

Effect of Phase Stability on the Microstructure Development of α -SiAlON Ceramics

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Abstract Alpha-SiAlON ceramics having various compositions and modifying cations were investigated with respect to their phase stability, transformation kinetics, and resulting microstructures. Each composition was heat treated at 1500°C for 1h and measured the α -SiAlON transformation. The phase-boundary composition in the single-phase α -SiAlON region showed sluggish transformation from α -Si₃N₄ to α -SiAlON compared to the phase-center composition in the diagram. Using the different rare earth modifying cations, dependence of transformation kinetics on the phase stability in a fixed composition was also explained. By changing size of the stable α -phase region with exchanging cations, systematic change in transformation was observed. Transformation rate of α -SiAlON at low temperature has an important role on controlling the final microstructure. Less transformation gives more chances to develop elongated grain in the microstructure.

Keywords : α -SiAlON, Phase stability, Elongated grain, Modifying cations

1. Introduction

Silicon aluminum nitride (SiAlON) ceramics are solid solution of Si₃N₄ with the Si-N bonds substituted by Al-N and Al-O bonds, which form α -SiAlON and/or β -SiAlON. Given the demand for hard materials that were intended for cutting tools, bearings, and engine components, research need about β -Si₃N₄ and β -SiAlON ceramics were steadily growing¹⁾. Because of low fracture toughness, however, α -SiAlON ceramics has been less attention even though it shows much higher hardness²⁾. Recently a family of *in-situ* toughened single-phase α -SiAlON has been discovered. In-situ toughened α -SiAlON ceramics possesses a whisker-like microstructure and has fracture toughness and strength values that are comparable to that of β -Si₃N₄ and β -SiAlON³⁻¹⁰⁾. Achieving a whisker-like microstructure in single-phase α -SiAlON, much more attention should be imposed then on that of β -SiAlON case.

α -SiAlONs are usually prepared from a mixture of Si₃N₄, AlN, and oxides of aluminum and one or several elements from the following list: lithium, magnesium, calcium, yttrium, and R (where R refers to rare-earth elements, excluding lanthanum). During sinter-

ing the reaction between surface oxide of nitride powders and included oxide powders forms a low temperature eutectic liquid as a transient phase, which contributes to transform from α -Si₃N₄ to α -SiAlON crystals as well as to densify and grow by way of solution and precipitation mechanism. In previous works, we have emphasized the importance of nucleation control and suggested the two-step processing as a controlling method, finally, to achieve *in-situ* toughened single-phase α -SiAlONs^{9,10)}. And we also have shown that not in the all compositions such microstructures could be obtained effectively, only in composition close to the phase boundary of the single-phase α -SiAlON region, and explained the reason using a relation with the reaction kinetics and phase stability¹⁰⁾.

In this paper we report about the relation between the transformation kinetics and phase stability in the entire α -SiAlON phase plane and in different interstitial cation systems. The results show low transformation kinetics for composition having low phase stability, and result in well-developed whisker-like microstructures eventually. Thus the phase stability and the composition can be used to predict the final microstructures in *in-situ* toughened α -SiAlON ceramics.

2. Experimental Procedure

Starting powders of α -Si₃N₄ (SN-E-10, Ube Ind., Japan), AlN (Type F, Tokuyama Soda Co., CA), Yb₂O₃, Y₂O₃, Gd₂O₃, Sm₂O₃, and Nd₂O₃ (99.9%, Aldrich Chem. Co., WI) were used to achieve the desired composition. In the formulation, the residual oxygen content of Si₃N₄ and AlN was considered. Powder mixtures, in batches of 50 g, were attrition milled in isopropyl alcohol for 2 h with high purity Si₃N₄ milling media in a Teflon-coated jar. The powder slurry was subsequently dried at 80°C under a lamp while being stirred. Using a hot press, the powder mixtures of approximately 10 g were heat-treated at 1500°C for 1 h in a nitrogen atmosphere with a graphite furnace, heating rate of 20°C/min and a uniaxial pressure of 30 MPa. Phase analysis of the sintered specimens was performed by X-ray diffraction using crushed powders. The relative amount of the α -SiAlON and α -Si₃N₄ was determined from the integrated peak intensities of their (210) and (102) diffractions.

