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Study on oxidation behavior of (Nd,Y)- and (Nd,Yb)-α-Sialon

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The oxidation behavior of multi-cation α-Sialons containing Nd and Y or Yb has been investigated for the compositions $(Nd_{0.18}Y_{0.18})Si_{10.38}Al_{1.62}O_{0.54}N_{15.46}$ and $(Nd_{0.18}Yb_{0.18})Si_{10.38}Al_{1.62}O_{0.54}N_{15.46}$ respectively in the temperature range of 1200°C to 1400°C in air. The grains of silicate containing Nd and Y as well as Nd and Yb were observed in preferred orientation on the surface of the materials oxidized at 1200°C or 1300°C for 20 h for (Nd,Y)- and (Nd,Yb)-α-Sialon respectively. By increase of oxidation temperature from 1300°C to 1400°C, bubble, which was caused by softening of silicate oxidation layer, occurred and glassy phase then appeared obviously. The phases formed on the surfaces of multi-cation α-Sialons during the oxidation were also discussed in this paper.

1. Introduction

It is well known that the densification of Si_3N_4-based ceramics is assisted by the liquid produced by the additives and the oxide layer on Si_3N_4 powder. The grain boundary phase, formed by this liquid after cooling down, is important for the high temperature properties. For α-Sialon [1] (abbreviated as α', $M_XSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$ with $x \leq 2$ and M = Li, Ca, Mg, Y and some of the lanthanide elements), the cation can be absorbed into α' structure in the later stage of sintering, thus cleaning the grain boundary.

It is understood that using multiple oxides as sintering additives to stabilize α' structure can lower the eutectic point of the system, thus facilitating the sintering process, as reported by Huang [2] and in our previous work on (Ca, Mg)-α-Sialon [3]. On the other hand, the influence of multi-cation on the formation behavior of α' phase and mechanical properties of Sialon materials would also be interesting to materials scientists [3–9]. The results have shown that when added with Y_2O_3 and CaO, the large rare earth ions such as Ce^{3+}, Sr^{2+} can be partially absorbed into the α' structure [4–6]. Using $(Y_2O_3 + La_2O_3)$ and $(Y_2O_3 + Nd_2O_3)$ as additives, Ekström etc have found that the Sialon materials are easy to densify while having similar mechanical property to Y-Sialon [7, 8].

It is noted in our recent research on the formation behavior of multi-cation α-Sialon, (Nd,Y)-α' and (Nd,Yb)-α' [9], that by the use of mixture of light and heavy rare earth oxides as additives to form α-Sialon, the eutectic temperature in the system could be lowered, thus promoting the dissolution of intergranular crystalline melilite solid solution phase (abbreviated as M′) into the liquid and facilitating the precipitation of α'. It was reported that the amount of α' phase (around 95 wt%) was higher than that of counterpart single rare earth doped α' composition, especially much higher than that of Nd-α'. TEM and EDS results further revealed that the small-radius ions intended to enter α' structure while the large-radius ions remained in the grain boundary [9]. In comparison with multi-cation α-Sialons, the crystalline phases of single-cation Nd-α' consisted of α', β-Sialon (abbreviated as β') and M′ and the amount of latter two phases for composition with x value of 0.36 was as high as 30 wt% and 10 wt% respectively [10].

The present paper focuses on the oxidation behavior of (Nd,Y)-α' and (Nd,Yb)-α' in the high temperature range (1200°–1400°C), with intention to explore the influence of the addition of multi-cation oxides on oxidation behavior.

2. Experimental

Compositions used in the present work were located on the join line Si_3N_4-R_2O_3 : 9AlN with a special formula $R_xSi_{12-4.5x}Al_{4.5x}O_{1.5x}N_{16-1.5x}$ ($x = 0.36$, R = 0.5Nd + 0.5Y and 0.5Nd + Yb), i.e. $(Nd_{0.18}Y_{0.18})Si_{10.38}Al_{1.62}O_{0.54}N_{15.46}$ and $(Nd_{0.18}Yb_{0.18})Si_{10.38}Al_{1.62}O_{0.54}N_{15.46}$ for (Nd,Y)-α' and (Nd,Yb)-α' respectively. The starting powders used were Si_3N_4(UBE-10, Japan, 2.0 wt%O), AlN(1.3 wt%O), Al_2O_3(CR30, Wusong Chemical Plant, China, 99.5%), R_2O_3(R = Nd, Y and Yb, Yaolung Chemical Plants, China, 99.9%). The powders were milled under absolute alcohol for 48 h in a plastic jar, using Si_3N_4 milling media. Pellets of dried powders were hot-pressed under nitrogen atmosphere in a graphite resistance furnace at 1750°C for 2 h.

