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WHISKER-REINFORCED OXIDE CERAMICS

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Résumé - Le renforcement par whiskers est une technique prometteuse pour l'amélioration significative des propriétés mécaniques des céramiques aussi bien pour les applications à haute température qu'à basse température. Les exemples discutés dans cet article concernent des matrices d' Al_2O_3 , cordiérite, mullite et zircone; toutes sont renforcées de whiskers de SiC.

Abstract - Whisker reinforcement represents a promising technique to significantly improve the mechanical behavior of oxide ceramics both for low and high temperature applications. Examples discussed in the paper include the matrix materials Al_2O_3 , cordierite, mullite and ZrO_2 ; all reinforced with SiC whiskers.

I - INTRODUCTION

Structural oxide ceramics are limited in their application not only because of their brittle nature, but also because of the high-temperature creep performance which is inferior to the covalently bonded ceramics. Transformation toughening has been successfully applied to a number of oxides /1/. However, the effectivity of this toughening mechanism decreases with increasing temperature, becoming ineffective at $T > \sim 700^\circ\text{C}$. Fiber reinforcement offers the opportunity to achieve valuable strength and toughness improvements both at low and high temperatures. This has been demonstrated mainly with glass and glass ceramic matrices /2/. For high-strength crystalline oxides, whiskers are a better choice than fibers because of their ability to survive the severe hot-pressing conditions necessary for incorporation into ceramic matrices /3-5/. The whiskers presently available have diameters of the same order of magnitude as the grain size of most of the strong oxides, their strengths and Young's moduli are much higher than those of the fibers, there are no out-gassing nor grain-growth problems as associated with fibers /6/ and normal ceramic powder processing can be applied without thermally and mechanically degrading the whisker properties /7/.

Another attraction of introducing whiskers is the prospect of increasing the room temperature strength of some transformation

toughened materials, especially tetragonal ZrO_2 polycrystals (TZP) and PSZ, where the strength is not controlled by the largest flaw but by the mean critical stress required to initiate the transformation [8,9]. This is schematically indicated in Fig. 1. E.g., Ce-TZP/10/ with a toughness of $\sim 500 \text{ MPa}\sqrt{\text{m}}$ and a strength of only $\sim 500 \text{ MPa}$ (right side of strength / toughness area) could be considerably strengthened by the incorporation of whiskers without loss in tough-

Fig. 1 - Schematic diagram of strength-toughness relation in TZP ceramics. The numbers represent the approximate range of values anticipated for 2-4 mole % Y_2O_3 -TZP.

ness. On the other hand, fine-grained, high-strength TZP could be toughened by the whiskers, however, with some loss in strength if the thermal mismatch between whiskers and the TZP matrix produces tensile stresses in the matrix [11].

The intent of the present work was to investigate possible preparation techniques to achieve a homogeneous whisker distribution and to study the effect of thermal mismatch on toughness and strength, mainly of ZrO_2 - containing oxides. SiC whiskers were used in most cases.

II - EXPERIMENTAL PROCEDURE

For most experiments in the present work, SiC whiskers of grade SCW-1 ("separated and dispersion improved") from Tateho Chem. Ind., Kariya, Japan, were used. The property data given for these whiskers by the supplier are a composition of $\sim 95\%$ β -SiC, an impurity content (%) of 0.15 Mg, 0.25 Ca, 0.31 Al, 0.04 Fe, a range of diameters from 0.06 to 0.2 μm and a range of lengths from 10 to 40 μm . Because the lot also contained larger SiC particles ($> 5 \mu\text{m}$), the whiskers were first ultrasonically dispersed in isopropanol and deagglomerated in a tumbling mixer with plastic balls (3 mm ϕ) for 24 h. Thereafter, most of the fragments $> 5 \mu\text{m}$ were eliminated by sedimentation. In two exploratory experiments were Al_2O_3 whiskers (Thermokinetics, Washington, D.C.) and Si_3N_4 whiskers (SNW-1, Tateho) incorporated into TZP and cordierite.

The ceramic matrix powders used for the oxide ceramic/whisker composites are given in Table 1. The cordierite is an experimental, fully crystallized powder which is readily sinterable. The other materials are well-characterized standard grades.

Table 1: Ceramic powders used for the whisker composites

Ceramic	Type	Supplier
Al ₂ O ₃	A16	Alcoa, USA
Mullite	Dynamullite (fused)	Dynamit-Nobel, FRG
Cordierite	experimental	Schott Glaswerke, FRG
m-ZrO ₂	SC 20	MEL, U.K.
t-ZrO ₂	TSK 3 (3 mole % Y ₂ O ₃)	Toyo Soda, Japan

Fig. 2 - Processing of the whisker Composites .