The same set of powder mixtures were hot-pressed at 1500°C for 1 h and followed by holding at 1950°C for 1 h. Full densification was achieved in all cases. The microstructures were observed using scanning electron microscopy (SEM) on polished sections after etching in molten NaOH.

3. Results and Discussion

All compositions investigated in this work lie on the α -plane that is depicted in Fig. 1, and their composition was referred as 'R10*m*10*n*' notation, where R is a rare-earth cation (ytterbium, yttrium, gadolinium, samarium, neodymium) and *m* and *n* are variables in

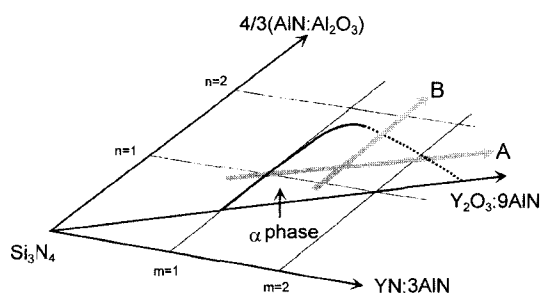


Fig. 1. Schematic phase diagram on the α -SiAlON plane, showing that trajectory A and B denote the direction of examined composition sets across the α -SiAlON single-phase region.

the formula for compositions in the α -plane: R_{*m*}Si_{12-(*m*+*n*)}Al_{*m*+*n*}O_{*n*}N_{16-*n*}. For instance, Y1512 represents Y_{0.5}Si_{9.3}Al_{2.7}O_{1.2}N_{14.8}. Two sets of composition trajectories are selected in Y- α -phase plane: one is trajectory A corresponding to the minimum accessible *n* compositions depending on the oxygen content of nitride powders, which means no aluminum oxide addition, the other is trajectory B to the constant *m* composition, direction to the apex composition.

Chen and Rosenflanz⁸⁾ recently showed that the size

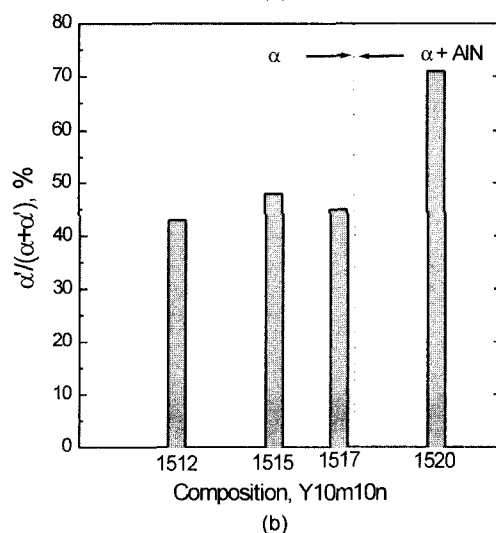
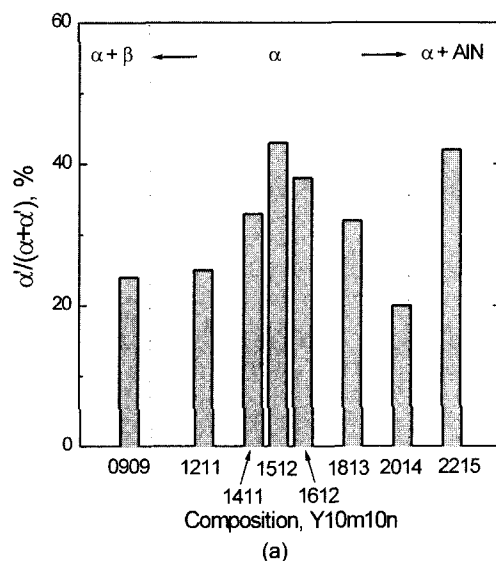


Fig. 2. Relative amount of transformed α -SiAlON from α -Si₃N₄ heat-treated at 1500°C for 1 h in N₂ at 30 MPa. The designated composition follows the trajectory (a) A and (b) B in Fig. 1.

