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The Effect of Heat-Treatment on the Performance of Submicron SiCp-Reinforced α-β Sialon Composites: III. Mechanical Properties

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Abstract

Agglomerate-free SiCp-reinforced Ln-sialon (Ln=Nd and Yb) composites were fabricated by hot-pressing and by pressureless sintering to evaluate the improvement in microstructure and mechanical properties that could be achieved by incorporating sub-micron SiC particles into a sialon matrix and then inducing α → β sialon transformation by heat-treatment. Both Nd_2O_3 and Yb_2O_3 were successful in producing dense samples by hot-pressing, but Yb_2O_3 produced a more stable α-sialon phase than Nd_2O_3. As a result, Yb-sialon/SiCp composites showed higher hardness (H_v), attributable to the higher percentage of α-sialon grains (formed in acicular morphology) in these materials. Under comparable heat-treatment conditions, the α-sialon phase present in Nd-sialon/SiCp composites was very unstable and almost completely transformed to β-sialon, with the aluminium-containing melilite phase (M') forming at pockets in grain junctions as the dominant grain-boundary phase. Even though the Nd-densified samples contained a large proportion of β-sialon, the fracture toughness(K_{Ic}) was not significantly improved by SiCp addition because of the decrease in aspect ratio and the coalescence of grains caused by the longer heat-treatment which resulted in degradation of mechanical properties, especially K_{Ic}. © 1997 Elsevier Science Limited. All rights reserved.

1 Introduction

Strengthening, toughening and hardening mechanisms and the relationship between microstructure and properties are important topics in current research programmes on ceramic matrix composites. It is now well-established that the selection of starting composition/starting materials and choice of processing route are the key parameters in determining the content, grain size and grain shape of the various components in the final microstructure, which in turn define the extent to which mechanical properties are improved. Previous investigations of $Si_3N_4SiC_p$ composites show that a Si_3N_4 matrix can be significantly reinforced by a dispersion of sub-micron SiC particles[1–6] because the latter allow very complex fracture paths compared to the monolithic ceramic. Moreover, the use of small second-phase particles does not lead to loss in strength of the composite—indeed, in some cases noticeable strength increases can be achieved.[7,8] The sintering temperature of silicon carbide is higher than that of the composite, so the SiC particles retain small grain sizes and remain well-dispersed throughout the matrix during sintering; in addition, it is possible to create effective local stresses in the matrix during cooling from the sintering temperature due to the mismatch in thermal expansion coefficients between Si_3N_4 and SiC. Finally, coherent bonding exists but with little chemical reaction between the SiC particles and the Si_3N_4 matrix in the final composites.

Sialon-based compositions offer significant advantages over silicon nitride as regards ease of sintering and improved control of properties by optimisation of α:β sialon ratio. For example, a high hardness α-sialon ceramic can be toughened and strengthened by the incorporation of high aspect-ratio, acicular, β-sialon grains. In the present study, agglomerate-free SiCp-reinforced α-β sialon composites were prepared and the change in microstructure and properties identified when the matrix phase was taken through α-β sialon transformation. Previous papers in this series have described the powder preparation[9] and heat-treatment behaviour[10] of mixed α-β sialon ceramics densified with neodymium and ytterbium. The first paper demonstrated that by using a surfactant (polyethylene glycol in alcoholic solution), it was

possible to effectively disperse sub-micron SiC grains within the sialon matrix without agglomeration; the second paper discussed the effect of the SiC grains on both the microstructure and the $\alpha \to \beta$ sialon transformation after extended heat-treatment at 1450°C. The present paper is concerned with the effect of these microstructural changes on selected mechanical properties (hardness, fracture toughness) of the final materials.

2 Experimental Procedure

Starting powder mixes corresponding to $m=1$, $n=1.7$ α-sialon compositions with Nd and Yb as the densifying additives were prepared as described previously.[9] The compacted powders were then hot-pressed at 1800°C for 45 min at 30 MPa pressure; in addition the Nd-containing composition was also pressureless sintered in a carbon resistance furnace at 1800°C for 2 h under a protective nitrogen atmosphere. Post-sintering heat-treatments were then carried out in an alumina tube furnace in flowing nitrogen at 1450°C for either one or four days. Densities were measured by immersion in mercury using Archimedes' principle. Phase identification was carried out by X-ray diffraction, using a Hägg-Guinier focusing camera and $CuK\alpha_1$ radiation; the intensities of the (102) and (210) peaks of α' and the (101) and (210) peaks of β' were used for determination of $\alpha:\beta$ phase ratio.[11] TEM and SEM studies of microstructure were carried out using a JEOL 200CX Transmission Electron Microscope and a Camscan S4-80DV Scanning Electron Microscope respectively, the latter equipped with EDX facilities. Details of TEM preparation have been given elsewhere.[10] Measurement of hardness and fracture toughness were made by indentation using a pyramidal indenter and applying a 10 kg load for 10 s.[12]

