ALUMINA/ZIRCONIA LAMINATED COMPOSITES

## SYNTHESIS AND MECHANICAL PROPERTIES

OF

# ELECTROPHORETICALLY DEPOSITED ALUMINA/ZIRCONIA

# LAMINATED COMPOSITES

By

## MICHAEL W. WHITEHEAD, B.Sc.(Eng.)

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in Partial Fulfilment of the Requirements

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AUTHOR: Michael W. Whitehead, B.Sc.(Eng.), Queen's University

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#### ABSTRACT

Al<sub>2</sub>O<sub>3</sub>/YPSZ laminates were fabricated by electrophoretic deposition (EPD) and pressureless sintering. Laminated composites with non-planar ("wavy") layers were produced by depositing powder from ethanol suspensions, onto a grid of Al<sub>2</sub>O<sub>3</sub> fibres. Laminates with thin (~3  $\mu$ m) YPSZ and thick (>10  $\mu$ m) Al<sub>2</sub>O<sub>3</sub> layers (12 vol % YPSZ) were produced. Deposition mass was a linear function of deposition time and current density. Al<sub>2</sub>O<sub>3</sub>-YPSZ interfaces were very strong and no delamination or crack deflection along the interface was observed. The flexural strength of the Al<sub>2</sub>O<sub>3</sub>/YPSZ laminates (tested at 25°C, 800°C and 1300°C) were slightly lower than monolithic Al<sub>2</sub>O<sub>3</sub>. This is attributed to crack-like defects which form during drying and to the deterioration of the strength of YPSZ at elevated temperatures. The fracture toughness of the Al<sub>2</sub>O<sub>3</sub>/YPSZ laminates were slightly higher than monolithic Al<sub>2</sub>O<sub>3</sub> over the temperature range tested (25°C - 1300°C). This is due to the stressinduced (t)->(m) phase transformation in the YPSZ layers at room temperature and to microplasticity in the YPSZ layers at 1300°C.

Room temperature crack trajectories were influenced by the residual thermal, and induced elastic stresses in the laminates. Cracks were deflected towards thin YPSZ layers because of the tensile induced elastic stresses in the thick  $Al_2O_3$  layers and the tensile thermal residual stresses in the thin YPSZ layers.

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# TABLE OF CONTENTS

ABST	RACI	<b>₹</b>	•	•	•	•	•		•	•	•	iii
ACKI	NOWL	EDGE	MENT	S	•	•	•	•	•	•	•	iv
TABL	LE OF	CONT	ENTS	•	•	•	•	•	•	•	•	v
LIST	OF FI	GURE	S	•	•	•	•	•	•	•	•	vii
LIST	OF TA	ABLES	•	•	•	•	•	•	•	•	•	xi
CHAI	PTER	1 - INT	RODU	JCTIO	N	•	•	•	•	•	•	1
CHAI	PTER	2 - LIT	ERAT	URE F	REVIE	W	•	•	•		•	5
	2.1 DEPO	COLL DSITIO	OIDA N	L PF	ROCES	SSING	ANI	D El	LECTI	ROPH	ORE	TIC 5
		2.1.1 ]	DLVO	THEC	RY	•	•	•••	•	•	•	б
		2.1.2 ]	ELECI	ROPH	IORET	TIC DE	POSIT	ION	•	•	•	<b>10</b> .
	2.2 C	ERAM	IC/CEI	RAMIO	C LAM	INATE	S	•	•	•	•	22
		2.2.1 0	CRACI	K DEF	LECTI	ON BY	( WEA	K INT	ERFA	CES	•	23
		2.2.2	CRACI	K PAT	HS IN	ELAST	TIC ST	RESS	FIELD	S	•	30
		2.2.3	Al <sub>2</sub> O <sub>3</sub> /Z	ZrO <sub>2</sub> L	AMINA	ATED (	COMP	OSITE	S	•	•	36
	2.3 M	ECHA	NICAI	L TEST	ING	•	•	•	•	•	•	38
		2.3.1 \$	STREN	IGTH	•	•	•	•	•	•	•	38
		2.3.2 ]	FRACT	FURE	TOUG	HNES	S	•	•	•	•	41

v

CHAPTER 3 - EXPERIMENTAL PROCEDURE	•	46
3.1 LAMINATE FABRICATION	•	46
3.2 CHARACTERIZATION OF ELECTROPHORETIC DEPOSI	TIO	N
• • • • • • • • • •	•	52
3.3 CHARACTERIZATION OF THE SINTERED MATERIALS	•	52
CHAPTER 4 - RESULTS AND DISCUSSION	•	56
4.1 STARTING MATERIALS AND PROCESSING	•	56
4.2 CHARACTERIZATION OF THE ELECTROPHON DEPOSITION PROCESS	ORI	ETIC 59
4.3 MICROSTRUCTURES OF EPD LAMINATES	•	62
4.4 INDENTATION CRACK PATHS	•	70
4.5 FLEXURAL STRENGTH	•	92
4.6 FRACTURE TOUGHNESS	•	101
CHAPTER 5 - CONCLUSIONS AND FUTURE WORK	•	108
REFERENCES	•	112
APPENDIX I		119

!

# LIST OF FIGURES

Figure 1.1 - A "wavy" laminate	straigh e	t crack	passing 1	through	1 a: (a) •	) plana	r and (	(b) noi	n-plan	ar or 3
Figure 2.1 - Sc spherical parti 1991)	hematic cles plo	of reproted as	ulsive, att s a func	ractive tion of	and to inter-	otal inte particle	eraction e dista	n energ nce (I	gies fo sraela	or two chvili 9
Figure 2.2 - Sci	hematic	of ζ-po	otential.	<b>`</b> •	•	•		•	•	11
<b>Figure 2.3</b> - Th (1940).	e proce	ess of de	posit for	mation	as preo.	dicted 1	by Ham	naker a	and Vo	erwey 13
Figure 2.4 - Tl (Hamaker and	ie conc Verwey	entratio 7 1940).	n in the .	suspens	sion du	iring el	lectropl	horetic	depo	sition 14
Figure 2.5 - Pot (Brown and Sa	ential e lt 1965)	nergy ve 	ersus inter	-partic	le dista	nce for	nickel	powde	r in et	hanol 17
Figure 2.6 - S deposition (Mi	chemati zuguchi	ic of po et al. 1	otential g 983).	radient	s whic	h are : ·	ideal fo	or elec	troph	oretic 20
Figure 2.7 - approaching a	Crack bimater	geomet ial inter	ry for a rface at 9	symm 0° (He	etrical and H	ly load utching	ded, se son 198	emi-infi 9).	inite	crack 25
<b>Figure 2.8</b> - Ra (G <sub>p</sub> ), for same 1989)	atio of e amoun	energy r t of cra	elease rat ck advan	te of de ce a as	flected a fund	crack ction o	(G <sub>d</sub> ) to f α (He	penetre and 1	ating: Hutch	crack inson 27
<b>Figure 2.9</b> - Ratio of energy release rate of deflected crack to maximum release rate of penetrating crack for wedge loaded cracks approaching an interface at angles of 30°, 45°, and 60° (He and Hutchinson 1989).										
Figure 2.10 - 0 interface at an	Crack g oblique	eometry angle	y for a w (He and )	edge la Hutchi	baded of some some som som 19	crack a 989).	ipproac	hing a	bima	terial 31

.

Figure 2.11 - Ratio of $K_{II}$ to $K_{I}$ for a wedge loaded straight crack approaching an interface at various angles (He and Hutchinson 1989)
Figure 2.12 - Conjectured trends for a crack approaching a bimaterial interface (Heand Hutchinson 1989)
Figure 2.13 - Normalized energy release rate for a straight crack approaching an interface at 60° for $\alpha = -0.5$ , 0.5 and 0, and $\beta = 0$ (He and Hutchinson 1989). 35
Figure 2.14 - Three and four-point bending geometries used to determine the flexuralstrength of ceramics <t< td=""></t<>
Figure 2.15 - Schematic of the volume of material subjected to the maximum tensile stress during three and four-point bending (Sung 1988)
Figure 2.16 - Geometry of bar used in four-point bending tests 42
Figure 2.17 - Geometry of a four-point-bend chevron-notched bar (Munz et al.1981)
Figure 3.1 - Schematic of apparatus used to fabricate monolithic samples and flat $Al_2O_3/YPSZ$ laminates.
Figure 3.2 - Actual EPD cell for producing monolithic $Al_2O_3$ and flat $Al_2O_3/YPSZ$ laminates.
Figure 3.3 - Schematic of apparatus used to fabricate non-planar laminates using electrophoretic deposition.
Figure 3.4 - Flow chart of the steps required to fabricate ceramic/ceramic laminates by electrophoretic deposition
Figure 4.1 - Particle size distributions for: (a) $Al_2O_3$ , and (b) YPSZ 57
Figure 4.2 - Supernatant liquid conductance versus number of washes for $Al_2O_3$ and YPSZ
Figure 4.3 - Deposit mass versus deposition time for $Al_2O_3$ and YPSZ using various current densities.
Figure 4.4 - Deposit thickness versus deposition time for Al <sub>2</sub> O <sub>3</sub> and YPSZ using

various currer	t densitie	s	•	•	•	•	•	•	•	61
Figure 4.5 - D	eposit ma	ss versus	total cl	harge (	ixt) fo	or Al <sub>2</sub> O	3 and Y	PSZ.	•	63
Figure 4.6 - laminate.	Low mag	nification	SEM	micro; ·	graph	ofano	on-plan	ar Al <sub>2</sub>	O₃/Y	PSZ 64
Figure 4.7 - In angle due to v	ndentation vavy morp	n crack pa bhology.	ath in a	ı wavy	lamina	te show	ving cha	anging	appr	oach 66
Figure 4.8 - M original ceram	icrograph uc fibres.	showing o	lefects :	at some	e positio	ons whic	ch were	occupi	ied b	y the 67
Figure <b>4.9</b> - S (~3 μm) YPS	EM micro Z layers (	graph sho (light).	owing tl •	hick (> ·	10 µm	) Al <sub>2</sub> O <sub>3</sub>	layers	(dark),	, and	thin 69
Figure 4.10 · perpendicular	Radial to the Al	$crack properties of _2O_3 and \Sigma$	oduced YPSZ la	by a ayers.	5 kg	Vickers	s inder	ntation	orie	ented 72
Figure 4.11 - YPSZ layer layer	SEM mic with the	rograph r radial cra	evealin ack pro	g a Vie eferenti	ckers in ally fo	ndentati orming ·	ion with in the ·	h its cc adjace	orner ent A	in a 41 <sub>2</sub> O <sub>3</sub> 75
Figure 4.12 - 2 and parallel to	10 kg Vick o the Al <sub>2</sub> C	ters inder $D_3$ and YF	ntation PSZ lay	with ra ers.	dial cra	acks ori	ented p	erpend	licula	ar to, 76
Figure 4.13 - ] the composite	Radial cra layers.	ck produo	ced by a	a 10 kg	Vickei	s inden	tation i	nclined	l at 3	10° to 78
Figure 4.14 -	Schematic	of strain	is induc	ed in o	constra	ined an	d unco	nstrain	ed la	iyers. 80
Figure 4.15 loading.	- Traject 	ories of	incline	d crao	ks un	der tei	nsile a	nd con	mpre	essive 84
Figure 4.16 - 3 and net total thin YPSZ lay	Schematic stress (N) ver and (b	of induc in the A ) crack le	ed elast l <sub>2</sub> O <sub>3</sub> an aving a	tic stres nd YPS 1 thin Y	sses (E Z layer PSZ la	), residu rs for: ( ayer.	al thei a) crac	rmal str k appro	resse oach	s (T) ing a 85
Figure 4.17 - illustrating or	Schemation of	tic of a of the poi	radial nt load	crack s (P) a	produc t the in	ed by dent.	a Vick	ers ind	lenta	ation, 89

t

Figure 4.18 - SEM micrograph of a radial crack intersecting a YPSZ layer at 30°. The YPSZ layer is situated far from the indentation. .
Figure 4.19 - Flexural strength versus testing temperature for monolithic $Al_2O_3$ and non-planar $Al_2O_3$ /YPSZ laminates
Figure 4.20 - SEM micrograph showing a machining defect that initiated failure of a monolithic $Al_2O_3$ sample
Figure 4.21 - SEM micrographs showing drying defects as the strength limitingflaws
Figure 4.22 - Low magnification micrograph of the cross-section of a typical $Al_2O_3/YPSZ$ laminate flexural strength bar.
Figure 4.23 - Fracture toughness versus testing temperature for monolithic $Al_2O_3$ and non-planar $Al_2O_3$ /YPSZ laminates.104
Figure 4.24 - A portion of a typical load-deflection curve obtained during a CNBtest105
Figure 5.1 - Fracture toughness ( $K_{IC}$ ) plotted against flexural strength ( $\sigma_f$ ) for non- planar Al <sub>2</sub> O <sub>3</sub> /YPSZ laminate, monolithic Al <sub>2</sub> O <sub>3</sub> (this investigation) and monolithic

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 YPSZ (Huang and Nicholson 1993).
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 <

# LIST OF TABLES

,

Table 4.1 - Summary of density data for non-planar $Al_2O_3$ /YPSZ laminates.	71
<b>Table 4.2</b> - Summary of crack length data for cracks parallel to and perpendiculatethe layers, and in monolithic $Al_2O_3$ using three indentation loads: 5 kg, 10 kg akg.	ılar to and 20 74
<b>Table 4.3</b> - Elastic properties (E and $\nu$ ), layer thicknesses (d) and CTE ( $\alpha$ ) usedestimation of residual thermal mismatch stresses<	in the 82
<b>Table 4.4</b> - Flexural strength data for monolithic $Al_2O_3$	93
Table 4.5 - Flexural strength data for non-planar Al <sub>2</sub> O <sub>3</sub> /YPSZ laminated comp   . <	osites. 94
<b>Table 4.6</b> - Fracture toughness data for monolithic $Al_2O_3$	102
Table 4.7 - Fracture toughness data for non-planar $Al_2O_3$ /YPSZ laminated comp<	osites. 103

, *\** 

4,

#### **CHAPTER 1 - INTRODUCTION**

There is considerable interest in producing materials for high temperature structural applications. Ceramics are the best materials available for use at temperatures >1200°C because of their good mechanical properties and excellent resistance to oxidation and corrosion. However, the inherent brittleness of ceramics limits their use in load bearing applications.

