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Microstructural Features of the α to β-SiAlON Phase Transformation

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Abstract

The microstructural characteristics of Sm (α + β) -SiAlON ceramics after post-sintering heat treatment at 1450°C are investigated by analytical electron microscopy (AEM). X-ray diffraction (XRD) analyses indicate that a significant amount of the α-SiAlON (α') phase has transformed to β-SiAlON (β') during the heat treatment. It is found that the transformation is nucleated on the existing β' phase and the transformed β' grains have unique microstructural features containing a high density of dislocations and ultra-fine spherical inclusions rich in Sm and O. Similar characteristics have also been observed in the Yb (α' + β') materials. It is suggested that the transformation from α' to β' proceeds via a nucleation-growth mechanism and may require only a small amount of liquid phase to promote atomic diffusion.

1 Introduction

Post-sintering heat treatment of SiAlON ceramics is used to crystallize the glassy grain boundary phase and subsequently improve the high temperature performance of the materials.[1,2] There have been many studies exploring the grain boundary crystallization phenomenon but very little attention has been paid to the effects of post-sintering heat treatment on the stability of the SiAlON phases. Recently, Mandal *et al.*[3] revealed that some rare earth α-SiAlON (α') phases could undergo transformation to β-SiAlON (β') in the temperature range 1100 to 1600°C. α and β-SiAlONs have different mechanical properties,[4] therefore, this discovery may open new routes for tailoring the microstructures and properties of (α + β) -SiAlON ceramics.

The α' and β' phases have distinct compositions and possess different crystal structures.[5] The transformation between the α' and β' phases involves lattice reconstruction and requires a high degree of atomic diffusion. As a result of the strong covalent nature of the bonding associated with both the α' and β' lattices, the atomic diffusivity of species making up the lattice is inherently low. This poses questions of how the α' to β' transformation could take place at relatively low annealing temperatures and what is the diffusion mechanism operating. The phenomenon of α' to β' transformation has now been observed in a number of rare earth α' systems;[6–9] however, little microstructural information has been reported. This paper presents some unique microstructural features observed in heat-treated Sm- and Yb-doped SiAlON samples that have experienced a substantial α' to β' transformation and attempts to provide some explanations for the mechanism of the transformation.

2 Experimental

Samples were prepared from Si_3N_4, AlN, Al_2O_3, Sm_2O_3 and Yb_2O_3 powders with a starting composition (in wt%) of 72·50 Si_3N_4, 14·27 AlN, 2·00 Al_2O_3 and 11·23 Sm_2O_3 for the Sm α' + β' sample and 79·82 Si_3N_4, 5·24 AlN, 4·92 Al_2O_3 and 10·02 Yb_2O_3 for the Yb α' + β' sample. The samples were pressureless sintered between 1800 and 1820°C in a nitrogen atmosphere. Full details of the sample preparation can be found in Refs 10 and 11. X-ray diffraction (XRD) analyses of the as-sintered materials revealed that both samples contained mainly α' and β' phases but in the case of the Sm-containing material traces of the 21R polytypoid phase were observed and in the Yb-containing sample, yttrium disilicate ($Yb_2Si_2O_7$) was present. In each of the samples an amorphous grain boundary phase was observed by transmission electron microscopy (TEM).

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The Sm sample was subsequently heat-treated at 1450°C for 120 h, and the Yb sample at 1300°C for 96 h, in an alumina tube furnace in flowing high purity nitrogen. Materials characterization was performed using a Rigaku X-ray diffractometer and Philips CM20 and CM30 analytical electron microscopes (AEM) fitted with ultra-thin window energy dispersive X-ray spectroscopy (EDXS) detectors for micro-analyses. Specimens for AEM were mechanically ground, dimpled to thickness of ~20 μm, and then ion-milled to electron transparency. All specimens were carbon-coated before AEM examination to avoid surface charging.

3 Results

Figure 1 shows the XRD pattern of the Sm sample before and after the heat treatment at 1450°C. A marked difference appears in the intensities of the characteristic XRD peaks between α' and β' phases, indicating the changes in the β':(α' + β') ratio. Approximately 11% β' was found in the as-sintered Sm sample; this was increased significantly to 57% after heat treatment at 1450°C for 120 h. This is the clear evidence of the α' to β' transformation during the isothermal heat treatment. Accompanying the transformation was crystallization of the glassy grain boundary phase to form melilite (M').[11] In the case of the Yb SiAlON sample, a less dramatic transformation was noticed by XRD with the β':(α' + β') ratio increasing from 48% in the as-sintered sample to 68% after heat treatment at 1300°C for 96 h. Yb YAG was the grain boundary phase in the heat-treated sample.

