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Processing and mechanical properties of biocompatible Al_2O_3 platelet-reinforced TiO_2

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The mechanical behaviour of Al_2O_3 platelet-reinforced TiO_2 bioceramics produced by hot-pressing has been investigated. The variation of the elastic constants, fracture strength and fracture toughness with the volume fraction of platelet content was studied. The addition of platelets did not affect the critical flaw size of the composites. This fact, and the good matrix/platelet interfacial bond resulted in a simultaneous increase of the fracture strength and toughness. The mechanical properties increased from $K_{Ic} = 2.4$ MPa m$^{1/2}$ and $\sigma_0 = 215$ MPa for pure TiO_2 to $K_{Ic} = 3.3$ MPa m$^{1/2}$ and $\sigma_0 = 265$ MPa for a 30 vol % platelet-containing composite. The indentation technique demonstrated the anisotropic behaviour of the fracture toughness in the composites due to platelet orientation during hot-pressing. Load transfer was identified as the main reinforcing mechanism and the toughening effect could be assessed by a load transfer-based model equation. Fracture surface analysis showed mainly intercrystalline fracture for the TiO_2 matrix, whilst with the composites, fracture became more transcrystalline with increasing platelet content.

1. Introduction

In the development of new biomaterials, although the achievement of the required mechanical properties is a prerequisite, the maintenance of biocompatibility with the human body is also necessary. While bioactive materials change their microstructure and properties by interactions with the living environment, bioinert materials do not show such changes and are therefore stable throughout the whole period of their application [1]. There are a few ceramic oxides which have been selected for these bioinert applications, including Al_2O_3, SiO_2 and TiO_2 [1, 2]. Although alumina is the most used inert bioceramic to date, TiO_2 has demonstrated a better biocompatible behaviour in some applications involving contact with blood [3]. TiO_2, however, has, in general, a worse mechanical behaviour than alumina, with lower fracture strength and fracture toughness values. It is therefore worthy to study reinforcing possibilities of the brittle TiO_2 matrix, for example by the incorporation of strengthening and toughening inclusions. The incorporation of Al_2O_3 in the form of platelets is an attractive alternative because it may provide the improvement of the mechanical properties without losing the bioinert character of the material. Platelet reinforcement has been shown to be a good alternative for improving the fracture behaviour of brittle ceramics, being relatively easy to disperse into a matrix and carrying no health risks [4]. Platelets have a toughening potential similar to whiskers with crack deflection, crack bridging, load transfer and, to a lesser extent, platelet pull-out being the operating mechanisms [4]. In particular, alumina platelets have been used to toughen different ceramics such as sialon [5], mullite [6, 7], zirconia [8, 9] and glass [10]. Moreover, some studies have reported a simultaneous increase in the fracture strength [6, 8, 10] indicating that the critical flaw size of the material was not increased by the incorporation of well-dispersed platelets. In this work, high-density TiO_2 matrix composite materials containing different volume fractions of Al_2O_3 platelets (10–30 vol %) were fabricated by an optimized hot-pressing technique. The composites were evaluated in terms of the dependence of their physical and mechanical properties on the platelet inclusion content, and the toughening and strengthening mechanisms were studied. The experimental values were compared with the prediction of a model derived on the basis of a load-transfer mechanism.

2. Experimental procedure

The TiO_2 powder investigated was of high-purity and high-sinterability. It was prepared by hydrolysis of metal alkoxides. Details about the powder production have been presented elsewhere [11, 12]. The powder was 100% in the rutile crystal modification of TiO_2. Using a powder with a high sinterability is necessary because the fabrication temperature of the composites must be kept low in order to avoid the formation of

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aluminium titanate (Al_2TiO_5). This compound would be detrimental to the mechanical behaviour of the final products.