The processing of the composites is summarized in Fig. 2. All matrix compositions with and without ZrO₂ additions were attrition milled for 2 h in isopropanol using TZP balls for the Al₂O₃ and cordierite composites and Al₂O₃-SiO₂ balls for the TZP and mullite composites. The whisker powder slurries were then tumble mixed with 3 mm plastic balls. In most cases, the mixtures were dried in a rotovap dryer followed by uniaxial hot-pressing in BN-washed graphite dies. The hot-pressing conditions were 30 min. at 1550°C for Al₂O₃, 30 min. at 1600°C for mullite, 10 min. at 1300°C for cordierite and 10 min. at 1450°C for TZP composites. In a few experiments, extrusion through a hypodermic syringe with a 1 mm orifice was tested with a plasticized mullite/whisker mixture as a mean of achieving uniaxial alignment of the whiskers. In this case, packages of aligned extruded rods were hot-pressed (Fig. 3).

The hot-pressed discs (35 mm in dia., 10 mm thick) were cut into rectangular bend bars (30 x 30 x 2.5 mm). The fracture toughness was measured by the ISB technique in 4-point bending. Controlled flaws were introduced by Vickers indentation with loads of between 10 and 1250 N. The fracture strength was measured in 4-point bending (20/7 mm), the orientation being such that the tensile surface was perpendicular to the HP direction. Six specimens were tested for each set of conditions.

The fracture surfaces were analyzed by SEM, and the microstructure was examined by TEM and STEM.

Fig. 3 - Schematic of uniaxial alignment of whiskers by hot-pressing packages of extruded ceramic whisker rods.

III - RESULTS AND DISCUSSION

The processing conditions used resulted in almost theoretically dense composites with very homogeneous distribution of the whiskers. The preferred long-axis orientation of the whiskers was on planes perpendicular to the hot-pressing direction (whisker-plane). The overview optical micrograph in Fig. 4a shows a whisker plane in a 10 vol. % ZrO_2 mullite composite with 20 vol. % SiC whiskers. The TEM overview of a 30 vol. % SiC whisker/TZP material (Fig. 4b) also demonstrates the homogeneity of the whisker distribution [11]. Fracture of whiskers was rarely observed. Reactions between the SiC whiskers and the ceramic matrices studied could not be detected, as was also the case for Al_2O_3 whiskers in TZP. Si_3N_4 whiskers, however, reacted severely with ZrO_2 -containing materials.

Results obtained with the various oxide matrix/SiC whisker systems are discussed in the following paragraphs.

Fig. 4 - Microsections of "whisker planes" in
a) 10 vol. % ZrO_2 mullite composite with 30 vol. % SiC whiskers (LM)
and b) TZP/30 vol. % SiC whisker composite (TEM).

a) Al₂O₃/SiC whisker composites

Table 2 lists strength and toughness data obtained at room temperature. For comparison, data from Ref. 12 are also included. The latter values, however, were obtained with different materials under different hot-pressing conditions.

Table 2: Strength and toughness of Al₂O₃/SiC whisker composites.

No.	Composition, vol.% Matrix	Whisker	K _{IC} MPa√m	Strength MPa
1	Al ₂ O ₃		4.7	520
2	Al ₂ O ₃	+ 20 SiC	8.5**	650*
3	Al ₂ O ₃ +15 t-ZrO ₂		6.2	1080**
4	(Al ₂ O ₃ +15 t-ZrO ₂)	+ 20 SiC	13.5+	~700
5	Al ₂ O ₃ +40 m-ZrO ₂		2	-
6	(Al ₂ O ₃ +40 m-ZrO ₂)	+ 20 SiC	8.5	880
7	m-ZrO ₂		< 1	-
8	m-ZrO ₂	+ 20 SiC	9.0**	n.d.

* data from Ref. 12, ** sample HIPped at 1600°C for 10 min.

+ annealed at 1500°C in Ar for 24h,

++ determined from indentation crack lengths.

The addition of t-ZrO₂ to Al₂O₃ is more effective in increasing the strength than the toughness, a feature which is due to the refined microstructure /13/. On the other hand, whisker reinforcement results in remarkable toughness enhancement, although the strength increase is less pronounced. This fact can be explained by the high tensile matrix stresses due to the thermal mismatch between Al₂O₃ ($\alpha_m = 8.5 \text{ MK}^{-1}$) and SiC ($\alpha_w = 4.7 \text{ MK}^{-1}$). An average value of 485 MPa for these stresses may be estimated /4/. In addition, the effect of a larger critical flaw size due to some whisker clustering has to be considered.

The combination of the two toughening methods (No 4 in Table 2) yields a toughness increase (~ 9.0 MPa√m) which is much more than the sum of the two single toughness increments (see Table 2, No 2: 3.8 MPa√m and No 3: 1.5 MPa√m). Hence, the existence of a positive interaction between transformation toughening and whisker reinforcement appears to be evidenced by the results.