To date two main approaches are commonly used to produce ceramics with higher mechanical reliability and fracture toughness. The first attempts to control the critical flaw size via colloidal powder processing techniques. Colloidal powder processing, in contrast to traditional dry processing, produces a more homogeneous green body free of agglomerates, thus creating a more uniform final material with a smaller critical flaw size (Lange 1989). The second approach involves creation of a microstructure with a greater resistance to crack propagation (Evans 1990). The mechanisms of resistance involved include: crack deflection at weak bimaterial interfaces, crack deflection by elastic or thermal residual stress fields, transformation and microcrack toughening at the crack tip and crack bridging by fibres, whiskers etc. in the crack wake. The present work employs both techniques to produce tough laminated ceramic/ceramic composites. The aim of the study was to fabricate laminated composites of alumina  $(Al_2O_3)$ , and Yttria-Partially-Stabilized-Zirconia (YPSZ), via electrophoretic deposition (EPD), (a technique which uses colloidal processing) and pressureless sintering. The intention was to increase toughness, compared with monolithic  $Al_2O_3$ , via crack deflection at the bimaterial interfaces, and/or crack interaction with the thermal and elastic mismatch stresses generated in the layers. Laminates with non-planar or "wavy" layers were produced by depositing alternating layers of  $Al_2O_3$  and YPSZ, onto a grid of polycrystalline  $Al_2O_3$  fibres. A "wavy" microstructure will, in theory, vary the angle of incidence of a propagating crack with the bimaterial interfaces within the laminate. Figure 1.1 (a) and (b) compare the path of a crack passing through a planar and a "wavy" laminate. The incidence angle of the crack as it grows in the latter will result in increased probability of crack deflection, and/or crack-stress field interactions at the various angles of incidence encountered (He and Hutchinson 1989).

The electrophoretic deposition process was studied by tracking deposition mass and thickness as a function of deposit time and current density. The resulting laminates were characterized with respect to density, grain size and layer thickness. Mechanical properties were evaluated up to 1300°C using 4-point bend tests to measure flexural strength and chevron-notched-bars to measure fracture toughness. Room temperature crack paths created by Vickers indentations, were studied as a function of angle of approach with respect to the layers, using a scanning electron microscope.



(b)

Figure 1.1 - A straight crack passing through a: (a) planar and (b) non-planar or "wavy" laminate.

The thesis begins with a comprehensive literature review of colloidal processing, electrophoretic deposition, ceramic laminates and mechanical property testing. A description follows of the processing methods employed, the techniques used to characterize electrophoretic deposition and the mechanical properties of the laminates. Chapter IV presents the results and a discussion thereof. The final chapter summarizes the important conclusions and discusses possible areas for future work with regard to ceramic/ceramic laminates produced by electrophoretic deposition.

### **CHAPTER 2 - LITERATURE REVIEW**

#### 2.1 COLLOIDAL PROCESSING AND ELECTROPHORETIC DEPOSITION

The processing of ceramic powders into an engineering shape involves four basic steps: (1) powder production, (2) powder preparation for consolidation, (3) consolidation of the powder into a green body and (4) densification at an elevated temperature (Lange 1989). Each step has the possibility of introducing a heterogeneity that may limit the final ceramic's engineering properties (Sung 1988; Lange 1989). Many researchers have demonstrated that more reliable ceramics can be formed using colloidal processing techniques (Sung 1988; Lange 1989).

Electrophoretic Deposition is a ceramic forming technique which utilises the advantages of colloidal processing. The phenomena of electrophoretic deposition was discovered in 1809 when Ruess noticed that clay particles suspended in water were attracted to the positive electrode upon application of an electric field. Since then EPD has been used to fabricate  $\beta$ "-Al<sub>2</sub>O<sub>3</sub> tubes for sodium/sulphur batteries (Powers 1975; Heavens 1986),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> bodies 40 cm high (Andrews et al. 1969), magnesia (MgO) (Krishna Rao and Subbarao 1979), high-T<sub>o</sub> superconducting thick films (Maiti et al. 1989; Sarkar and Nicholson 1991) and yttria-stabilized-zirconia (YSZ) for use in oxide fuel cells (Ishihara et al. 1993). More recently Sarkar et al.

(1992) have fabricated ceramic/ceramic laminates and functionally gradiented materials (Sarkar et al. 1993) using EPD followed by pressureless sintering.

#### **2.1.1 DLVO THEORY**

Electrophoretic deposition requires that the suspension (or colloid) must be stable against coagulation. The electrically induced stability of colloids has been developed via double layer electrostatic repulsion models independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). This is known as the DLVO theory.

According to the DLVO theory, the interaction between colloidal particles involves the superposition of electrostatic repulsion and van der Waals attraction. Colloids are stable because particles are charged and hence repel each other, however electroneutrality demands that a particle and its immediate surroundings have no net charge. Thus, the surface charge is compensated by a countercharge and these combine to form the electric double layer (Lyklema 1968). The DLVO theory assumes that the distribution of charge in the outer component of the double layer is diffuse with a morphology predicted by the Poisson-Boltzman distribution (Lyklema 1968; Chapman 1913). For spherical double layers with low potential (<25 mV) the potential of the double layer is given by;

$$\psi(r) = \psi_o \left(\frac{a}{r}\right) e^{-\kappa(a-r)} \tag{6-1}$$

where  $\psi(\mathbf{r})$  is the potential at a distance r from the particle centre,  $\psi_o$  the potential

at the particle surface and a the particle radius (Lyklema 1968). If the double layer thickness is defined as the distance over which the potential drops to (1/e) of its initial value at the particle surface, then  $\kappa$  is equivalent to the reciprocal of the double layer thickness.  $\kappa$  controls the rate at which potential decays with distance from the particle surface and for a symmetrical electrolyte is defined as;

$$\kappa = \left(\frac{4\pi e^2 n z^2}{\epsilon k T}\right)^{\frac{1}{2}} \tag{7-1}$$

where  $\epsilon$  is the dielectric constant of the suspending medium, n the number of ions of charge z, k Boltzman's constant and T the absolute temperature (Lyklema 1968).

When two particles of like charge approach, their diffuse counter layers begin to overlap. The free energy of the double layers increases during their interaction (Verwey and Overbeek 1948) and work must be done to bring the particles closer. For low potentials and small values of  $\kappa a$  (ie. thick double layers) the DLVO theory predicts the repulsive energy between two spherical particles is;

$$V_R = \frac{\epsilon a^2 \psi_o^2}{R} e^{-\kappa H}$$
(7-2)

where H is the shortest distance between the two particle surfaces (H=R-2a if R is the distance between the particle centres and a is the particle radius) and  $\epsilon$  and  $\psi_o$ are given above (Lyklema 1968).

It has long been recognized that London-van der Waals attractive forces large enough to compete with double layer repulsion (Hamaker 1936) also exist between particles in colloidal suspensions. For two spherical particles of material 1 in !

medium 2, the London-van der Waals attractive energy over short distances is given by;

$$V_A = -\frac{A_{1(2)}}{12} \frac{a}{H}$$
(8-1)

where  $A_{1(2)}$  is the Hamaker constant for material 1 in medium 2, and a and H are as previously stated (Lyklema 1968).

The repulsive and attractive energies between two particles are scalars, thus can be combined to give the total interaction energy. Equations (7-2) and (8-1) show that  $V_A$  and  $V_R$  are dependent upon the inter-particle distance (H) in different ways. The London-van der Waals attractive forces fall off as the inverse of H whereas the repulsive forces decay exponentially with negative H. Figure 2.1 (Israelachvili 1991) is a schematic of the repulsive, attractive and total interaction energies plotted as a function of inter-particle distance. Van der Waals attraction dominates at small and large separations. Repulsion dominates at intermediate distances. These opposing forces give rise to an unsymmetrical repulsive maximum, V<sub>max</sub>. This "potential energy barrier" must be overcome if two approaching particles are to coagulate. The height of the barrier is determined by the double layer thickness  $(1/\kappa)$ , the Hamaker constant (A), and the particle radius (a). The critical  $V_{max}$  needed to confer complete stability on both particles is arbitrary and depends on the stability criterion Vold (1961) estimated that  $V_{max} > 10kT$  is necessary for a stable applied. suspension; Verwey and Overbeek (1948) estimated that  $V_{max} \sim 15$ kT will retard coagulation by a factor of  $10^5$ .





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## 2.1.2 ELECTROPHORETIC DEPOSITION

Electrophoretic deposition (EPD) is a combination of two processes: electrophoresis (the motion of charged particles in a suspension in a potential gradient) and deposition (the coagulation of particles into a dense mass at an electrode).

Many researchers have investigated the EPD process (Hamaker and Verwey 1940; Hill et al. 1947; Koelmans 1955; Brown and Salt 1965), however no generally accepted model describes the process. The DLVO theory provides a good starting point since electrophoresis requires the suspension be stable against coagulation. On application of a potential gradient, the particles in a suspension move towards an electrode. This is because some of the diffuse double layer around the particle is stripped away when the particles move, ie. the double layer now terminates at a plane of shear (Hunter 1988). The potential in the double layer no longer falls to zero and a residual potential, termed the  $\zeta$ -potential, exists (Figure 2.2). The intrinsic charge of the particles is no longer balanced and the particle and its double layer have an overall charge of the same sign as the particle. This charge repels particles of the same sign and causes particles to be attracted to the oppositely charged electrode. For deposition at the electrode, the particles must be brought sufficiently close together for the London-van der Waals forces of attraction to dominate. To accomplish this, the particles must overcome the "potential energy" barrier" responsible for stability (Figure 2.1).

The first attempt to explain the process of EPD was made by Hamaker and



Figure 2.2 - Schematic of  $\xi$ -potential.

Verwey (1940). They compared the formation of a deposit by electrophoresis to the formation of an adherent layer by sedimentation and assumed the two phenomena were identical. They neglected the electrical nature of the phenomenon and treated it as a purely mechanical problem. In this theory, the electric field moves the particles to the electrode and produces a force which presses the particles together on the surface of the electrode (like gravity in sedimentation). Thus Hamaker and Verwey assume the electric charge on the particles plays no role in EPD. They rationalized this approach on the observation that, left to stand long enough, a stable suspension will produce a dense layer on the bottom of a vessel. The force arising during electrophoretic deposition can be schematically represented by a straight line through the origin of the energy versus distance plot in Figure 2.1. The slope of the line increases with increasing pressure. This new force is added to the total interaction energy curve (ie. sum of attractive and repulsive energies), to create a new resultant energy curve. A set of resultant curves for increasing pressure is given in Figure 2.3. As the pressure increases the distance between the maximum, S, and the minimum, M, gradually reduces. At some point the difference between S and M will become so small that the particles will be pushed individually, by simple thermal agitation, from M, over S, into the energy minimum. When this occurs the particles are systematically deposited into a layer and form a homogeneous deposit.

Verwey and Overbeek proposed the concentration profile in Figure 2.4 during EPD. The region between A and B represents an already deposited layer, as indicated by a high constant concentration. Point B represents the surface of the



Figure 2.3 - The process of deposit formation as predicted by Hamaker and Verwey (1940).



Figure 2.4 - The concentration in the suspension during electrophoretic deposition (Hamaker and Verwey 1940).

deposit and the concentration drops corresponding to the transition from the deposit to the suspension. From B to C the concentration decreases; it is the surplus of particles in this region that causes the pressure needed to form the deposit. The suspension has its normal concentration between C and D. D to E represents a region which has been deprived of particles.

Many researchers (Hill et al. 1947; Koelmans 1955) observed a critical time  $t^*$ , for electrophoretic deposition, such that for  $t < t^*$  no adherent deposit forms. At this critical time practically the whole deposit becomes rigid within a few seconds (Koelmans 1955).

The theory presented by Hamaker and Verwey only considers the accumulation of particles at the depositing electrode. However, Koelmans (1955) pointed out that the electric field also causes a transport of ions which, combined with the electrode reactions, leads to an increase in the concentration of electrolyte near the depositing electrode. This in turn will decrease the stability of the suspension near the electrode. Koelmans analyzed whether this effect is sufficient to explain deposition via the flocculation of particles at the electrode. He estimated the electrolyte concentration at the electrode as a function of time and compared the concentration of electrolyte known to induce flocculation. In the calculations he considered the transport of ions to the electrode by migration, and from the electrode by diffusion.

He observed that the concentration of electrolyte built up by electrolysis was

of the same order of magnitude as the observed flocculation concentrations. He concluded that formation of the particles into a dense layer occurs by flocculation at the electrode.

Hill et al. (1947) expanded on the model proposed by Hamaker and Verwey and derived an equation to predict the critical time for deposition,  $t^*$ . They proposed that  $t^*$  is the time needed to create a layer thickness BC, (Figure 2.4) such that the force exerted by all the particles in this layer is sufficient to push the particles over the critical potential barrier. Their experiments confirmed the existence of a critical time, however yields were not zero for  $t < t^*$  as predicted by their model. This is because the interaction forces for the first layer of particles are not between two particles but between a particle and the depositing electrode. Critical times were between 10<sup>-3</sup> and 10 seconds, depending on the experimental conditions.