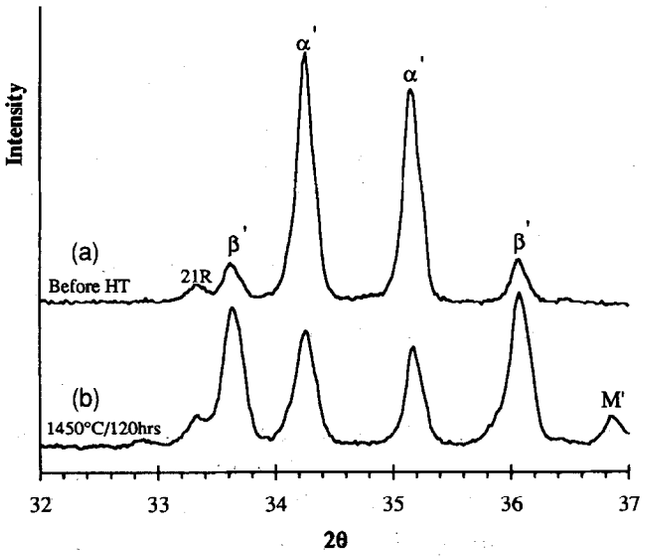

Fig. 1. XRD patterns for the Sm (α + β)-SiAlON specimens (a) before and (b) after heat treatment at 1450°C for 120 h, showing that a significant amount of α' phase has transformed to β' phase during the heat treatment. 21R and M' are 21R SiAlON polytypoid and Al-containing melilite phases, respectively.

Microstructures of the samples after the heat treatments were studied using AEM. Based on the XRD results, the microstructure should consist of two β' phases: the 'original' β' formed at sintering temperature and the transformed β' resulting from the transformation. Figures 2(a) and (b) show typical bright-field and dark-field images of the Sm sample after heat treatment, in which a β' grain with unique microstructural features is revealed. This microstructure in fact comprises two distinct grains, one is basically a defect-free β' crystal whereas the other contains a high density of dislocations and a large amount of ultra-fine (~40 nm) spherical inclusions which are often associated with the dislocations. It is emphasised that this kind of microstructure is commonly observed in the heat-treated Sm (α' + β') samples. Electron diffraction patterns in the (1 0 $\bar{1}$ 0) zone [Figs 2(c) and (d)] positively identify that both grains have the β-Si_3N_4 structure and a similar crystallographic orientation with a very small angle of misfit between them. EDXS analyses [Fig. 2(e)] from the two grains, excluding the spherical inclusions, showed the presence of Si, Al, O and N but no Sm, further confirming the grains to be β-SiAlON.

Burgers vector analysis using two-beam conditions and $\mathbf{g}\cdot\mathbf{b} = 0$ criteria verifies that the dislocations have $\mathbf{b}$ = [0 0 0 1], which is a common type of dislocations found in β-Si_3N_4/SiAlON materials.[12,13] The ultra-fine spherical inclusions, examined by nano-probe EDXS analysis, have different compositions from both the α' and β' grains and are particularly rich in Sm and O (Fig. 3). It should be noted that, although an 8 nm electron probe was used in the EDXS analysis, the surrounding β-SiAlON matrix may have made a significant contribution to the EDXS result of the inclusions, increasing their apparent Si and N concentrations. As a consequence, the actual Sm and O or even Al contents of the inclusions can be higher than that apparently observed in the spectrum shown in Fig. 3(a). It is seen from Fig. 2 that dislocations change their directions when passing through the fine spheroids. This feature discounts the possibility that the spheroidal inclusions are some artefacts of specimen preparation. Figure 4 shows a high magnification TEM image of a region that contains a number of fine spheroidal inclusions. It is clear that even within a single spheroid, the moiré pattern and lattice fringes may vary, suggesting a complex nature of these spheroids; i.e. a single spheroid may consist of several crystals as well as an amorphous region. A similar microstructure has also been observed in the Yb (α' + β') sample after heat treatment at 1300°C for 96 h (Fig. 5), which confirms the