The as-fired samples were cut into rectangular pieces with dimensions of 6 mm × 7 mm. After grinding into 1 mm in thickness, the samples were carefully polished on both surfaces. Prior to oxidation, the samples

were ultrasonically cleaned in acetone, followed by a cleaning in ethanol. The specimens, holding in an alumina tray, then were put in a muffle furnace at 1200°, 1300°C and 1400°C for 20 h respectively. Typical heating rate of the furnace was around 200°C/h. Weight gains of the specimens were measured using a balance with resolution of 0.1 mg. The phase analysis of the oxidized surfaces was performed by X-ray diffractometer. Microstructure observation of the oxidized surfaces was carried out in a scanning electron microscope (SEM) (KYKY 2000 equipped with a Link ISIS 3.00 EDX system, China), using secondary electron for imaging. For the cross-section observation, the oxidized samples were immersed in polymer and polished along the cross-section. The analysis of EDAX was also performed for element analysis when SEM observation was carried out.

3. Results and discussion

Table I lists the phase assemblages of the 1750°C hot pressed samples. As shown in the table, the phase assemblages mainly consist of α', along with a small amount of β' and M′ phase ($R_{2-x}Si_{3-x}Al_xO_{3+x}N_{4-x}$).

The polished samples were oxidized at temperature ranging from 1200°C to 1400°C for 20 h. The weight increase and the phase assemblage of the oxidized samples are listed in Table II. It can be seen that the weight increase of (Nd,Yb)-α' is less than that of (Nd,Y)-α' at the same oxidization temperature, especially at higher temperature. XRD results indicated that, similar to the ones of oxidized single cation R-α' (R = Nd, Dy and Y) [11], the oxidized surfaces contained preferentially-oriented silicate crystallites at oxidation temperatures 1200°C and 1300°C, while mainly consisted of SiO_2 at 1400°C. It was necessary to note that, besides A-$Nd_2Si_2O_7$, no any XRD peak of A-$Y_2Si_2O_7$ and A-$Yb_2Si_2O_7$ was detected for (Nd,Y)-α' and (Nd,Yb)-α' samples respectively oxidized at both 1200°C and 1300°C, although β-$Yb_2Si_2O_7$ phase appeared on the 1300°C-oxidized surface of (Nd,Yb)-α'.

TABLE I Phase assemblages of $Nd_{0.18}(Y/Yb)_{0.18}Si_{10.36}Al_{1.62}O_{0.54}N_{15.46}$ hot-pressed at 1750°C for 2 h

	Phase assemblage			
Sample	α'	β'	M′[a]	Density (g/cm^3)
(Nd,Y)-α'	96	3	1	3.32
(Nd,Yb)-α'	93	5	2	3.41

[a]see text.

SEM micrographs of (Nd,Y)-α' and (Nd,Yb)-α' samples oxidized at 1200°C, 1300°C and 1400°C are shown in Figs 1 to 5. As seen from Fig. 1, the 1200°C-oxidized surfaces contain extensive silicate crystallites, along with some small holes (3–8 μm) due to the N_2 evaporation in the oxidation process. The crystallites are tetragonal and longitudinal on oxidized (Nd,Y)-α' surface while mainly tetragonal on oxidized (Nd,Yb)-α' surface. The composition of silicate crystallites was further analyzed with EDS. The results (see Fig. 1c and Fig. 1f) revealed that both Nd and Y, Nd and Yb have been found in silicate crystallites on the surfaces of (Nd,Y)-α' and (Nd,Yb)-α' oxidized samples respectively, suggesting that the $Nd_2Si_2O_7$ phase, identified by the XRD, was actually $(Nd,Y)_2Si_2O_7$ or $(Nd,Yb)_2Si_2O_7$ solid solubility. The fact that the ratios of (Nd + Y) or (Nd + Yb) to Si were much lower than 1 : 1, which was about 0.3 for (Nd,Y)-α' sample, for example, may be due to the influence of background on EDS signal, since the silicate crystallites were smaller than the depth range of EDS signal (around 1–2 μm).

