that the high temperature fracture process had yet to start taking place, and the drop in strength shows the trend that the material would follow when the failure is dominated only by the fabrication surface defects. On the other hand, the small amount of alumina impurity may have enhanced the flow process at the initiation sites, so that this material would show a strength increase at a temperature lower than 950°C, and by 950°C the strength was decreasing rapidly.

On comparing the strength data from the bulk and thin-film samples (sets A to D), it can be seen that the material made by the thin-film processes was much stronger - in spite of using a more severe stress distribution in the flexure test. No SEM examination of the bars was performed, but from previous work it is assumed that the failure initiation sites would usually be damage at the surface from grinding - hence the scatter of data within the sets of bars was generally lower than for the discs.

The room temperature strengths of all the sets are higher than those determined previously (Gut, 1994; Basu, 1993), but are still of the order expected, and the Weibull modulus (~ 5) is as expected for an industrially manufactured ceramic (Ashby, 1991).

It was stated in section (2.5) that Siemens required a failure probability of 10^{-6} . Using the Weibull strength and modulus data obtained, and scaling up from the area of the discs subjected to the maximum tensile stress to the area of an electrolyte plate, it is found that the maximum stress that should be applied to the plate is ~ 74 MPa.

5.3.3 Summary of Main Points

The strengths of the different sets of tape-cast material were not identical, with sets B and D, produced by Kerafol and Siemens respectively, considered the same at room temperature, whilst set C, also made by Kerafol, was stronger.

At room temperature the strength of the tape-cast material was dominated by processing defects at the surface; the fracture path was transgranular in sets B and D, and intergranular in set C.

Ageing was shown to have no effect on strength in either the bulk or tape-cast material.

At 950°C the strength of both sets C and D decreased, and there was also a change in the fracture mechanism, with the processing defects no longer being so dominant in initiating failure. This 'high temperature' mechanism seemed to be more pronounced in set D at 950°C, and set D was also examined at a higher temperature of 1050°C, where the strength was actually increasing and the fracture path was virtually completely intergranular.

Set A, manufactured by the viscous processing and tape-calendering route, rather than tape-casting, failed in a transgranular manner at room temperature and 950°C, although there was a drop of 57% in strength at the higher temperature. It is believed that the presence of a small amount of alumina impurity may be the cause of such a large drop in this material.

5.4 Fracture Toughness

Each technique yielded a different value for K_{Ic} , with the overall range in toughness values being from 0.94-3.87 MNm^{-3/2} (table (4.16)). However, each technique has limitations, and when these are taken into consideration, the discrepancy in the toughness is not as serious as initially appears.

5.4.1 Bulk Samples - Single-edge Notched Beam Tests

The purpose of the SENB was to see whether ageing at 950°C for 1000 hours had an effect on the toughness of bulk FSZ. Three sets were tested, rather than just two, in order to verify whether any change detected was actually the effect of the heat treatment on toughness, or merely an effect on the notch-tip. However, the results seem to show (table (4.13)) that the ageing affected both the bulk toughness and the crack tip, since the K_{Ic} value calculated for each set was different.

From the literature (Dalglish, 1980), some form of crack tip healing might be expected to occur from the ageing treatment, although the temperature of 950°C is quite low. If so, the damage at the notch tip of the notched/aged (N/A) samples would be reduced, so that the notch tip is no longer atomically sharp; this could give an anomalously high measured K_{Ic} value. i.e. the results for N/A may overestimate K_{Ic} . However, for the bars notched after ageing (A/N), there would be more damage at the notch tip, and consequently the actual 'a' would be longer than that used in the equation (2.18); this would mean that the true K_{Ic} would be higher than that measured, i.e. the results obtained for the A/N samples are underestimates of the actual K_{Ic} . The error caused by the damage at the notch tip was quoted in the literature (Dalglish, 1980) as being up to 12%; if the A/N toughness is increased by this amount, the difference between the two aged sets is no longer significant, but the toughness of the unaged is still lower; this does suggest that the ageing conditions had changed the structure in some way.

There was an obvious difference in the crack path through the bars between the aged and unaged sets at the macro-level, with the crack passing directly through the A/N and N/A samples rather than following the convoluted path seen in the unaged set; these crack paths are illustrated in figure (5.1). This cannot be associated with crack healing at the notch-tip, since if crack healing was responsible samples from the unaged and A/N sets would be expected to fail in a similar manner, which would be different to the N/A. This also suggests that the ageing must have altered the microstructure in some way. The microstructure of the bulk samples have not been investigated in any detail, but the more extensive studies of the tape-cast samples did not reveal any major microstructural changes on holding at temperatures up to 1050°C.

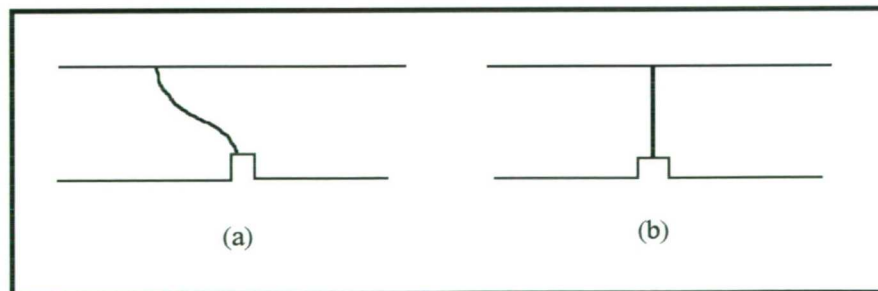


Figure (5.1) - diagram illustrating the difference in crack paths through heat treated SENB samples; (a) - unaged; (b) - aged.

From the examination of the cross-sections of the notches (figure (4.18)), there seemed to be very little damage (microcracking, etc) behind the crack front or around the notch tip of any of the samples. Either insertion of the notch did not cause much damage, and so the calculated values in table (4.13) are the actual values, or (more probably) the thermal etch at 1300°C of the sectioned samples eliminated the damage. In either case, the toughness did appear to be affected by the heat treatment, and further information was required from the post-indent and ISB tests concerning the influence of the heat treatment.