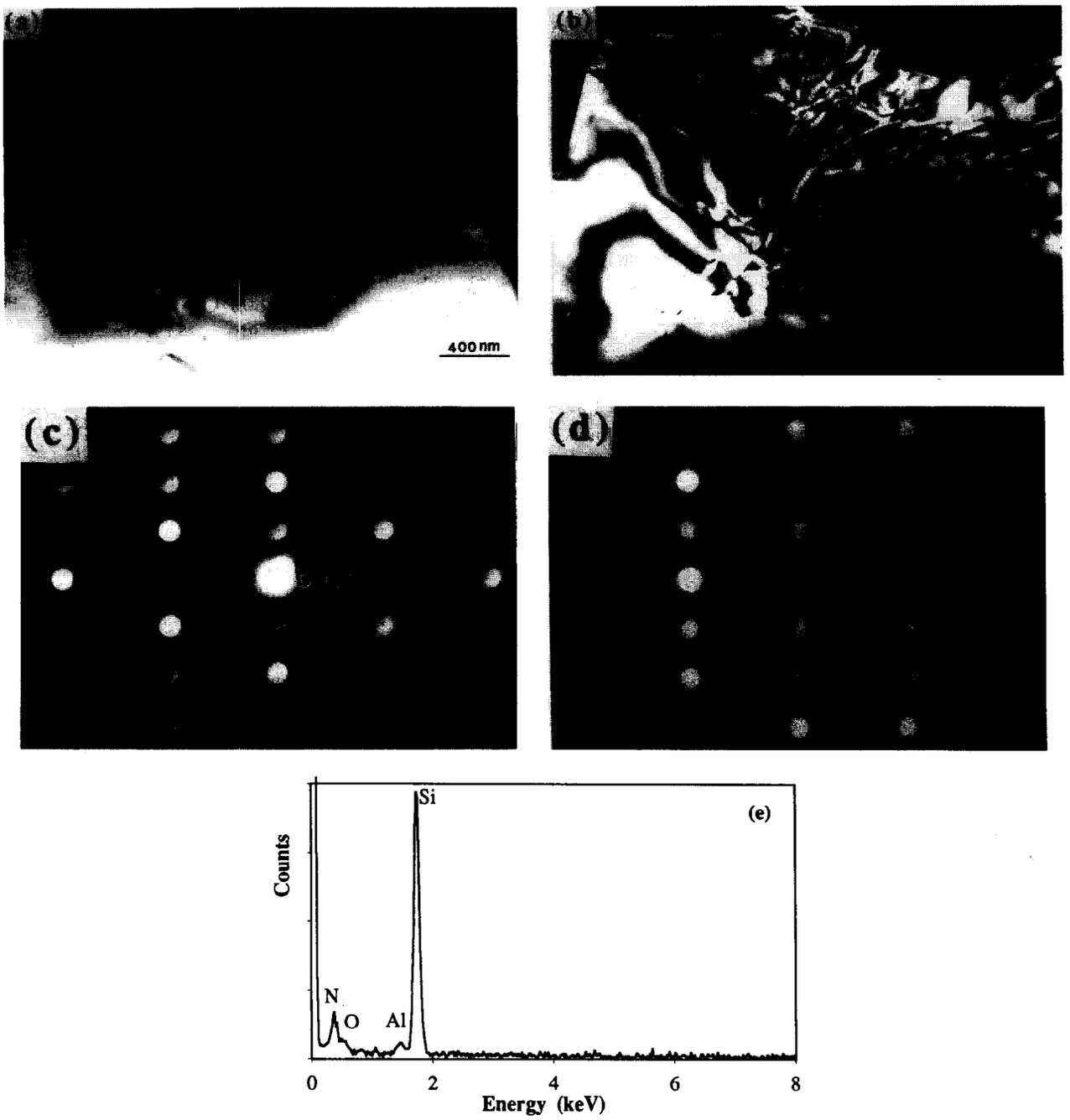

Fig. 2. (a) Bright-field and (b) dark-field TEM images of a β' grain in the heat-treated sample. Electron diffraction patterns in the (1 0 $\bar{1}$ 0) zone (c) from defect-free region and (d) from dislocated region, and (e) EDXS spectrum has confirmed both regions to be the β' phase.