After oxidization at 1300°C for 20 h, a lot of bubbles formed on the surface (see Fig. 2 and Fig. 3). On these bubbles, some longitudinal silicate crystallites were present. EDS results also confirmed the existence of both Nd, Y and Nd, Yb in silicate crystallites for (Nd,Y)-α' and (Nd,Yb)-α' oxidized samples respectively.

When oxidation temperature was increased to 1400°C, a transparent glassy film was formed (see Fig. 4). The observation of cross-section of oxidized samples, as shown in Fig. 5, exhibited the transition of the oxidized layer from dense layer to porous structure.

It is interesting to be pointed out that the ratio of Nd to Y in silicate crystallites for (Nd,Y)-α' oxidized surface was different from the one of Nd to Yb in (Nd,Yb)-α' case. For the former sample, the Nd : Y ratio (around 1 : 1) remained almost constant when the oxidization temperature increased from 1200°C to 1300°C. On the contrary, the Nd : Yb ratio was around 1 : 1 for those crystallites formed on the 1200°C-oxidized (Nd,Yb)-α' surface while those crystallites, formed on the 1300°C-oxidized (Nd,Yb)-α' surface, were found to have two different compositions with Nd : Yb ratios around to be 6 and 1.5 respectively. This suggests the diffusion of Yb^{3+} is accelerated at high oxidation temperature.

Except for 1300°C-oxidized (Nd,Yb)-α' sample, the fact that only XRD peaks of preferentially oriented A-$Nd_2Si_2O_7$ are present on the surfaces of multi-cation-α' oxidized at both 1200°C and 1300°C, suggesting that the $(Nd,Yb/Y)_2Si_2O_7$ crystallites

TABLE II Oxidation weight gain and phase assemblages of the oxidized surfaces of multi-cation α-Sialons ceramics

			Phase assemblage	
Sample	Oxid. temp. (°C)	Weight gain (mg/cm^2)	Major phase	Minor phase
(Nd,Y)-α'	1200	0.3	A-$Nd_2Si_2O_7$, α'[a]	SiO_2, β'[a]
	1300	2.3	A-$Nd_2Si_2O_7$, α'[a], SiO_2	β'[a]
	1400	9.0	SiO_2	
(Nd,Yb)-α'	1200	0.3	A-$Nd_2Si_2O_7$, α'[a]	SiO_2, β'[a]
	1300	1.7	α'[a], β-$Yb_2Si_2O_7$, A-$Nd_2Si_2O_7$, SiO_2	β'[a]
	1400	3.8	SiO_2	

[a]X-ray diffraction patterns from bulk material.