5.4.2 Tape-cast Samples

5.4.2.(i) Sources of Error in Indentation and ISB Tests

Difficulties in measuring crack lengths accurately may introduce errors in the results of the indent-based techniques. It had been pointed out in the literature (Jones, 1987; Ponton, 1989(b)) that it is difficult to obtain very accurate results from optical indent measurements of $2c$, and this was found to be the case, with the error compared with the SEM measurements being greater for the smaller indent loads. However, if it is assumed that the error in $2c$ for different samples at the same indent load is constant, then the measurements can be used to rank different materials.

The difference in the post-indent toughness (table (4.15)) from using indent loads of 100g and 350g was $\sim 30\%$, found by equation (2.20), which is of a similar magnitude to the error associated with that from the optical and SEM measurements. This implies that the higher values for K_{Ic} found with the lower loads (100g and 200g for set C; 100g for set D) could be a consequence of underestimating the optically measured radial crack lengths. This would tend to make the results found using the higher loads (300g and 350g) more reputable, since the error in K_{Ic} resulting from poorly measured crack lengths is much lower. However, on examining the fracture faces of ISB samples in the SEM (figure (4.20)), the damage associated with the indentation was shown to be extensive, such that every test lay outside the limits concerning the ratio of crack lengths to sample thickness. In figure (4.20) the plastic damage immediately around the indent was shown, but also the radial and median cracks extending far beyond the $t/10$ limit (Ponton, 1989(b); Zhang, 1991). The median cracks produced using the lower indent loads were smaller, and so the error associated with this effect would be less at loads of 100g and 200g. Thus it would appear that the most reputable results from the indentation processes would be those found from the ISB test at 100g, although even using this load was not totally acceptable.

In addition to the above problems, it was also difficult to determine exactly at what point fast fracture commenced in the samples used in the ISB tests, since sub-critical crack growth was not obvious from the SEM images. Thus the crack lengths used to calculate K_{Ic} from the ISB equation (equation (2.21(a))) were estimates; overestimating the crack lengths by $\sim 2\mu\text{m}$ would result in a K_{Ic} value about 20% too low, which is similar to the discrepancy found between the results from the ISB equation and graphical methods. Finding K_{Ic} from the ISB graph (figure (4.22)) does not depend on measuring crack lengths, but may still be affected by the 'forbidden' crack length to sample thickness ratio.

If the above experimental difficulties concerning the indentation techniques are taken into account, then the variation in the post-indent toughness of both sets C and D (table (4.15)) is shown to be a consequence of experimental error, and the true toughness of each set is constant over the load range used. It can also be concluded that the toughness of sets C and D is the same, within experimental error. The ISB data for set D also showed that the toughness was constant with indent load, in agreement with the post-indent results, but the ISB data for set C was shown to vary with load, and was always lower than that for set D. More meaningful results for set C would have been obtained if there had been more samples available for testing.

It is still expected that the indent-based techniques can rank K_{Ic} for different materials, so long as the same indent loads are used for comparison, but with samples as thin as the tape-cast material these techniques may not be suitable for obtaining absolute data; the damage produced from the indent is quite extensive below the sample surface. Using smaller indent loads, and the SEM to measure the crack lengths, would improve the post-indent accuracy, except that at very small indent sizes the surface cracks may be affected by the local microstructure, e.g. the crack may lie within the same grain, or be dominated by a pore, so that the bulk toughness is no longer being measured. Using smaller loads in the ISB test will not necessarily help, since even at 100g some samples failed from porous defects in the vicinity of the indent, rather than from the indent itself. At lower loads failure would be initiated increasingly from natural defects, rather than from the inserted flaw.

5.4.2.(ii) Double Torsion Tests

K_{init} , the stress intensity to initiate the crack propagation, was always greater than K_{prop} , the stress intensity required to propagate the crack through the sample (table (4.14)). Since the elastic energy released on crack initiation is often greater than that needed to fracture a sample, K_{prop} is considered more representative of the toughness of the material (Davidge,

1979). The scatter within the tests was low, and the toughness calculated was of a similar magnitude to that from the indentation techniques (table (4.16)). It is often found that DT toughness values are higher than those found using natural flaws (Bleise, 1994; Dransmann, 1994); in this case the DT value for set D material was ~ 33% higher than that found using the ISB technique from figure (4.22).

5.4.2.(iii) Toughness of Tape-cast Samples

The toughness of set C found from the ISB test was in reasonable agreement with the values quoted in the literature for Kerafol material (Basu, 1993; Brocco, 1994), and the ISB data for set D was of a similar magnitude. However, the value for set D from the DT test was greater than the ISB results, and the post-indent values for sets C and D (table (4.15)) are clearly not in good agreement with these tests. The equation used in the post-indent calculation (equation (2.20)) was one of many that could be used; it was noted in the literature (Ponton, 1989(b)) that most post-indent equations will rank materials in the same order as other techniques, although often there is discrepancy in the actual data, and this seems to be the situation in the present work. Use of a different equation, e.g. equation (5.1) (Ponton, 1989(b)), would give toughness values closer to the ISB values; in this case, the toughness for aged set C with an indent load of 200g would be $0.77 \text{ MNm}^{-3/2}$.

$$K_{Ic} = \frac{0.0101P}{a\sqrt{c}} \quad \text{Equation (5.1)}$$

The important point in using the post-indent equations is that they reveal trends in the toughness of different materials, rather than obtain absolute data.

The results in table (4.16) show that the toughness for the unaged and aged samples of set C was the same. The lack of effect contrasts with the bulk samples, where the toughness of the aged material was significantly higher than the unaged; however, no change in toughness of the tape-cast samples is consistent with all the microstructural and bulk properties evidence (strength, E, SEM, phase stability), so the change in toughness brought about by ageing is specific to the bulk material. Possibly the difference in processing routes would account for the different response to the heat treatment demonstrated by the toughness results.

The gradient (-0.24) of the $\log(\sigma)$ versus $\log(P)$ graph for set D (figure (4.21)) was a little lower than the theoretical value of -0.33 expected if the microstructural effects are negligible. Bleise (1994) suggested this could be a result of changes in the crack system or front, but from the SEM examination, the crack system in operation was always median, and

the crack front always appeared to be semi-circular at the point where it was assumed fast fracture commenced (figure (4.20)). A deviation at lower loads would be a sign that the material was displaying R-curve behaviour, which occurred in alumina when using indent loads below 10N (Cook, 1987). However, the graph of $1/\sigma_f^3$ versus P for set D (figure (4.22)) fitted well to a straight line (despite the median crack size being so large compared to the sample thickness) and gave a P^* value of 0.2N, which was much lower than the indent loads used in the test. This suggests that no R-curve behaviour was occurring throughout the range of loads used in this work. Since the value of toughness found from figure (4.22), $1.99 \text{ MNm}^{-3/2}$, did not depend on any crack size measurements, and also used natural sized defects, it is considered the most accurate value for the toughness of set D.