3 Results and Discussion

3.1 Dispersion of SiC particles in the matrix

Figure 1 (b) shows that unless care is exercised in the incorporation of sub-micron SiC powders into the sialon composites, serious agglomeration of the SiC grains can occur. In this case, the SiC particles had been suspended in isopropanol to which PEG surfactant had been added, and the mixed oxides and nitrides comprising the sialon mix had been suspended in separate alcoholic solutions. Agglomeration occurred when the two solutions were dried separately and the resulting powders then mixed. Successfully deagglomerated powders were obtained when the two suspensions were mixed and the whole solution carefully dried (see Fig. 1(a)). More details of this work have been discussed elsewhere.[9]
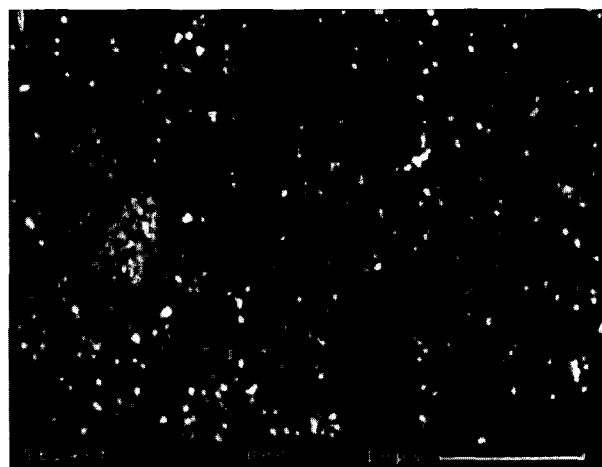
(a)
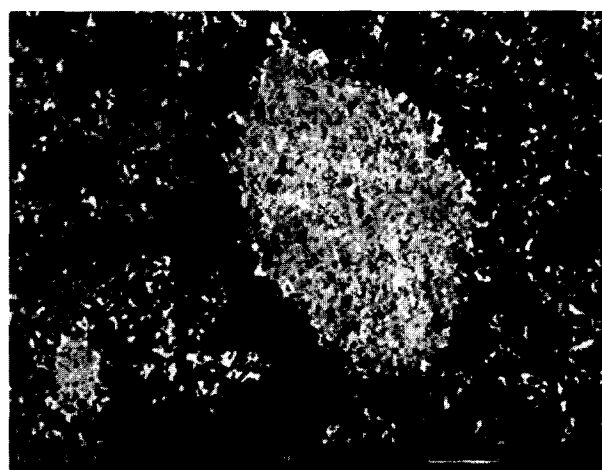
(b)

Fig. 1. Dispersion of SiC particles in a sialon matrix, (a) well-dispersed SiC_p in a Yb-sialon/SiC_p composite containing 10 wt% SiC and (b) seriously agglomerated SiC_p in a Nd-sialon/SiC_p sample containing 10 wt% SiC.

3.2 Properties and phase stability of sintered SiC_p/Ln-Sialon composites

Dense, agglomerate-free Ln-sialon/SiC_p composites were obtained by hot-pressing at 1800°C for 45 min. Similar samples were prepared by pressureless sintering under similar conditions, but these samples gave lower densities. Various properties of these composites are listed in Tables 1 and 2.

From the tables it can be seen that Yb_2O_3-densified materials had higher densities than Nd_2O_3-densified ones, but this is almost totally due to the higher molecular weight of the former. Also, the higher density of α-sialon, compared with an equivalent mixture of β-sialon plus glass gives some density advantage. The microstructure of the Yb-sialon/SiC_p composites consisted of equiaxed α-sialon grains with very little grain-boundary phase in the form of Yb-garnet and Yb-J-phase plus some residual glass. On adding silicon carbide, densities decreased with increasing SiC content, partly due to the lower density of SiC and