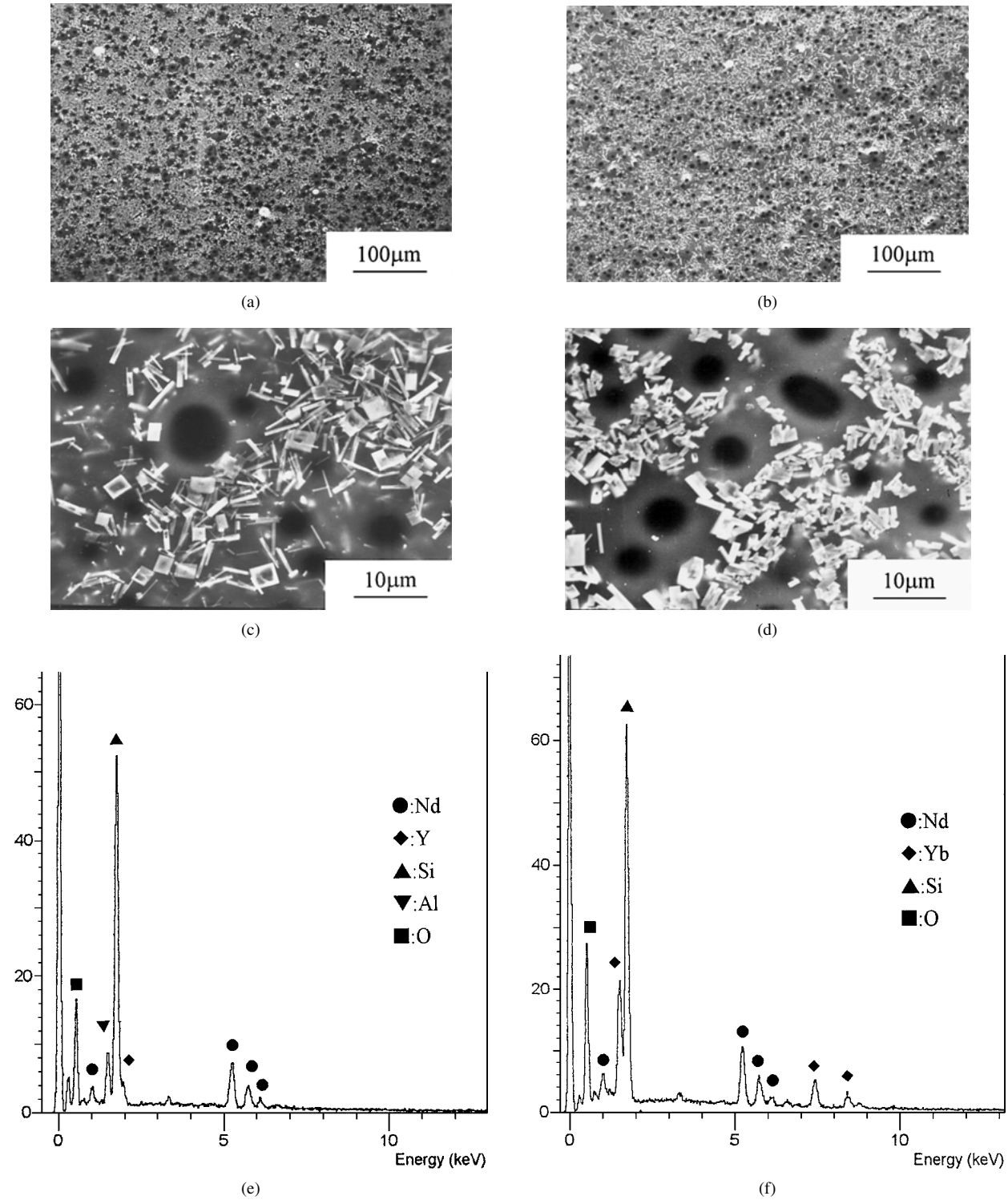
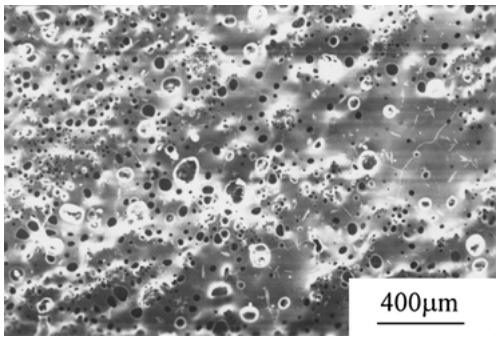
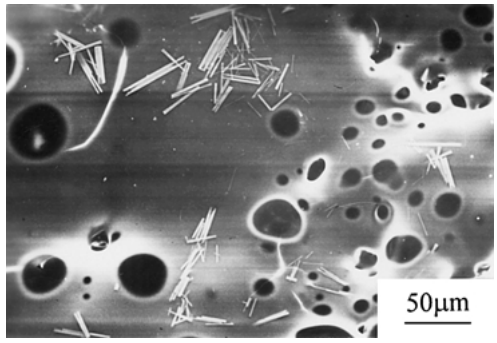


Figure 1 SEM micrographs of surfaces of (a) (Nd,Y)-α', (b) (Nd,Yb)-α' oxidized in air at 1200°C for 20 h. (c) and (d) are the enlarged photos of (a) and (b) respectively. (e) and (f) are the typical EDS patterns of the white grains shown in (c) and (d) respectively. Note that the ratios of Y : Nd and Yb : Nd estimated from the EDS patterns are ∼1.