The large decrease in toughness of set C found using the ISB equation between loads of 100g and 200g, in contrast with the constant toughness found from the post-indent data when allowances for experimental error have been made, can probably be attributed to difficulties in measuring the crack lengths. However, the toughness found from figure (4.22) ($1.13 \text{ MNm}^{-3/2}$) may not represent the true toughness of this material, since there are only two data points on this graph. It would be surprising for the toughness of set C to be lower than that of set D, as indicated by the ISB results, because the grain size of set C is smaller. Grain boundaries tend to inhibit the crack's progress as it crosses grains, and since the grain size of set C was half that of set D, crack propagation would be obstructed more in this material; thus the toughness would actually be expected to be higher. Since the post-indent results show that the toughness of sets C and D are the same, then a value of $1.99 \text{ MNm}^{-3/2}$, which is the most accurate value determined for set D, can also be taken as the toughness of set C.

The critical flaw sizes of set D found from the fast fracture tests were $\sim 15\text{-}20\mu\text{m}$ (section (4.3.2.(ii))). Using the room temperature Weibull strength of 294 MPa, together with these flaw sizes, a range in K_{Ic} for set D can be calculated using equation (2.17), and found to be $1.41\text{-}1.63 \text{ MNm}^{-3/2}$, which is similar to that found from the ISB technique. For set C a slightly higher toughness is calculated, at $1.84 \text{ MNm}^{-3/2}$, which compares well with the value of $1.99 \text{ MNm}^{-3/2}$ taken from the ISB technique.

The ISB test was intended to be used at high temperatures as well, and although these tests were not actually performed, the method does seem to be suited for this. However, an indication of the toughness at 950°C can be obtained using the residual strength data from the samples loaded at $18\%\sigma_o$, and the room temperature fast fracture strength and toughness data of set C.

Putting values of 332MPa and $1.99\text{MNm}^{-3/2}$ as the respective room temperature strength and toughness values into equation (2.17), a critical flaw size of $23\mu\text{m}$ is obtained. (This agrees very well with the flaw sizes actually observed in section (4.3.2.(ii)), where the defects extended $\sim 20\mu\text{m}$ into the sample.) The critical defect size for the samples loaded under $18\%\sigma_0$ is calculated, using the residual strength value of 248MPa, as $42\mu\text{m}$ (thus the defects grew from $23\mu\text{m}$ - $42\mu\text{m}$ within 1000 hours at 950°C). Under a stress of 46MPa, the stress intensity factor, K_{I_1} , at the crack tip was $0.40\text{MNm}^{-3/2}$, approximately one fifth of the room temperature K_{I_c} value, and since the sample did not fail at high temperature under this load, the K_{I_c} value at 950°C would have to be greater than this.

5.4.3 Summary of Main Points

The increase in toughness of the bulk samples after ageing was not mirrored in the unaged and aged tape-cast material; this illustrates the importance of testing on material which will actually be used in service.

It was believed that the indentation processes would be the most suitable techniques for determining toughness of the thin tape-cast material, yet difficulties concerning the size of the indent cracks with respect to the sample thickness were found. Despite these problems, reasonable agreement between the DT, $\sim 3\text{MNm}^{-3/2}$, ISB, $\sim 2\text{MNm}^{-3/2}$, and literature values for toughness were found. The post-indent test confirmed that, if experimental errors were taken into account, the K_{I_c} value of set D was constant with indent load (although the actual data values were not the same), and also that the toughness of sets C and D was the same.

No toughness tests were performed at high temperature, but it was estimated from the fast fracture and sub-critical crack growth results that K_{I_c} would be greater than $0.40\text{MNm}^{-3/2}$.

5.5 Static Fatigue Tests

5.5.1 Sub-critical Crack Growth (sccg) and Strength-Probability-Time Diagram

The median strength of each set of bars fell into two groups, with the strength increasing as loading rate increased within each group (figure (4.23)), because less sccg is able to occur before the fracture stress, σ_F , is reached. The samples tested at 5 and 100 N/min. were made at a different time than the rest, so although the processing conditions were nominally the same, possibly there was some slight difference in preparation which would account for the data falling into two groups. There was less scatter within the sets tested at 5 and 100 N/min., implying that the surface finish was different, and the median strengths were lower than would be necessary to fit with the other data; thus the grinding process may have been the stage at which the variation was introduced, producing larger, yet more consistent, defects.

The value of 10.2 found for n_{sf} from figure (4.23) is quite low compared with the general range of 10 - 200 for ceramics given in the literature (Morrell, 1985). Resistance to sccg increases as n_{sf} increases, so this low value found from the bar samples means that sccg will be very significant in the FSZ material.

The assumptions made when calculating the static stress required for discs to fail within 1000 hours at 950°C from the room temperature data determined for bars meant that the value calculated for the discs would be approximate, and subsequent work showed that the load of 1N was lower than would have been needed for all the set of samples to fail. However, the errors in expected sccg behaviour resulting from these assumptions were not as significant as those from the assumption that the failure mechanism at high temperature under prolonged loading would be the same as that under fast fracture, and that the strength drop which occurred under fast fracture from room temperature to high temperature would correspond to that under static loading.

This was proved by the subsequent behaviour of the samples from set C tested in static fatigue. From the room temperature SPT plot, ~ 70% of the samples loaded under 1 N (18% σ_o) at 950°C were predicted to fail by 1000 hours, so the lack of any failures was initially surprising. No deflection or deformation was visible by eye, so the samples were broken under fast fracture to test whether there was a drop in residual strength from sccg, without measuring the profiles beforehand (afterwards it was not possible to measure accurately the

deflection, because the fragments were too small). The drop in Weibull strength compared with the aged samples was almost 30%, which does imply that either sccg was occurring during the test, but obviously not at the rate found at room temperature, or that another deformation mechanism was occurring in addition to sccg.

