JOURNAL OF MATERIALS SCIENCE **36** (2001) 807– 810

Anisotropic grain growth of R-α-sialon (R = Nd and Er)

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Two R-α-sialon ($R_{0.6}Si_{9.3}Al_{2.7}O_{0.9}N_{15.1}$, R = Nd and Er) compositions were first fired at 1750°C/25 min and 1650°C/2 h respectively for completion of the $\alpha \rightarrow \alpha'$ phase transformation. Elongated α-sialon grain morphology was developed in both samples after being re-fired at 1800°C for different periods of time. The growth in width of R-α-sialon grains is controlled by diffusion in the liquid, while the length growth tends to be interfacial reaction controlled. The anisotropic growth of R-α-sialon is attributed to the large difference in the growth rate constant between the length and the width directions of the grain. *© 2001 Kluwer Academic Publishers*

1. Introduction

The ceramic family of sialon has gained wide research interest owing to its excellent performance such as high strength, high hardness, and good resistance to erosion and wear, which is more pronounced at elevated temperatures. Of the two commonly used modifications of sialon ceramics, i.e., α-sialon and β-sialon, the latter has been successfully applied in many engineering components because of the high fracture toughness originating from its elongated grain morphology. On the other hand, the application of α-sialon, despite its high hardness, has been hampered by its frequently occurred equi-axed morphology associated with low toughness and reliability. Recent experimental findings of elongated α-sialon in the rare earth and Ca systems, especially the subsequent toughness enhancement to the material [1, 2], have prompted great enthusiasm in understanding the grain growth behavior of α-sialon.

It is generally accepted that the grain growth of sialon follows the empirical equation defined by the LSW theory [3, 4]:

$$d^n - d_0^n = kt \qquad (1)$$

here d and d_0 are the final and initial grain sizes, k is the growth rate constant, and n is the growth exponent to determine whether the grain growth is controlled by diffusion in the liquid or interfacial reaction. In our recent work [5], we studied the grain growth kinetics of Ca α-sialon after the α-Si_3N_4 (α) → α-sialon (α') transformation and found interesting similarities and differences comparing to β-Si_3N_4/sialon systems reported in previous literature. In the present paper, we extended the study to the rare earth doped α-sialon. Both Nd (light rare earth) and Er (heavy rare earth) were chosen as the modifying cations to study the influence of rare earth ion radius on the grain growth behavior of α-sialon.

2. Experimental

R-α-sialon compositions were chosen along the join line Si_3N_4-R_2O_3·9AlN on the α-sialon plane ($R_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}$), i.e. $m = 2n$, with $x = 0.6$ and R = Nd and Er, giving specific compositions of $R_{0.6}Si_{9.3}Al_{2.7}O_{0.9}N_{15.1}$. Samples were designated as Nd60 and Er60. Starting powders were α-Si_3N_4 (UBE E-10, Japan, 2.0 wt% O), AlN (Wuxi, 1.3 wt% O), R_2O_3 (R = Nd and Er) (Yaolung Chemicals, 99.9%). Powder mixtures were ball milled with absolute alcohol for 24 h.

Following the convention used in our previous study on the Ca α-sialon system, the completion of $\alpha \rightarrow \alpha'$ phase transformation is assumed when a sample contains less than 5 wt% unreacted α-Si_3N_4 after firing. Based on this criterion, to achieve the completion of $\alpha \rightarrow \alpha'$ phase transformation it required a firing at 1750°C for 25 min for Nd60 composition and at 1650°C for 2 hours for Er60 composition by hot-pressing. After initial firings at these conditions, bulk materials with a rectangular shape (30 × 37 mm) were then cut into small pieces. Each piece was re-fired under 0.1 MPa nitrogen atmosphere at 1800°C for 1 min, 1 h and 3 h respectively in a graphite resistance furnace by pressureless sintering.

