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Materials Chemistry and Physics 48 (1997) 156–159

MATERIALS
CHEMISTRY AND
PHYSICS

The coarsening behavior of duplex $Al_2O_3/NiAl_2O_4$ composites

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Received 6 October 1995; accepted 4 January 1996

Abstract

In the present study, the grain growth behavior of $Al_2O_3/NiAl_2O_4$ composite is compared with that of Al_2O_3 and of $NiAl_2O_4$. Duplex $Al_2O_3/NiAl_2O_4$ composite shows strong resistance to coarsening. The activation energy for the grain growth of monolithic Al_2O_3 is the same as that of Al_2O_3 in composite. However, the activation energy for the grain growth of $NiAl_2O_4$ is changed as $NiAl_2O_4$ is surrounded by Al_2O_3. The shape of Al_2O_3 grains in composite is also different from that of Al_2O_3 in monolithic alumina. The coarsening of one phase in the composite is thus constrained by the presence of another phase.

Keywords: Duplex composite; Coarsening; Activation energy

1. Introduction

Ceramics exhibit superior hardness, chemical stability and high temperature strength. However, they suffer from poor toughness at room temperature. The application of ceramics under ambient conditions is therefore limited. Nevertheless, the potential of applying ceramics at high temperature is very high because of their high melting points and superb oxidation resistance. As ceramics are used at elevated temperature, grain growth may take place at the same time. It can seriously degrade the performance of ceramics. Therefore, the microstructural stability at high temperature for ceramics is essential for high temperature applications.

The presence of a small amount of second phase slows down the coarsening of matrix grains [1]. Recent studies have suggested that the coarsening of $50\%Al_2O_3/50\%ZrO_2$ composite is dramatically slower than that of monolithic ceramics and of composites containing less second phase [2,3]. The potential of duplex composites for elevated temperature applications is therefore worth noting. The mutual solubility between Al_2O_3 and ZrO_2 is limited. The coarsening resistance of the duplex Al_2O_3/ZrO_2 composite has been attributed to the physical constraint (due to the space-filling requirement) [3], the change of coordination number and of dihedral angle [2]. The mutual solubility of $Al_2O_3/NiAl_2O_4$ system is higher than that of Al_2O_3/ZrO_2 system [4]. For example, the solubility of Al_2O_3 in $NiAl_2O_4$ increases by 10 mol.% from 1000 to 1700°C. In the present study, the grain growth behavior of duplex $Al_2O_3/NiAl_2O_4$ composite during sintering is investigated. Furthermore, the process conditions to prepare dense $Al_2O_3/NiAl_2O_4$ composite are proposed.

2. Experimental

Duplex $Al_2O_3/NiAl_2O_4$ composites and monolithic $NiAl_2O_4$ specimens were prepared by reaction sintering Al_2O_3 and NiO powder mixtures [5]. Alpha alumina (TM-DR, Taimei Chem. Co. Ltd., Tokyo, Japan, particle size ≈ 0.2 μm) and 0, 25 and 50 mol.% nickel oxide (Johnson Matthey Co., USA, particle size ≈ 16 μm) were ball milled in alcohol for 4 h with zirconia balls. The slurry was dried with a rotary evaporator. The dried lumps were crushed and passed through a plastic sieve. Powder compacts were first formed by uniaxial pressing at 18 MPa, then by cold isostatic pressing (CIP) at 250 MPa. Sintering was performed in a box furnace at 1500–1700°C in air. Sintering was also performed in a dilatometer (differential dilatometer, Theta Co., USA) that allowed continuous monitoring of the shrinkage kinetics. The heating rate was kept constant as $5°C\ min^{-1}$.

Phases were identified on fired powder compacts by X-ray diffractometry (XRD). The final density was determined by the water displacement method. Before the specimens were submerged in water, a wax was applied to the surface to prevent water penetration. The theoretical densities of composites were calculated from the theoretical density for alumina of $3980\ kg\ m^{-3}$, for nickel oxide of $6800\ kg\ m^{-3}$, and for nickel aluminate spinel of $4000\ kg\ m^{-3}$. The polished

PII S0254-0584(96)01865-2

surfaces were prepared by cutting the samples along the axial direction of the discs and polishing with diamond paste to 6 μm and silica powder to 0.05 μm. The samples were thermally etched at 1550°C for 30 min. The grain size was determined by the linear intercept technique [6].

