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Laminar Ceramic Composites

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Abstract

The processing of laminar ceramic composites from stacking of layers obtained by tape casting is described. In the case of composites for structural applications, the reinforcement mechanisms are briefly reviewed. It is shown that both strength and toughness can be improved. The evaluation of residual stresses allows a strategy for tailoring the mechanical properties of such composites to be developed. As an example, results are given in the case of laminar composites with layers made of alumina with various zirconia contents.

1 Introduction

Designers require materials with higher and higher performances. Sometimes, materials must be corrosion resistant at elevated temperatures while retaining high mechanical properties (rupture strength and toughness). Ceramic materials, such as alumina, silicon carbide, silicon nitride or mullite seem to be potential candidates for such applications. However, these materials, like all the monolithic ceramics, are brittle, which limits their use in numerous systems.

The usual approach to improve the mechanical behaviour is to eliminate the flaws that initiate the catastrophic failure, or at least to reduce their size. Recently, new strategies have emerged that are fundamentally different from the conventional approach. These strategies involve energy dissipative mechanisms to develop ‘flaw-tolerant’ materials. Among them are the ceramic–ceramic composites. In the flaw tolerance approach, the microstructure is designed to promote the bridging of the cracks which leads, in the ideal case, to the strength being independent of flaw size. The process must produce a material generally with two phases, with a controlled heterogeneous microstructure. The presence of the second phase, either long fibres, whiskers or particles (zirconia, for instance) enhances the mechanical properties.

Long fibre-reinforced ceramics exhibit high mechanical and thermomechanical properties. However, the routes available to process the matrix (i.e. infiltration or impregnation across a fibre fabric) are expensive, and only parts with limited thickness can be obtained. Moreover, carbon or silicon carbide fibres, which are the most used, exhibit a limited thermal stability in oxidizing environments.

By contrast, whisker- or particle-reinforced ceramic composites can be processed following classical routes. The reinforcing phase may be dispersed quasi-isotropically in the matrix, whereas some processing techniques, such as tape casting, allow a preferential orientation of whiskers.

Special attention must be focused on laminar composites. Whereas laminar composites with organic matrix are well developed, laminar composites with ceramic matrix are relatively new. These structures provide the advantage for tailoring the properties by stacking layers of different compositions in a suitable sequence.[1–17] Then, it is possible to produce functionally gradient ceramics. Tape casting, which is extensively used for electronic ceramics, is well suited to the fabrication of ceramic sheets that can be reinforced by whiskers or particles.

In this paper, the different mechanisms that can be used to reinforce laminar composites will be briefly reviewed in the first section. Then, the next section will deal with the processing by tape casting of laminar ceramic composites. The classical laminated plate theory will be used to predict the composite behaviour in the third section and the results compared with the experimental data obtained for alumina–zirconia composites.

2 Strengthening and Toughening Mechanisms in Laminar Ceramic Composites

Laminar ceramic composites consist of alternate layers reinforced by whiskers or particles. This type of composite allows the association of two

Table 1. Strength to failure σ_f (MPa) (four-point bend test) and toughness K_c (MPa$\sqrt{m}$) (SENB)

Forming		SiC$_w$ (vol· %) 0	10	20	30	40	50	Ref·
Tape casting	σ_f	320	470	560	670	940	805	1
	K_c	2·73	3·46	4·54	5·69	6·85	6·5	
Extrusion moulding	σ_f			407				18
	K_c			4·6				
Slip casting	σ_f			452				18
	K_c			4·44				
Slip casting	σ_f			438				20
	K_c			4·6				

reinforcing mechanisms: the first one, acting at the scale of the microstructure, inside the layers, due to the second phases, leading to flaw-tolerant materials; the second one, acting at a macroscopic scale, due to the interfaces between the layers. The aim is to improve both the toughness and the strength.

2.1 Reinforcement mechanisms inside the layers

2.1.1 Whiskers

The incorporation of whiskers allows load transfers from the matrix to the whiskers (crack bridging) and crack deflection. An optimum toughening is achieved by loading whiskers by internal compressive stresses. Hence, the matrix–whisker couple must be judiciously chosen with a thermal expansion coefficient mismatch and chemical compositions leading to an appropriate bonding.