Brown and Salt (1965) approached the problem by comparing observed electrophoretic behaviour with the DLVO theory of colloid stability. They calculated  $V_R$  and  $V_A$ , using equations (7-2) and (8-1) respectively, for various powder/liquid combinations. These values were then used to obtain a curve for the total interaction energy ( $V_A + V_R$ ) as a function of the inter-particle distance. As an example, the potential energy/distance plot for nickel powder in ethanol is reproduced in Figure 2.5 (Brown and Salt 1965).

The maximum slope of the curve to the right of the peak represents the minimum force (F) required to overcome the repulsion between two particles. The field strength (E) required to overcome repulsion can be calculated by equating the



Figure 2.5 - Potential energy versus inter-particle distance for nickel powder in ethanol (Brown and Salt 1965).

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electrophoretic velocity with the Stokes' law velocity. This gives;

$$E = \frac{2F}{3\epsilon a\zeta} \tag{18-1}$$

where  $\epsilon$  is the dielectric constant of the suspending medium, a the particle radius and  $\zeta$  the zeta-potential (Brown and Salt 1965). The field strength (E) needed to overcome repulsion was calculated for many powder/liquid systems and compared with the experimental field needed to produce a deposit. The two field strengths differed by a factor of less than 5 when no electrolyte was present. This agreement was excellent considering the many assumptions involved in their calculations. However, in the presence of an electrolyte, the calculated field strengths were 40-1000 times greater than the observed values suggesting the electrolyte is playing a role other than simply altering the  $\zeta$ -potential (Brown and Salt 1965). This work suggests that with no electrolyte, the electric field moves the particles to the electrode and exerts sufficient force to overcome double layer repulsion.

Mizuguchi et al. (1983) considered the different potential gradients necessary for electrophoresis and deposition. According to Mizuguchi the suspending liquid must contain species that adsorb on the particles and act over relatively large distances thus providing stability. Therefore, the suspending medium must have a high dielectric constant. If there are not enough charge-carrying species in the solvent, the potential gradient will increase and may induce electronic charges on the particles. These charges operate over very small distances and do not combat coagulation. Furthermore, the gradient must remain relatively high (ie. the suspension must be very conductive) as it provides the force to move the particles.

Deposition has very different requirements of potential gradient. During deposition the particles must overcome their double layer repulsion so the Londonvan der Waals forces of attraction can dominate. This requires much larger potential gradients. Figure 2.6 illustrates the ideal potential gradient for electrophoretic deposition (Mizuguchi et al. 1983). The potential distribution must supply voltages at the electrode interfaces ( $V_{DA}$  and  $V_{DC}$ ) sufficient for deposition, whilst retaining the potential gradient in the bulk suspension ( $V_B$ ) necessary for electrophoresis. Mizuguchi et al. found that adding appropriate amounts of electrolyte created this distribution. If insufficient electrolyte is added, the deposition voltages are too small and no deposition will occur. Conversely, if too much electrolyte is added, the potential gradient in the solvent will be flat and no electrophoresis will occur (Mizuguchi et al. 1983). They reported a highly stable, non-aqueous suspension which enables deposition of many oxide, phosphor, and metallic powders.

Hamaker (1940) investigated the experimental aspects of EPD and formulated an expression for the yield (Y) with time, ie.

$$Y = \sigma \ c \, \iint \, \frac{dV}{dn} \, dS \, dt \tag{19-1}$$

where c is the concentration of the suspension,  $\sigma$  a constant which depends only on the chemical composition of the suspension, S the surface area, t time and dV/dn the electric field perpendicular to the surface, S (Hamaker 1940). If every particle partakes in the formation of a deposit,  $\sigma$  will be equal to the electrophoretic velocity,



Figure 2.6 - Schematic of potential gradients which are ideal for electrophoretic deposition (Mizuguchi et al. 1983).

otherwise it will be a fraction of this value (Hamaker 1940). Hamaker performed a range of experiments to confirm Equation (19-1) and found that deviations exist for low voltages, short times and low concentrations.

In the same paper, Hamaker also investigated the green density of the deposits. Densities >60 % were determined for  $Al_2O_3$  powder but those for MgO were as low as 36 %. Density decreased slightly with increasing applied voltage. When the voltage is high the layer forms at a greater velocity thus leading to an irregular structure (Hamaker 1940).

Krishna Rao and Subbarao (1979) investigated the electrophoretic deposition of magnesia. They found amyl alcohol was the best suspending media (compared with benzyl alcohol and dichloromethane) based on yield rate, suspension behaviour and deposit quality. They observed an abnormal increase in yield rate (not predicted by Equation 19-1) for suspension concentrations >20g/100cm<sup>3</sup>. They attributed this to rapidly moving particles dragging slower particles along thus increasing the yield rate. Relationships between yield, applied voltage, deposition time and electrode separation as predicted in Equation 19-1, were all verified.

Ishihara et al. (1993) investigated the EPD of zirconia for use in solid oxide fuel cells. They produced good quality green films of uniform thickness using acetone, acetylacetone and cyclohexanone as the suspending media. Stable suspensions were formed through additions of  $I_2$ . Linear relationships between deposit mass, applied voltage and deposition time were again confirmed.

Andrews et al. (1969) used EPD to manufacture thick, hollow alumina bodies

with a good surface finish. They found suspensions in ethanol with additions of dewaxed shellac as a binder produced the best deposits. Deposits 5 mm thick were formed in 15 minutes at a potential difference of 120 V and a current density of 0.3  $mA/cm^2$ . Green densities between 45 and 53 % were achieved depending on the deposition conditions. Alumina bodies 15 cm high were produced with an average standard deviation in thickness of 2.7 %.

Powers (1975; 1986a; 1986b) has produced many papers on the EPD of beta alumina ceramics. He observed that, when the suspension contains particles of different composition, they deposit in the same ratio as they are found in the suspension. High forming voltages resulted in the evolution of gases during deposition which introduced large pores into the deposit. He attributed the excellent sinterability of electrophoretic deposits to deagglomeration during particle charging.

#### 2.2 CERAMIC/CERAMIC LAMINATES

The reliability of structural ceramics depends upon their ability to resist catastrophic failure via the growth of a single crack originating at a pre-existing defect (flaw). The low reliability of monolithic ceramics can be improved by control of flaw size or by enhancing the resistance of the material to crack propagation. The first approach, as discussed in Section 2.1, involves reduction of the maximum flaw size using colloidal processing techniques. The second involves creation of a microstructure with greater resistance to crack propagation (Evans 1990). The mechanisms of increased crack resistance can be divided into three categories: 1. crack deflection, either at a weak bimaterial interface (He and Hutchinson 1989; Cook and Gordon 1964), or by suitably oriented residual and/or induced stress fields (Sarkar et al. 1994), 2. phase transformations (Porter et al. 1979) and microcracking (Ruhle et al. 1986) which take place in a "process zone" at the crack tips and 3. crack-wake bridging by whiskers, fibres, platelets and grains resulting in crack closing forces (Swanson et al. 1987). The present work utilizes colloidal processing techniques to reduce maximum flaw sizes and produces laminated  $Al_2O_3/YPSZ$ ceramic/ceramic composites with microstructures designed to promote crack deflection.

The stress-induced tetragonal-to-monoclinic phase transformation in the zirconia layers will to contribute to the laminate toughness at room temperature. However, as stated in the introduction, the main goal is to increase toughness through crack deflection so the extensive literature on toughening by the stress-induced phase transformation in zirconia is not reviewed. Crack wake bridging is not expected to contribute significantly to the toughness and will not be discussed.

## 2.2.1 CRACK DEFLECTION BY WEAK INTERFACES

Energy dissipation in brittle materials involves the creation of new surfaces. Thus ceramic/ceramic composites are designed to generate large amounts of interfacial area on crack propagation. This can be accomplished by adding a second phase in the form of whiskers, platelets, fibres or particles or by laminating two ceramics with or without the use of a discontinuous reinforcing phase. The deflection of a crack along a weak interface or the opening of a weak interface ahead of a propagating crack, is an important toughening mechanism in ceramic matrix composites (Evans 1990; Cook and Gordon 1964). Cracks can also be deflected by local elastic stress fields in composite materials due to differences in Coefficients of Thermal Expansion (CTE) and/or elastic properties (E and  $\nu$ ) (Binns 1962; Sarkar et al. 1994).

He and Hutchinson (1989) analyzed crack deflection at an interface between two isotropic, elastic materials. When a crack intercepts a bimaterial interface it can deflect along the interface or penetrate through the interface. He and Hutchinson analyzed the competition between these two paths by comparing the strain energy release rate for both processes.

They considered the case of a symmetrically loaded, semi-infinite crack approaching a bimaterial interface at 90° (Figure 2.7). The ratio of the energy release rate for crack deflection ( $G_d$ ) and crack penetration ( $G_n$ ) is given by;

$$\frac{G_d}{G_p} = \left[\frac{(1-\beta^2)}{1-\alpha}\right] \left[\frac{d^2 + e^2 + 2R_e(de)}{c^2}\right]$$
(24-1)

where  $\alpha$  and  $\beta$  are Dundurs parameters (Dundurs 1969), and c, d and e are dimensionless complex valued functions of  $\alpha$  and  $\beta$  (He and Hutchinson 1989). Dundurs parameters are non-dimensional combinations of the elastic properties of the two materials in the composite and are given by;


Figure 2.7 - Crack geometry for a symmetrically loaded, semi-infinite crack approaching a bimaterial interface at 90° (He and Hutchinson 1989).

$$\alpha = \frac{\mu_1(1-\nu_2)-\mu_2(1-\nu_1)}{\mu_1(1-\nu_2)+\mu_2(1-\nu_1)}$$
(26-1)

$$\beta = \frac{\mu_1(1-2\nu_2)-\mu_2(1-2\nu_1)}{\mu_1(1-2\nu_2)+\mu_2(1-2\nu_1)}$$
(26-2)

where  $\mu$  is the shear modulus,  $\nu$  the Poisson's ratio and the subscripts 1 and 2 refer to the arrangement shown in Figure 2.7 (Dundurs 1969).  $\alpha$  has been shown to be the more important of the two parameters (He and Hutchinson 1989) and most investigators consider  $\beta = 0$ . For example, in equation (24-1),  $\beta$  appears as  $\beta^2$  and since  $\beta < 1$ , its effect will be small.

When  $\mu_1 > \mu_2$ , the crack is approaching a stiffer material across an interface and  $\alpha > 0$ . When  $\mu_1 < \mu_2$ , the crack is approaching a more compliant material across the interface and  $\alpha < 0$ . He and Hutchinson used integral equation methods to determine c for the penetrating crack and d and e for the deflected crack. The ratio  $G_d/G_p$  for a crack approaching a bimaterial interface at 90°, is plotted in Figure 2.8 as a function of Dundurs  $\alpha$  parameter (He and Hutchinson 1989). For the singly deflected crack with -0.5 <  $\alpha$  < 0.25, the ratio  $G_d/G_p$  is ~1/4.  $\alpha$  = 0.25 corresponds to the plane strain tensile modulus of material-1 being 1.5 times that of material-2. In short, for crack deflection to occur, the toughness of the interface must be < 1/4 of the Mode I toughness of the material across the interface. The singly deflected crack generally controls the condition for deflection (as compared to the doubly deflected crack) since it has the higher ratio  $G_d/G_p$ . In more simplistic terms, the crack will deflect along the interface if;



Figure 2.8 - Ratio of energy release rate of deflected crack  $(G_d)$  to penetrating crack  $(G_p)$ , for same amount of crack advance a as a function of  $\alpha$  (He and Hutchinson 1989).

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$$\frac{G_{ic}}{G_c} < \frac{G_d}{G_p} \tag{28-1}$$

where  $G_{ic}$  is the toughness of the interface and  $G_c$  the Mode I toughness of the material across the interface (He and Hutchinson 1989).

He and Hutchinson also studied the effect of crack approach angle by considering wedge-loaded cracks approaching an interface at angles of 30°, 45° and 60°. Once again they compared the energy release rate for a deflected crack to the maximum release rate for a penetrating crack. The results of their analysis are shown in Figure 2.9 as a plot of  $G_d/G_p$  as a function of Dundurs  $\alpha$  parameter. The curve for the symmetrically loaded crack approaching the interface at 90° (Figure 2.7) is also reproduced. As anticipated, the competition between deflection and penetration becomes favourable to deflection as the crack approach angle is reduced. For an approach angle of 30° the ratio  $G_d/G_p$  is only slightly less than 1 over the range -0.25 <  $\alpha$  < 0.25. This suggests the crack will be deflected if the toughness of the interface is only slightly less than the Mode I toughness of the material across the interface.

If we intend to design an interface such that all cracks will be deflected, the result for cracks approaching at 90° will control the choice of interface toughness (He and Hutchinson 1989). This is because cracks oriented at this angle require minimum interfacial toughness to guarantee crack deflection.



Figure 2.9 - Ratio of energy release rate of deflected crack to maximum release rate of penetrating crack for wedge loaded cracks approaching an interface at angles of 30°, 45°, and 60° (He and Hutchinson 1989).

## 2.2.2 CRACK PATHS IN ELASTIC STRESS FIELDS

Cracks may also be deflected by suitably-oriented residual or induced stress fields. The former arise from differences of Coefficients of Thermal Expansion (CTE), the latter from differences in the elastic properties of the two materials in the composite.

He and Hutchinson (1989) analyzed the induced elastic mismatch stresses by considering the Mode II opening induced as a wedge loaded crack approaches an interface at an oblique angle (Figure 2.10). When the crack is far from the interface (ie.  $1/1_{\circ} << 1$ ), the crack tip suffers pure Mode I opening with;

$$K_I \to (\frac{2}{\pi})^{\frac{1}{2}} P l^{-\frac{1}{2}}$$
 (30-1)

where P is the wedge-opening-force per unit thickness and 1 the distance from the applied loads to the crack tip (He and Hutchinson 1989).