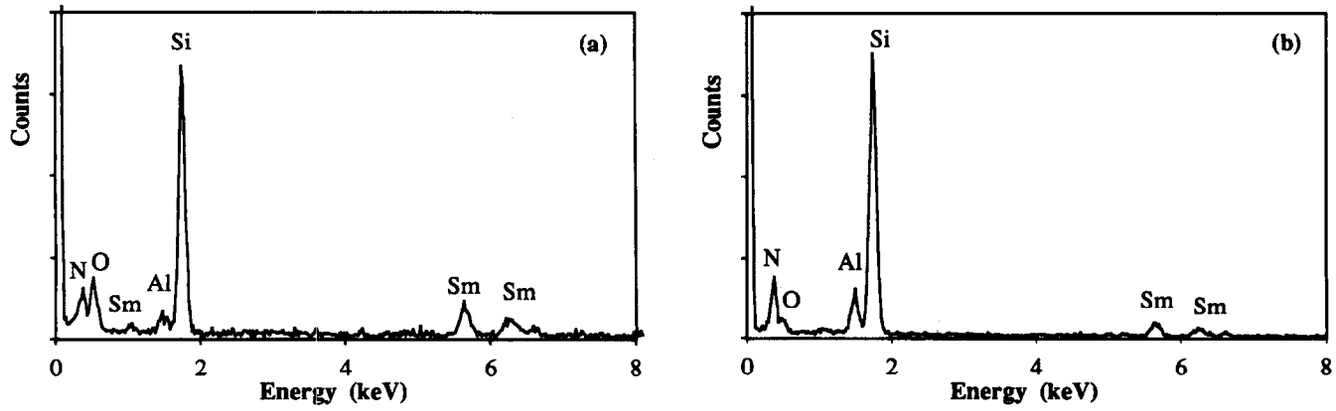

Fig. 3. EDXS spectra for (a) the ultra-fine inclusions and (b) α' grains in the heat-treated Sm sample. Note the Sm and O peaks in (a) are higher than those in (b).

Fig. 4. High magnification image of ultra-fine inclusions in a β' grain. The contrast of the inclusions shows different moiré patterns, indicating a complicated nature of the inclusions. Note the association of dislocation with the inclusions.

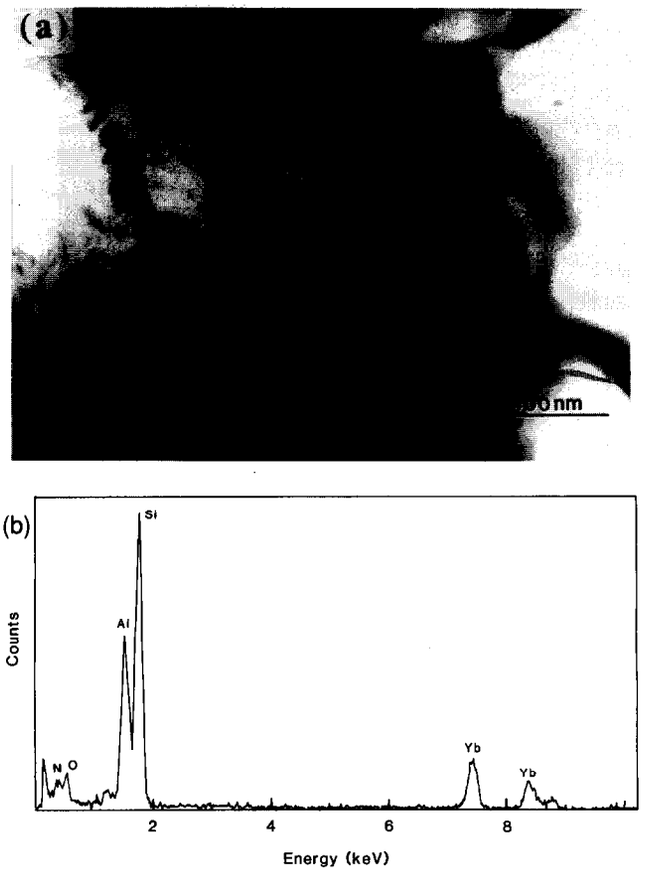

Fig. 5. (a) TEM micrograph of Yb SiAlON sample heat-treated at 1300°C for 96 h; (b) EDXS of spheroids in the microstructure.

commonality of the spheroid/dislocation features in the materials undergoing the α' to β' transformation. Extensive TEM studies failed to identify the similar feature in the Sm sample prior to the heat treatment and, to the knowledge of the authors, this type of microstructure has not been observed or reported in the as-sintered SiAlON materials. It is, therefore, suggested that this microstructure is a unique feature associated with the α' to β' transformation.