Alumina platelets (TS100, Lonza-Werke, Waldshut-Tiengen, Germany) having a hexagonal shape and a medium size of ~ 4.5 μm in the major axis were used in the as-received condition as reinforcing component. They are specified as being quasi-monocrystalline and defect-free by the manufacturer. The TiO_2 powder and Al_2O_3 platelets were investigated by scanning electron microscopy (SEM). Mixtures with the following volume fractions of platelet content were made: 0, 10, 20 and 30 vol %. For obtaining well-dispersed platelets in the matrix, the mixtures were wet-milled using isopropanol in a rotation mixer–dryer. The platelet/powder mixture, placed in a recipient which rotated in a water bath maintained at 85 °C under a low pressure (80 mbar), was mixed at a speed appropriate for obtaining a good powder dispersion via centrifugal forces. The binder evaporated at ~ 60 °C leaving the dried, well-mixed, composite powder after the process. Cylindrical samples (50 mm diameter, 6 mm height) were fabricated by hot pressing (KCE-Sondermachinen, Germany) using a graphite die under a flowing nitrogen atmosphere. The processing parameters of temperature, pressure and time were optimized for obtaining high-density samples. The optimized hot-pressing involved heating at a rate of 20 K min^{-1} with a simultaneous, continuous increase of the pressure. An optimum pressure of 25 MPa was reached when the temperature was 1050 °C. Whilst maintaining the pressure constant at 25 MPa, the temperature was further increased at 20 K min^{-1} until reaching the sintering temperature of 1150 °C. After a sintering period of 10 min at this temperature, the furnace was cooled down at a cooling rate of 5 K min^{-1}. After cooling, the samples were heat treated for 10 h at 800 °C to allow relaxation of the internal thermal stresses developed. The density of all samples was determined using the Archimedes' principle. The hot-pressed samples were plain parallel machined using a diamond tool (Fa. Okamoto, ACC-DX, Japan) and polished using SiC 1200-powder to a 4 μm finish. The parallel character of the machined faces was controlled to be ~ 0.01 mm. The ultrasonic technique was used to obtain the elastic constants (Young's modulus, Poisson's ratio) of the composite on the polished hot-pressed plates. Bars for four-point bend tests were cut from the hot-pressed plates using a diamond saw. The final dimensions of the bars were 3 mm × 4 mm × 45 mm. The edges of the bars were bevelled using SiC powder. The fracture strength (modulus of rupture) was determined in four-point bend (Instron 1121) using a crosshead speed of 0.5 mm min^{-1}. The samples were placed such that the load was applied parallel to the hot-pressing direction during fabrication. At least 14 samples were tested for each composition and the data were evaluated using Weibull statistics. In addition, the single-edge-notched beam (SENB) technique was used to obtain fracture toughness data. For these measurements, a crack of 100 μm length was introduced perpendicular to the longitudinal axis of the samples with a geometry $a/W \sim 0.4$ (a is the crack length, W the sample height). The crosshead speed was 0.5 mm min^{-1} and average values of at least five measurements were determined. The fracture toughness was evaluated also using the indentation crack length technique (ICL). A Vickers' indentor (Duromat, Fa. Leitz, Germany) working at a load of 20 N was used and the length of the diagonals of the indentations and the cracks emanating from the apices were measured with high precision using a quantitative microstructural analyser (Quantimet 570, Cambridge Instruments). At least five indentations per specimen were made on polished sections prepared in the planes perpendicular and parallel to the hot-pressing axis. The fracture toughness, K_{Ic}, was calculated using the equation of Anstis *et al.* [13]. Quantitative microstructural analysis of polished and thermally etched (1000 °C, 1 h) sections was performed in order to obtain the relevant parameters to characterize the microstructure.

3. Results and discussion

Fig. 1 shows a scanning electron micrograph of the high-purity, fine TiO_2 powder used. The particles have spherical shape and a mean radius of 100–150 nm. Fig. 2 is a scanning electron micrograph of the Al_2O_3 platelets used showing their pronounced hexagonal morphology. The mean aspect ratio of these platelets has been measured to be $z/x = 0.2$ [10]. Using a TiO_2 powder of high sinterability enabled dense samples to be produced at relatively low temperatures (1150 °C) and therefore avoided the formation of the undesired aluminium titanate phase at the matrix/platelet interface. This has been demonstrated by means of XRD analysis of selected samples for all platelet contents investigated [12]. The results of the density measurements are shown in Table I. Even for the composite with the highest concentration of platelets (30 vol %), near theoretical density has been achieved by hot-pressing at 1150 °C. The fine and homogeneous