formed during oxidation possess the same structure and preferential orientation as A-$Nd_2Si_2O_7$. As mentioned above that smaller rare earth ions $Yb^{3+}(Y^{3+})$ entered more easily into the α' structure than the larger Nd^{3+} reported in our previous study on formation behavior of multi-cation α-Sialons containing neodymium and ytterbium or yttrium [9]. Therefore, $Yb^{3+}(Y^{3+})$ content is higher than that of Nd^{3+} in α' grain. On the other hand, more Nd^{3+} are founded in the grain boundary phase of the materials. It is well known that the oxidation occurs firstly at grain boundary of the material, thus the rare-earth ions inside the boundary diffuse outward to the surface silicate layer in the beginning of the oxidation. Consequently, the initial oxidized silicate layer contains more Nd ions and facilitates the crystallization of preferentially oriented $Nd_2Si_2O_7$ grains. When the oxidation further proceeds, the α' grains start to oxidize, which increases the relative content of Yb/Y ions in the surface silicate layer. Some of these Yb/Y ions solve into the previously formed $Nd_2Si_2O_7$ crystalline



(a)



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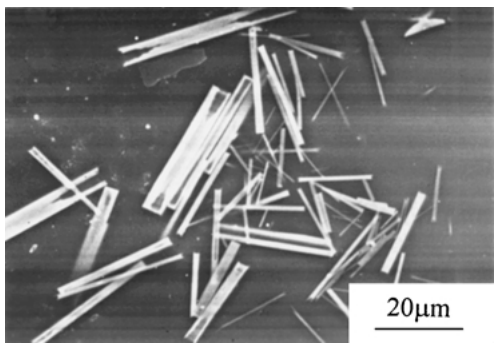
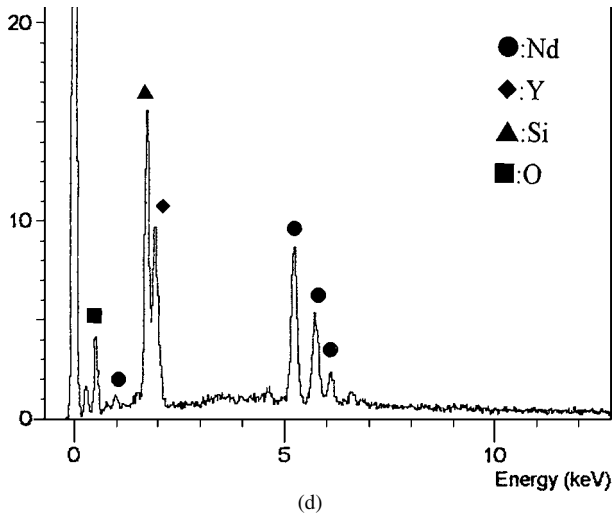
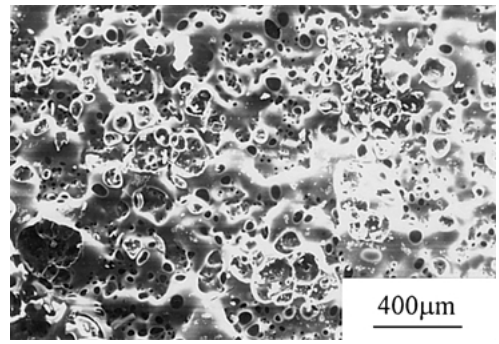


(c)

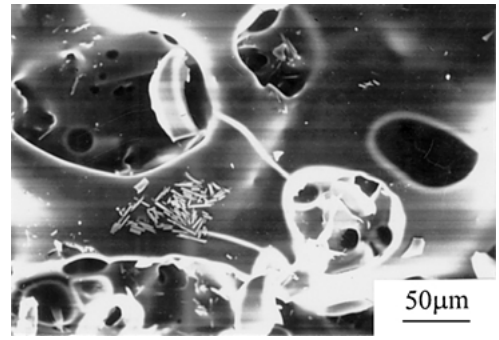


(d)

Figure 2 (a) SEM micrograph of surface of (Nd,Y)-α' oxidized in air at 1300°C for 20 h. (b) and (c) are the enlarged photos of (a). (d) is the typical EDS pattern of the white grains shown in (c). Note that the ratio of Y : Nd estimated from the EDS pattern is ∼1.