The rate of sccg under 46 MPa at 950°C can be estimated by the growth of the sub-critical defect from 23µm to 42µm in 1000 hours, which corresponds to a rate of $5.3 \times 10^{-6} \mu\text{ms}^{-1}$. Taking the room temperature value for toughness, $1.99 \text{ MNm}^{-3/2}$, would give a critical flaw size of 1200 µm, which is eight times the sample thickness, i.e. the crack will not propagate catastrophically, but will grow sub-critically through the electrolyte. (This can be compared to the 'leak before break' scenario in pressure vessels, where the crack grows sub-critically through the vessel wall and can be detected by a leakage of steam before catastrophic failure occurs.) At the above rate, the crack would take just under one year to grow to the electrolyte thickness, and could possibly be detected by a non-destructive testing technique before reaching this stage; however, it is also likely that over such a time scale creep would intervene to reduce the stresses on the electrolyte, slowing the rate of sccg, so that failure of the cell due to sccg would take even longer.

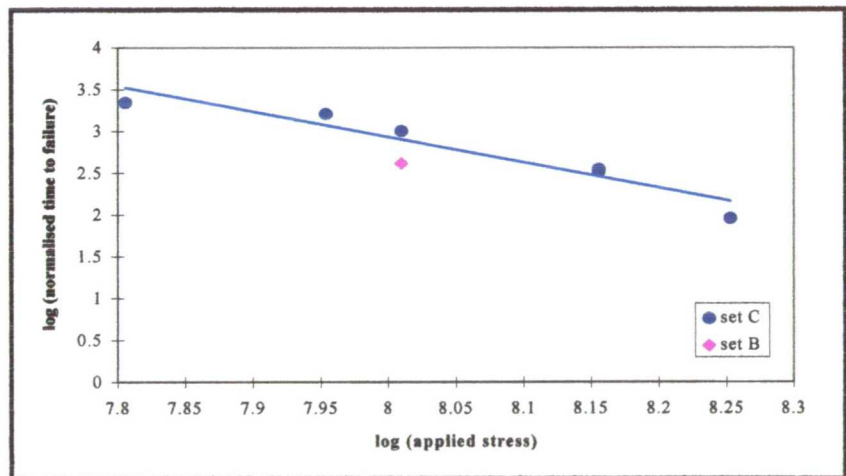
When higher loads were applied to set C, three scenarios were found (table (4.17)): samples could fail instantly, or after a delay ranging from 0.6 - 27 minutes after applying the load, or samples would not fail but were found to deform. This would correspond to the natural scatter of strengths found in a set of samples, linked to the range in defects. Instant failure would occur for any samples which had a strength lower than the applied stress, which occurred in those samples where a large porous defect was found to be within the maximum stress region. The samples which did not fail instantly did not contain a critical sized defect, and sccg occurred, either from a porous defect as was found for those which failed at room temperature, or from a region where there was a featureless site, which was the case for delayed failure at 950°C. It must be assumed that sccg was still occurring in those samples which did not fail within the allotted test time, but it occurred either more slowly, or from much smaller defects, so that fracture was not observed and the operation of other forms of deformation were revealed. Porous defects were present in these samples, since when the samples were fractured at room temperature, they were found to be the failure initiation sites in those which were examined.

The profiles of the deformed samples measured using the Talysurf were quite symmetrical around a central axis, which means that the samples and apparatus were aligned concentrically, producing a symmetrical stress distribution. Exceptions to this were some of

the samples under the 45% and 50% σ_o loading; possibly this misalignment is the reason for the lack of failure from sccg, since this was not the case for the samples under lower loads.

The fracture of samples within a short space of time, or not at all, made the obtaining of sccg data difficult. The fact that some samples within a batch did not fail distorted the mean failure time found for the particular stress, and so the times to failure in table (4.17) were normalised by multiplying them by the ratio of samples failed to samples tested. The resultant plot of log (normalised times to failure) against log (applied stress) is given in figure (5.2), which shows the expected trend: as applied stress increases, the normalised time to failure decreases. The normalised time to failure (6.8 mins) for set B, which had a larger grain size and was tested only under 103MPa at 950°C, is lower than that found for set C under the same test conditions (16.7 mins), but is of a similar magnitude to these values, as can be seen in figure (5.2).

Figure (5.2) - showing the plot of log (normalised time to failure) versus log (applied static stress) for sets B and C tested at room temperature and 950°C; values for set C from the 45 and 50% load not shown, due to the misalignment of rig.



It was surprising that all the samples under 56% σ_o and 70% σ_o failed so quickly, since from the SPT plot the expected failure time would have been up to ~ 27 hours (for 56% σ_o). Initially samples were loaded at room temperature, and then the temperature was raised, but since the sccg was so rapid they all failed below 200°C; it was wondered whether at 950°C processes were occurring which would suppress the sccg, so that some samples would survive and deform plastically; hence three samples were loaded under 56% actually at 950°C, rather than at room temperature. The results were the same, in that delayed failure still occurred for all the samples (table (4.17)), and t_f was very similar to the value obtained with the loads initially applied at room temperature; thus the higher temperature did not prevent sccg occurring in favour of another deformation mechanism at these high loads.

The rate of sccg at low and high loads can be compared using the value of n_{sc} calculated from figure (4.23). Taking an initial crack size of $23\mu\text{m}$, the K_I values under 56% and $18\%\sigma_o$ are calculated as 0.86 and $0.27\text{ MNm}^{-3/2}$ respectively. The velocity under $18\%\sigma_o$ is $5.3 \times 10^{-6}\mu\text{ms}^{-1}$, and using equation (2.26) this gives the rate of sccg under $56\%\sigma_o$ as $0.7\mu\text{ms}^{-1}$, which is $\sim 1.3 \times 10^5$ times faster than that at the lower load, and illustrates once again how significant the applied stress is on the rate of sccg.

From the SEM examination of the fracture faces of a selection of samples it would appear that the short-term fracture behaviour at room and high temperature reflects the fast fracture behaviour at room and high temperature, with large defects dominating the source of failure at room temperature and in the weaker samples at 950°C , whereas the initiation area in the stronger samples which failed at 950°C after longer times up to 27 minutes was often featureless.

Samples which survived without failure from sccg at 950°C for several hours went on to experience permanent deformation. The intervention of permanent deformation prevented long term failure by sccg under the conditions of this study.

5.5.2 Creep

The plot of deflection versus time from the LVDT (figure (4.30)) shows two regions. During the first 400 hours the amount of deflection which occurred was small compared with the overall deflection, and the rate of deflection was also increasing, which suggests that the steady state creep processes were not yet functioning. In the second region the rate of deflection is constant, implying steady state creep (since strain was proportional to deflection).