The same arguments as for the No 2 composite apply to the strength of the No 4 composite. Further increases in strength should be possible by reducing the thermal mismatch stresses, e.g., by introducing Al₂O₃ whiskers or by utilizing the phase transformation (see chapter IV).

SEM evaluation of the fracture surfaces suggests crack deflection as the main whisker toughening mechanism. Pull-out was rarely observed.

b) mullite/SiC whisker composites

Room temperature strength and toughness data are given in Table 3. In mullite composites, whisker and ZrO₂ toughening appear to be additive. There is no obvious additional interaction effect. Since the thermal mismatch is negligible between mullite and SiC, the strength and K_{IC} are improved to the same degree. The relatively low strength of the aligned whisker composites (Nos. 6 and 7 in Table 3, Fig. 5), may be explained by the fact that stress singularities at strongly bonded whiskers can lead to premature failure and that crack deflection is less effective as a mechanism if the crack plane is perpendi-

cular to the whiskers. At high temperature, when whisker pull-out may become effective due to interface softening, the aligned composites may exhibit superior strengths.

Table 3: Strength and toughness of mullite/SiC whisker composites.

No	Composition, vol. % Matrix	Whisker	K_{Ic} , $MPa\sqrt{m}$	Strength, MPa
1	Mullite		2.8	244
2	Mullite + 10ZrO ₂		3.5	
3	Mullite	+ 20 SiC	4.4	452
4	(Mullite + 10ZrO ₂)	+ 20 SiC	5.4	580
5	(Mullite + 10ZrO ₂)	+ 30 SiC	6.7	551
6	Mullite	+ 10 SiC	4.1	277
7	Mullite	+ 20 SiC	4.6	407

Fig. 5 - Mullite/10 vol. % SiC whisker composite extruded through a 1 mm orifice of a hypodermic syringe.

a) SEM fractograph of the green extruded rod and
b) microsection of the "whisker plane".

c) Cordierite/SiC whisker composites

Table 4 gives some preliminary K_{Ic} and strength results obtained at room temperature and at 1000°C.

Table 4: Strength and toughness of cordierite/SiC whisker composites.

No	Composition, vol. % Matrix	Whisker	K_{Ic} , $MPa\sqrt{m}$ RT	Strength, MPa RT	1000°C
1*	Cordierite		2.2	180	170
2	Cordierite + 20 ZrO ₂		n.d.	190	160
3*	Cordierite	+ 20 SiC	3.7	260	245
4	(Cordierite + 20 ZrO ₂)	+ 20 SiC	n.d.	380	300

* Hot pressed at 1250°C for 30 min.

The favorable thermal mismatch becomes obvious from the greatly improved strength of the whisker composites. The higher strength of composite No 4 when compared to that of No 3 is partly due to the enhanced densification behaviour associated with ZrO₂ dispersions in cordierite.

(d) TZP/SiC whisker composites

The TZP matrix consisted of tetragonal grains, typically $< 0.5 \mu\text{m}$ in size, this microstructure being a result of the short time and low temperature of the hot-pressing. No crystalline phases were detected other than t-ZrO_2 and SiC. An amorphous phase at the whisker matrix interface, 1-5 nm thick, was observed in TEM [11]. In some cases, glassy pockets had formed adjacent to the whiskers (Fig. 6).

Fig. 6 - Dark-field TEM of SiC whisker/TZP composite showing glass pockets (g) near radial whisker cross section.

Table 5: Strength and toughness of TZP/SiC whisker composites.

No	Composition, vol. % Matrix	Whisker	K_{IC} , $\text{MPa}\sqrt{\text{m}}$	Strength, MPa	
			RT	RT	1000°C
1	3Y-TZP		6.8	1150	160
2	3Y-TZP	+ 20 SiC	10.2	600	340
3	3Y-TZP	+ 30 SiC	11.0	590	380

The toughness values and strengths of 3Y-TZP with 0, 20 and 30 vol. % SiC whiskers are given in Table 5. The matrix shows the characteristic properties of high-strength TZP with relatively low toughness. The latter may be attributed to the small size of the t-ZrO_2 grains which prevents their transforming on stress loading. Thus, the increase in fracture toughness of the whisker composites is assumed to originate from the whiskers where crack deflection appears to be the dominant toughening mechanism.

Whisker debonding and pull-out at room-temperature was rarely observed, probably due to the strong interfacial bonding, and so did not contribute much to the toughening. The bond strength may result from chemical bonding, thermal mismatch strains and interfacial roughness. Only in cases where the whiskers were nearly parallel to the fracture plane did some debonding take place. In all cases, the matrix fracture was predominantly intergranular.

Fig. 7 - Flexural strength of TZP with and without SiC-whisker reinforcement. Thermal mismatch stresses reduce the strength at RT, while modulus load transfer becomes effective at 1000°C.