3. Results and discussion

The expansion curves for the powder mixtures of Al_2O_3 and NiO are shown in Fig. 1. Owing to the density difference between Al_2O_3, NiO and $NiAl_2O_4$, the reaction

$$Al_2O_3 + NiO = NiAl_2O_4 \qquad (1)$$

induces a volume expansion. The expansion curves in Fig. 1 indicate that the reaction starts from 1000°C as the powder mixtures are heated with a heating rate of 5°C min^{-1}. As the holding time at 1000°C is prolonged, the amount of $NiAl_2O_4$ can be increased. Fig. 2 shows the XRD pattern for the Al_2O_3/25%NiO compact after heating at 1000°C for 50 h. No residual NiO is found within the detection limit of the instrument (about 1%). It suggests that NiO reacted fully with Al_2O_3 to form $NiAl_2O_4$. Since there is 75 mol% Al_2O_3 in the starting powder, residual Al_2O_3 is indicated in Fig. 2. Therefore, a duplex $Al_2O_3/NiAl_2O_4$ composite resulted after the heat treatment. According to the phase diagram [4], 25 mol.% NiO powder mixture results in 55 mol.% $NiAl_2O_4$, whereas 50 mol.% NiO powder mixture results in only $NiAl_2O_4$ after the heat treatment. To avoid the complexity induced by the expansion of $NiAl_2O_4$ formation, all specimens were first heat treated at 1000°C for 50 h.

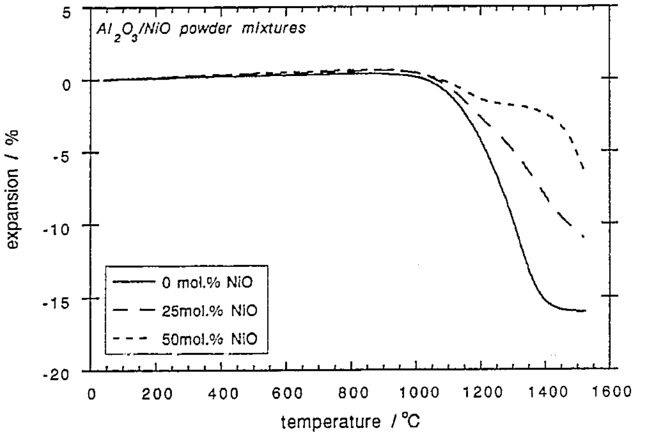

Fig. 1. The expansion curves for the Al_2O_3/NiO powder mixtures as a function of temperature. The heating rate is 5°C min^{-1}.

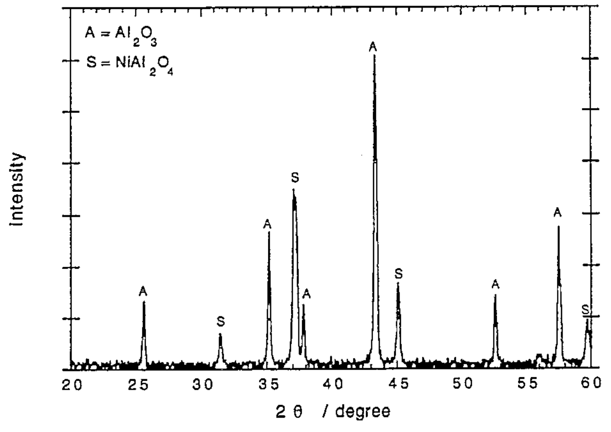

Fig. 2. The XRD pattern for the Al_2O_3/25%NiO compact after heat treated at 1000°C for 50 h.

The density for the heat treated powder compacts is shown as a function of temperature in Fig. 3. The sintering is carried out in the dilatometer. Owing to a volume expansion accompanied by the formation of $NiAl_2O_4$, the particles are pushed apart as the reaction is taken place [7]. A larger pore size thus results. The density of the specimens is decreased with the increase of $NiAl_2O_4$ content. As the heat-treated compacts are sintered in a box furnace, the relative density is shown as a function of sintering temperature in Fig. 4. The specimens are sintered at the indicated temperatures for 5 h. The fired density is also decreased with the increase of $NiAl_2O_4$ content.