Whisker reinforced composites have already been the subject of numerous studies.[1,6,18–23] Some results concerning SiC$_w$ reinforced mullite are reported in Table 1.

2.1.2 Particles

Zirconia-toughened ceramics are the best example of particle-reinforced materials.[24–30] The most effective toughening mechanism in ZrO_2-containing ceramics is the stress-induced transformation of small ZrO_2 particles in their metastable tetragonal state. Both toughness and strength can be increased, although a compromise between these two effects must be accepted.[31] Other mechanisms, that is, crack deflection and microcracking around monoclinic particles, increase toughness but generally at the expense of strength.

The transformation of zirconia particles is also used to develop compressive surface stresses, increasing the modulus of rupture.

Some results obtained on zirconia-reinforced alumina are given in Table 2.

Table 2. Strength to failure σ_f (MPa) (four-point bend test) and toughness K_c (MPa$\sqrt{m}$) (SENB)

Forming		ZrO_2 (vol.%) 0	5	10	15	20	Ref.
Pressing	σ_f		459	412	285		30
	K_c		5·8	6·2	6·2	5·7	
Slip casting	σ_f		382	390	370		30
	K_c		5·7	5·5	4·9		
Tape casting	σ_f	335	441	444			3
	K_c	4·6	4·9	5·4			

2.2 Reinforcement mechanisms at layer interfaces

The laminar ceramic–ceramic composites must fulfill two requirements:

—improve the toughness and the work of rupture,

—improve the modulus of rupture in bending.

The first objective is obtained using mechanisms involving crack 'clamping' stresses, crack deflection or microcracking, that operate at a macroscopic scale, thanks to the laminar structure of the material, instead of operating at a local scale (microstructure).

In the laminar structure, residual stresses develop during cooling from the sintering temperature because of the difference in thermal expansions between layers of different compositions. But, contrary to the case of monoliths, these stresses built up in the whole volume of the layers. The sign and the magnitude of these stresses may be adjusted through the compositions (ZrO_2 amount in Al_2O_3–ZrO_2 composites), but also through the layer thickness. Hence, it is possible to develop high compressive stresses in thin layers whereas the tensile stresses remain low in the associated thick layers. The propagation of the crack in mode I being impeded by the compressive stresses, propagation modes I and III can occur, leading to crack deflection at the interface and to an increase of the surface of rupture. An example is given by Chartier and coworkers[3,5] for alumina–zirconia composites.

Crack deflection at the layer interface can be favoured by a weak interlayer bond. Clegg *et al.*[10] have fabricated SiC-graphite laminar composites that, although the onset of microcracking appears at 500 MPa, exhibit an ultimate strength three times higher, an apparent toughness (calculated from the ultimate strength) of 15 MPa$\sqrt{m}$ and a work of fracture of 4625 Jm^{-2}. For comparison, the modulus of rupture, the toughness and the work of fracture of monolithic SiC were 500 MPa, 3·6 MPa$\sqrt{m}$ and 25 Jm^{-2}, respectively.

Toughness can also be enhanced by deflection of the growing crack at a porous layer in laminar composites consisting of a sequence of dense and porous layers.[9]

Folsom *et al.*[11] have developed composites with alumina and carbon fibre-reinforced epoxy resin layers in which alumina sheets provide high strength, high stiffness and abrasion resistance, whereas the fibre-reinforced sheets provide high toughness and flaw tolerance. They suggest that composites for high-temperature applications could be designed in a similar way, replacing the epoxy resin by an inorganic glass.

The second objective is reached by choosing for the outer layers a material with a thermal expansion coefficient smaller than the inner layer one. In this configuration, the outer layers sustain compressive stresses.[2,5]

3 Processing of Alumina–Zirconia Laminar Composites

Laminar composites consisting in a regularly alternate stacking of $(2n + 1)$ layers made of alumina with various zirconia content (Al_2O_3 = A; Al_2O_3 + 5 vol.% ZrO_2 = AZ5; Al_2O_3 + 10 vol.% ZrO_2 = AZ10) were fabricated by tape casting, stacking, thermocompression, pyrolysis of organic components and sintering. The sequences were chosen to put the outer layers in a compressive state. The layer thickness was adjusted by superposing a variable number of individual identical tapes. So the AZ10/AZ5/AZ10 composite with $n = 2$ was fabricated by stacking five layers, each consisting in three identical tapes whereas the AZ10/AZ5/AZ10 composite with $n = 10$ was fabricated with 21 alternate tapes.