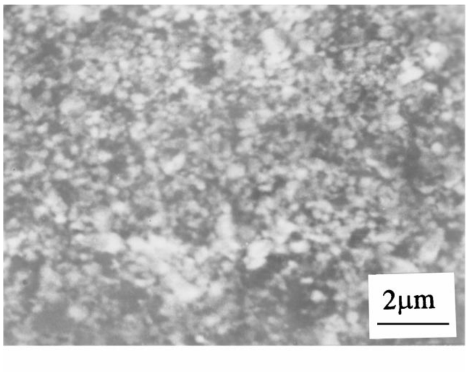
Microstructural observation of the fired samples was carried out on a KYKY-2000 scanning electron microscope (Keyi Inc., China). Polished surfaces of the samples were etched in molten NaOH for a few seconds and then carbon coated prior to SEM observation. An image analyzer (IBAS/C, Kontron Elektronik, Germany) was used for quantitative analysis of the microstructure taking into account the three-dimensional random distribution of the elongated α-sialon grains. Details of the method were given elsewhere [5].

3. Results and discussion

3.1. Grain morphology

Fig. 1 shows the microstructures of Nd60 and Er60 samples after the initial hot-pressing. Like in the Ca α-sialon system, the grain morphology of R-α-sialon was rounded at the completion of the $\alpha \rightarrow \alpha'$ transformation. This morphological feature of the α-sialon grains represents a fundamental difference with the elongated β-Si_3N_4/sialon grain morphology upon completion of the $\alpha \rightarrow \beta$ transformation [6, 7].

Sialon is formed via a solution-precipitation process in which α-Si_3N_4 is dissolved into a transient liquid upon firing, from which the α- and/or β-sialon phases are precipitated. It is generally thought that the development of sialon grains involves nucleation and grain growth. Owing to the persistence of the highly refractory Nd melilite phase, the completion temperature of the $\alpha \rightarrow \alpha'$ transformation for Nd60 was 100°C higher than for ER60, as shown in Fig. 1. However, the Nd60 composition revealed a much finer grain morphology than sample Er60. This may be attributed to a relatively higher nucleation rate and/or a lower growth rate for grains in the Nd composition comparing to that in the Er composition. The difference in the nucleation rate accords with the acid-base property of the two rare earth oxides [8]. During sintering, the more basic Nd-containing melt preferentially wets and reacts with Si_3N_4, which is favorable to the nucleation of α-sialon on existing α-Si_3N_4 particles. A high density of nuclei could lead to a microstructure with large amounts of fine grains. However, the difference in the growth rate of Nd and Er α-sialon grains needs some analyses. It is known that the ionic field strength increases with increasing atomic number (from Nd to Er); thus the viscosity of the Nd-containing liquid should be lower than the Er-containing liquid [9]. A low viscosity liquid should facilitate easy diffusion of ions and thus promote grain growth. But this seems not to agree with the observed facts here that a faster growth rate appeared in the Er composition instead of in the Nd composition. This inconsistency can be rationalized if a catalytic effect of rare earth ions on the growth rates of α-sialon is assumed. The catalytic effect was employed in previous studies of β-Si_3N_4/sialon materials to explain the fine-grained microstructure observed in the light rare earth containing samples compared to that in the heavy rare earth containing ones [10, 11]. In our following discussion on different grain growth kinetics of the Nd and Er doped systems, it is seen that the same catalytic effect still holds for the α-sialon grain growth.


(a)

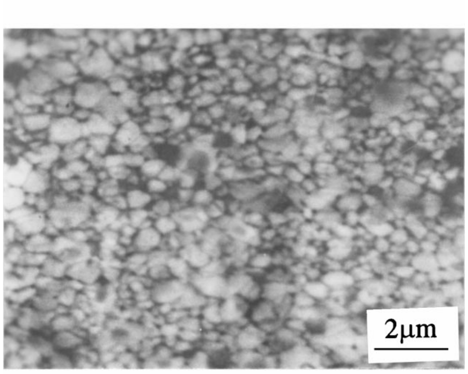

(b)

Figure 1 Microstructure of samples Nd60 (a) and Er60 (b) upon completion of the $\alpha \rightarrow \alpha'$ transformation.

After firing at 1800°C for prolonged time, a gradual increase in the grain size of α-sialon was detected, as shown in Fig. 2. As the $\alpha \rightarrow \alpha'$ transformation was completed in both samples prior to the firing at 1800°C, the growth of α-sialon grains followed an Ostwald ripening process through a transient liquid. Similar to the Ca doped system, R-α-sialons began to show an anisotropic grain morphology in the subsequent grain growth period, evidenced by the increasing α-sialon aspect ratio with increasing holding time (see Fig. 3). It can therefore be concluded that the development of grain morphology of α-sialons, either Ca doped or rare earth doped, follows the same rule. That is, fine spherical grains are the initial appearance at completion of the $\alpha \rightarrow \alpha'$ transformation and elongated grains are subsequently developed through prolonged holding at high temperatures, providing the necessary kinetics for this evolution.