of single-phase α -SiAlON stable region in the phase diagram depends on the temperature: smaller at lower temperature and *vice versa*. A high m -side boundary, especially, such a trend is much enormous, now has been understood as reverse transformation phenomena. During heating, because α -SiAlONs were usually prepared from a mixture of Si_3N_4 , AlN , and other oxides, the composition near phase boundary is supposed to have low driving force for the formation of α -SiAlON. The amount of transformations after low temperature heat-treatment at the compositions following the trajectory A show the corresponding trends with the driving force consideration for transformation, as shown in Fig. 2(a). The compositions far from the phase boundary and rather inside have higher transformation rate than that of near the boundary ones. Furthermore, the difference in amount of transformation shows a direct relation with the final microstructure. Less transformation at low temperature gives more chance to have elongated grains in final micro-

structure after the high temperature sintering, as shown in Fig. 3.

Such a difference in transformation rate does not likely relate with the properties of transient liquid that forms from oxides during transformation reaction. Because the liquid should have a eutectic composition of Al_2O_3 , SiO_2 , and Y_2O_3 , at first, and then follows identical liquidus line at 1500°C , the liquid lies within a nearly same composition range regardless of the initial compositions investigated here. In addition, according to the calculation by ternary phase diagram of Al_2O_3 , SiO_2 , and Y_2O_3 ⁸⁾, the amounts of liquid phase in each composition increases as the m and n values increase, therefore if we assume the transformation rate is dependent on the amount of liquid phase, the rate should increase gradually. Therefore, the maximum transformation rate at the center of the α -single-phase region and minimum at the boundary do not relate with the liquid phase properties.

Another possibility is the dependence of viscosity

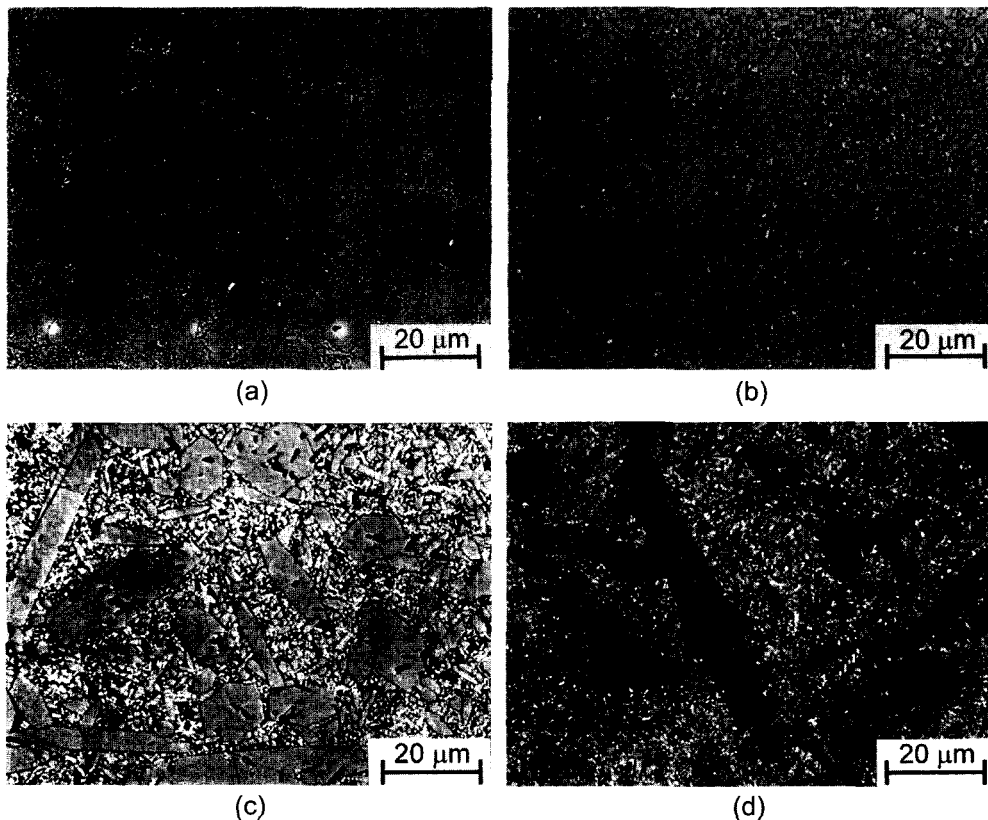


Fig. 3. Microstructures of single-phase (a) Y1211, (b) Y1512, (c) Y1813 and (d) Y2014 α -SiAlON samples hot-pressed at 1500°C for 1 h and 1950°C for 1 h.