Tape casting is the prominent process for producing homogeneous wide and thin (25–1000 μm) ceramic sheets with controlled thicknesses and smooth surfaces.[32] Tape casting, basically, consists in depositing a suspension composed of the ceramic powder and organic components on a support, either by spreading under a blade (doctor blade process) or by coating. Typical applications are substrates of Al_2O_3 (or AlN) for thick- and thin-film circuitry and $BaTiO_3$ for multilayer capacitors, which represent the two principal markets in electronic ceramics. Tape casting is now used on a larger scale to produce thin ceramic sheets and multilayer structures of various materials for different applications. The evaporation of the solvents leads to a dried green tape with sufficient strength and flexibility to be handled and cut to the proper shape. After removal of organic components, green sheets or multilayer systems made by stacking and laminating green sheets are sintered.

3.1 Slurry formulation

The composition of the slurry and the drying stage greatly affect the microstructure and hence the properties of the green tapes (density and strength). The rheological behaviour of the slurry is an important parameter for the homogeneity and the microstructure of the green tape, and for the reproducibility of the process. Tape-casting slurries are complex, multicomponent systems, which contain ceramic powders (including sintering aids), solvents, dispersants, binders and plasticizers. The control of such a system requires the knowledge of the role of each component.

3.1.1 Powder

Powders of fine particle size are used to obtain thin films, smooth surfaces, high densities and small critical flaw size. The particle size distribution greatly influences the rheology of the slurry. The starting powders are 99·7 wt% purity, 0·5 μm grain size alumina (P172SB, Péchiney, France) and 97·5 wt% purity, 0·4 μm grain size zirconia (UPH 12, Criceram, France).

3.1.2 Solvent

The solvents ensure the dissolution of all organic components (i.e. dispersant, binders and plasticizers) to give an homogeneous slurry. Interactions between the solvent and the solid surfaces influence the further adsorption of the dispersant and of the binders, and then the stability and the rheological behaviour of the slurry. Mixtures of organic solvents, and particularly binary systems, are preferred for solubility reasons: the various organic additives have their higher solubility in different solvents. The solvent used is an azeotropic mixture of methyl ethyl ketone (MEK) and ethanol (40/60).

3.1.3 Dispersant

Dispersants are necessary to obtain a good deagglomeration and dispersion of the ceramic particles in the solvent, and to stabilize the tape-casting suspensions with a high ceramic–organic ratio. A stable dispersion of deagglomerated particles leads to a dense particle packing and to a homogeneous microstructure.

The best stabilization is given by a combination of electrostatic and steric repulsion (referred as electrosteric stabilization). The steric hindrance prevents contact between particles and the double layer, which may be due to net charge on the particle surface and/or charges associated with the adsorbed polymer, providing repulsion by a potential energy barrier at larger distances.

The dispersant used is a phosphate ester (Beycostat C213, CECA, France).

3.1.4 Binder

After evaporation of the solvent, the binders provide the strength to the green tape, to enable handling and subsequent processing steps like punching. Binders are polymeric molecules which adsorb on the particle surfaces and form organic bridges between them. The slurry should exhibit a shear thinning behaviour caused by an alignment of the binder molecules at high shear rate.

The binder used is a poly(vinyl butyral) (PVB).

3.1.5 Plasticizer

Most binders require the addition of plasticizers to improve the flexibility and workability of the green tape. Plasticizers are low molecular weight species which can reduce the glass transition temperature of the binder at room temperature or below, leading to a better plasticity. The addition of plasticizers modifies the mechanical properties of the green tape, the strain to failure increases but the strength decreases.

The plasticizer used is a mixture of poly(ethylene glycol) (PEG) and dibutyl phthalate (DBP).

The slurry must be adjusted, not only for tape casting but taking into account other processing parameters such as shaping (cutting, punching, thermocompression), pyrolysis of organic components and sintering (Table 3).