As the crack advances it begins to interact with the interface and some Mode II opening is induced. He and Hutchinson used integral equation techniques to determine the  $K_{II}/K_{I}$  ratio as a function of  $1/l_{o}$ , for three angles of approach (30°, 45° and 60°) and two materials combinations ( $\alpha = 0.5$  and  $\alpha = -0.5$ , with  $\beta = 0$ ). Their results are shown in Figure 2.11. When the crack approaches a more compliant material across the interface ( $\alpha = -0.5$ ),  $K_{II}$  becomes negative (Figure 2.11). This crack would turn towards the interface if it were free to follow the path defined by  $K_{II}=0$ , since the straight crack has  $K_{II}<0$ . Likewise, a crack approaching a stiffer material across the interface ( $\alpha = 0.5$ ) will tend to curve away from the interface as







Figure 2.11 - Ratio of  $K_{II}$  to  $K_I$  for a wedge loaded straight crack approaching an interface at various angles (He and Hutchinson 1989).

 $K_{II}$  becomes positive. These trends are shown schematically in Figure 2.12 (He and Hutchinson 1989). Erdogen and Arin (1975) drew similar conclusions.

A stress field may also be generated in composite materials during cooling from the fabrication temperature because of differences of CTE. Ceramic/ceramic composites are usually densified at temperatures >1300°C. During cooling to ~0.5  $T_m$  (~ 1200°C for the ceramics used in this investigation) the stress is dissipated by plastic deformation near the interfaces. However, upon further cooling to room temperature, no mechanism for stress relaxation exists and significant residual stresses can develop (Chen and Mecholsky 1993; Li and Bradt 1989). These stresses will be maximized near the interfaces and can cause cracks to form during cooling (Bhattacharya and Petrovic 1992). The induced elastic mismatch stresses and residual thermal mismatch stresses are both elastic and can be superimposed to create a net elastic stress field. It is the magnitude and orientation of this stress field that will influence the trajectory of a crack.

He and Hutchinson (1989) also looked at the variation of strain energy release rate as a crack approaches an interface at an oblique angle. Their results are shown in Figure 2.13 as a plot of the normalized energy release rate as a function of distance from the interface ( $M_0 = 1$  represents the interface). When  $\alpha = 0$ , the crack is in a monolithic material and the energy release rate remains constant as the crack propagates (Figure 2.13). When the crack is approaching a stiffer material across the interface ( $\alpha > 0$ ), the energy release rate falls to zero as the interface is approached (Figure 2.13). When  $\alpha < 0$ , the crack is approaching a more compliant



Figure 2.12 - Conjectured trends for a crack approaching a bimaterial interface (He and Hutchinson 1989).



Figure 2.13 - Normalized energy release rate for a straight crack approaching an interface at 60° for  $\alpha = -0.5$ , 0.5 and 0, and  $\beta = 0$  (He and Hutchinson 1989).

material across the interface and the energy release rate rises to infinity (Figure 2.13). This behaviour is well documented for cracks approaching interfaces at 90° (Lu and Erdogan 1983a; Lu and Erdogan 1983b; Hilton and Sih 1971; Cook and Erdogan 1972).

This behaviour is governed by the stress singularity exponent  $\lambda$ , which equals 0.5 in a monolithic material. For the semi-infinite crack approaching an interface at 90° (Figure 2.7), the stress intensity factor for the penetrating crack is given by;

$$K_I = c(\alpha, \beta) k_I a^{1/2 - \lambda}$$
(36-1)

where  $k_I$  is proportional to the applied load, c a dimensionless function of  $\alpha$  and  $\beta$ , and a is shown in Figure 2.7 (He and Hutchinson 1989). When  $\alpha > 0$ ,  $\lambda$  becomes < 0.5 and  $K_I$  tends to zero at the interface. Likewise, if  $\alpha < 0$ ,  $\lambda$  becomes > 0.5 and  $K_I$  tends to infinity at the interface (He and Hutchinson 1989).

## 2.2.3 Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> LAMINATED COMPOSITES

Laminated composites of  $Al_2O_3$  and various forms of  $ZrO_2$  have been fabricated using many techniques, each giving unique material properties. Tape casting combined with pressureless sintering (Boch et al. 1986; Chartiful et al. 1988) has been utilized to fabricate laminates of  $Al_2O_3$  and  $Al_2O_3+ZrO_2$  (up to 10 vol%  $ZrO_2$ ), with a minimum layer thickness of 150 µm. The laminates exhibited strengths of ~ 375 MPa, which was comparable to monolithic  $Al_2O_3$  produced by the same researchers. The laminates did however exhibit a higher fracture toughness (up to 5.65 MPa $\sqrt{m}$ ) than was measured for monolithic Al<sub>2</sub>O<sub>3</sub> (4.8 MPa $\sqrt{m}$ ). Lower strengths were observed when the difference in ZrO<sub>2</sub> content of the layers was large. This is due primarily to the development of cracks during processing.

Requena et al. (1989) produced laminates with alternating layers of  $Al_2O_3$  and  $Al_2O_3 + 4 \text{ vol}\% \text{ m-ZrO}_2$  using slip casting and pressureless sintering. Samples with >98 % density, well defined interfaces and a minimum layer thickness of ~ 100  $\mu$ m, were produced. Due to the nature of the slip casting process, the casting rate decreased with casting time. No mechanical properties were reported.

Marshall et al. (1991) used a colloidal processing technique to produce laminates with layers of Ce-ZrO<sub>2</sub> and either Al<sub>2</sub>O<sub>3</sub>, or a mixture of Al<sub>2</sub>O<sub>3</sub> and Ce-ZrO<sub>2</sub>. The technique consisted of centrifuging solutions containing suspended particles to form a layered green body, followed by drying and pressureless sintering. A minimum layer thicknesses of 10  $\mu$ m was produced, however their samples were quite porous. Their aim was to increase the room temperature fracture toughness of Ce-ZrO<sub>2</sub> by the introduction of a large scale microstructural unit in the form of Al<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> + Ce-ZrO<sub>2</sub> layers. The purpose of these Al<sub>2</sub>O<sub>3</sub>-based layers was to stop the formation of a long narrow transformation zone ahead of the crack tip in Ce-ZrO<sub>2</sub>, which has been shown to degrade the toughness of Ce-ZrO<sub>2</sub> (Marshall et al. 1991). The presence of Al<sub>2</sub>O<sub>3</sub>-containing layers lead to an increase of toughness and extensive R-curve behaviour at room temperature. Enhanced fracture toughness was observed for cracks running both parallel to and perpendicular to, the layers.

It is important to note that all work to date on  $Al_2O_3/ZrO_2$  laminates has

focused on characterizing the room temperature properties. The main intent of the investigators described in this section, was to take advantage of the stress induced  $(t) \rightarrow (m)$  phase transformation in the  $ZrO_2$  layers, to increase the laminate toughness. In contrast the present study concentrates on increasing toughness (through crack deflection) in the high temperature regime where ceramic materials must be used.

#### **2.3 MECHANICAL TESTING**

#### 2.3.1 STRENGTH

Fracture strength is an important mechanical property for design purposes. The tensile strength is defined as the maximum Mode I fracture stress under a uniform stress state. As a result of the difficulties associated with performing tensile tests on ceramics, the bend or flexural test is used to measure strength. In this test, the flexural strength is defined as the maximum outer fibre stress sustainable in a rectangular beam. Three and four-point-bend geometries can be used (Figure 2.14), however the four-point configuration is preferred as a larger volume of material is subjected to the maximum tensile stress (Figure 2.15). This results in a higher probability of stressing a critical flaw. The flexural strength of a rectangular beam loaded in four-point-bending is given by;

$$\sigma_f = \frac{3 P L}{4 b d^2} \tag{38-1}$$

where P is the load at fracture and b, d and L are illustrated in Figure 2.16 (ASTM C1211-92; ASTM C1161-90). This calculation assumes the material is homogeneous,





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isotropic and linear elastic with moduli of elasticity in tension and compression that are identical.

Ceramic flexural test specimens are very sensitive to edge and surface flaws (Hanney and Morrell 1982) and therefore extreme care must be exercised in their preparation. Testing standards have been developed for ambient (MIL-STD 1942(A) 1983; ASTM C1161-90) and elevated temperatures (ASTM C1211-92). These standards give rigorous requirements for specimen size, shape and surface finish, as well for fixture configuration, loading rate and number of samples needed to give reliable results.

## **2.3.2 FRACTURE TOUGHNESS**

Fracture toughness relates the fracture stress of a material with the critical flaw size and associated geometrical factors. The plane strain fracture toughness  $(K_{IC})$  is an important parameter for evaluating structural ceramics, however there is no standard testing method for determining  $K_{IC}$ .

A valid  $K_{IC}$  test measures the difficulty of initiating fracture in a sample containing a stress free, sharp crack (Bloyce 1993). A wide variety of techniques are used to determine  $K_{IC}$  including: double torsion (DT) (Freiman 1988), double cantilever beam (DCB) (Gillis and Gillman 1964), indentation strength-in-bending (ISB) (Chantikul et al. 1981), single-edge pre-cracked-beam (SEPB) (Nose and Fujii 1988) and the chevron-notched-bend-bar method (CNB) (Munz et al. 1980). The chevron-notched-bend-bar technique was adopted in this investigation. This





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test method has the major advantage in that it does not require the induction of a pre-crack.  $K_{IC}$  is calculated directly from the maximum load with no prior knowledge of the initial crack length (Barker 1977). Although many different chevron-notch specimens exist (Newman 1984), the bend-bar specimen is best suited for elevated temperatures and was used in the present study. The geometry of the four-point-bend chevron-notched bar is shown in Figure 2.17 (Munz et al. 1981). A chevron-shaped notch is cut into one side of the sample and, upon loading, a crack propagates from the tip of the chevron. The crack width, b, continuously increases from zero at the chevron apex, to B, for a crack of length  $a_1$ . The geometry of the chevron-notched bar requires that an increasing load is needed to maintain crack extension. This can result in stable crack growth.

Munz et al. (1981) obtained a relationship between the maximum load ( $P_{max}$ ), and  $K_{IC}$  by considering the available and the necessary energy for crack propagation. The solution involved the introduction of a compliance function ( $Y^*$ ) such that  $Y^*$ is minimized ( $Y^*_m$ ) when P is maximized, and;

$$K_{IC} = \frac{P_{\max}}{B\sqrt{W}} Y_m^*$$
(43-1)

where B and W are the sample width and height respectively (Munz et al. 1981). The compliance function  $(Y^*)$  was derived using a straight-through-crack assumption (Munz et al. 1981), or the slice model of Bluhm (1975). The minimum for  $Y^*$  is obtained by curve fitting with;







$$Y_{m}^{*} = (3.08 + 5.00\alpha_{o} + 8.33\alpha_{o}^{2})(\frac{S_{1} - S_{2}}{W})(1 + 0.007\frac{S_{1}S_{2}}{W^{2}})^{\frac{1}{2}}(\frac{\alpha_{1} - \alpha_{o}}{1 - \alpha_{o}}) \qquad (45-1)$$

where all variables are as specified in Figure 2.17 (Munz et al. 1980).

Stable crack growth must precede final failure to ensure that Equation (43-1) is valid. This appears as a non-linear region on the load-displacement curve between the initial elastic region and final failure (Munz 1983). The influence of notch geometry on  $K_{IC}$  has been extensively studied (Munz et al. 1981; Salem and Shannon 1987). It is generally agreed that, in the range  $\alpha_0 = 0.07$  to 0.37 and  $\alpha_1 = 0.85$  to 1.0 the measured value of  $K_{IC}$  is independent of the chevron geometry.

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#### **CHAPTER 3 - EXPERIMENTAL PROCEDURE**

## **3.1 LAMINATE FABRICATION**

Commercially available  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (AKP-50, Sumitomo, Tokyo) and 3.0 mol % Y<sub>2</sub>O<sub>3</sub> partially-stabilized-zirconia (YPSZ) (TZ-3Y, Tosoh, Tokyo) were the starting powders used in this study. The particle size distributions were measured by an optical transmission method (CAPA-700 Horiba particle size analyzer, SSCAN, Richmond Hill, Ontario) based on the principle of sedimentation.

The powders were washed using a centrifuge to remove any adsorbed ions which lead to instability and irreproducible suspensions. The powder was repeatedly centrifuged in distilled H<sub>2</sub>O until the conductivity of the suspender equalled that of distilled H<sub>2</sub>O. The washed powders were then dried at 120°C for 24 hours. Slurries consisting of 100 grams of ceramic powder, 200 ml of ethyl alcohol (EtOH) and 250 grams of 5 mm diameter zirconia balls were prepared in 500 ml PE bottles. EtOH was chosen as the suspending liquid because it has a relatively high dielectric constant ( $\epsilon = 24$ ), low cost and is safe. Water would be the ideal suspending medium based on its dielectric constant ( $\epsilon = 80$ ) and cost, but electrolysis occurs at low voltages, resulting in pin holes in the deposit. The slurries were vibromilled for 20 hours, the zirconia balls removed and sufficient EtOH added to produce 5 vol. % solid suspensions. The as-produced suspensions were highly unstable, ie. they flocculated very quickly if left undisturbed. The suspensions had a pH > 8 and the particles moved to the cathode in a dc field giving a very wet deposit that fell off the electrode upon removal of the suspension. The  $\zeta$ -potential versus pH curves for Al<sub>2</sub>O<sub>3</sub> and YPSZ in EtOH (Sarkar et al. 1994) indicate stable suspensions (ie. high  $\zeta$ -potential) are formed for pH < 5. HCl:EtOH (1:25) was used to reduce the pH and form stable suspensions. Based on deposit mass and quality, the optimum pH range for the EPD of Al<sub>2</sub>O<sub>3</sub> and YPSZ is between 3 and 3.5, corresponding to a  $\zeta$ -potential of ~ 35 mV (Sarkar et al. 1994) for both powders. At this pH ~ 60 % dense, uniform deposits formed on the cathode.