The grain size of the specimens in Fig. 4 is shown as a function of temperature in Fig. 5. The grain size of Al_2O_3/

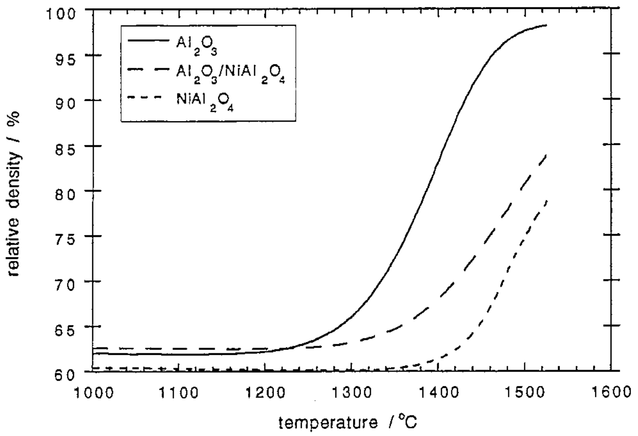

Fig. 3. The densification curves for the $Al_2O_3/NiAl_2O_4$ powder compacts. The heating rate is 5°C min^{-1}.

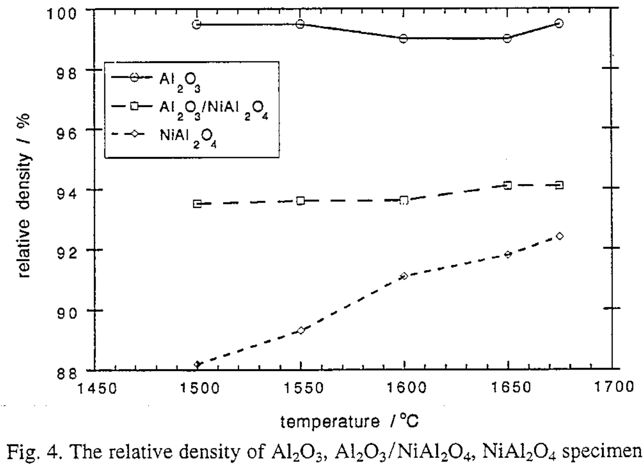

Fig. 4. The relative density of Al_2O_3, $Al_2O_3/NiAl_2O_4$, $NiAl_2O_4$ specimens as a function of temperature. The specimens are sintered at the indicated temperatures for 5 h.

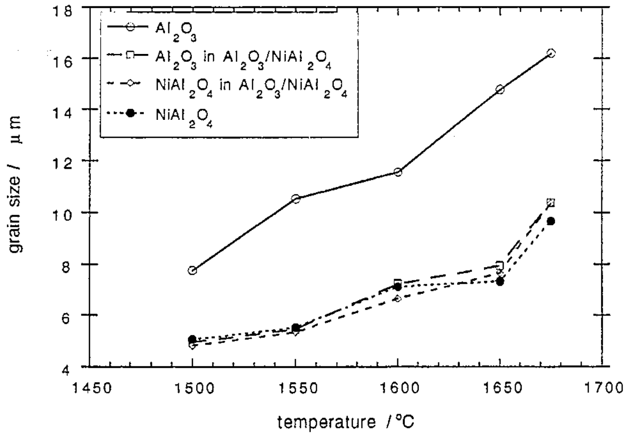

Fig. 5. The grain size of Al_2O_3, $Al_2O_3/NiAl_2O_4$, $NiAl_2O_4$ specimens as a function of temperature. The specimens are sintered at the indicated temperatures for 5 h.