3.2 Slurry preparation

The preparation of slurries is carried out in two stages, namely (i) deagglomeration and dispersion of powders in the solvent with the aid of the dispersant, and (ii) homogenization of the slurry with binders and plasticizers. The sequence of component addition is critical. The dispersant has to be added before the binders to prevent competitive adsorption. The initial adsorption of the binder on the particle surfaces would prevent the dispersant from being subsequently adsorbed, thereby decreasing its effectiveness. Furthermore, the deagglomeration is more efficient in a low viscosity system (i.e. without binders and plasticizers) and the mechanical damage of the binder molecules is minimized by this sequence of addition. The deagglomeration is done by ultrasonic treatment. The second stage of homogenization is performed by milling for 24 h. The slurry is kept rotating at a slow speed for deairing and to prevent settling.

Table 3. Composition of a tape casting slurry

Component	*Function*	*vol.%*
Alumina + zirconia	Ceramic powder	30·6
MEK/ethanol	Solvent	57·6
Phosphate ester	Dispersant	0·8
PVB	Binder	4·6
PEG 300	Plasticizer	2·9
DBP	Plasticizer	3·5

3.3 Tape casting

Tape casting is performed with a laboratory tape-casting bench (Cerlim Equipement, Limoges, France). Slurries were tape cast onto a fixed glass plate with a moving double blade device at a constant speed of 1 m min^{-1}.

4 Evaluation of Residual Stresses in Alumina-Zirconia Laminar Composites

The determination of the distribution of the residual stresses allows the appropriate choice of the layer composition and thickness and of the stacking sequence, for an optimum reinforcement. Models have previously been developed for organic composites[33] or glass-to-metal seals.[34]

During cooling, the difference in deformation, due to the different thermal expansion coefficients of the layers, is accommodated by creep, as long as the temperature is high enough. Below a certain temperature, that will be called the 'joining' temperature, the different layers become bonded together and internal stresses appear.

For laminar composites with symmetrical stacking (odd number of layers) and with a low thickness compared with the plate size, the problem is that of an in-plane stress state with the stress normal to the surface equal to zero ($\sigma_{33} = 0$) (Fig. 1).

In the case of a solid with an isotropic, linear elastic behaviour, the mechanical strains are expressed as follow:

$$\varepsilon_{ij\mathrm{el}} = \frac{1+\nu}{E}\,\sigma_{ij} - \frac{\nu}{E}\,\mathrm{Tr}\tilde{\sigma}\,\delta_{ij} \qquad (1)$$

$$\varepsilon_{11} = \frac{1}{E}\,(\sigma_{11} - \nu\sigma_{22})$$

$$\varepsilon_{22} = \frac{1}{E}\,(\sigma_{22} - \nu\sigma_{11})$$

$$\varepsilon_{12} = \frac{1+\nu}{E}\,\sigma_{12}$$

$$\varepsilon_{33} = -\,\frac{\nu}{1-\nu}\,(\varepsilon_{11} + \varepsilon_{22})$$

$$\varepsilon_{13} = \varepsilon_{23} = 0$$

where $\tilde{\varepsilon}$ is the strain tensor, $\tilde{\sigma}$ the stress tensor, ν the Poisson ratio and E the Young modulus.

In a loading configuration which is symmetrical in respect to directions 1 and 2, and the axes 1 and 2 are equivalent (orthotropic system), then:

$$\sigma_{11} = \sigma_{22} \qquad (2)$$

and

$$\varepsilon_{11} = \frac{1-\nu}{E}\,\sigma_{11} = \varepsilon_{22}$$

$$\varepsilon_{12} = \frac{1+\nu}{E}\,\sigma_{12}$$

In each layer I, the total deformation after sintering, is the sum of an elastic component and of a thermal component. In the case of a perfectly rigid bonding between the layers, the total deformation will be the same for all the layers, then:

$$\varepsilon^{I}_{11} = \frac{1-\nu_I}{E_I}\,\sigma^{I}_{11} + \alpha_I\,\Delta T = \text{constant} \qquad (3)$$

where ΔT is the difference in temperature between the actual temperature, T_0, and the joining temperature, T_j.

The force balance requires (in normal stresses):

$$\textstyle\sum_I \sigma^{I}_{11} d_I = 0 \qquad (4)$$

where d_I is the thickness of the Ith layer.