(a)



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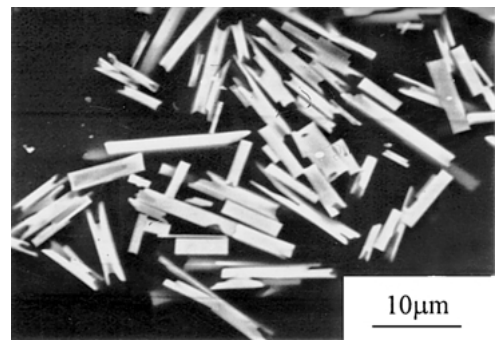
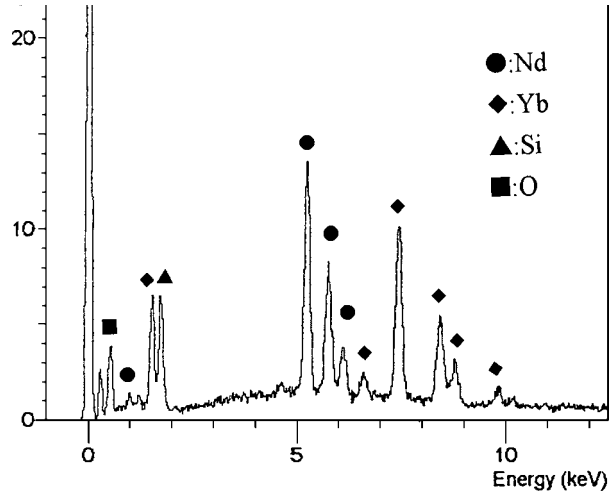


(c)

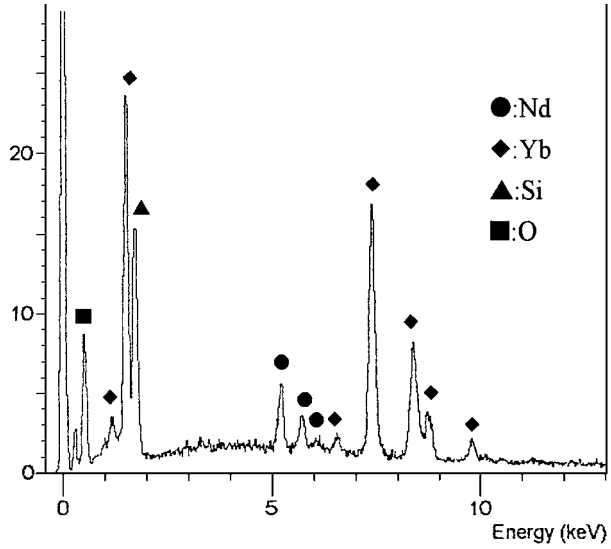
Figure 3 (a) SEM micrograph of surface of (Nd,Yb)-α' oxidized in air at 1300°C for 20 h. (b) and (c) are the enlarged photos of (a). (d) is one typical EDS pattern of the white grains shown in (c). (e) is another EDS pattern of the white grains shown in (c). Note that the Yb : Nd ratios are estimated to be ∼1.5 in (d) and ∼6 in (e) respectively. (*Continued.*)

and form the $(Nd,Yb/Y)_2Si_2O_7$ with the ratio of Nd to Yb/Y around 1 : 1. On the other hand, the ratio of Yb to Nd around 6 is attributed to the contribution of β-$Yb_2Si_2O_7$ formed at 1300°C-oxidized (Nd,Yb)-α' surface. For (Nd,Yb)-α' composition, Yb ions intend to solve into the A-$Nd_2Si_2O_7$ crystalline when oxidized at 1200°C. With increasing oxidation temperature, significant Yb ions diffuse to the oxidized layer and thus β-$Yb_2Si_2O_7$ crystalline is formed instead. The fact that the crystalline formed at different temperatures possesses different morphologies may be related to the viscosity of the silicate layer and rare earth ions concentration, which needs to be further investigated.

As discussed above, during oxidation process, a silicate layer with rare earth silicate crystallites forms on the surfaces of (Nd,Y/Yb)-α'. When oxidation temperature is high enough as to close to the eutectic point of rare earth silicate, the layer softens and consequently, bubbles form due to N_2 evaporation. When temperature further increases to 1400°C, liquid is formed in the oxidized surface layer, in which the rare-earth ions dissolve. SiO_2 phase is therefore the only phase to be present on the surface layer.