Table 1. Properties and β: α sialon ratio in Nd-sialon/SiC$_p$ composites

| | | 0 wt% SiC$_p$ | | 10 wt% SiC$_p$ | | 20 wt% SiC$_p$ | |
		Before HT^a	After HT	Before HT	After HT	Before HT	After HT
d	HPS^b	3.354	3.334*3.274**	3.332	3.288*3.314**	3.296	3.301*3.281*
(g/cm^3)	PLS^c	3.165	3.161*	3.138	3.124*	2.890	2.823*
H_{v10}	HPS	17.78	17.43*15.89**	19.10	18.17*17.58**	22.25	19.26*19.73*
(GPa)	PLS	14.88	13.71*	14.33	14.00*	13.03	13.00*
K_{IC}	HPS	7.19	6.34*5.40**	5.24	6.46*5.16**	5.53	6.41*5.54**
(MPa m$^{1/2}$)	PLS	6.87	6.80*	6.16	6.04	5.38	5.16*
β/α	HPS	55/45	66/34*100/0**	52/48	74/26*100/0**	53/47	82/18*91/9*
	PLS	27/73	47/53*	28/72	50/50*	35/65	25/75*

^{a} HT = heat treatment, 1450°C, * — 24 h; ** — 96 h.
^{b} HPS = hot-pressed sintered.
^{c} PLS = pressureless sintered.

Table 2. Properties and β:α sialon ratio in Yb-sialon/SIC$_p$ composites

| | 0 wt% SiC$_p$ | | 10 wt% SiC$_p$ | | 20 wt% SiC$_p$ | |
	HPS	After HT	HPS	After HT	HPS	After HT
d (g/cm^3)	3.418	3.412* 3.387**	3.394	3.381*3.385**	3.369	3.331*3.288**
H_{v10} (GPa)	21.53	21.17* 21.85**	21.81	21.67*23.70**	22.30	22.15*23.61**
K_{IC} (MPa m$^{1/2}$)	5.04	4.94*4.54**	4.93	4.59*5.40**	4.57	4.50*5.27**
β/α	6/94	12/88*10/90**	10/90	19/81*20/80**	6/94	15/85*12/88**

^{a} HT = heat treatment, 1450°C, * — 24 h; ** — 96 h.
^{b} HPS = hot-pressed sintered.
^{c} PLS = pressureless sintered.

also due to the relatively inert SiC grains tending to hinder densification processes. The table shows that the samples become harder on adding SiC particles partly because of the intrinsically higher hardness of SiC compared to α-sialon, but also because the grains of SiC are well-bonded to sialon grains. For the Nd-sialon/SiC$_p$ composites, the β:α sialon ratio is much higher than for the Yb samples, (basically slightly larger than 50:50); the M' (melilite) phase[13–16] remains as the dominant crystalline phase at grain boundaries plus some glassy phase, and therefore these composites possess higher toughness but lower hardness than Yb-doped materials. In contrast, pressureless-sintered samples show lower hardnesses even when SiC particles are present in the matrix because of residual porosity due to SiC grains interfering with sintering processes. Moreover, large amounts of glassy phase remained in the grain boundaries in the pressureless-sintered samples; this is another reason why the samples exhibited reduced hardness.