It is also noted that both the width and length of α-sialon grains in sample Nd60 were shorter than those in Er60 at the same holding time, while the aspect ratio showed the inverse trend (e.g. Fig. 2e, f). This feature resembles that of the β-Si_3N_4/sialon system, where a nearly one-dimensional growth was observed for the light rare earth doped system in contrast to the predominantly diameter growth for the heavy rare earth doped system. Hoffmann *et al*. attributed this difference to the influence of the rare earth additives on the Si_3N_4 surface energy, which caused a change of the basal and prism plane growth rates [12]. Similarly, the different microstructure of the R-α-sialon can be understood in terms of the different growth rates in the width and length directions, as supported by the kinetic parameters discussed below.

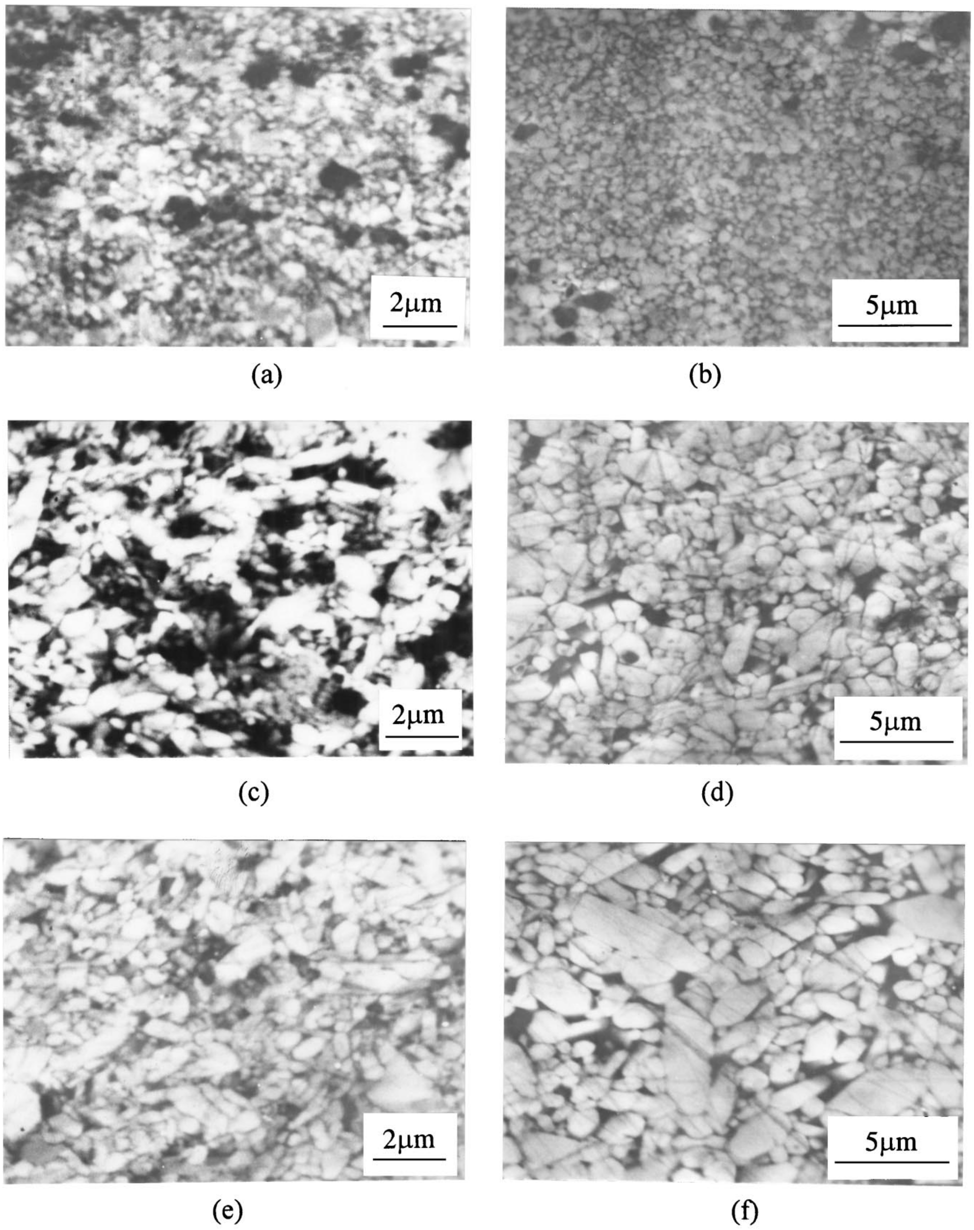