Monolithic  $Al_2O_3$  and flat  $Al_2O_3$ /YPSZ laminated samples were deposited on a cathode (depositing electrode) of graphite paper (3 cm x 3 cm) glued to a teflon support base. The anode (counter electrode) was platinum foil 2 cm distant from the cathode. A constant current (0 - 100 mA) dc power source (Keithley 237 High Voltage Source Measure Unit) was used for deposition and current densities between 0.5 mA/cm<sup>2</sup> and 2.0 mA/cm<sup>2</sup> were employed. Laminated composites for indentation crack path experiments were fabricated by sequentially depositing alternating layers of  $Al_2O_3$  and YPSZ of desired thickness. Suspensions were continually mixed between depositions with a magnetic stirrer. Monolithic  $Al_2O_3$  samples were made by continually depositing from an alumina suspension until the desired thickness was obtained. It required ~ 3 hours to deposit a 200-layer flat laminate 3 cm x 3 cm, ~4 mm thick. Figure 3.1 is a schematic of the apparatus used to fabricate monolithic



Figure 3.1 - Schematic of apparatus used to fabricate monolithic samples and flat  $Al_2O_3$ /YPSZ laminates.

 $Al_2O_3$  and flat  $Al_2O_3/YPSZ$  laminates by EPD. The cell used for electrophoretic deposition is shown in Figure 3.2.

Non-planar Al<sub>2</sub>O<sub>4</sub>/YPSZ laminates for electron microscopy and indentation crack path experiments were fabricated using a grid of polycrystalline Al<sub>2</sub>O<sub>3</sub> fibres (ALMAX, Mitsui,  $\sim 10 \ \mu m$  diameter) as the depositing electrode. The fibres were received in a tow which was treated at 700°C for 2 hours in flowing gas to remove its polymeric sizing. Individual, 10 µm diameter, fibres were then sputter-coated (SPI-Module Sputter Coater) with  $\sim 15$  nm of Au to make them conducting and rows of fibres were glued onto acetate sheet frames with an inter-fibre spacing of  $\sim 0.5$  mm. The frames were then glued together to form a grid of conducting fibres with 0.5 mm spacing. The anode was two platinum foils on either side of the fibre grid. The electrodes were 2 cm apart. A schematic of EPD using a grid of fibres as the depositing electrode is shown in Figure 3.3. Alternating layers of Al<sub>2</sub>O<sub>3</sub> and YPSZ were deposited onto the fibres using current densities between  $1 \text{ mA/cm}^2$  and 3 mA/cm<sup>2</sup>. Non-planar samples for mechanical testing ( $\sigma_f$  and  $K_{IC}$ ) were prepared using a single row of approximately 20 conducting fibres (~0.5 mm spacing) as the depositing electrode. Samples 3 cm x 2 cm x 5 mm thick with more then 300 total layers were deposited in  $\sim$  3 hours.

The samples were placed in a plastic dish after deposition and covered with plastic wrap to control the rate of drying. It was observed that samples dried slowly in this manner cracked less than samples dried quickly in air. The deposits were allowed to dry for 24 to 48 hours, depending on the size of the sample. Dry



Figure 3.2 - Actual EPD cell used in this investigation to produce monolithic  $Al_2O_3$  and flat  $Al_2O_3/YPSZ$  laminates.



Figure 3.3 - Schematic of apparatus used to fabricate non-planar laminates using electrophoretic deposition.

specimens were densified by pressureless sintering (1700S-E, CM Furnace, Inc., Bloomfield, NJ, USA) in air at 1550°C for 6 hours with heating and cooling rates of 300°C per hour. Densities were determined using Archimedes method in water. A flow chart of the fabrication steps for producing ceramic/ceramic laminates by electrophoretic deposition is shown in Figure 3.4.

## **3.2 CHARACTERIZATION OF ELECTROPHORETIC DEPOSITION**

The rate of deposition was studied by tracking the deposit mass as a function of time and current density. A deposit was laid onto a single alumina fibre 10  $\mu$ m in diameter and 3 cm long. The anode was platinum foil and the electrode separation was 2 cm. The Al<sub>2</sub>O<sub>3</sub> and YPSZ suspensions contained 26.2 and 40.3 grams of powder respectively, in 250 ml of EtOH (2.5 vol % solids) at pH = 3.3. Three current densities: 0.06 mA/mm<sup>2</sup>, 0.11 mA/mm<sup>2</sup> and 0.23 mA/mm<sup>2</sup> were employed for deposition times up to 200 seconds. The deposit mass was measured on a balance accurate to 5 decimal positions (Mettler AE 240). The mass of the fibre (< 2.0x10<sup>-5</sup> g) was ignored in the calculations. The mass of powder deposited (< 0.25 grams) was less than 0.01% of the total powder in the suspension. The theoretical densities of Al<sub>2</sub>O<sub>3</sub> and YPSZ were used to calculate the deposit thicknesses, based on the mass data and fibre geometry.

# **3.3 CHARACTERIZATION OF THE SINTERED MATERIALS**

Flexural strength was measured using the four-point flexure method (ASTM



Figure 3.4 - Flow chart of the steps required to fabricate ceramic/ceramic laminates by electrophoretic deposition.

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C1161-90; ASTM C1211-92). Tests bars of nominal dimension 2.0 mm x 1.5 mm x 25 mm were cut from the sintered samples. The non-planar laminates were cut such that the layer of fibres used as the depositing electrode was located in the center of the test bar. The shortest "wavelength" attainable was such that, over the cross section of a flexural bar (1.5 mm x 2.0 mm), the layers were essentially planar. This artifact is discussed in more detail in Chapter 4. The tensile and side surfaces of the bars were polished to 1  $\mu$ m on a diamond wheel. As it is well known that grinding YPSZ induces surface compressive stresses (Virkar et al. 1987), the bars were annealed at 1275°C for 10 hours.

The samples were loaded in a very stiff,  $(0.5 \ \mu m/N)$  (Huang and Nicholson 1993) screw driven machine (Wykeham Farrance Ltd., model no. 10053, England). Crosshead rates between 0.2 - 0.5 mm/min were employed. The inner and outer loading-spans were 10 and 20 mm, respectively. Samples were tested at 800°C and 1300°C using a furnace controlled to  $\pm 2^{\circ}$ C. An equilibration time of 15 minutes was employed. All samples tested at high temperatures failed in < 30 seconds. Four bars were tested at each temperature.

Fracture toughness was determined using the chevron-notched-bend-bar (CNB) method (Munz et al. 1980). Bars of nominal dimension, 3 mm x 4 mm x 25 mm were prepared and a 0.2 mm wide chevron notch was introduced into the centre of the bar. The geometry of all notches was such that  $a_0/W = 0.04$  to 0.27, and  $a_1/W = 0.8$  to 1.0, where  $a_0$  = the initial crack length,  $a_1$  = the crack length on the side surface and W = the specimen height (Figure 2.17). Samples were annealed at

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1275°C for 10 hours to remove residual stress due to machining. A crosshead speed of 5  $\mu$ m/min was used for the room temperature tests. High temperature testing was performed at 800°C and 1300°C using crosshead speeds between 50 and 100  $\mu$ m/minute. All samples tested at the elevated temperatures failed in less than 1 minute. The notch geometry (a<sub>o</sub>/W, a<sub>1</sub>/W) was determined after the sample was tested using an optical microscope. The fracture toughness was calculated using the slice model proposed by Munz et al. (1980), and the maximum load from the loaddisplacement plot.

Vickers indentations at room temperature were used to investigate how cracks interacted with the layers and interfaces. Samples > 2 mm thick were cut from bulk materials, polished to 1  $\mu$ m and annealed at 1275°C for 10 hours to remove grinding stresses. Indentations were made using loads between 5 kg and 20 kg. The radial cracks, emanating from the corners of the Vickers impression were analyzed using a scanning electron microscope. Cracks lengths were measured using an optical microscope.

SEM specimens were cut, ground flat and polished to  $0.3 \ \mu m \ (Al_2O_3 \ suspended in H_2O)$  on a cloth covered wheel. Samples were thermally etched for 10 hours at 1275°C and coated with 15 nm of Au to make them conducting. Electron microscopy was performed using an ISI-DS 130, Dual Stage SEM.

## **CHAPTER 4 - RESULTS AND DISCUSSION**

### 4.1 STARTING MATERIALS AND PROCESSING

The particle size distributions of the  $Al_2O_3$  and YPSZ powders, as determined by an optical transmission method, are shown in Figures 4.1 (a) and (b) respectively. The  $Al_2O_3$  has a bimodal distribution with an average size of 0.23 µm for particles, and ~0.9 µm for agglomerates of particles. The YPSZ powder is similarly distributed but the average sizes are 0.20 µm for the particles and ~0.8 µm for agglomerates of particles.

The powders were washed in distilled water using a centrifugal technique, prior to forming the suspensions. Figure 4.2 is a plot of the supernatant liquid conductance (HP 4192A LF Impedance Analyzer) versus number of washes for both powders. After 3 washes the conductance of the supernatant from Al<sub>2</sub>O<sub>3</sub> was  $\sim 3 \mu$ S, ie. the value for distilled water, indicating all the impurity ions adsorbed on the surface of the particles had been removed. The conductance of the YPSZ supernatant was still >10  $\mu$ S after 12 washes, ie. significant impurity ions still remained on the particles. Unwashed YPSZ powder did not form a stable suspension and deposits thereof had a much higher tendency to crack during drying.



Figure 4.1 - Particle size distributions for: (a)  $Al_2O_3$  and (b) YPSZ.



Figure 4.2 - Supernatant liquid conductance versus number of washes for  $Al_2O_3$  and YPSZ.

# 4.2 CHARACTERIZATION OF THE ELECTROPHORETIC DEPOSITION PROCESS

Figure 4.3 is a plot of deposit mass versus deposition time for  $Al_2O_3$  and YPSZ. The relationship is linear as predicted by the Hamaker equation (Hamaker 1940). The deposit mass increases linearly with increasing current density, however gas evolution was observed at the cathode at very high current densities. This resulted in pin-holes in the deposits. The deposit mass for  $Al_2O_3$ , at a given time and current density is always higher than that of YPSZ. Many ions were adsorbed on the surface of the YPSZ powder when it was introduced into the EtOH (Figure 4.2). Once in the EtOH, many of the adsorbed ions leave the YPSZ particles, to exist as free ions in the suspension. During EPD these ions decrease the potential gradient in the cell thus decreasing the deposition rate.

Figure 4.4 is the data from Figure 4.3 plotted as calculated deposit thickness versus deposition time. The theoretical deposit thicknesses were calculated using measured densities ( $Al_2O_3 = 3.94$  g/cm<sup>3</sup> and YPSZ = 6.10 g/cm<sup>3</sup>) and the fibre electrode dimensions. The relationship is not linear due to the cylindrical nature of the depositing electrode; the surface area to be covered increases with deposition time. This factor is important if laminates with constant layer thickness are desired.

The linear relationship between deposit thickness and deposition time is realized when the depositing electrode is flat as the surface area to be covered remains constant during deposition. Design incorporating this type of data allows accurate synthesis of composites with precise layer thickness.



Figure 4.3 - Deposit mass versus deposition time for  $Al_2O_3$  and YPSZ using various current densities.


Figure 4.4 - Deposit thickness versus deposition time for  $Al_2O_3$  and YPSZ using various current densities.

Figure 4.5 is a plot of the mass data as a function of the total charge (current x deposition time). All the data falls on two straight lines. The higher deposition rate of the  $Al_2O_3$  powder is again clear. This graph suggests the total charge controls the amount of deposited material. Therefore, constant layer thicknesses can be achieved by simply controlling the total charge during deposition.

## **4.3 MICROSTRUCTURE OF EPD LAMINATES**

Figure 4.6 is a low magnification SEM micrograph of a non-planar  $Al_2O_3$ /YPSZ laminate. The 20 large circular dark regions (~ 250  $\mu$ m in diameter) are the first  $Al_2O_3$  layers deposited onto the Au-coated  $Al_2O_3$  fibres. The centres of these regions were occupied by the twenty 10  $\mu$ m diameter Al<sub>2</sub>O<sub>3</sub> fibres that formed the depositing electrode for this sample. The starting Al<sub>2</sub>O<sub>3</sub> fibres are no longer distinguishable due to their polycrystalline nature. A thick first layer is necessary to avoid cracking during further processing. Thin initial layers of Al<sub>2</sub>O<sub>3</sub> dried very quickly and cracked as the electrode form was moved to the YPSZ suspension for the first time. The first layer cracked as it dried and contracted around the rigid Al<sub>2</sub>O<sub>3</sub> fibres. Cracking occurred both parallel to and perpendicular to, the fibre axis. In many cases the cracked deposit flaked off the  $Al_2O_3$  fibres. Initial layers thicker than  $\sim 100 \ \mu m$  did not have time to dry before the first YPSZ layer was deposited and thus they survived. Alternating layers of  $Al_2O_3$  (dark) and YPSZ (light) surround the  $Al_2O_3$  cores. All regions between the fibres were filled during deposition and the material is >99 % dense.

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Figure 4.5 - Deposit mass versus total charge (i x t) for  $Al_2O_3$  and YPSZ.

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Figure 4.6 - Low magnification SEM micrograph of a non-planar  $Al_2O_3/YPSZ$  laminate.