It must be mentioned that the samples were not profiled before the test, but it is assumed that they would not be flat or smooth, but warped (figure (4.2) and table (4.3)). This was not seen in the profiles after the test (figure (4.27)), but does mean that the deflection for each sample would not be identical, and so is one source of error in the strain calculated from the deflection data. It is also encouraging that the Talysurf and LVDT deflection readings were so similar; the sample deflection from the creep test was in the same direction as the warpage of the samples illustrated in figure (4.2), and so the Talysurf profile would be a combination of these readings. The LVDT readings only registered the deflection during creep, and so would be expected to be slightly less, which was found to be the case. The roughness of the surface would be insignificant compared to the overall deflection.

The strain rates calculated by the two techniques would not be expected to be the same, since they operated over different areas of the samples. The stress at the central region would always be greater than at the edges, and hence the strain rate calculated by 'Fett's' method should always be faster than that from the 'triangle', which was an average of the rate over the whole sample, including the slower regions at the perimeter. The strain rate results confirmed this (table (4.18)). The difference in the rates found from the two methods was fairly constant for all the tests performed at different loads at 950°C and at 40% σ_0 at different temperatures, with the exception of an anomalous result at 40% σ_0 at 1000°C, where the rate was much faster in the central region. This implies that the strain rate distribution across the samples was constant for all the test conditions.

The values of n_c (0.5 or 0.8) and Q (320 or 260 kJ/mol) found by Fett and triangle methods respectively do not agree with values quoted in the literature (section (2.8.4)); n_c is less than the range of 1-1.5 for polycrystalline YSZ (for FSZ, PSZ, and TZP material), and Q is also lower than the range 360-590 kJ/mol quoted. The values found from the two techniques also do not agree with each other: Q is greater and n_c less for the central region than for the average across the samples. These discrepancies are probably the product of using the biaxial flexure geometry for the creep rig, and also the methods used to calculate strain from the deflection.

n_c is calculated from the logarithmic plot of strain rate versus applied stress. In figure (4.28), the applied stress is taken as the maximum stress that would be experienced at the tensile surface below the loading ring, at the start of the test. The Fett technique applies only to the region which lies within the load ring, where the stress is constant and equiaxial, and hence the strain rate would also be. The stress which would correspond to the triangle technique needs to be an average value across the sample, which would be less than the applied stress.

As mentioned in section (2.8.3), if $n \neq 1$ then the stresses may redistribute through the sample thickness, so that the actual tensile stress is reduced; it is possible that this could occur during these creep tests. The 'Fett' technique was based on geometry, so factors which could affect the strain calculations would be the neutral axis shifting upwards, due to creep occurring more easily in tension than compression, and the equations used for elastic deformation are not always suitable for plastic deformation. To counter these effects, a small radius was considered specifically to avoid the discrepancy between elastic

and plastic geometry, so that the deflection can still be considered as part of a sphere. Also, the Talysurf profile of a sample plastically deformed under 25% was compared with the elastic deformation predicted by Kao (1971), and the two did not look dissimilar. This is encouraging for the applicability of Fett's equation.

The above problems tend to be found when performing creep tests on bulk samples with any flexure test. Using the biaxial flexure test with such thin samples presented the additional problem of membrane stresses, since discs were found to deflect to twice their thickness. An FEA model was developed in the Department of Mechanical Engineering (Adamson, 1996) to show the effect that the membrane stresses could have, by assuming the simplest case of $n_c = 1$ in equation (2.34), and plotting the stress redistribution through the sample thickness and along the tensile face as the system moves, due to creep, into the large displacement regime. The difference is displayed in figure (5.3) for a sample under 50% initial stress, which shows the stress across the tensile face decreasing with time, most notably in the central region. (A similar plot along the compression face shows the stress increasing.)

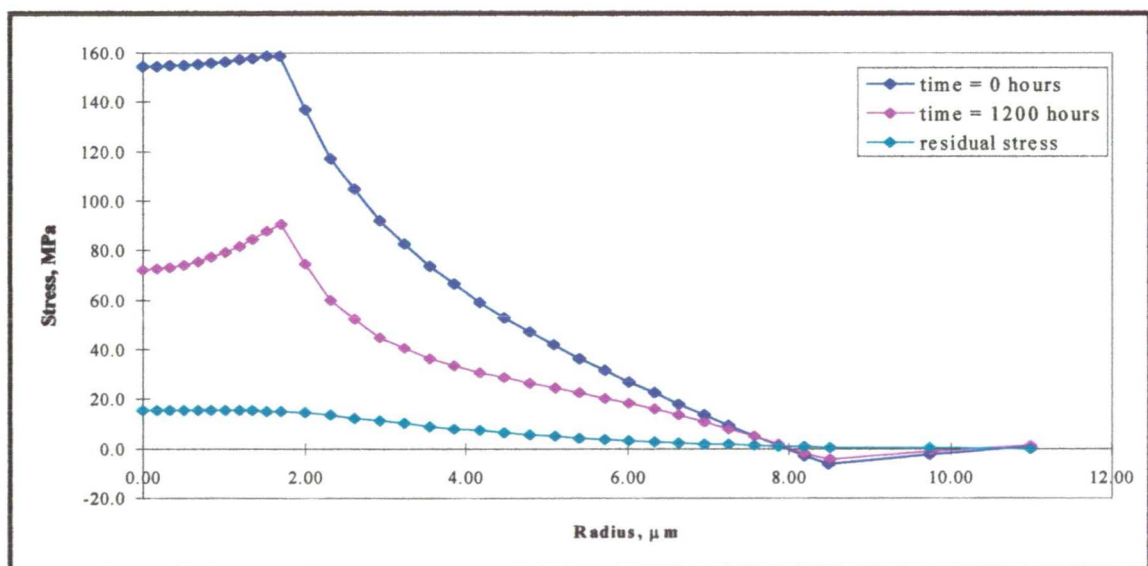


Figure (5.3) - showing the change in stress experienced with time along the tensile face, due to the large displacement, for a sample held under an initial load of 129 MPa at 950°C for 1200 hours.