4 Discussion

4.1 Identification of the transformed β' particles

The β' form of the SiAlON structure is unable to accommodate any detectable amount of the rare earth cations; conversely the α' form requires the cations to stabilize its structure.[4] The dispersion of large amounts of Sm-rich inclusions in a β' grain represents a thermodynamically unstable state and this microstructure is unlikely to be developed during sintering at 1800°C. Post-sintering heat treatment at 1450°C produces M' ($Sm_2Al_xSi_{3-x}O_{3+x}N_{4-x}$) as a stable grain boundary phase,[11] during which the free energy of the system is reduced. Clearly redispersing of Sm from grain boundaries into β' grains would increase the free energy and hence it is unreasonable to assume these inclusions to be a result of diffusion of components from the grain-boundary phase during heat treatments. Considering the fact that the α' phase must effectively reject the stabilizing rare earth cation to proceed the transformation, we suggest that the Sm- or Yb-rich spheroids are originally a part of the α' composition which has been excluded from the structure during the transformation from α' to β' structures. Therefore the spheroidal inclusions described above are a unique feature resulting from grains which have undergone the α' to β' phase transformation.

The observed α' to β' transformation indicates that the β' phase has a lower free energy than the α' composition at 1450°C and hence the reduction in free energy ensures a thermodynamic driving force for this transformation to take place. In the α-Si_3N_4 to β-SiAlON transformation during sintering, the process can be facilitated as existing β' grains provide effective nucleation sites which would significantly reduce the interfacial energy.[13] There is no apparent reason why the two adjacent β' grains observed in Fig. 2 should develop such distinct microstructural features if they both formed in the primary sintering process. It is, therefore, very likely that the defect-free β' grain adjacent to the spheroid/dislocation-containing β' grain in Fig. 2 is a pre-existing β' phase which acts as a heterogeneous nucleus for the transformation to occur. The close crystallographic relationship between the two neighbouring β' grains provides evidence of epitaxial heterogeneous nucleation. After the phase transformation, the β' particle size is increased and its grain morphology becomes erratic (Fig. 6), further supporting that nucleation and growth is a mechanism of the transformation.

4.2 Microstructural development in the transformation

Because of the reconstructive nature of the transformation and low diffusivity of SiAlON lattices,