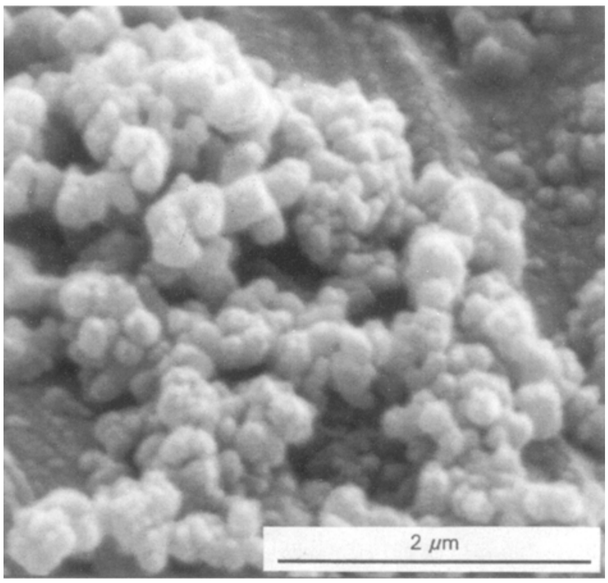

Figure 1 Scanning electron micrograph of the high-purity, high-sinterability sol–gel TiO_2 powder used.

microstructure of a hot-pressed unreinforced TiO_2 sample is shown in Fig. 3. The average grain size, as measured by the mean linear intercept length, is ~ 6 μm. The success of dispersion reinforcement of brittle matrix depends on the achievement of a homogeneous distribution of the reinforcing component in the matrix avoiding formation of clusters and agglomerates [6]. The wet processing route used in this study has lead to such homogeneous microstructures. This is evident in Fig. 4, which shows a scanning electron micrograph of a polished cross-section parallel to the hot-pressing direction for a composite containing 20 vol % platelets. Moreover, the mean linear intercept length of the TiO_2 matrix in the composites was lower than that of the TiO_2 sample free from platelets. This would indicate that the platelets are also acting as grain-growth inhibitors. Indeed it has been shown that when the platelets were dispersed badly in the matrix, the mean intercept length in the platelet-free regions was much larger than in regions which contained a high concentration of platelets [12]. This phenomenon was not studied further in this work.

Platelet orientation was observed in the hot-pressed samples, as a careful observation of Fig. 4 reveals. By means of quantitative microstructural analysis of the polished sections and stereological equations, the orientation angle of the platelets axis to the hot-pressing direction could be determined, as has been shown previously for glass matrix/platelet composites [10]. The values of the orientation angle for the different volume fraction of inclusions are given in Table I. Similar orientation of platelets in different composite ceramic bodies fabricated by hot-pressing have been reported in the literature [9, 14, 15].

The results of the Young's modulus and Poisson's ratio ultrasonic measurements are shown in Table I. The Young's modulus of the composites increases with increasing platelet content up to a volume

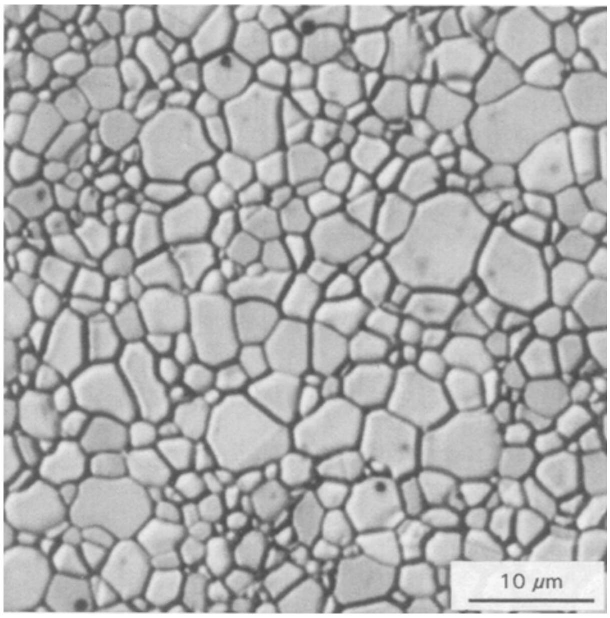

Figure 3 Optical micrograph showing the microstructure of the hot-pressed TiO_2 matrix without inclusions (after thermal etching in air for 1 h at 1000 °C).