The change in maximum stress experienced by samples was plotted against time in figure (5.4) for the loads in the range 25 - 50% σ_c . The plots are approximately linear and therefore the stress at 600 hours was taken and used as an average stress over the 1200 hour period of the tests to re-plot log (strain rate) versus log (stress). This yielded slightly higher values for n_c of 0.7 and 1.0 for the Fett and Triangle techniques respectively than obtained

previously using the initial stress. (Note that the reason the n_c values change is because the plots of figure (5.4) are not parallel.)

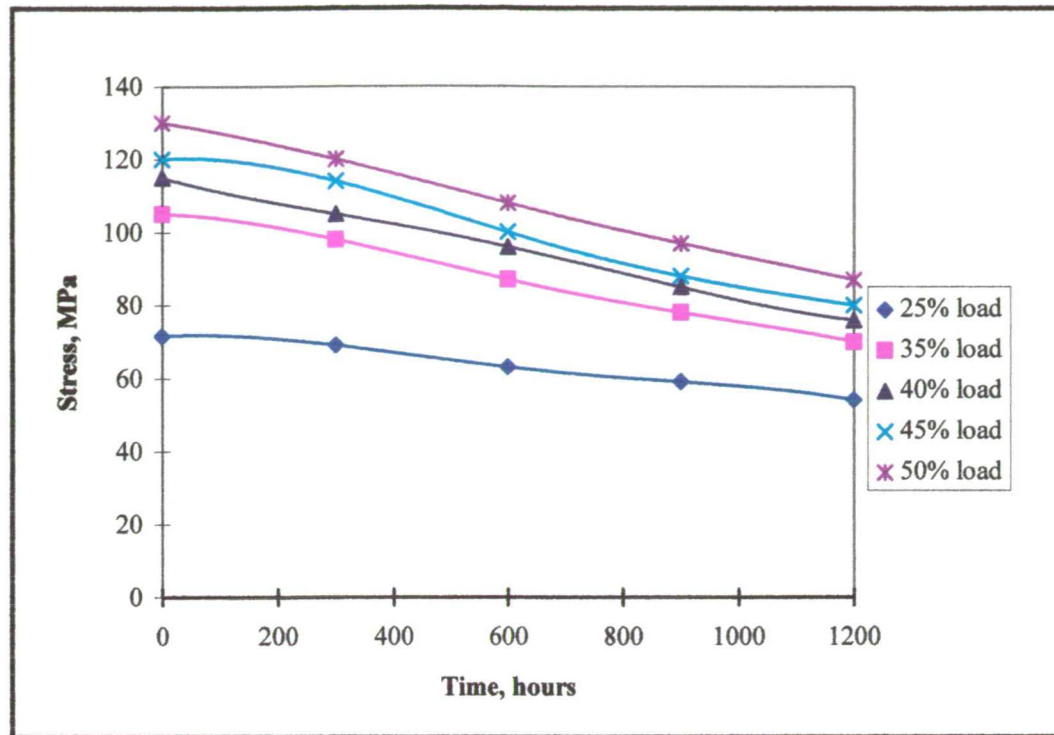


Figure (5.4) - shows the change in maximum tensile stress for the initial loads over period of 1200 hours.

Thus initially Fett's technique would yield a more accurate value for n_c than the triangle method, since this measures strain only in the centre where the stresses are constant. However, as creep occurs and the stresses change, Fett's method becomes less accurate; for the time period used the central stress continued to decrease, and so the strain rate in the centre would also decrease, whilst the reduction in the surrounding stress, and hence surrounding strain rate, was less pronounced. As time proceeds, the average stress value used above would probably become more similar to the average stress that would be experienced across the entire sample, and that is needed for the 'triangle' method, so that this method would give more accurate data.

The values for n_c obtained with the adjusted stress values are only accounting for the change due to membrane stresses, but are probably more accurate than those found assuming that the initial stress remained constant. (It is quite likely that any additional stress redistribution would seek to decrease the central stresses even more.) The linear plot obtained from the LVDT, indicating an overall constant rate of creep, suggests that the effect of the stress redistribution may be self-cancelling, such that the drop in stress and rate on the tensile

surface may be balanced by the increase in stress and rate closer to the compression surface. From the work performed it seems reasonable to take a value of 1 for the stress exponent, n_c , which is consistent with a diffusion creep mechanism.

It was mentioned that no deformation of the samples loaded under $18\%\sigma_0$ was noticed by eye. Using the stress exponent of 0.7 found by the Fett method, the deformation that would have occurred in the central region of these samples after 1000 hours would have been $\sim 8\mu\text{m}$, which would correspond to a total deformation of $\sim 40\text{--}80\mu\text{m}$ across the sample diameter. In order to have been noticed the deformation would probably need to be $120\mu\text{m}$; this would have been attained after ~ 1500 hours under these test conditions. (Taking a value of $n = 1$ would give a longer time, ~ 1850 hours, for this noticeable amount of deformation to occur.)

The difference in Q values (which are notorious for error - Rawlings, 1996) found by either method implies that different creep mechanisms were occurring at the centre and the edge, most probably as a result of the different stress regimes in these regions. The range of $260\text{--}320\text{ kJ/mol}$ is much higher than the activation energy for diffusion of oxygen ions in YSZ, 86 kJ/mol (table (2.2)), but more similar to that for cation diffusion, 461 and 462 kJ/mol for Zr^{4+} and Y^{3+} respectively, although still low in comparison.

The SEM showed that microcracking was occurring only at the central regions, where the stresses were greater, rather than at the edges. This was also only in the samples under the higher loads. Thus the commencement of creep rupture processes was influenced strongly by stress.

The TEM examination did not show any evidence of new phases precipitating out as a result of the heat treatment, nor were any dislocations detected. The microstructure was also examined in the SEM and the grains were undeformed; both these results suggest that the creep was occurring by a diffusion, rather than a dislocation, process. In addition, the SEM showed that micro cracking was occurring only at the central regions, where the stresses were greater, rather than at the edges, and this only in the samples under the higher loads. This is consistent with the cavitation processes that ultimately lead to failure, and which would occur in regions of higher stress, where the creep rate is not sufficiently rapid to accommodate all the strain. The fracture mechanism map for materials with the CaF_2 structure (Gandhi, 1979), of which YSZ is one, predicts that failure would occur by brittle intergranular fracture under all the creep conditions used in the project. No samples actually

failed during creep, but the lack of dislocations and grain deformation would support this failure mode.