The technique of depositing onto a grid of ceramic fibres created a "wavy" microstructure, ie. the interfaces take many different orientations. Figure 4.7 shows a crack produced by a Vickers indentation that has passed through the laminated structure. As the crack moved from left to right its orientation with respect to the layers changed from  $\sim 70^{\circ}$  to  $<35^{\circ}$ . A straight crack proceeding through a planar laminate always intersects the layers at the same angle. The varied approach angle made possible in these laminates is beneficial as it has been shown that crack deflection at a weak bimaterial interface is more likely for oblique angles-of-approach (He and Hutchinson 1989). The scale of the microstructure controls the distance the crack must travel to sample a range of interfacial orientations. The "wavy" structure of the present laminates is quite coarse; a crack must travel >100  $\mu$ m to significantly change its orientation with respect to the intercepted bimaterial interfaces. The scale of the structure achievable using this technique is controlled by two factors:

1. The inter-fibre spacing in the electrode grid.

2. The thickness of the first layer deposited.

The first factor is controlled by the operator's ability to arrange the fibres into a grid by hand. The smallest inter-fibre spacing presently achieved was  $\sim 0.5$  mm. Even if smaller inter-fibre spacings were possible the cracking problem associated with the first layer deposited, would have to be solved for a finer microstructure to result.

Figure 4.8 is a higher magnification micrograph of the same laminate. It



Figure 4.7 - Indentation crack path in a wavy laminate showing changing approach angle due to wavy morphology.



Figure 4.8 - Micrograph showing defects at some positions occupied by the original  $Al_2O_3$  fibres.

reveals a few defects (marked by the arrows) at positions occupied by the original ceramic fibres. These void-like defects occurred at  $\sim$ 50% of such positions and are thought to form during drying of the material (these defects result from the shrinkage stresses which develop during drying). These stresses will be largest at the fibre surface, and cracking will begin thereat. The defects ranged from <10 µm to 100 µm in diameter.

Figure 4.9 is a high magnification micrograph showing thin YPSZ layers,  $\sim$  3 µm (light), and > 10 µm Al<sub>2</sub>O<sub>3</sub> layers (dark). Note the layers appear almost planar at this magnification. The Al<sub>2</sub>O<sub>3</sub> and YPSZ layers had average grain diameters of 2.1 µm and 0.56 µm respectively, using the linear intercept method. The interfaces between the two materials are completely dense and perfect on a micron scale.

This micrograph demonstrates EPD can be used to fabricate perfect laminates with very thin layers (< 3  $\mu$ m). Layer thickness represents the distance the crack must travel before intersecting an interface. Slip casting, tape casting and centrifugal casting can only achieve minimum layer thicknesses of 100  $\mu$ m (Requena et al. 1989), 150  $\mu$ m (Boch et al. 1986) and 10  $\mu$ m (Marshall et al. 1991) respectively.

The Archimedes method was used to determine the density of both sintered monolithic  $Al_2O_3$ , and laminated samples. The  $Al_2O_3$  had an average density of 3.94 g/cm<sup>3</sup> (alumina density of 3.96 g/cm<sup>3</sup>). Assuming that the laminated samples are theoretically dense, the density measurements were used to determine the volume



Figure 4.9 - SEM micrograph showing thick (> 10  $\mu$ m) Al<sub>2</sub>O<sub>3</sub> layers (dark), and thin (~3  $\mu$ m) YPSZ layers (light).

percent of YPSZ in the laminates. The density data is summarized in Table 4.1 for the nine flexural strength bars which were tested. The mean density of the laminates was 4.22 g/cm<sup>3</sup> which corresponds to a YPSZ volume fraction of 0.12 ( $\rho$ Al<sub>2</sub>O<sub>3</sub> = 3.96 g/cm<sup>3</sup> and YPSZ = 6.10 g/cm<sup>3</sup>). The standard deviation over the 9 samples was 0.02, indicating the samples have nearly constant composition.

## **4.4 INDENTATION CRACK PATHS**

Figure 4.10 is an SEM micrograph showing a radial crack from a 5 kg loadinduced Vickers indentation oriented perpendicular to the Al<sub>2</sub>O<sub>3</sub>/YPSZ interfaces. The crack proceeds straight through all the layers with no crack deflection. This behaviour was observed for all cracks which intersected the layers at an angle greater than 60°. Using typical values of  $\mu$  and  $\nu$ , for Al<sub>2</sub>O<sub>3</sub> and YPSZ, Dundurs  $\alpha$ parameter (Equation 26-1) was calculated as 0.28 for a crack approaching the stiffer Al<sub>2</sub>O<sub>3</sub> across the interface and -0.28 when approaching the more compliant YPSZ. The ratio G<sub>d</sub>/G<sub>p</sub> is ~0.25 for these values of  $\alpha$  and a 90° approach angle (Figure 2.8). Thus if crack deflection is to be realized, the toughness of the interface must be <1/4 of the Mode I toughness of the material across the interface. This condition was not met in the present composites as no interface deflection was observed for cracks approaching at 90°.

The lengths of radial cracks (c, where 2c is the distance between crack tips on opposite sides of an indentation) oriented perpendicular to the layers were measured and compared to those of cracks running parallel to the layers and to crack lengths

sample #	density(g/cm <sup>3</sup> )	vol % YPSZ	vol % Al <sub>2</sub> O <sub>3</sub>
1	4.29	0.15	0.85
2	4.15	0.09	0.91
3	4.19	0.11	0.89
4	4.29	0.15	0.85
5	4.21	0.12	0.88
6	4.16	0.09	0.91
7	4.19	0.11	0.89
8	4.29	0.15	0.85
9	4.22	0.12	0.88

Table 4.1 - Summary of density data for non-planar  $Al_2O_3/YPSZ$  laminates.



Figure 4.10 - Radial crack produced by a 5 kg Vickers indentation oriented perpendicular to the  $Al_2O_3$  and YPSZ layers.

in monolithic  $Al_2O_3$  (Table 4.2). Three indentation loads were used in this investigation: 5 kg, 10 kg and 20kg. The length of a radial crack emanating from a Vickers indentation gives an estimate of  $K_{IC}$  (Anstis et al. 1981) to within ~40%. However, a number of conditions must be realized including that the material is isotropic and homogeneous. These two conditions are not met in the  $Al_2O_3/YPSZ$  laminate in this investigation and it was decided not to estimate  $K_{IC}$  from the crack length date here reported. The crack lengths do however, still indicate the materials resistance to crack propagation.

The laminate data was obtained from a planar  $Al_2O_3/YPSZ$  laminate with uniform layer thicknesses of 40 µm and 4 µm, (0.10 vol % YPSZ) for the  $Al_2O_3$  and YPSZ layers respectively. The data lists the mean value and standard deviation for >15 cracks in each material and each indentation load.

The mean lengths of the cracks, oriented parallel to the interfaces and randomly oriented in the monolithic  $Al_2O_3$  were equal (within the experimental error of the test) for all three indentation loads. This result is not surprising as the radial cracks directed parallel to the interfaces travelled almost exclusively in the thick  $Al_2O_3$  layers. Even when the corner of the Vickers indentation was placed within a YPSZ layer, or on a bimaterial interface, the radial crack preferentially formed in the adjacent  $Al_2O_3$  layer (Figure 4.11).

The cracks oriented perpendicular to the  $Al_2O_3$  and YPSZ layers were significantly shorter than those running parallel to the layers, or in the monolithic  $Al_2O_3$ . Figure 4.12 is an SEM micrograph revealing two cracks emanating from two

	Al <sub>2</sub> O <sub>3</sub>	perpendicular	parallel
5 kg	119±10 µm	102±11 μm	116±11 µm
10 kg	196±16 µm	140±12 μm	221±40 μm
20 kg	309±26 µm	240±25 μm	330±57 μm

 $Al_2O_3$  - monolithic  $Al_2O_3$ , random directions with respect to the sample

perpendicular - cracks perpendicular to Al<sub>2</sub>O<sub>3</sub> and YPSZ layers

parallel - cracks parallel to  $Al_2O_3$  and YPSZ layers

Table 4.2 - Summary of crack length data for cracks running parallel to and perpendicular to the layers, and in monolithic  $Al_2O_3$  using three indentation loads: 5 kg, 10 kg and 20 kg.



Figure 4.11 - SEM micrograph revealing a Vickers indentation with its corner in a YPSZ layer with the radial crack preferentially forming in the adjacent  $Al_2O_3$  layer.



Figure 4.12 - 10 kg Vickers indentation with radial cracks oriented perpendicular to and parallel to the  $Al_2O_3$  and YPSZ layers.

corners of the same indent. The crack directed perpendicular to the layers is much shorter than the crack which travelled parallel to the layers. Shorter cracks perpendicular to the layers should be anticipated as these cracks must pass through the much tougher YPSZ layers. YPSZ has a room temperature fracture toughness of 4.3 MPa $\sqrt{m}$  (Huang and Nicholson 1993), compared to 2.9 MPa $\sqrt{m}$  (determined in this investigation) for monolithic Al<sub>2</sub>O<sub>3</sub> (both of these K<sub>IC</sub> values were determined using the CNB test at the same laboratory).

Residual thermal stresses will also influence the length of radial cracks produced by a Vickers indentation (Marshall and Lawn 1977). Residual thermal stresses will be present in the  $Al_2O_3$  and YPSZ layers due to differences of CTE. These stresses will be oriented parallel to the interfaces and will be tensile in the YPSZ layers and compressive in the  $Al_2O_3$  layers. However, these stresses will form such that the net force summed over the sample will be zero. Thus, if a radial crack traverses many layers the net force exerted on the crack by the residual stress fields will be ~ zero. Each radial crack measured in this investigation spanned between ~5 and 11 total layers.

Figure 4.13 is a micrograph of a radial crack inclined at  $\sim 30^{\circ}$  to the interfaces. No crack deflection is observed along a bimaterial interface, but the crack does deviate from its preferred path (dotted lines) on crossing each YPSZ layer. The crack travelled from the lower right corner to the upper left corner of the micrograph. When the crack is  $\sim 5 \mu m$  from a YPSZ layer it turns into and penetrates the YPSZ layer at an angle >80°. In the YPSZ the crack remains



Figure 4.13 - Radial crack produced by a 10 kg Vickers indentation inclined at 30° to the composites layers.

~ perpendicular to the layer, however it reassumes its original path upon entering the next  $Al_2O_3$  layer. This process is repeated for every YPSZ layer. This phenomena was observed for incident angles between 15° and 60°. The observed "bending" of the crack paths near the YPSZ layers is the direct result of residual thermal mismatch and induced elastic mismatch stresses in the material.

The laminates were densified at 1550°C and during cooling from this temperature residual stresses develop as a result of the difference in CTE of the Al<sub>2</sub>O<sub>3</sub> and YPSZ (Al<sub>2</sub>O<sub>3</sub>: 8.3 x 10<sup>-6</sup>/°C and YPSZ: 10.0 x 10<sup>-6</sup>/°C).

The magnitude of the thermal stresses induced during cooling can be estimated using a force balance (Virkar et al. 1987). Assuming the laminate is stress free at 1550°C, and that stresses induced upon cooling to 1200°C (~0.5 T<sub>m</sub> for YPSZ) are relived by plastic deformation then, if the layers were unconstrained (ie. free to shrink) the difference of length between the Al<sub>2</sub>O<sub>3</sub> and YPSZ layers would be  $\Delta \epsilon_o$  (Figure 4.14). However, the layers are constrained and upon cooling they strain such that the forces balance. If  $\sigma_A$  is the stress in the Al<sub>2</sub>O<sub>3</sub> layers and  $\sigma_Z$  the stress in the YPSZ layers, it can be shown (see Appendix I) that;

$$\sigma_{A} = \left(\frac{E_{A}}{1-\nu_{A}}\right) \frac{\left(\frac{-\Delta \varepsilon_{o} E_{Z} \Sigma d_{Z}}{1-\nu_{Z}}\right)}{\left(\frac{E_{A} \Sigma d_{A}}{1-\nu_{A}} + \frac{E_{Z} \Sigma d_{Z}}{1-\nu_{Z}}\right)}$$
(79-1)





$$\sigma_{Z} = \left(\frac{E_{Z}}{1-\nu_{Z}}\right) \frac{\left(\frac{\Delta \varepsilon_{o} E_{A} \Sigma d_{A}}{1-\nu_{A}}\right)}{\left(\frac{E_{A} \Sigma d_{A}}{1-\nu_{A}} + \frac{E_{Z} \Sigma d_{Z}}{1-\nu_{Z}}\right)}$$
(81-1)

where  $d_A$  and  $d_Z$ ,  $E_A$  and  $E_Z$ , and  $\nu_A$  and  $\nu_Z$  are the thicknesses, Young's moduli and Poisson's ratios for the Al<sub>2</sub>O<sub>3</sub> and YPSZ layers respectively (Virkar et al. 1987). Substituting the elastic properties and layer thicknesses given in Table 4.3, into equations 79-1 and 81-1, ( $\Delta T = 1200^{\circ}$ C) one obtains a compressive stress of 58.6 MPa (acting parallel to the layers) in the Al<sub>2</sub>O<sub>3</sub> layers, and a tensile stress of 586 MPa in the YPSZ layers. This calculation assumes that no stress gradients exist across the layers. This assumption probably holds for the thin YPSZ layers, but steep stress gradients will exist in the thicker Al<sub>2</sub>O<sub>3</sub> layers very close to the interface. These residual thermal stresses will survive in the laminate at room temperature.