with different composition. Based on the same properties of liquid phase previously discussed, that can be neglected either. The outside composition of α -SiAlON single-phase region, Y2215, however, shows the highest transformation rate, which means that, within the limited driving force (minimum driving force), the amount of transformation depends on the amount of liquid. The amount of transformation in composition following the trajectory B shows about the same transformation within the α -phase region but the highest outside region, as shown in Fig. 2(b), this also shows importance of driving force for transformation in such a *solution and precipitation process*.

The driving force and phase transformation relation seems to be hold even in a same composition with different modifying cation systems. Fig. 4 shows the transformation rate when different cations were used for stabilization of α -SiAlON phase. The solubility ranges of α -SiAlON phase are known for yttrium, samarium modified system, as described by Sun *et al.*^{11,12)} and Nordberg *et al.*¹³⁾, respectively: the α -SiAlON field is smaller with samarium than with yttrium. More is known along the Si_3N_4 - R_2O_3 - 9AlN line, because Huang *et al.*¹⁴⁾ have shown that the minimum solubility of rare earth cations is the same for all rare earth ions but the maximum solubility larger for smaller ions. Recently, Rosenflanz and Chen^{7,8)} have explained the solubility changes with different temper-

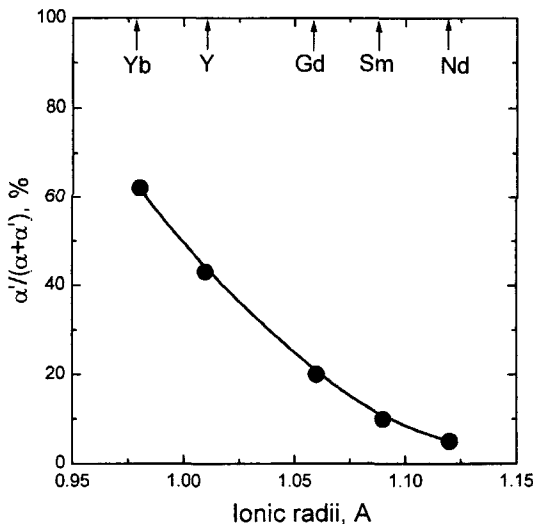
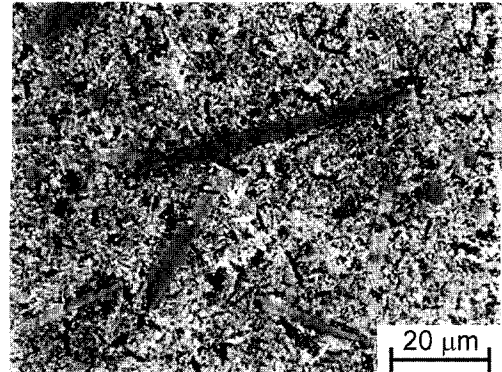
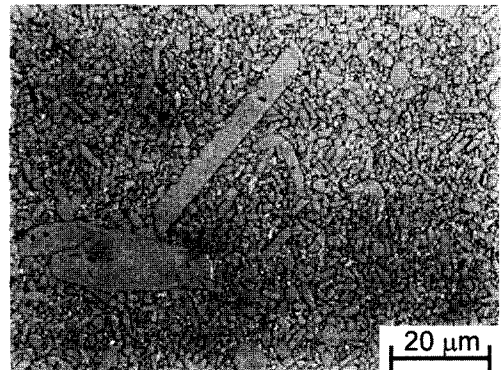


Fig. 4. Relative amount of transformed M- α -SiAlON from α - Si_3N_4 heat-treated at 1500°C for 1 h in N_2 at 30 MPa. The designated composition is fixed with M1512.