Using samples with a different grain size, to analyse the effect of grain size on strain rate, would have provided additional clues to the creep process occurring. Unfortunately, the samples from set B, which had a larger grain size, did not survive sccg to undergo creep. However, this in itself suggests that creep was slower in the large grain samples, which is consistent with diffusion creep rather than dislocation creep.

The creep is occurring at a relatively low temperature ($\sim 0.4T_m$), and the activation energy is less than that for cation diffusion through the bulk material. This implies that the creep process is most likely Coble creep, by diffusion along the grain boundaries. Using for the grain boundary diffusion coefficient, D_{GB} , the self-diffusion coefficient given in table (2.2) but now calculated using the experimentally determined activation energy of 320 kJ/mol, the Coble creep rate was calculated for a grain size, d , of $3.2\mu\text{m}$ under an average stress, σ , of 60MPa at 950°C , from equation (5.2) (Evans, 1993):

$$\dot{\varepsilon} = \frac{D_{GB}\delta\Omega\sigma}{d^3kT} \quad \text{Equation (5.2)}$$

where δ = grain boundary zone ~ 5 atomic widths

Ω = vacancy volume

k = Boltzman's constant

This gives a strain rate of $9.5 \times 10^{-10} \text{ s}^{-1}$, which is in good agreement with the rates actually determined during this project.

5.5.3 Summary of Main Points

The static fatigue tests proved that sccg occurs at room temperature and 950°C in 8 mol% FSZ, at a similar rate in both cases. The low value for n_{sf} means that FSZ is very susceptible to sccg. It was found that another deformation process intervened at higher temperatures, which could prevent failure from sccg at low loads. At high loads sccg was so rapid, and the K_I at the crack tip would also be so high, that this other mechanism could not prevent failure from sccg. This high temperature mechanism was found to be creep.

The creep work performed has shown that plastic deformation occurs in 8 mol% YSZ at 950°C , and follows the stress and temperature dependence expected. The values of the

stress exponent, n_c , and the activation energy for creep, Q , calculated are approximate, since there is not enough detail known about how the applied stress may change with time, but they are of roughly the same magnitude as values previously determined. The findings were that n_c was ~ 1 ; Q was less than that for cation-diffusion, but too high for anion motion; there was no dislocation substructure within the grains; and limited evidence that material with a larger grain size displayed less creep. From these results it can be concluded that creep is occurring by a diffusion process, most likely Coble creep at such a low temperature.

This is consistent with the literature on creep for polycrystalline YSZ, summarised in table (2.6), although the temperatures in this project were generally lower, and the stress range higher, than previously used. Failure would be expected to ultimately occur from cavitation processes, which were shown to be in operation in this project, although the actual fracture could not be monitored.

CHAPTER 6
CONCLUSIONS

CHAPTER 6

CONCLUSIONS

6.1 Conclusions of Work Performed

The bulk and thin-film (tape-calendered and tape-cast) samples used in this project all consisted of cubic YSZ, with some variation in microstructure and composition. No structural instability was displayed after ageing at 950°C for 1000 hours.

The topography of the samples was affected by the processing routes; tape-cast samples contained large (~20-60µm) porous defects along one surface, whereas the surface defects resulting from the tape-calendering process were smaller. In addition, all the thin-film samples were warped.

Young's modulus of the bulk and tape-cast materials was determined at room temperature by a dynamic method to be ~ 200 GPa. The modulus of tape-cast samples at elevated temperatures was measured using static techniques and a finite element analysis solution, and was shown to vary non-linearly with temperature, initially decreasing by 40% over a temperature rise of 500°C. Explanations for this behaviour which are given in the literature are not considered to be adequate for the materials used in this project.

The fracture strength of the thin-film materials was determined using biaxial flexure tests. The room temperature strength of the tape-cast samples was controlled by surface defects, and ranged from 290 - 350 MPa. The strength of all the thin-film materials decreased at 950°C, more so for the tape-calendered material, which was attributed to the softening of a small amount of alumina impurity. The processes of crack initiation and propagation during fast fracture changed over the temperature range 850 - 1050°C.

Fracture toughness of the tape-cast material was determined using two indentation-based techniques. The techniques gave different values, but it was shown that the toughness of the tape-cast material was constant over the range of indent loads used, and a value of 1.99 MNm^{-3/2}, determined from the indentation-strength-bend test, was considered to be the most accurate.

The mechanical properties of all the samples tested were unaffected by ageing at 950°C for 1000 hours, with the exception of the toughness of bulk samples, found by the single-edge notched beam test; a value of 1.29 MNm^{-3/2} was measured for the unaged material, but the value of the aged material was almost double this.

Sub-critical crack growth was exhibited in the bulk material at room temperature, and shown to be sensitive to the applied stress, with a value of 10 calculated for the exponent. Scgc also occurred in the tape-cast material, at room temperature and 950°C.

At elevated temperatures and low loads, creep was also observed to occur in the tape-cast samples, and this was monitored from 925°C - 1000°C, and over a range of applied stress. The stress exponent for creep was determined as approximately 1, and the activation energy as 320 kJ/mol; these values, in addition to the results of the microstructural examination, indicated that creep was occurring by a grain-boundary diffusion process.

6.2 Significance for the SOFC

The results can be considered purely in terms of the behaviour of FSZ, but also their impact on the SOFC needs to be related. The actual stress conditions that the electrolyte will operate under are not known, so the following comments are general observations which can be applied to specific conditions.

The sample analysis and mechanical tests showed that the tape-casting process produced warpage in the disc samples. This made the mechanical tests more difficult, yet since the warpage in the tape-cast plates was so small, it will probably not be a problem when fitting the SOFC together - and so it is pointless to change the tape-casting process merely to obtain samples more suitable for mechanical testing when such changes are not required for the actual SOFC component.

The surface defects are more relevant to the survival of the electrolyte. The electrolyte is probably most likely to fail by fast fracture when actually being stacked together at room temperature, so although there is a drop in strength at high temperature, and the changeover in fracture process at higher temperatures is interesting, it is not very relevant to the SOFC once it is in operation. If the surface defects can be reduced by making slight alterations to the tape-casting process, it may be worthwhile doing this - otherwise a proof test is a simple way of ensuring that all the electrolytes will have the required strength to be fitted into the stack.