Stress fields will also develop in a composite material due to differences of the elastic properties (E and  $\nu$ ) of the two materials forming the composite (see Chapter 2.2.2). An elastic stress field exists in front of a crack tip, the magnitude of the stress at a given point near the crack tip being proportional to the stress intensity factor (K) from;

$$\sigma_{ij} = \frac{K}{\sqrt{2\pi r}} f_{ij}(\theta) + \dots \qquad (81-2)$$

where r and  $\theta$  are the cylindrical polar coordinates with respect to the crack tip (Ewalds and Wanhill 1984). As the crack tip approaches an Al<sub>2</sub>O<sub>3</sub>/YPSZ interface,

	Al <sub>2</sub> O <sub>3</sub>	YPSZ	
E (GPa)	380	210	
ν	0.26	0.31	
α (/°C)	8.3 x 10 <sup>-6</sup>	10 x 10 <sup>-6</sup>	
d (µm)	40	4	

Table 4.3 - Elastic properties (E and  $\nu$ ), layer thicknesses (d) and CTE ( $\alpha$ ) used in estimation of the residual thermal stresses.

both materials will feel an equal stress. However, since  $E_A > E_Z$  the materials will respond differently to this applied stress. Since the two materials are constrained by very strong interfaces, they will elastically strain by the same amount. This results in a tensile stress acting parallel to the interface in the  $Al_2O_3$  layer and a compressive stress in the YPSZ layer. These induced elastic mismatch stresses are opposite in sign to the residual thermal stresses previously described. Quantitative estimation of the stresses induced at the tip of a propagating radial crack in a laminated composite is not trivial and was not attempted in this investigation.

The thermal and elastic mismatch stresses described here are elastic and operate in the same direction (parallel to the layers) and can be superimposed to give a net stress which will influence the crack path.

The preferred trajectory for a crack approaching a net residual stress field can be predicted from fracture mechanics (He and Hutchinson 1989, Atkinson 1979, Ewing et al. 1976), but it is not easy to decide which criteria is the most precise (the criteria used by He and Hutchinson was summarized in 2.2.2). A simple interpretation considers the growth of centrally located cracks in a monolithic material under compressive and tensile loading (Sarkar et al. 1994). Figure 4.15 illustrates the well known result that a crack inclined to an applied tensile stress will tend align itself perpendicular to the applied stress. Likewise, a crack inclined to an applied compressive stress will tend to align itself parallel to the applied stress.

The observed crack trajectories can now be explained by considering the induced elastic and residual thermal stresses in the laminates. Figure 4.16 (a)





Figure 4.16 - Schematic of the induced elastic stresses (E), residual thermal stresses (T) and net total stress (N) in the  $Al_2O_3$  and YPSZ layers for: (a) crack approaching a thin YPSZ layer and (b) crack leaving a thin YPSZ layer.

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is a schematic of a crack approaching a thin YPSZ layer illustrating the direction, and predicted magnitude of the thermal (T), elastic (E) and net total (N) stresses present in the  $Al_2O_3$  and YPSZ layers. As the crack approaches the more compliant YPSZ across the first interface, the analysis performed by He and Hutchinson (1989) predicts that the stress intensity factor will tend to infinity (Figure 2.13). Therefore, the magnitude of the elastic stress field at the crack tip will also tend to infinity since its magnitude is directly proportional to the stress intensity factor (Equation 81-2). In turn, the large elastic stress field at the crack tip induces large tensile and compressive elastic mismatch stresses in the  $Al_2O_3$  and YPSZ layers, respectively. The magnitude of these stresses will increase as the crack tip approaches the interface. The thermal stress in the  $Al_2O_3$  layer is compressive in nature but small in magnitude (58.6 MPa) and, given the size of the layer, its magnitude is expected to diminish quickly away from the interface.

When the crack tip is  $-5 \,\mu m$  from the YPSZ layer the crack turns into the approaching interface (Figure 4.13). This suggests that the induced tensile stress in the Al<sub>2</sub>O<sub>3</sub> layer is much larger than the residual compressive stress resulting in a net tensile stress in this layer. Once the crack penetrates the interface the elastic stress is locally relaxed and the stress intensity factor will return to a value controlled by the indentation.

The penetrated crack is now almost normal to the interfaces with its tip just inside the YPSZ layer (Figure 4.16 (b)). This layer is under a residual tensile thermal stress estimated at 586 MPa thus the crack will traverse the YPSZ orthogonal to the next interface. As it approaches the stiffer  $Al_2O_3$  the analysis by He and Hutchinson (1989) predicts the stress intensity factor will decrease to zero (Figure 2.13). However, as the crack does not terminate, K must remain above the critical stress intensity factor for YPSZ. Since the crack is almost normal to the layers, a very large compressive stress field would be necessary to deflect it parallel to the layers (away from the interface). No such deflection is evident in Figure 4.13. Therefore, either the net stress in the thin YPSZ layer is tensile (tensile thermal mismatch stress > compressive elastic mismatch stress) thus keeping the crack perpendicular to the layers, or the net stress is compressive (tensile thermal mismatch stress < compressive elastic mismatch stress) but of magnitude insufficient to deflect the crack.

Once the crack penetrates the interface and enters the next  $Al_2O_3$  layer, the elastic mismatch stresses are relieved. After penetrating the interface the crack turns to reassume its original orientation with respect to the indentation (~30° to the  $Al_2O_3$  and YPSZ layers). The next YPSZ layer is 40 µm away and does not effect the crack trajectory. The process repeats as the crack tip approaches the next YPSZ layer.

The radial cracks produced by a Vickers indentation are driven by point loads at the indent (Figure 4.17). For this loading arrangement the stress intensity factor at the crack tip is given by;

$$K = \frac{P}{\sqrt{\pi a}} \tag{88-1}$$





where P is the applied point load per unit thickness and a the crack length (Ewalds and Wanhill 1984). Therefore, the stress intensity factor decreases as the crack extends until it reaches a subcritical value and the crack arrests. The magnitude of the elastic stress field at the crack tip also decreases as the crack extends since it is directly proportional to the stress intensity factor (K) (Equation 81-2). The elastic stress field is responsible for the elastic mismatch stresses in the  $Al_2O_3$  and YPSZ layers. Therefore, as the crack extends, the magnitude of the induced elastic mismatch stresses will decrease. Hence, the influence of the magnitude of the induced elastic mismatch stresses can be studied by observing how a crack interacts with the layers as it propagates.

The three YPSZ layers in Figure 4.13 were all situated very close to a 20 kg indentation and they all illustrate the same effect, however slight variations were observed when the layers were far from the indentation, or the indentation load was very small. Figure 4.18 is an SEM micrograph of a radial crack intersecting a YPSZ layer far from the indentation. The crack approaches the layer at 30° and is not deflected until it reaches the interface. (The crack in Figure 4.13 turned while it was still in the Al<sub>2</sub>O<sub>3</sub> layers.) As previously mentioned, this layer is far from the indent and the stress intensity factor of the radial crack will have considerably decreased. Therefore, the induced elastic mismatch stress will be much smaller than the case illustrated in Figure 4.13. The tensile stress induced in the Al<sub>2</sub>O<sub>3</sub> is unable to deflect the crack into the approaching interface. However, when the crack penetrates the interface and responds to the tensile thermal stress in the YPSZ layer, it turns



**Figure 4.18** - SEM micrograph of a radial crack intersecting a YPSZ layer at 30°. The YPSZ layer is situated far from the indentation.

towards the next interface (and the tensile thermal stress). The crack travels at an angle of 50° with respect to the layers whilst within the YPSZ layer so the change in orientation is less severe than in Figure 4.13. Subsequently as the crack leaves the YPSZ layer it reassumes its original orientation with respect to the indentation. The elastic mismatch stresses appear to have no effect on the crack path in this situation.

As previously mentioned cracks oriented almost parallel to the layers (< 15°) prefer to travel in the thicker Al<sub>2</sub>O<sub>3</sub> layers. No crack deflection was observed when cracks oriented at very low angles did cross an interface. From Figure 2.9 one can see that for an approach angle of < 30°, the ratio of the energy release rate for the deflected crack to that for the penetrating crack ( $G_d/G_p$ ), for  $\alpha = \pm 0.28$ , is only slightly less than unity. Therefore, if the toughness of the interface is only slightly lower than the toughness of the material across the interface crack deflection will occur. The absence of crack deflection in the present laminates is further evidence of the high toughness of the interfaces.

## **4.5 FLEXURAL STRENGTH**

The flexural strength of the composites and monolithic  $Al_2O_3$  was measured and the results are summarized in Tables 4.4 and 4.5. The data is also presented in Figure 4.19 as a plot of flexural strength versus testing temperature. The room temperature flexural strength of monolithic  $Al_2O_3$ , (556±11 MPa) compares favourably with values reported in the literature (Boch et al. 1986; Chen and Mecholsky 1993). As expected the strength of monolithic  $Al_2O_3$  decreased with

T (°C)	b (mm)	d (mm)	P (N)	$\sigma_{\rm f}$ (MPa)
25	1.492	2.059	232.2	550.9
25	1.473	1.842	182.1	546.5
25	1.473	1.846	191.1	571.1
25	1.520	2.051	236.6	555.0
Avg.				556±11
800	1.492	1.854	164.2	480.3
800	1.483	1.893	166.4	469.7
800	2.026	1.514	143.2	462.5
800	1.496	1.984	190.6	485.5
Avg.				475±10
1300	2.027	1.501	111.2	365.2
1300	1.487	2.060	127.7	303.6
1300	1.493	2.067	147.5	346.9
1300	2.033	1.513	122.8	395.8
Avg.				353±39

Table 4.4 - Flexural strength data for monolithic  $Al_2O_3$ .

T (°C)	b (mm)	d (mm)	P (N)	$\sigma_{\rm f}$ (MPa)
25	1.466	1.917	193.3	538.2
25	1.505	1.996	222.9	557.2
25	1.507	1.914	206.4	560.8
25	1.497	2.010	229.5	569.2
Avg.				556±13
800	1.493	1.990	169.2	429.3
800	1.506	1.994	183.0	458.4
800	1.488	1.914	186.2	512.4
800	2.036	1.464	122.6	421.6
Avg.				455±41
1300	1.500	2.017	102.3	251.5
1300	1.486	2.031	111.6	273.1
1300	1.498	1.991	125.7	317.5
1300	1.511	1.907	118.2	322.7
Avg.				291±35

Table 4.5 - Flexural strength data for the non-planar  $Al_2O_3/YPSZ$  laminated composites.

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Figure 4.19 - Flexural strength versus testing temperature for monolithic  $Al_2O_3$  and non-planar  $Al_2O_3/YPSZ$  laminates.

increasing temperature to  $475\pm10$  MPa at  $800^{\circ}$ C and  $353\pm39$  MPa at  $1300^{\circ}$ C. Fractography was used to determine the failure initiation points. Figure 4.20 shows the machining damage that led to failure of an Al<sub>2</sub>O<sub>3</sub> sample. Machining damage was found to be the major source of failure in monolithic Al<sub>2</sub>O<sub>3</sub> samples. The satisfactory strength values of monolithic Al<sub>2</sub>O<sub>3</sub> indicate that electrophoretic deposition and pressureless sintering is an effective technique for producing ceramic materials with small critical flaws.

No delamination or evidence of crack deflection was observed during the testing of laminated samples at any temperature. All load-deflection graphs were linear to failure with no evidence of the graceful failure exhibited by weak interfaced SiC/C laminated composites (Clegg et al. 1990). This further substantiates that the laminate interfaces are dense and strong. The non-planar  $Al_2O_3$  laminate had a room temperature strength of  $556\pm13$  MPa,identical to that of monolithic  $Al_2O_3$ . Monolithic YPSZ has a room temperature fracture strength of  $\sim$ 935 MPa (Huang and Nicholson 1993) and additions of YPSZ to  $Al_2O_3$  should increase the composite strength. Fractography of failed samples however, revealed crack-like defects near the tensile surface of many laminated samples (Figure 4.21). These defects probably originate during drying as the deposit contracts around the rigid fibres.

The larger void-like defects described in Chapter 4.3 were also observed on many laminate fracture surfaces. These defects were associated with the original  $Al_2O_3$  fibres and were aligned along the neutral axis of the flexural bars. Figure 4.22 is a low magnification micrograph of a cross section of a typical flexural strength bar.


Figure 4.20 - SEM micrograph showing a machining defect that initiated failure of a monolithic  $Al_2O_3$  sample.

Figure 4.21 - SEM micrographs showing drying defects as the strength limiting flaws.



The original fibres are in the centre of the bar and therefore any defects associated with these positions will not suffer significant stress during a bend test. It is also important to note that, over the cross-section of the bar (2 mm x 1.5 mm), the layers are almost planar. Therefore, these "wavy" laminates should behave in a similar fashion to the planar  $Al_2O_3/YPSZ$  laminates produced by Sarkar et al. (1994). The room temperature strength for the planar laminates is 488 MPa, ie. 12 % lower than the laminates tested in this investigation. Laminate fracture at room temperature was intra-granular in the YPSZ layers and mixed inter-/intra-granular in the  $Al_2O_3$  layers.

At 800°C and 1300°C the strength of the non-planar laminate decreased to  $455\pm41$  MPa, and  $291\pm35$  MPa respectively. These values are 4 and 18 % lower than monolithic Al<sub>2</sub>O<sub>3</sub> at the same temperatures. The lower strengths can be attributed to processing defects in the laminate and the significant deterioration in the strength of YPSZ at elevated temperatures (Claussen 1985, Wakai 1991). At these temperatures monolithic ZrO<sub>2</sub> has a flexural strength of 176 MPa (800°C) and 113 MPa (1300°C) (Huang and Nicholson 1993). The planar Al<sub>2</sub>O<sub>3</sub>/YPSZ laminates fabricated by Sarkar et al. (1994) had a strength of 317 MPa at 1300°C, ie. 9 % higher than the present laminates. At elevated temperatures fracture was intergranular in the YPSZ layers and mixed inter-/intra-granular in the Al<sub>2</sub>O<sub>3</sub> layers.