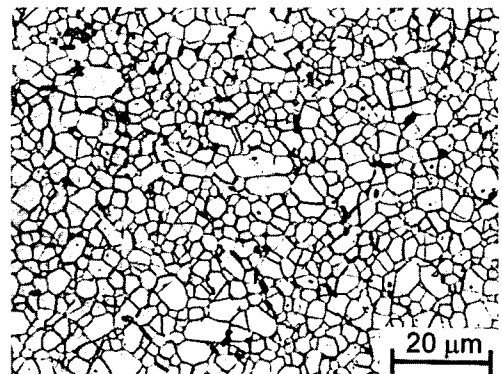
ature in several modifying cation systems more generally. Such changes in solubility with different modifying cations give different driving force for phase transformation although in the fixed composition, which is one of the most important reasons that



(a)



(b)



(c)

Fig. 5. Microstructures of single-phase (a) Nd1512, (b) Y1512 and (c) Yb1512, α -SiAlON samples hot-pressed at 1500°C for 1 h and 1950°C for 1 h.

transformation rate is faster when the smaller modifying ion used than when the larger modifying ion. The different modifying oxide could effect on the viscosity of transient liquids, which has an important role on transformation reaction. However, the viscosity is inversely proportional to the ionic radii, and the diffusion coefficient of Si_3N_4 in the residual glass also has on inverse relationship with the viscosity. Therefore, the fastest diffusion (i.e. Nd) in the glass phase achieves the lowest transformation, which means that the viscosity of liquid is never able to explain the results.

The differences of transformation rate in several modifying cation systems directly affected on the hot-pressed microstructures. The microstructures of Nd-, Y-, and Yb-1512 α -SiAlON ceramics hot-pressed at 1500°C for 1 h, and 1950°C for 1 h were shown in Fig. 5. Combining with the X-ray analysis results as shown in Fig. 4, less transformation at low temperature gives more chances to have elongated grains in the final microstructure after high temperature sintering.

4. Conclusions

The correlation between the phase stability and transformation kinetics and its effect on the microstructure development of α -SiAlON were investigated. Composition near the phase boundary in a single-phase region shows slow transformation kinetics from α - Si_3N_4 to α -SiAlON, which was very useful to control nucleation and growth, and finally to achieve *in-situ* toughened α -SiAlON ceramics. And composition near the center, however, showed the fastest transformation rate. Such a difference of transformation rate in this composition range was due to a

difference in driving force resulting from the variation of phase stability. In the same manner, the solubility change with different rare earth cation resulted in transformation kinetic changes. Such experimental results supported the explanation of nucleation and growth of *in-situ* toughened α -SiAlON ceramics.

References

1. H. Takao: Proc. of 4th Intl Symp. Ceram. Mater. Comp. for Engines, (1991) 118.
2. T. Ekström and M. Nygren: J. Am. Ceram. Soc., **75** (1992) 259.
3. M. Zenotchkine, R. Shuba, J. Kim and I. Chen: J. Am. Ceram. Soc., **84** (2001) 1651.
4. R. Shuba and I. Chen: J. Am. Ceram. Soc., **85** (2002) 1260.
5. M. Zenotchkine, R. Shuba, J. Kim and I. Chen: J. Am. Ceram. Soc., **85** (2002) 1254.
6. M. Zenotchkine, R. Shuba, J. Kim and I. Chen: J. Am. Ceram. Soc., **84** (2001) 884.
7. A. Rosenflanz and I. Chen: J. Eu. Ceram. Soc., **19** (1999) 2337.
8. A. Rosenflanz and I. Chen: J. Am. Ceram. Soc., **82** (1999) 1025.
9. I. Chen and A. Rosenflanz: Nature, **389** (1997) 701.
10. J. Kim, A. Rosenflanz and I. Chen: J. Am. Ceram. Soc., **83** (2000) 1819.
11. W. Y. Sun, T. Y. Tien and T. S. Yen: J. Am. Ceram. Soc., **74** (1991) 2547.
12. W. Y. Sun, T. Y. Tien and T. S. Yen: J. Am. Ceram. Soc., **74** (1991) 2753.
13. L. Nordberg and M. Nygren: J. Am. Ceram. Soc. **81** (1998) 1461.
14. Z. K. Huang, D. S. Yan and T. Y. Tien: J. Am. Ceram. Soc., **69** (1986) C241.