The fracture strength is reduced to almost half the TZP matrix strength by the incorporation of whiskers because of the high tensile matrix stresses due to the thermal mismatch ($\alpha_{TZP} = 11 \text{ MK}^{-1}$).

The situation is markedly different at high temperatures. At 1000°C, the strength of the whisker composite is nearly twice that of the TZP matrix (Fig. 7). The thermal mismatch stresses are much lower than at room temperature and the interfacial layer has softened to the extent that some whisker pull-out (Fig. 8) can take place.

Fig. 8 - Scanning electron micrographs of TZP/30 vol. % whisker composites fractured at 1000°C. Some debonding and pull-out occurred.

In samples annealed for 120 h at 1030°C in air, the thickness of the amorphous layer increased drastically at the interface ($\sim 50 \text{ nm}$, Fig. 9) and between the TZP grains near SiC whiskers. Besides Si and Zr, the glasses phase contained Y and some Al. The formation of ZrSiO_4 was not observed. Furthermore, most of the grains close to the whiskers were transformed to m symmetry with microcracks along the grain boundaries. This can be explained by the oxidation of SiC whiskers under the annealing conditions contributing to the amorphous silicate phase and by dissolution of Y_2O_3 into the glassy phase, leading to Y-depletion of the t- ZrO_2 grains which then easily transform. Microcracking is then caused by the transformation and possibly by some CO pressure build-up.

Fig. 9 - TZP-30 vol. % SiC-whisker composite annealed for 120 h at 1030°C in air. The glassy interface layer is ~ 50 nm thick (g). Almost all grains have transformed to monoclinic symmetry. Some microcracks (mc) are visible.

IV - CONTROL OF THERMAL MISMATCH

In oxide ceramics with coefficients of expansion larger than that of SiC, thermal mismatch stresses are produced on cooling the composite from the preparation temperature which can considerably decrease the strength. These detrimental stresses, however, can be reduced by utilizing a proper amount of thermally transformable ZrO_2 . The principle of controlling the thermal mismatch stresses by this method is explained in Fig. 10. This schematic diagram shows the temperature dependence of the average residual matrix stresses without (v_0) and with (v_1, v_2) two different volume fractions of transformable ZrO_2 . The matrix stresses in the composite without transformable ZrO_2 ; i.e., containing only retained t- ZrO_2 , are tensile at room temperature for $\alpha_m > \alpha_w$, while the stresses at v_1 are just balanced and those at v_2 are compressive. The average matrix stresses at $T < M_f$ (martensite finish temperature, ~ 700°C) can be estimated from:

$$\sigma_{mT} = \frac{[(\alpha_m - \alpha_w)(T_g - T) - \epsilon^T_v] E_w w}{1 + w (E_w/E_m - 1)}$$

where E_m (~ 400 GPa) and E_w (~ 580 GPa) are the matrix (Al_2O_3 - ZrO_2) and whisker (SiC) Young's moduli, w is the whisker volume fraction and T_g (~ 1200°C) the temperature below which interfacial relaxation no longer takes place. ϵ^T_v is the dilational transformation strain.

The method was tested with composite No 6 (Table 2). While a whisker-free Al_2O_3 with 40 vol. % m- ZrO_2 (No 5) was heavily cracked due to the large volume change (~ 5 %) associated with the zirconia transformation, the same system when used as matrix with 20 vol. % SiC whiskers exhibited both high K_{IC} and strength. Since the two-phase matrix is not transformation toughened, the enhanced performance, especially in strength, has to be attributed to the reduced thermal mismatch stresses in the matrix. The residual stress in the No 6 composite is -190 MPa, hence compressive. Even composites consisting of m- ZrO_2 as the only matrix phase could, with 20 vol. % SiC whiskers, be fabricated with high toughness (No 8).

Fig. 10 - 1) Schematic dilatometer curve of a whisker composite without (v_0) and with two different volume fractions of thermally transformable ZrO_2 (v_1 , v_2).

b) Average residual matrix stresses in the whisker composite for $\alpha_m > \alpha_w$. M_S and M_F are the martensite start and finish temperature, A_S the austenite start temperature.

V - CONCLUSIONS

1. The thermal mismatch stresses strongly affect the strength of the composites, e.g. the room-temperature strength of TZP is reduced, while that of mullite and cordierite based composites is increased by the incorporation of SiC whiskers. The strength at 1000°C of TZP and cordierite was considerably enhanced by the incorporation of SiC whiskers.
2. The fracture toughness of all oxide ceramics studied was enhanced by the incorporation of SiC whiskers. The dominant toughening mechanism appears to be a crack deflection.
3. An additional toughness contribution may result from the interaction of the stress-induced transformation and the whisker reinforcement.
4. The thermal mismatch stresses in TZP- and Al_2O_3 -based composites can be reduced by adding an appropriate amount of thermally transformable ZrO_2 .

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