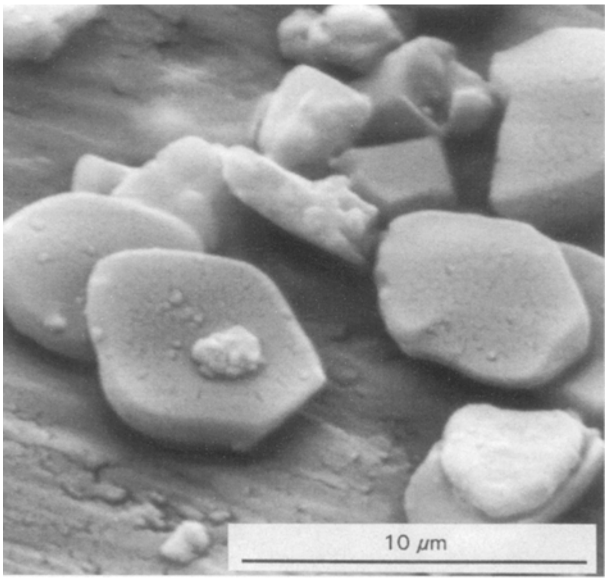

Figure 2 Scanning electron micrograph of the Al_2O_3 platelets used as reinforcement.

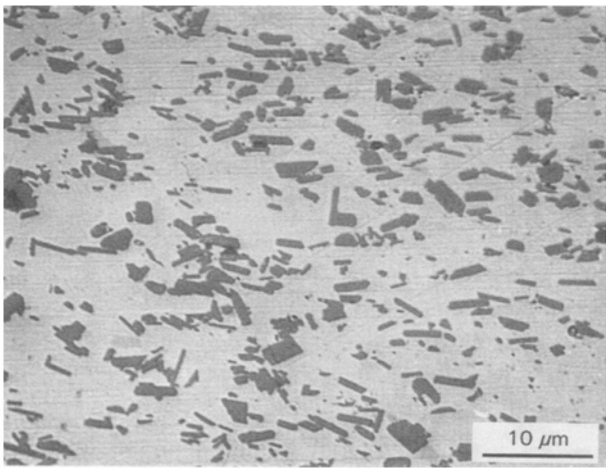

Figure 4 Optical micrograph showing the microstructure of a composite containing 20 vol % platelets (section parallel to hot-pressing direction).

TABLE I Density, microstructural information and elastic constants of the fabricated materials

Platelet content (vol %)	Density (% theoretical)	Orientation angle (deg)	Young's modulus (GPa)	Poisson's ratio
0	99.5	–	284	0.285
10	98.5	65	298	0.270
20	97.9	62	310	0.266
30	97.1	60	312	0.260

fraction of 20%. The proportionally lower increment of the Young's modulus for the composites containing 30 vol % platelets is attributed to the higher residual porosity of these samples. Moreover, the 30 vol % platelet-containing composites are likely to be cracked because of the higher residual stresses developed after fabrication. This would also negatively affect the Young's modulus. The Poisson's ratio shows negligible variation with platelet addition.

The fracture strength data are summarized in Table II. The maximum of the mean fracture strength is obtained for the 20 vol % platelet-containing composite, being ~25% higher than the fracture strength of pure TiO_2. Fig. 5 shows the Weibull plots for the different materials investigated. The Weibull modulus for all composites up to 20 vol % platelet inclusions is high and is in the range normally reported for structural ceramics [16]. The 30 vol % platelet-containing composites showed a slight decrease in the Weibull modulus and this can be correlated with a less homogeneous microstructure and residual porosity at this high inclusion content level [12]. The most important conclusion that can be drawn from the fracture strength data is that the critical flaw size in the material was not increased by the platelet addition, confirming the optimum processing route used for fabrication of the composites. As mentioned in the introduction, most studies on platelet toughening of ceramics have also reported a simultaneous decrease of the fracture strength due to microstructural inhomogeneities [4, 6, 8].

The fracture toughness values determined by the SENB and ICL methods are shown in Table III. An increase in K_{Ic} with platelet content was found using both techniques. The ICL values were determined on the basis of crack length measurements of the crack pattern produced by Vickers' indentations on three mutually perpendicular sections of the sample and therefore they can give evidence for the anisotropy in the materials. This is indeed demonstrated by the values in Table III. While in sections parallel to the hot-pressing direction the crack can meet the basal plane (direction I) and the edges of the platelets (direction II), in sections perpendicular to the hot-pressing direction the crack always meets the same type of obstacles (direction III), and therefore can be considered isotropic in this plane. This is evident by observation of the micrograph in Fig. 6 which shows the crack pattern of an indentation made on a section perpendicular to the hot-pressing direction. Similar anisotropy effects of oriented platelets in ceramic matrix composites have been reported in the literature [9, 14, 15]. As stated in the introduction, a number of mechanisms can be responsible for the increase of the