The variation in Young's modulus with temperature was intriguing, yet unlikely to affect the life of the cell. The drop in modulus from the room temperature to the operating temperature of the cell was between 25 - 30%, and it is assumed that this value will remain constant at the high temperature, and can be incorporated into the SOFC models.

More pertinent to the lifetime of the cell are sub-critical crack growth (sccg) and creep, processes which were both shown to occur at 950°C. The creep may actually benefit the cell initially, by enabling any stress concentrations that are produced when the stack is put together to dissipate, but if it assumed that the lifetime of the fuel cell will be several years, then the electrolyte may actually deform beyond the dimensional tolerances of the cell (which at the time of this project are unknown) and impair operation. It is more difficult to predict the effect of sccg, since the SPT plot produced concerned the room temperature failure of bulk samples. However, the work performed did show that rate of sccg in FSZ is sensitive to stress - under low stresses the rate will be so slow that a propagating crack should be detected before catastrophic failure in the cell occurs, and creep, which may reduce the sccg rate, will also be able to occur; as the applied stress is increased failure from sccg becomes more likely. One way of reducing the operational costs of the fuel cell is to lower the temperature (and hence the electrolyte thickness); a drop in temperature of, e.g. 50°C, would reduce the creep rate four times, and so sccg would become even more important in determining the fuel cell lifetime. Another factor on the rate of sccg through the electrolyte could be the atmosphere conditions. Oxides are generally more susceptible to sccg in the presence of water, and the atmosphere at the anode in the cell will contain ~ 80% steam (Steele, 1996); this could increase the rate of sccg even more than found from the static fatigue tests performed in air in this project. Thus damage in the electrolyte from sccg could be very significant during fuel cell operation.

CHAPTER 7

FURTHER WORK

CHAPTER 7

FURTHER WORK

This section contains suggestions for additional work which could be performed, both in the short-term, as a continuation of this project, and in the longer-term, considering the behaviour of YSZ as an electrolyte in the SOFC.

7.1 Short-term Research

It needs to be ascertained whether the defects produced on tape-casting can be modified by a change in the drying rate, and also whether the warpage that was detected in all the thin-film samples was a result of the stamping and sintering stages of production, and could be reduced by modifications in these processes.

To complete the work on Young's modulus, the determination of E of the bulk material, by the dynamic technique, needs to be continued above 200°C, to confirm that the variation found in the tape-cast material is the response of 8 mol% YSZ and not a consequence of the tape-cast samples. In addition, the hysteresis behaviour detected by some authors should be investigated with tape-cast and bulk material, by repeated temperature runs on the same samples. It would be interesting to test samples of PSZ too, containing varying amounts of the cubic phase, to verify whether it is the behaviour of the constituent cubic phase which can cause the rapid drop in E of PSZ as the temperature is raised which has been reported in literature; if this is the case, the decrease in E should vary with the amount of cubic phase present.

The variation of strength with temperature needs to be monitored over a wider temperature range than was performed in this project, to examine the changeover in fast fracture mechanism more fully, and to establish how the processes are affected by the grain size and composition of different materials.

The fracture toughness value of the tape-cast material needs to be determined at elevated temperatures, which should be straightforward using the ISB technique. However, the effect of a variation in the indent crack length : sample thickness ratio has not been investigated, either in the literature or in this project; since indentation-based techniques

are probably the most practical method of measuring the fracture toughness of such thin samples it would be useful to study this, because it is unlikely that the ratio will be within the 1:10 limit specified in the literature.

7.2 Long-term Research

The above suggestions could be performed to complete some of the issues raised in this project. However, an understanding of the long-term, high temperature, failure processes of the electrolyte is essential when predicting the operating lifetime of the SOFC, and so the sccg and creep work need to be expanded, since these seem to be the processes most likely to influence the electrolyte behaviour once the cell is in operation. Both these effects will take longer to monitor.

Creep has been shown to occur at the operating temperature of the SOFC, and so the entire creep curve needs to be analysed around this temperature range, to gain a more complete understanding of the mechanisms involved than have been suggested by the preliminary work in this project. Since the samples are so thin a flexure test is probably the most practical way of performing the creep test, which means the stress and strain distributions will be more complicated than in, e.g. a tensile test, and need to be monitored by a suitable apparatus design and/or computer modelling.

The creep processes will operate in conjunction with the sccg process, and as mentioned in section (6.2) the rate at which each of these processes are able to occur will be affected by the operating conditions and environment (temperature, atmosphere, stress). Thus long-term tests, up to failure, on electrolyte material must be carried out under the actual operating conditions of the SOFC, so that the processes by which the electrolyte material will fail can be determined, and hence an accurate lifetime predicted.

Two topics which have not been mentioned in this project are thermal cycling, which could cause fatigue in the electrolyte, and the effect of the electrodes which the electrolyte must support and separate. Both these factors could further complicate the long-term high temperature behaviour, and this should be investigated.

APPENDIX

APPENDIX

The F-test

This statistical technique enables several sets of data (or treatments) to be compared together, in order to verify whether they can be considered as belonging to the same distribution, or whether there is a significant difference between them. It must be assumed that all the sets of data follow a normal distribution; the technique then assumes that there is no difference between the means of each set, and then calculates the probability that this is true.

The test statistic, F , must be calculated, from:

$$F = \frac{MST}{MSE}$$

where $MST = \text{mean square for treatments} = \frac{SST}{p - 1}$

$$SST = \text{sum of squares for treatments} = \frac{T_1^2}{n_1} + \frac{T_2^2}{n_2} + \dots + \frac{T_p^2}{n_p} - CM$$

$T_1, T_2, \dots = \text{treatment total}$

$n_1, n_2, \dots = \text{number of observations for each treatment}$

$$CM = \text{correction for mean} = \frac{(\text{total of all observations})^2}{\text{total number of observations}}$$

$$\text{MSE} = \text{mean square for error} = \frac{SSE}{n - p}$$

$$SSE = \text{sum of squares for error} = SS(\text{Total}) - SST$$

$$SS(\text{Total}) = \text{total sum of squares} = (\text{sum of squares of all observations}) - CM$$

$$n = \text{total number of observations}$$

$$p = \text{number of treatments}$$

If the final value for F is greater than F_R , the hypothesis that the sets are the same is rejected. F_R will vary with n and p , and can be looked up in tables. Usually a probability $\leq 5\%$ is taken as being statistically significant, and the sets considered different.

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LIST OF REFERENCES

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