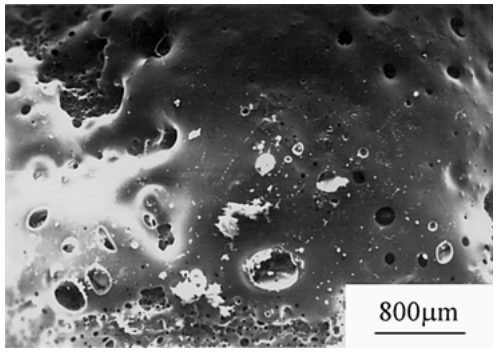


(d)

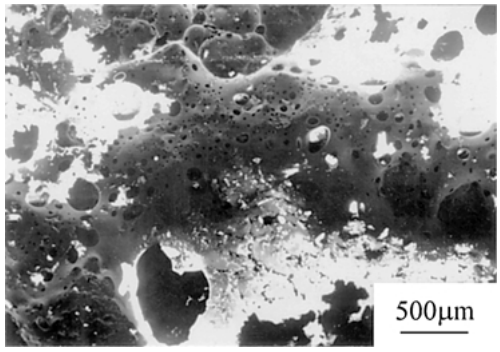


(e)

Figure 3 (*Continued.*)

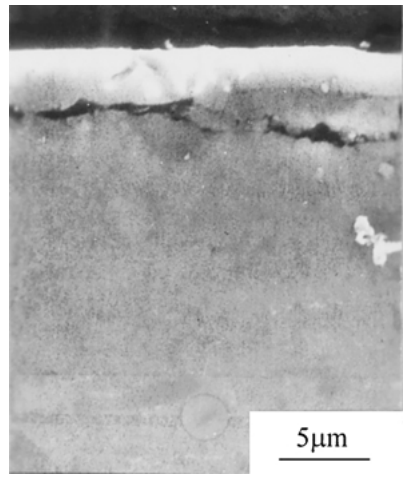


(a)

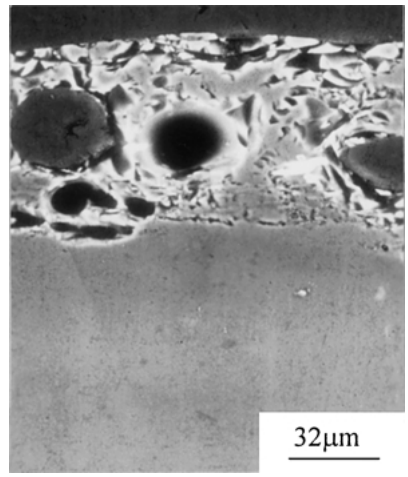


(b)

Figure 4 SEM micrographs of surfaces of (a) (Nd,Y)-α' and (b) (Nd,Yb)-α' oxidized in air at 1400°C for 20 h.



(a)



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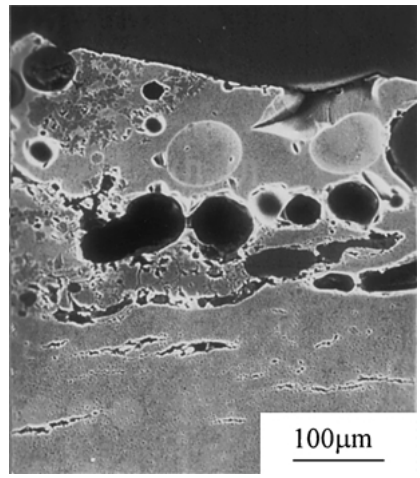

(c)

Figure 5 SEM micrographs of the cross section of (Nd,Y)-α' oxidized at (a)1200°C, (b)1300°C and (c)1400°C for 20 h.

4. Conclusion

1. Preferentially oriented silicate crystallites are present on the surfaces of multi-cation (Nd,Y/Yb)-α', after oxidized at 1200° and 1300°C for 20 h. With increase of the oxidation temperature, the dense oxidized silicate layer softens to form bubbles. When oxidation temperature further increases to 1400°C, transparent glassy phase is formed on the oxidized surface.

2. During initial oxidation process, relatively more Nd ions in the grain boundary diffuse to the oxidized

layer and form preferentially oriented A-$Nd_2Si_2O_7$ crystallites. The Y(Yb) ions released from further oxidation of α' grains tend to dissolve into the A-$Nd_2Si_2O_7$ crystallites.

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