TABLE II Fracture strength data and results of the Weibull statistics evaluation of the fabricated materials

Platelet content (vol %)	Characteristic strength, σ_0 (MPa)	Weibull modulus m	Mean bend strength (MPa)
0	215	10	204 ± 24
10	252	11	242 ± 25
20	265	12	244 ± 24
30	260	9	228 ± 32

TABLE III Fracture toughness data of the fabricated materials

Platelet content (vol %)	K_{Ic} (SENB) ($MPa\,m^{1/2}$)	K_{Ic} (ICL) ($MPa\,m^{1/2}$)		
		Direction 1	Direction 2	Direction 3
0	2.38	[a]	[a]	[a]
10	2.85	2.22	1.76	2.22
20	3.01	2.87	2.11	2.69
30	3.23	3.51	2.00	3.13

[a] Not measured.

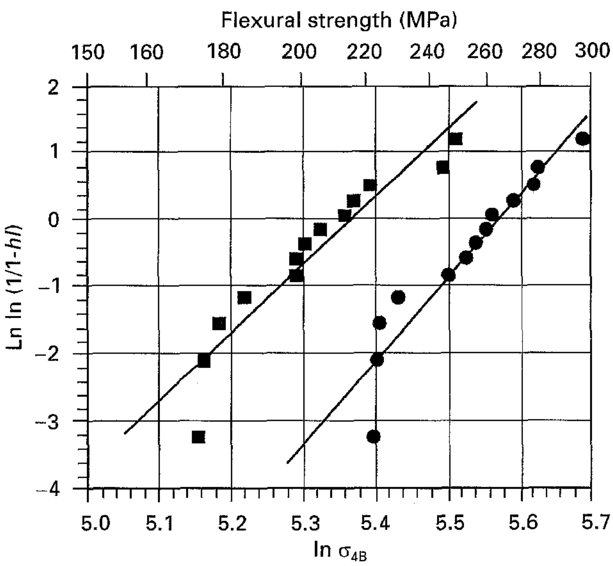

Figure 5 Weibull plot summarizing the strength data for the materials investigated: (■) TiO_2 matrix, (●) composite with 20 vol % platelets.

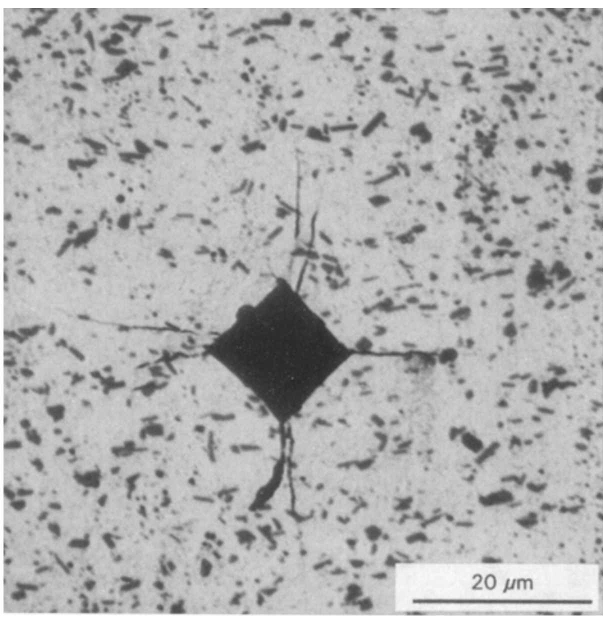

Figure 6 Vicker's indentation and crack pattern produced on a section perpendicular to the hot-pressing direction for a 20 vol % composite.

fracture toughness with increasing volume content of platelets. Crack deflection, crack bridging and load transfer have been identified to be the most effective [4, 7]. Although no detailed characterization of the platelet/matrix interface has been performed, the simultaneous increase of Young's modulus, fracture strength and fracture toughness indicate that the platelets are well bonded to the matrix. This would support the suggestion that a load-transfer mechanism is occurring. Load transfer has also been suggested to explain the increase of strength and toughness in SiC platelet-reinforced mullite [6].