Table 1
The density and grain size of Al_2O_3, $Al_2O_3/NiAl_2O_4$ and $NiAl_2O_4$ specimens after sintering at 1700°C for 1 h

	Relative density (%)	Grain size of Al_2O_3 (μm)	Grain size of $NiAl_2O_4$ (μm)
Al_2O_3	98.6	15.1	–
$Al_2O_3/NiAl_2O_4$	96.6	12.8	9.4
$NiAl_2O_4$	97.8	–	16.8

$NiAl_2O_4$ composite and of $NiAl_2O_4$ specimen is smaller than that of Al_2O_3. The relative density of the $Al_2O_3/NiAl_2O_4$ composite is lower than 95%, as the composite sintered at 1675°C for 5 h. A higher sintering temperature, 1700°C, is used to densify the composite. The density and grain size of the specimens sintered at 1700°C for 1 h are shown in Table 1. The densities of the specimens in Table 1 are very close to one another. However, the grain size of the composite is the smallest. It thus suggests that the composite is resistant to coarsening at high temperature. Typical microstructures of the specimens are shown in Fig. 6.

The grain growth kinetics can be expressed in terms of the relation

$$G^n - G_o^n = Kt \tag{2}$$

where G is the grain size at time t, n the grain growth kinetic exponent, G_o the grain size in the beginning, and K the grain growth rate constant. When the specimens are sintered at high temperature for 5 h, the grain size G is much greater than G_o. Therefore, Eq. (2) can be simplified to

$$G^n = Kt \tag{3}$$

Grain growth is a thermally activated process. The grain growth rate constant K is thus a function of temperature T as

$$K = K_o \exp(-Q/RT) \tag{4}$$

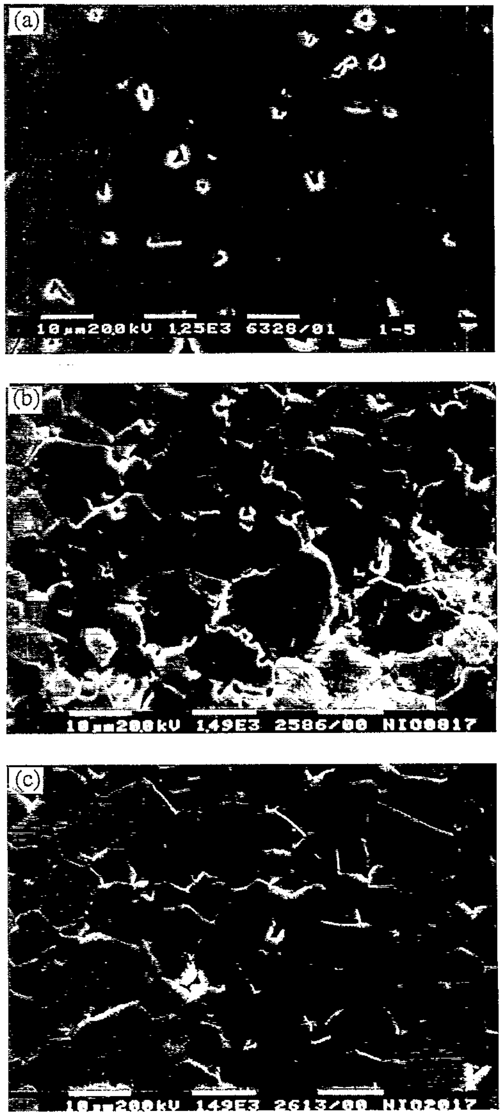

Fig. 6. The microstructures for (a) Al_2O_3 (b) $Al_2O_3/NiAl_2O_4$ and (c) $NiAl_2O_4$ specimens. The specimens are sintered at 1700°C for 1 h. The small particles on the surfaces are the contamination from the polishing suspension. In (b), the dark grains are Al_2O_3, the bright grains $NiAl_2O_4$.

where K_o is a constant, Q the activation energy, and R the gas constant. The values of n for ceramics have been suggested to vary from 2 to 4 [8]. The exact value of n is difficult to be determined with limited data points [9]. A value of $n = 3$ was thus chosen to provide a basis for comparison of the values of K. The grain growth rate constant is shown as a function of inverse temperature in Fig. 7. The activation energy for the grain growth is shown in Table 2. The activation energy for Al_2O_3 is slightly lower than the reported value for the diffusion of Al ions along grain boundaries [10]. This may result from the composition difference. The activation energy of Al_2O_3 in the composite is the same as that of monolithic Al_2O_3. However, the activation energy of $NiAl_2O_4$ in the composite is different from that of monolithic $NiAl_2O_4$.