3.3 Effects of heat-treatment on mechanical properties
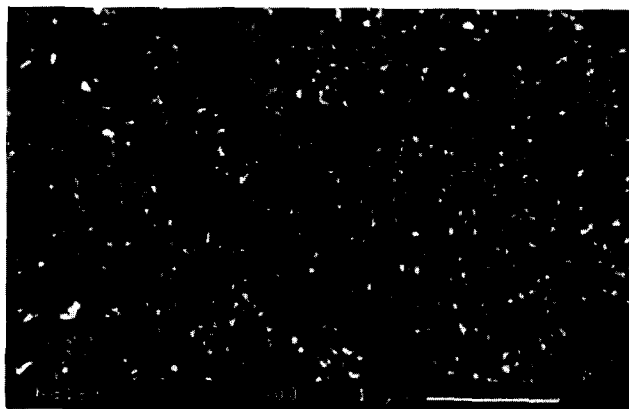
All samples sintered at 1800°C were heat-treated at 1450°C in flowing nitrogen for 24 and 96 h. Nd- and Yb-sialon/SiC$_p$ composites gave quite different responses to the heat-treatment. In both cases, the grain boundaries were essentially fully crystallised after the first 24 h of heat-treatment (as shown by X-ray diffraction and selected area electron diffraction), with slightly different crystalline phases occurring in the two systems. However, the main difference is that in the Yb-densified sample, relatively small amounts of $\alpha \rightarrow \beta$ sialon transformation occur, whereas in the Nd-densified system much more $\alpha \rightarrow \beta$ transformation occurs with consequent changes in the microstructure. The second paper in the present series has summarised in some detail the microstructural changes that take place when these samples are heat-treated.[10] The present paper focuses on the changes in mechanical properties that arise from these heat-treatments.
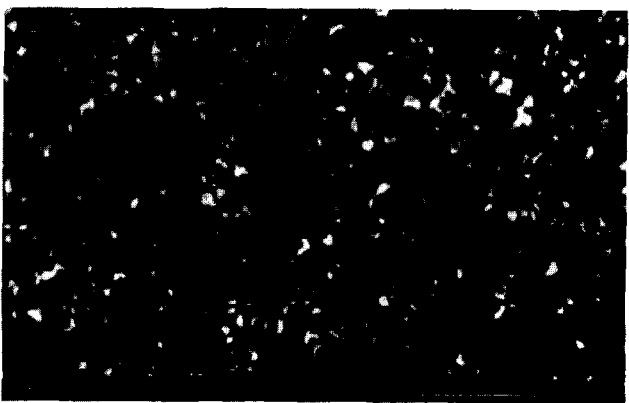
3.3.1 Nd-sialon/SiC$_p$ composites

Experiments showed that in both systems, $\alpha \rightarrow \beta$ sialon transformation occurred, to an extent determined by the temperature, time, type of additive and the amount of SiC$_p$ added, and in Nd-densified samples, almost total transformation from α-sialon to β-sialon always occurred, accompanied by the formation of large amounts of grain-boundary material, mainly in the form of the M' (melilite) phase accompanied by some

residual glass. Addition of SiC particles promoted an increase in % β-sialon, possibly because the additional silica on the surface of the SiC resulted in generation of increased amounts of liquid. However, what was surprising was that the K_{Ic} values did not improve significantly as a result of heat-treatment, either for the hot-pressed or pressureless sintered materials; the values of K_{Ic} before heat-treatment were high due to the existing network of large β needles but even though the amount of β formed during heat-treatment increased, the aspect ratio did not significantly increase beyond a certain value. Instead, grain growth occurred and continued up to the end of the heat-treatment process, influenced by coalescence of grains and also the increased liquid content.[17-19] Figure 2 illustrates the change in β-sialon grain morphology in Nd-sialon/SiC$_p$ before and after heat treatment; here the fibre-like grains are β phase, but some pores (dark) remain on the surface of samples, arising because of weight loss after the longer heat-treatment history. It would appear that the SiC grains interfere with the growth of β grains during heat-treatment; clearly the saturation in aspect ratio prevents an increase

in fracture toughness compared with the as-sintered materials.

3.3.2 Yb-sialon/SiC$_p$ composites

As mentioned above, Yb$_2$O$_3$ is equally effective as a densifying additive for sialon composites but is more useful for stabilising α-sialon than Nd$_2$O$_3$. Table 2 shows the change in properties of these samples before and after heat-treatment. After a longer time of heat-treatment, only a few percent of α-sialon transformed to β-sialon partly due to the absence of grain-boundary liquid, partly due to the absence of β-sialon grains which aid nucleation, and partly because of the inherent higher stability of the α-sialon phase in this system, as compared with the Nd-sialon/SiC$_p$ system, the α-sialon remaining in the form of fairly equiaxed grains. In addition, after four days of heat-treatment, glassy phase at grain boundaries was nearly fully crystallised to Yb-garnet and Yb-J phases (as deduced from analysis of electron diffraction patterns), so the average H_v values increased gradually. In contrast, the K_{Ic} values for these compos-

(a)

(b)

Fig. 2. Change in β-sialon grain morphology in Nd-sialon/SiC$_p$ composites (a) before and (b) after a four-day heat-treatment of 1450°C.
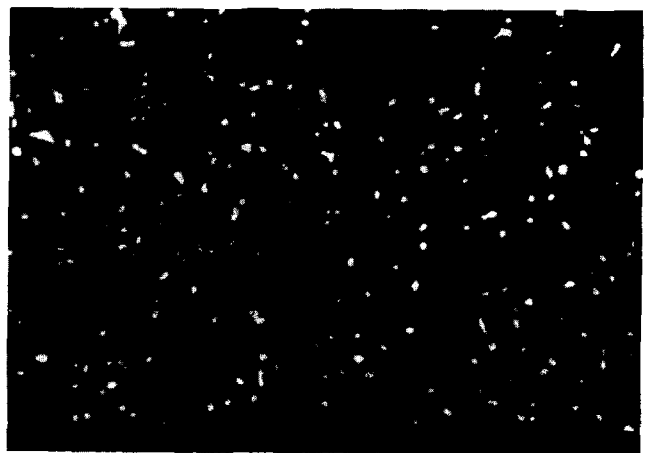