Assuming that the platelets and matrix strains under loading are equal and that fracture toughness scales with fracture strength, the following relation is valid for the effective fracture toughness of the composite [10]

$$K_{Ic}^{c} = K_{Ic}^{M} \frac{E_c}{E_M} \tag{1}$$

where E_c, E_M are the Young's modulus of the composite and the matrix, and K_{Ic}^{c}, K_{Ic}^{M} are the fracture toughness of the composite and the matrix, respectively. The Young's modulus of a composite material containing a low volume fraction (< 40 vol %) of second-phase spheroidal dispersions has been derived elsewhere [17] as a function of E_M and microstructural parameters. The final equation for the effective fracture toughness of a composite containing spheroidal inclusions results as [10]

$$K_{Ic}^{c} = K_{Ic}^{M}\left\{1 - \frac{\pi}{A}\left[1 - \frac{1}{\left(1 + \frac{1.99}{B}\eta\right)} - \frac{1}{3\left(1 + \frac{1.68}{B}\eta\right)} - \frac{1}{\frac{9}{5}\left(1 + \frac{1.04}{B}\eta\right)}\right]\right\} \tag{2a}$$

with

$$\eta = \frac{E_M}{E_D} - 1 \tag{2b}$$

$$A = \left(\frac{4\pi}{3c_D}\right)^{2/3}\left(\frac{z}{x}\right)^{-1/3} \bigg/ \left\{1 + \left[\left(\frac{z}{x}\right)^{-2} - 1\right]\cos^2\alpha\right\}^{1/2} \tag{2c}$$

$$B = \left(\frac{4\pi}{3c_D}\right)^{1/3}\left(\frac{z}{x}\right)^{1/3} \left\{1 + \left[\left(\frac{z}{x}\right)^{-2} - 1\right]\cos^2\alpha\right\}^{1/2} \tag{2d}$$

where E_D is the Young's modulus of the inclusion phase, c_D is the volume fraction, z/x the axial ratio and α the orientation of the inclusions. Equation 2 has been used successfully to predict the toughening of whiskers-reinforced ceramics by load transfer mechanism [10]. Using $E_D = 400$ GPa for Al_2O_3, $z/x = 0.2$ for the platelets [10] and the average measured orientation angle $\alpha = 65°$, the effective fracture toughness of the Al_2O_3 platelet-containing TiO_2 matrix composites can be calculated by means of Equation 2. The comparison of the calculated values with the experimental data determined by the SENB technique is shown in Fig. 7. Good agreement between calculated and experimental values is found. The low residual stresses in the material due to the low thermal expansion and elastic mismatch between matrix and platelets and the strong interfacial bonding may be responsible for this behaviour. An observation should be made, however, for the 30 vol % composite: as shown in Table I, the Young's modulus of this material is lower than the value which should result from load transfer [10] and this would result in a lower fracture toughness value than that predicted by Equation 2. Therefore, the agreement between the calculated and the experimental value for the fracture toughness for the 30 vol % composite must be considered as fortuitous. An increase of crack deflection at this high platelet content may explain the higher fracture toughness value measured. Fracture path observations provide more evidence for this approach for the composites with 30 vol % platelets, as shown in Fig. 8. There is evidence of crack-deflection and crack-bridging processes together with platelet fracture,

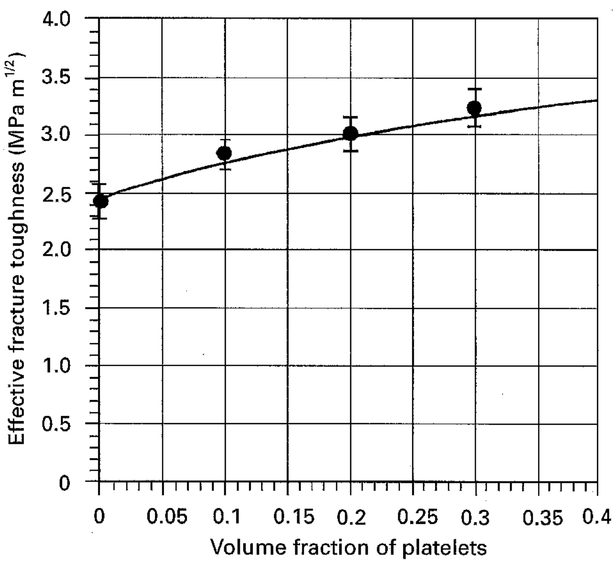

Figure 7 (—) Calculated (Equation 2) and (●) experimental (SENB technique) values for the fracture toughness of Al_2O_3 platelet-reinforced TiO_2 matrix composites.