Based on the flexural strength data here presented, the "wavy"  $Al_2O_3/YPSZ$  laminates fabricated in this investigation have no advantage over "flat"  $Al_2O_3/YPSZ$  laminates. This is because the interfaces of both laminates are very strong and



Figure 4.22 - Low magnification micrograph of the cross-section of a typical non-planar  $Al_2O_3/YPSZ$  laminate flexural strength bar.

therefore they behave like monolithic materials in bending. The "wavy" laminates might exhibit different flexural properties in a composite with weak interfaces.

## **4.5 FRACTURE TOUGHNESS**

The fracture toughness data is summarized in Tables 4.6 and 4.7 for monolithic  $Al_2O_3$  and the non-planar  $Al_2O_3$ /YPSZ laminates respectively. This data is also illustrated in Figure 4.23 as a plot of fracture toughness versus testing temperature. All tests reported exhibited stable crack growth indicated by a "rolling over" of the load displacement plot before final failure. Figure 4.24 is a portion of a typical load-displacement curve obtained during a CNB test illustrating this effect. The room temperature fracture toughness determined for monolithic  $Al_2O_3$ (2.91±0.49 MPa $\sqrt{m}$ ) is in excellent agreement with data obtained by other researchers, using different testing geometries (Chantikul et al. 1981; Bloyce 1993) This suggests the laminate data is reliable. The fracture toughness of the monolithic  $Al_2O_3$  decreased to 2.80±0.39 MPa $\sqrt{m}$ , and 2.38±0.32 MPa $\sqrt{m}$  at 800°C, and 1300°C respectively.

At room temperature the fracture toughness of the Al<sub>2</sub>O<sub>3</sub>/YPSZ laminate was  $4.57\pm0.73$  MPa $\sqrt{m}$ . This represents an increase of 57% compared to monolithic Al<sub>2</sub>O<sub>3</sub> (2.91 MPa $\sqrt{m}$ ), and is about 9% higher than the K<sub>IC</sub> reported for monolithic YPSZ (~4.2 MPa $\sqrt{m}$ ) using the CNB test (Huang and Nicholson 1993). This value (4.57±0.73 MPa $\sqrt{m}$ ) is 49% higher than the value calculated using the rule of mixtures (3.07 MPa $\sqrt{m}$ ).

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T (°C)	W (mm)	B (mm)	α,	α <sub>1</sub>	P (N)	K <sub>IC</sub> (MPa√m)
25	4.211	2.953	0.08	0.91	89.9	3.63
25	4.097	2.892	0.1	0.89 <sup>.</sup>	63.6	2.76
25	4.089	2.946	0.15	0.91	52.5	2.51
25	3.659	2.886	0.21	0.97	39.6	2.75
Avg.						2.91±0.49
800	3.665	2.871	0.18	0.95	34.9	2.23
800	3.671	2.735	0.22	0.96	39.1	2.88
800	3.642	2.896	0.11	0.92	55.9	3.07
800	3.557	2.872	0.14	0.82	57.9	3.03
Avg.		_				2.80±0.39
1300	3.676	2.907	0.09	0.94	36.3	1.92
1300	3.702	2.879	0.27	0.93	34.5	2.48
1300	3.621	2.947	0.16	0.95	43.0	2.66
1300	3.702	2.870	0.06	0.98	45.8	2.44
Avg.						2.38±0.32

Table 4.6 - Fracture toughness data for monolithic  $Al_2O_3$ .

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T (°C)	W (mm)	B (mm)	α <sub>o</sub>	α <sub>1</sub>	P (N)	K <sub>IC</sub> (MPa√m)
25	3.990	3.008	0.09	0.93	117.9	5.30
25	3.564	2.769	0.16	0.91	55.2	3.60
25	3.498	2.690	0.14	0.89	77.5	4.92
25	4.009	3.021	0.09	0.91	103.0	4.46
Avg.						4.57±0.73
800	3.975	2.989	0.10	0.89	72.3	3.17
800	3.204	3.048	0.16	0.85	44.4	2.82
800	3.576	3.086	0.10	0.92	68.7	3.57
800	4.020	3.078	0.13	0.89	88.5	3.88
Avg.						3.36±0.46
1300	3.789	2.934	0.15	0.89	65.6	3.46
1300	3.970	2.977	0.11	0.87	67.2	2.92
1300	4.034	2.991	0.14	0.90	62.1	2.93
1300	4.045	2.954	0.04	0.90	79.2	3.15
Avg.						3.12±0.25

Table 4.7 - Fracture toughness data for non-planar  $Al_2O_3/YPSZ$  laminated composites.

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Figure 4.23 - Fracture toughness versus testing temperature for monolithic  $Al_2O_3$  and non-planar  $Al_2O_3$ /YPSZ laminates.

104



Figure 4.24 - A portion of a typical load-displacement curve obtained during a CNB test.

105

The increase in fracture toughness at room temperature (as compared to monolithic  $Al_2O_3$ ) is probably due to the stress induced (t) $\rightarrow$ (m) transformation in the YPSZ layers.  $Al_2O_3$ -YPSZ dispersed composites exhibit similar increases in fracture toughness. Lange (1982) reported an increase in  $K_{IC}$  of 27% for  $Al_2O_3 + 12$  vol % dispersed YPSZ (2 mol %  $Y_2O_3$ ) as compared to monolithic  $Al_2O_3$ .

It is interesting to note that assembly of the YPSZ into layers (laminate) as opposed to a homogeneous distribution (dispersed) increases the  $Al_2O_3$  toughness by 57% as compared to 27%. Assuming the zirconia transformation contribution is identical in each case, the difference (+ 30%) must be due to the action of inhomogeneously distributed stress fields experienced by a crack propagating through the laminate. The existence of such fields is evidenced by the regular disturbance of a crack propagating through the layers (Figure 4.13) and the relative length of cracks parallel to and perpendicular to the layers (Figure 4.12).

At 800°C the fracture toughness of the laminates decreased to  $3.36\pm0.46$  MPa $\sqrt{m}$ . This value is still 20% higher than monolithic Al<sub>2</sub>O<sub>3</sub> at 800°C ( $2.80\pm0.39$  MPa $\sqrt{m}$ ) and 68% higher than YPSZ at 800°C ( $2.0\pm0.3$  MPa $\sqrt{m}$ ) (Huang and Nicholson 1993). In the ZrO<sub>2</sub> ( $3.0 \mod \% Y_2O_3$ ) used in this investigation the tetragonal phase is stable above ~750°C (Scott 1975). Therefore, at 800°C no stress induced (t) $\rightarrow$ (m) transformation occurs in the YPSZ layers.

At 1300°C the toughness of the laminate decreased slightly to  $3.12\pm0.25$  MPa $\sqrt{m}$ , which represents an increase of 31% compared to monolithic Al<sub>2</sub>O<sub>3</sub> (2.38±0.32 MPa $\sqrt{m}$ ) and a 160% increase compared to monolithic YPSZ (1.2±0.2)

MPa $\sqrt{m}$ ) (Huang and Nicholson 1993).

The small improvements in  $K_{IC}$  at 1300°C are probably due to the plasticity exhibited by YPSZ at this temperature (Huang and Nicholson 1993). During sintering a thin layer of a continuous glassy phase forms at the  $ZrO_2$  grain boundaries (Huang and Nicholson 1993). At high temperatures this phase softens, and flows viscously. This results in inter-granular fracture in the YPSZ at high temperatures. The YPSZ layers are highly constrained by the thicker and stiffer  $Al_2O_3$  layers in the laminate and this will inhibit their ability to deform plastically. However, limited microplasticity may blunt crack tips thus increasing the toughness of the composite.

## **CHAPTER 5 - CONCLUSIONS AND FUTURE WORK**

The main goal to establish electrophoretic deposition as an effective technique for fabricating  $Al_2O_3/YPSZ$  laminated composites with improved toughness (compared to monolithic  $Al_2O_3$ ) was achieved. Electrophoretic deposition combined with pressureless sintering is an effective technique for producing dense laminated composites of thin, uniform layers with strong interfaces. Deposition using a grid of fibres as the depositing electrode resulted in composites with a "wavy" microstructure but the scale of the structure was too coarse to influence crack paths. Drying defects associated with the rigid fibres eliminated the possibility of higher curvatures by this method. The "wavy" laminates fabricated thus have no major advantages over the more simple planar laminates.

The strength of the non-planar  $Al_2O_3/YPSZ$  laminates and monolithic  $Al_2O_3$ were the same at room temperature. At elevated temperatures (800°C and 1300°C) the strength of the laminates were only slightly lower than monolithic  $Al_2O_3$ . This result is encouraging as the strength of most ceramic/ceramic composites are significantly lower than monoliths. The reduced strength is due to drying defects in the laminates and to the deterioration in the mechanical integrity of YPSZ at temperatures >800°C.  $Al_2O_3$  for all temperatures tested. At room temperature this is due to the stress induced (t) $\rightarrow$ (m) transformation in the YPSZ layers. At 800°C and 1300°C the transformation does not occur and the observed increase is probably due to microplasticity in the YPSZ layers (1300°C).

No crack deflection was observed along  $Al_2O_3/YPSZ$  interfaces under any conditions. The interfaces produced by EPD are very strong and dense. Room temperature cracks inclined at an oblique angle to the layers were influenced by the residual thermal mismatch stresses and induced elastic mismatch stresses. Cracks approaching a thin YPSZ layer at an angle between 15° and 60° were observed to turn into the interface and pass through the layer at ~90°. In all the laminated composites tested, cracks aligned perpendicular-to or parallel-to the interfaces were not deflected.

Most work to date concerned with synthesis of tough ceramic composites has focused on deflecting cracks at weak interfaces. The present work suggests that cracks inclined to a strong interface may also be deflected, by thermal and elastic mismatch stress fields. However, unlike a weak interface, these stress fields do not influence the trajectory of cracks which run perpendicular to, or parallel to the interfaces. This problem can be solved by producing non-planar laminates or by inclusion of ceramic platelets to deflect cracks from their orthogonal paths.

The introduction of weak interfaces in laminated materials is a non-trivial process. In ceramic-fibre-reinforced-ceramics, carbon (Bischoff et al. 1989) and boron nitride (Shen et al. 1993) coatings are used to create weak interfaces and thus

boron nitride (Shen et al. 1993) coatings are used to create weak interfaces and thus promote crack deflection. However, these materials oxidize at the working temperatures (>1200°C) of ceramics. Recently McMaster researchers (Bissinger et al. 1994) have incorporated thin porous layers with strong interfaces into ceramic laminates to act as planes of weakness and thus promote crack deflection.

By way of summary, a plot of fracture toughness versus flexural strength (at room temperature and 1300°C) for the non-planar  $Al_2O_3/YPSZ$  laminates of this investigation, and monolithic  $Al_2O_3$  and YPSZ is shown in Figure 5.1. The mechanical properties of the materials are more easily compared via this type of graph.

Future work in this area should take two directions. The first should utilize the induced and residual stress fields in the laminate to deflect cracks from their preferred path. A complete knowledge of the magnitude and influence of the induced and residual stress fields is needed. The second direction involves the introduction of weak bimaterial interfaces or porous layers into the laminate. All work should focus on improved high temperature (>1200°C) properties. !



Figure 5.1 - Fracture toughness ( $K_{IC}$ ) plotted against flexural strength ( $\sigma_f$ ) for nonplanar Al<sub>2</sub>O<sub>3</sub>/YPSZ laminate, monolithic Al<sub>2</sub>O<sub>3</sub> (this investigation) and monolithic YPSZ (Huang and Nicholson 1993).

111

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## **APPENDIX I**

Simple beam theory can be used to determine the residual thermal stress distribution in multi-layered ceramic laminates with uniform layer thickness. Consider the laminate in Figure 4.14 where  $\Delta \epsilon_0$  is the difference in thermal contraction between the Al<sub>2</sub>O<sub>3</sub> and YPSZ layers during cooling from the sintering temperature (Virkar et al. 1987). The Young's modulus and thickness of the Al<sub>2</sub>O<sub>3</sub> and YPSZ layers are E<sub>A</sub>, E<sub>Z</sub>, d<sub>A</sub> and d<sub>Z</sub> respectively. A force balance for the entire beam gives:

$$\sigma_A \Sigma d_A + \sigma_Z \Sigma d_Z = 0 \tag{119-1}$$

which in terms of strains in the Al<sub>2</sub>O<sub>3</sub> ( $\epsilon_A$ ), and YPSZ ( $\epsilon_Z$ ) layers is:

$$\frac{\epsilon_A E_A}{1 - \nu_A} \Sigma d_A + \frac{\epsilon_Z E_Z}{1 - \nu_Z} \Sigma d_Z = 0$$
(119-2)

We also know that:

$$-\epsilon_A + \epsilon_Z = \Delta \epsilon_o \tag{119-3}$$

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Solving for  $\epsilon_A$  and  $\epsilon_Z$  using equations (A2) and (A3) we obtain:

$$\epsilon_{A} = \frac{\left(\frac{-\Delta \epsilon_{o} E_{Z} \Sigma d_{Z}}{1 - \nu_{Z}}\right)}{\left(\frac{E_{A} \Sigma d_{A}}{1 - \nu_{A}} + \frac{E_{Z} \Sigma d_{Z}}{1 - \nu_{Z}}\right)}$$
(119-4)

$$\epsilon_{z} = \frac{\left(\frac{\Delta \epsilon_{o} E_{A} \Sigma d_{A}}{1 - \nu_{A}}\right)}{\left(\frac{E_{A} \Sigma d_{A}}{1 - \nu_{A}} + \frac{E_{z} \Sigma d_{z}}{1 - \nu_{z}}\right)}$$
(119-5)

The corresponding stresses are then given by:

$$\sigma_A = \frac{\epsilon_A E_A}{1 - \nu_A} \tag{120-1}$$

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$$\sigma_{z} = \frac{\epsilon_{z} E_{z}}{1 - \nu_{z}}$$
(120-2)

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