That gives, for a symmetrical composite with $2n + 1$ alternate layers of type 1 and 2:

$$(n+1)\sigma^{1}_{11} d_1 + n\sigma^{2}_{11} d_2 = 0 \qquad (5)$$

From eqns (3) and (5), it comes:

$$\sigma^{1}_{11} = \frac{nE_1E_2d_2(\alpha_2-\alpha_1)\,\Delta T}{n(1-\nu_1)E_2d_2 + (n+1)(1-\nu_2)E_1d_1} \qquad (6)$$

and

$$\sigma^{2}_{11} = -\frac{(n+1)E_1E_2d_1(\alpha_2-\alpha_1)\,\Delta T}{n(1-\nu_1)E_2d_2 + (n+1)(1-\nu_2)E_1d_1} \qquad (7)$$

The magnitude of these stresses depends on the thermal expansion coefficient mismatch (that must be small enough to avoid delamination) and on the relative thickness of the layers.

In order to limit the sensitivity to surface flaws, the composite is tailored to develop compressive residual stresses in the outer layers. In the case of a symmetrical laminate, this is obtained by choosing the layer compositions so that the thermal expansion of the odd layers is smaller than the even ones ($\alpha_1 < \alpha_2$).

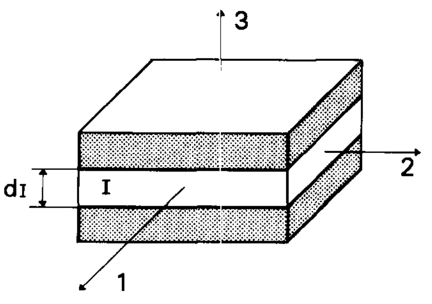

Fig. 1. In-plane stress state with a stress normal to the surface equal to 0 ($\sigma_{33} = 0$) in a laminar composite with a symmetrical stacking.

Table 4. Young modulus, Poisson ratio and thermal expansion coefficient of 'pseudo-laminar composites' consisting of 21 identical layers with a thickness of 160 μm in the green state

	E (GPa)	ν	$\alpha\Delta T$
A/A	341	0·234	-120×10^{-4}
AZ5/AZ5	328	0·241	-125×10^{-4}
AZ10/AZ10	325	0·242	$-121{\cdot}5 \times 10^{-4}$

For a three layer composite ($n = 1$), the change in compressive (σ^{1}_{11}) and tensile (σ^{2}_{11}) stresses with the thickness ratio ($x = d_2/d_1$) of the layers, taking $\nu_1 = \nu_2 = \nu$, is given by eqns (8) and (9):

$$\sigma^{1}_{11}(x) = \frac{E_1E_2(\alpha_2-\alpha_1)\,\Delta T}{(1-\nu)}\,\frac{x}{2E_1 + E_2x} \qquad (8)$$

$$\sigma^{2}_{11}(x) = -2\,\frac{\sigma^{1}_{11}(x)}{x} \qquad (9)$$

Figure 2 illustrates these changes for an A/AZ5 composite. The characteristics of the constitutive materials are given in Table 4.

The compressive stress increases when the d_2/d_1 ratio increases, whereas the tensile stress decreases. In the case of brittle materials, which have a high sensitivity to cracking under tensile stresses, the thickness of the layers in tension must be high enough to avoid catastrophic failure.

This result is consistent with Amateau & Messing[2] who observed a decrease in crack frequency in the inner layer (under tension) in a $Al_2O_3 + y$ vol.% SiC_w (20/0/20) when d_2/d_1 increases from 1 to 4.