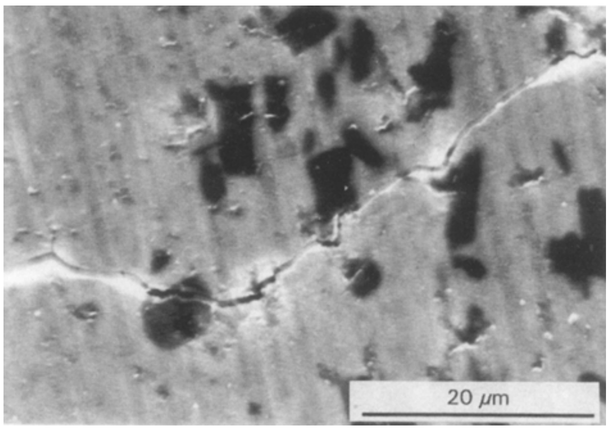

Figure 8 Scanning electron micrograph of the fracture path of a 30 vol % platelet-containing composite showing crack deflection and platelet fractures.

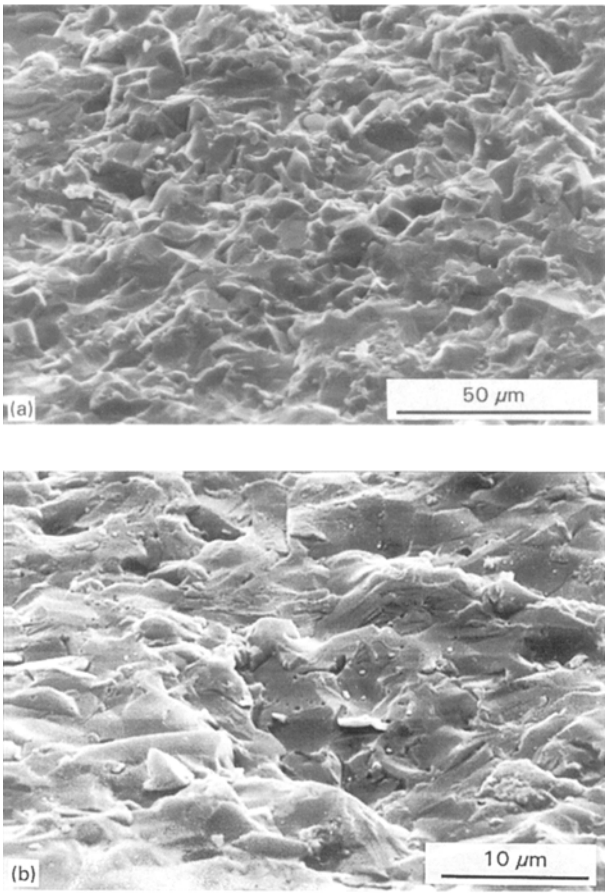

Figure 9 Scanning electron micrograph of fracture surfaces of (a) pure TiO_2 matrix and (b) composite containing 20 vol % platelets.

confirming that the crack path was affected by the presence of the inclusions in these composites of high platelet content.

The platelet inclusion also affects the failure mode of the material from essentially intercrystalline for the pure TiO_2 matrix, to a more transcrystalline fracture mode with increasing platelet content. This is documentated in Fig. 9a and b which shows fracture surfaces of the pure TiO_2 matrix and of a composite containing 20 vol % platelets. Further investigation of this behaviour will be the objective of future work.

4. Conclusion

A hot-pressing route has been optimized for preparation of dense TiO_2 matrix composites reinforced with Al_2O_3 platelets with potential for using as biomaterials. Both the fracture strength and fracture toughness improved with the platelet volume fraction, indicating that the critical flaw size of the material was not affected by the platelet addition. A load-transfer mechanism was suggested as being responsible for the improvement of the mechanical properties up to a platelet content of 20 vol %. The effective fracture toughness of the composite could be predicted by a load transfer-based equation which considers the microstructural characteristics of the material. The composites showed anisotropy of the fracture toughness according to the orientation of the platelets during processing. The reinforced TiO_2 bioceramics are candidate materials for fabrication of cardiac valves and other human implants.

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