Figure 2 Microstructural evolution of R-α-sialon after the $\alpha \rightarrow \alpha'$ transformation (a) Nd60 1800°C/1 min (b) Er60 1800°C/1 min (c) Nd60 1800°C/1 h (d) Er60 1800°C/1 h (e) Nd60 1800°C/3 h (f) Er60 1800°C/3h.

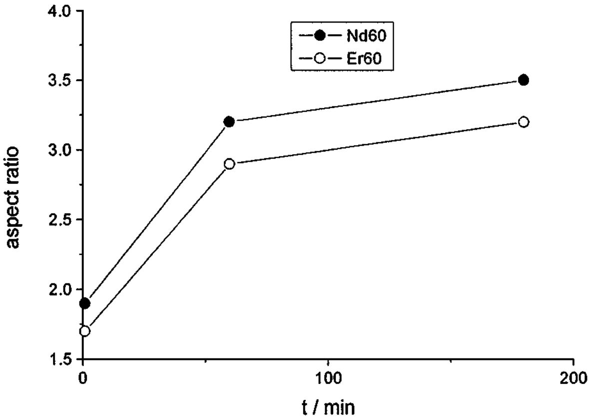


Figure 3 Aspect ratio of R-α-sialon grains after firing at 1800°C for different time.

TABLE I Grain growth exponent (n) and growth rate constant (k) for Nd and Er α-sialon compositions

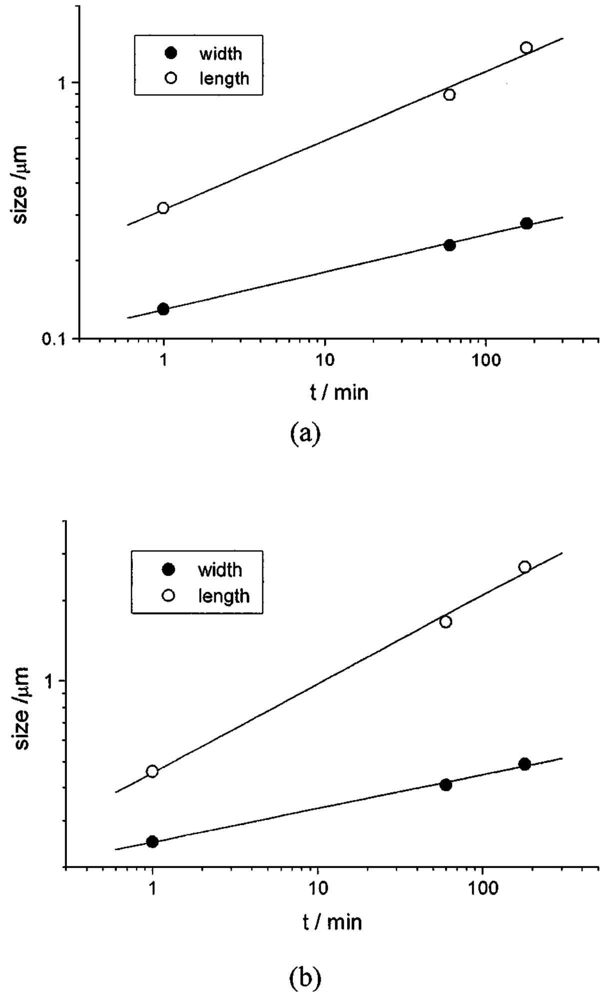
	n		k	
	n_w	n_l	k_w	k_l
Nd60	6	4	4.6×10^{-6}	1.0×10^{-2}
Er60	7	3	6.3×10^{-5}	9.5×10^{-2}

Note: w and l = width and length of the α-sialon grains.

3.2. Growth kinetics

The grain size data (length and width) in Fig. 2 were plotted on a log-log scale in Fig. 4. From the slope and intercept of the lines fitted according to Equation 1, the growth exponent and rate constant of the two dimensions of α-sialon grains can be determined, as listed in Table I.