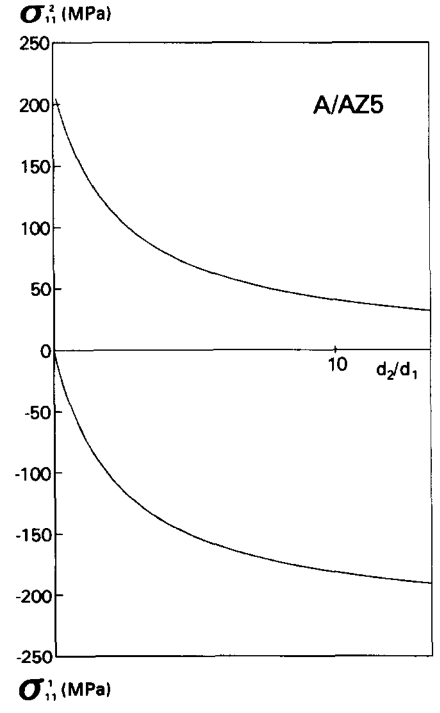

Fig. 2. Compressive stresses (σ^{1}_{11}) developed in alumina layers and tensile ones (σ^{2}_{11}) in alumina containing 5 vol.% zirconia layers versus the thickness ratio (x = d_2/d_1) in a A/AZ5 composite.

Table 5. Strength to failure σ_f (MPa) (three and four-point bend tests), toughness K_c (MPa√m) (SENB) and residual and calculated stresses

	K_c (MPa√m)	σ_f (three-point) (MPa)	σ_f (four-point) (MPa)	σ^1_{11} (MPa)	σ^2_{11} (MPa)	σt (calculated) (MPa)
A/A	4·6	335				
AZ5/AZ5	4·9	441	357			
AZ10/AZ10	5·4	444	351			
A/AZ5, n = 10	5·1	437		−114	126	449
AZ10/AZ5, n = 2			404	−60	90	411
AZ10/AZ5, n = 10	8·0	560		−118	130	562

5 Mechanical Properties of Alumina—Zirconia Laminar Composites

5.1 Characteristics of the layer materials

Young modulus and Poisson ratio of the materials were measured using a vibrating technique[35] on monoliths fabricated by stacking 21 identical layers ('pseudo-laminar composites'). The thermal expansion coefficient was measured from 20°C to 1400°C. 1400°C was taken as the joining temperature. The data are given in Table 4.

5.2 Mechanical properties

Table 5 shows the experimental results for ultimate strength in three-point and four-point bending (load normal to the layers), toughness measured by the SENB method (beam notched perpendicularly to the layer planes) together with the internal stresses and the calculated strength.

5.2.1 Flexural strength

In this sollicitation, and taking into account the fact that ceramics are more resistant in compression than in tension, the rupture is initiated in a zone in tension. It can develop either from surface flaws, or from internal defects located in the outest layer in tension.

In the first case, the rupture strength will be equal to the strength of material constituting the outer layer increased of the compressive residual stress.

In the second case, in contrast, the tensile internal stress overlaps the applied stress, leading to a strength lower than the strengths of the constitutive materials of the composite.

The experimental results in Table 5 show a good agreement with the strength calculated under the assumption of a rupture initiated from surface flaws. In fact, the processing flaws have their size limited to the thickness of the individual layer (about 135 μm after sintering) and their growth is impeded by the compressive stresses in the adjacent layers and by the deflection effects at the interfaces.

5.2.2 Toughness

The higher toughness of 'pseudo-laminar composites' AZ5/AZ5 and AZ10/AZ10 reflects the reinforcement due to the tetragonal–monoclinic transformation of zirconia particles. A slight increase of toughness is observed for A/AZ5/A composites in which the compressive stresses in the alumina layers contribute to the lowering of the stress field at the crack tip. The improvement is much higher for AZ10/AZ5/AZ10 composites in which the compressive stresses, induced by the phase transformation of the zirconia particles, are superimposed to the internal compressive stresses in the AZ10 layers, leading to a synergetic effect. Toughness increases from 4·9–5·4 to 8 MPa√m.

6 Conclusion

These results illustrate the interest of laminar ceramic–ceramic composites for structural applications. A similar concept could be used to design materials with an improved resistance to high-temperature corrosion. To achieve this goal, a corrosion-resistant material will be chosen for the outer layers and the inner layer will provide mechanical resistance.

Besides composites with layers differing by their mechanical, chemical or thermal properties, it is possible to create sequences of microstructures with different porosities or grain sizes. Hence, it could be possible to have a fluid to flaw through the composite or even to impregnate the composite with a metal (Ni, Al, etc.).

Laminar ceramic–ceramic composites afford an outstanding opportunity to create materials with functional gradients and have immense potential applications.

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