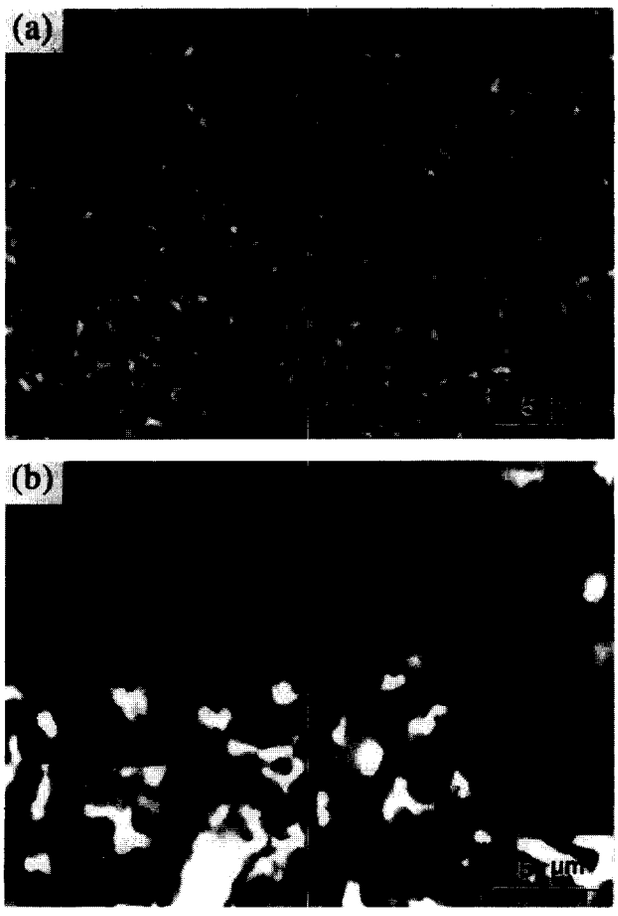

Fig. 6. SEM images of the Sm samples (a) as-sintered and (b) heat-treated at 1450°C for 120 h. The multiphase feature comprises β' (dark grey), α' (light grey), 21R (dark needle shape) and grain boundary phases (white). Note the increase in β' content and changes in its morphology after the heat treatment.

the α' to β' transformation must involve a liquid phase to promote diffusion and hence may only occur above the eutectic temperature of the system. The Sm sample shown in Fig. 2 was heat-treated at 1450°C for 120 h. It was found that after the initial 24 h heat treatment, very little glass was remained at SiAlON grain boundaries but the α' to β' transformation proceeded continuously with a constant rate in the subsequent heat treatment.[6] It seems that a large amount of liquid phase may not be a necessary premise for the α' to β' transformation although liquid is essential to this process. The spherical shape of the inclusions suggests these particles to be liquid at the heat treatment temperature but the exact origin of this liquid is equivocal at this stage. There is a possibility that, after facilitating the transformation, the residual liquid at interfaces between the nuclei and the transforming grains is left behind in the grain as the transformation frontier is advanced. It is also possible that when the transformation is initiated, the rejected Sm^{3+} cations may react with other SiAlON elements upon diffusion and create ultra-fine local liquid regions within the transforming α' grain, which could further assist the transformation. Clearly more studies are required to further understand the nature of these super-fine inclusions. The structural complication of the spheroids demonstrated in Fig. 4 indicates compositional inhomogeneity among these inclusions. This is a feature contrary to the generally homogeneous grain boundary liquid but corresponds to the local compositional fluctuation in solid solutions. In either cases, however, it seems that the amount of liquid phase involved in the phase transformation is insignificant.

The transformation from α' to β' phases depends on atomic diffusion. The formation of large amounts of dislocations in the transformed β' grains is an indication of imperfection of the diffusion, which is a combined effect of strong atomic bonding, low thermal energy and a limited amount of liquid phase. The bending of dislocations around the spheroids suggests that these super-fine aliens may also be a cause for the formation of dislocations. On the other hand, the association of these spheroids with dislocations ensures a relatively easy diffusion because the activation energy for pipe (dislocation) diffusion is less than for lattice diffusion and this is particularly evident at relatively low temperatures.[14] The feature observed in Fig. 2 may imply the characteristic of a medium stage of the transformation, in which the fine liquid regions have been solidified on cooling. During the transformation, these Sm-rich liquid spheroids would gradually diffuse out of the transformed grain along the dislocations and form a crystalline phase(s) at grain boundaries. The completion of the transformation is marked by the elimination of these inclusions from the transformed β' grains. This would further reduce the free energy of the system and induce an additional driving force to encourage the transformation. Previous studies on the Sm SiAlON samples have observed an increase in the amount of the grain boundary phase (M') and a decrease in the z value of the β' phase following the prolonged transformation process.[6,8] These results support the present assumption. In addition, it was found that the dislocation density of silicon nitride grains decreased with extending the heat treatment time.[12] This may explain why the amount of the transformed β' grains containing the spheroid/dislocation feature in the heat-treated samples is less than the proportion of the $\alpha' \rightarrow \beta'$ transformation recorded by XRD.

5 Conclusions

Unique microstructural features resulting from the α to β-SiAlON transformation have been observed in Sm and Yb ($\alpha + \beta$)-SiAlON samples.

Heterogeneous nucleation on pre-existing β' phases occurs in the transformation and the transformed grains contain large amounts of Sm/Yb-rich ultrafine spherical inclusions which are associated with dislocations. These inclusions may be a liquid phase accompanying the transformation that is solidified on cooling. The microstructure of spheroid/dislocation in a β' grain presents a unique feature of the α' to β' transformation. The diffusion of the rejected elements, namely Sm and Yb, from a transformed α' structure proceeds mainly along dislocations, which has a lower activation energy than lattice diffusion.

Acknowledgements

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