Like the Ca doped α-sialon, the two rare earth doped systems had higher n_w than n_l values. Thus the width growth tends to be diffusion controlled and the length growth is more prone to interfacial reaction controlled. The higher diffusivity in the multi-grain junctions than at the two-grain boundaries might be the cause for the



(a)

(b)

Figure 4 Isothermal grain growth behavior of (a) Nd60 and (b) Er60 compositions.

lower n value in the length direction. It is also interesting to note that the n values for the Nd system are just the same as for the Ca doped system, i.e., $n_w = 6$ and $n_l = 4$, implying a similar growth behavior for the two systems. Whilst the Er composition had quite different values with $n_w = 7$ and $n_l = 3$. The growth rate constant of the length is three orders of magnitude higher than that of the width. The much higher k_l than k_w for the two compositions dictates the preferred growth along the length direction of R-α-sialon grains.

It is seen from Table I that Er60 had much higher k values than Nd60, which contradicts with the higher viscosity of the Er-containing liquid than the Nd-containing liquid. The seemingly inconsistencies can be rationalized if we also assume a catalytic effect of rare earth ions on the grain growth rates of the basal and prism planes of α-sialon so that the Nd composition has much lower rate constants than the Er composition. This is consistent with the calculated k values as listed in Table I. To rationalize this difference, more work is needed to investigate the interface between the α-sialon and glassy phase.

4. Conclusion

The grain growth kinetics of α-sialon in the rare earth doped systems was studied. A comparison of the experimental results with those of Ca α-sialon and β-Si_3N_4/sialon systems revealed the following features of the grain growth of R-α-sialon:

1. Like Ca α-sialon, rare earth doped α-sialon takes an equi-axed grain morphology at the temperature of $\alpha \rightarrow \alpha'$ transformation. Prolonged holding at higher temperatures provides necessary kinetics for the development of elongated α-sialon.
2. The growth in width of R-α-sialon grains is controlled by diffusion in the liquid, while the length growth tends to be interfacial reaction controlled. The Nd composition has similar growth behavior to the Ca α-sialon in that both have the same n values.
3. Like the β-Si_3N_4/sialon system, the light rare earth (Nd) doped composition has a much finer microstructure with high aspect ratio comparing to the heavy rare earth (Er) doped composition. The assumption that the catalytic effect of the rare earth ions on the growth rates of the basal and prism plans of α-sialon can explain this difference.
4. The rate constant of the length is three orders of magnitude higher than that of the width so that anisotropic growth occurs and elongated grains are developed. The Er composition shows a higher grain growth rate in both the width and length than the Nd composition.

Acknowledgments

This work has received financial support from the National Natural Science Foundation of China.

References

1. I. W. CHEN and A. ROSENFLANZ, *Nature* **389** (1997) 701.
2. C. WOOD, H. ZHAO and Y.-B. CHENG, *J. Amer. Ceram. Soc.* **82** (1999) 421.
3. I. M. LIFSHITZ and V. V. SLYOZOV, *J. Phys. Chem. Solid* **19** (1961) 35.
4. C. WAGNER, *Z. Electrochem.* **65** (1961) 581.
5. Y. W. LI, P. L. WANG, W. W. CHEN, Y. B. CHENG and D. S. YAN, *J. Amer. Ceram. Soc.* in review.
6. D. D. LEE, S. J. L. KANG, G. PETZOW and D. N. YOON, *ibid.* **73** (1990) 767.
7. M. KRÄMER, M. J. HOFFMANN and G. PETZOW, *Acta Metall. Mater.* **41** (1993) 2939.
8. M. MENON and I. W. CHEN, *J. Amer. Ceram. Soc.* **78** (1995) 545.
9. J. E. SHELBY and J. T. KOHLI, *ibid.* **73** (1990) 39.
10. M. J. HOFFMANN, in "Tailoring of Mechanical Properties of Si_3N_4 Ceramics," edited by M. J. Hoffmann and G. Petzow (Kluwer Academic Publishers, Netherlands, 1994) p. 59.
11. M. KITAYAMA, K. HIRAO, M. TORIYAMA and S. KANZAKI, *Ceram. Proc. Sci.* (1998) 517.
12. M. J. HOFFMANN and G. PETZOW, *Pure & Appl. Chem.* **86** (1994) 1807.

Received 31 March
and accepted 6 July 2000