(a)

(b)

Fig. 3. Change in β-sialon grain morphology in Yb-sialon/SiC$_p$ composites (a) before and (b) after four-day heat-treatment at 1450°C.

ites remained constant, independent of the time of heat-treatment and the volume fraction of SiC particles, even though SiC particles were well dispersed in the matrix. From the SEM observations, it was also found that the aspect ratio of β' grains decreased and coalescence of small β' grains took place during heat treatment. The change in β-sialon morphology is not beneficial to the improvement of K_{Ic} as it degrades the in-situ reinforcement of fibre-like β-sialon grains. The changes in β-sialon grain morphology are shown in Fig. 3.

Considering the effect of added SiC particles on the transformation and properties, it was found that the β:α ratio decreased with increasing SiC$_p$ content up to 20 wt%, more noticeably after the longer period of heat-treatment. In our previous paper[10] it was reported that sub-micron SiC particles are mainly located at grain boundaries. As microcracks propagate along the grain boundaries, SiC particles sited there may stop or deflect the microcracks in other directions (shown in Fig. 4), so that they also contribute towards a mechanism of adsorption of fracture energy and hence affect K_{Ic}. However K_{Ic} values are less strongly influenced by adding SiC$_p$ than by the change in β grain morphology. Since the $\alpha \rightarrow \beta$ sialon transformation is via a solution-diffusion-precipitation route, the SiC particles sited at the boundaries interfere with the solution-reprecipitation process and in particular interfere with the growth of β grains and other crystallisation processes involving liquid phase.[20] Despite the low value of K_{Ic}, the SiC grains and the high proportion of equiaxed α-sialon grains combine to give good hardness for these materials.

4 Conclusions

(1) Nd- and Yb-sialon/SiC$_p$ composites exhibit very different responses to heat-treatment,

which allows easy evaluation of the effect of differences in microstructure on mechanical properties achieved by long heat-treatments of the two materials.

(2) Yb$_2$O$_3$ is equally good as an additive for densifying the composites and is more efficient for stabilising the α-sialon structure than Nd$_2$O$_3$. As a result, Yb-sialon/SiC$_p$ materials possess higher hardness because of the high proportion of equiaxed α-sialon grains in these composites.

(3) α-Sialon is very unstable in the Nd-sialon/SiC$_p$ system on heat-treatment at 1450°C. Under the same conditions of heat-treatment as in Yb$_2$O$_3$-doped samples, Nd-α-sialon almost completely transformed to β-sialon with aluminum-containing melilite (M') left at pockets of grain junctions as the dominant grain-boundary phase. Higher K_{Ic} values are observed in this system compared with the Yb-system.

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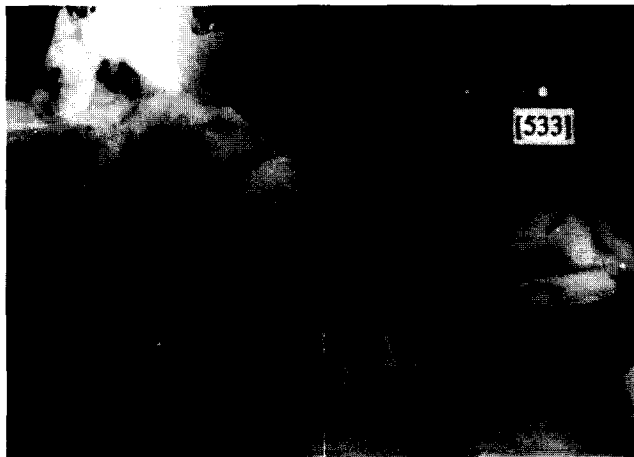

Fig. 4. Dispersion of SiC particles in the Yb-sialon sample. Larger SiC particles are located at grain boundaries and smaller ones in sialon grains as indicated by arrows. Inserted is the diffraction pattern of the Yb-garnet grain boundary phase.

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