For monolithic ceramics, the mass can be transported along the grain boundaries. However, the grain boundaries in a

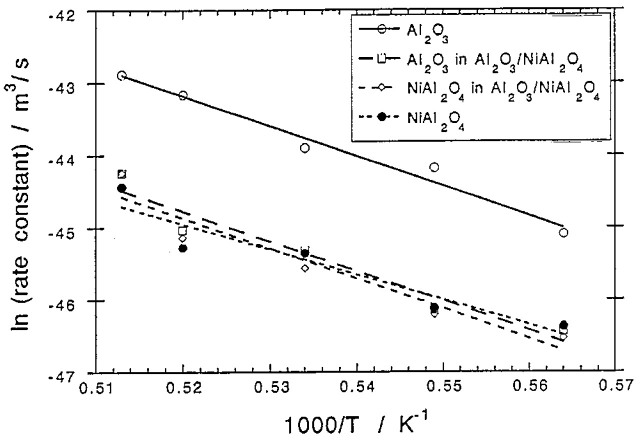

Fig. 7. The grain growth rate constant as a function of temperature.

Table 2
The activation energy for the grain growth of Al_2O_3 and $NiAl_2O_4$ in Al_2O_3, $Al_2O_3/NiAl_2O_4$ and $NiAl_2O_4$ specimens

Specimen	Activation energy (kJ mol^{-1})
Al_2O_3	343
Al_2O_3 in $Al_2O_3/NiAl_2O_4$	342
$NiAl_2O_4$ in $Al_2O_3/NiAl_2O_4$	347
$NiAl_2O_4$	290

monolithic microstructure are replaced by the interphase boundaries in a duplex microstructure. Good lattice matching has been observed in the $Al_2O_3/NiAl_2O_4$ interphase boundary [11]. The structure of the interphase boundary may thus be similar to the structure of the grain boundary of monolithic Al_2O_3 and of monolithic $NiAl_2O_4$. Since the activation energy of Al_2O_3 in a composite is the same as that of monolithic Al_2O_3, the grain growth of the composite is likely to be controlled by the diffusion of Al ions along the interphase boundary. From Fig. 6(a), the aspect ratio of Al_2O_3 grains is slightly higher than unity. However, the Al_2O_3 grains in the $Al_2O_3/NiAl_2O_4$ composite are equiaxed instead, Fig. 6(b). The $NiAl_2O_4$ grains in $NiAl_2O_4$ or in $Al_2O_3/NiAl_2O_4$ composite are all equiaxed. This suggests that the coarsening of one phase in the composite is constrained by the presence of the other phase and the space filling requirement.

To achieve high density, either the sintering temperature or the sintering time can be increased. The duplex microstructure is resistant to coarsening. Therefore, even if a higher temperature or a longer time is used, the sintering-accompanied coarsening is limited. This can be demonstrated by sintering the specimens at 1700°C, Table 1. A relative density of 97% for the composite is achieved. Furthermore, the grain size of duplex $Al_2O_3/NiAl_2O_4$ composite is smaller than that of monolithic Al_2O_3 and $NiAl_2O_4$.

4. Conclusions

The grain growth behavior of Al_2O_3, $Al_2O_3/NiAl_2O_4$ and $NiAl_2O_4$ is studied. Duplex $Al_2O_3/NiAl_2O_4$ composite is resistant to coarsening at high temperature. The grain growth of duplex $Al_2O_3/NiAl_2O_4$ composite is controlled by the diffusion of Al ion along the interphase boundary. Because of the space filling requirement, the coarsening of each phase in the composite is constrained. Even though dense duplex $Al_2O_3/NiAl_2O_4$ composite can only prepared by sintering at a high temperature, 1700°C. For its coarsening resistance, the microstructure of the composite is still refined. The potential of applying the duplex composite at high temperature is thus high for its microstructural stability.

Acknowledgements

The present study is supported by The National Science Council, ROC, through the contract number of NSC82-0405-E002-63.

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