Kinetics of rare earth incorporation and its role in densification and microstructure formation of α-SiAlON

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Abstract

The reproducible sintering and microstructure formation of α- and α/β-SiAlONs is a precondition for the production of such materials with reproducible properties.

The Rietveld method was used for quantitative analysis of the phase composition and the kinetics of incorporation of the rare earth into the α-SiAlON structure. The analysis showed that in the early stages of sintering more rare earth cations were incorporated into the grains than would be expected from the equilibrium conditions. This was observed for all investigated rare earths (Y, Nd and Yb) with different ionic radii. The consequences for sintering and microstructure formation are the fast disappearing of the transient liquid and the formation of polytypes. The use of excess of rare earth in comparison to the stoichiometric SiAlON composition results in a stable residual liquid. It allows reproducible densification, anisotropic grain growth and materials with high fracture toughness.

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Keywords: Sintering; Microstructure; SiAlONs

1. Introduction

Development of α- and α/β-SiAlON ceramics has increasingly gained interest over the last few years due to the higher hardness and higher chemical resistance of these materials in comparison with those of β-Si₃N₄ materials and the correspondingly better wear properties in cutting tool applications.[1–3] α-SiAlON ($M_x Si_{12-(m+n)} Al_{m+n} O_n N_{16-n}$, ($x = m/v$ and v is the valance of the cation M^{+v}; M = Li, Mg, Ca, Y and some rare earth elements $Z > 60$) has the same structure as α-Si₃N₄. This structure is stabilized by simultaneously incorporating the stabilizing cation M, Al, and O into the α-Si₃N₄ lattice. Al and O partially replace Si and N, whereas the stabilizing cation occupy an interstitial whole in the lattice.[1] The stability region of the α-SiAlON strongly depends on the nature of the cations. The smaller rare earth cations fit better into the α-SiAlON lattice and therefore a larger homogeneity region of the α-SiAlON is formed[1,3,16] (Fig. 1). The stability region of the α-SiAlON does not include the pure Si₃N₄ composition, because the α-Si₃N₄ is metastable at high temperatures. It is well known that the densification of β-Si₃N₄, and of α- and β-SiAlON materials is a liquid phase

sintering process. Above 1250 °C (depending on additives) an oxide liquid forms in which Si₃N₄ solves with increasing temperature, and β-Si₃N₄ or β- or α-SiAlON precipitates depending on the composition. In the case of α-SiAlON solved in the liquid rare earth oxide and, AlN/Al₂O₃, precipitated together with Si₃N₄ forming the α-SiAlON phase. By this chemical reaction the amount of the liquid strongly reduces or completely disappears. The kinetics of the consumption of the liquid strongly depends on the nature of the rare earth.[9,19] A fast consumption of the liquid results in a retardation of the densification and a small-grained equiaxed microstructure. Therefore it is difficult to completely densify materials with *m*- and *n*-values less than 1 without external pressure.[1,14] Because of that the existence of a liquid up to high temperatures is a precondition for a good densification behavior and grain growth in α-SiAlON materials.

Despite thoughts to the contrary in the 1980s and 1990s, it is now well established that α-SiAlON and α/β-SiAlON ceramics can also be sintered in such a way that the grain morphology becomes elongated as in β-Si₃N₄ materials. The result of this changed microstructure is an increase in the fracture toughness and strength of the materials to levels comparable to those of the β-SiAlON materials. Analysis of the literature revealed the following conditions for formation of elongated α-SiAlON grains:

- Nordberg showed that elongated grain growth can be achieved for high *n* and *m* values and sintering temperatures in the range
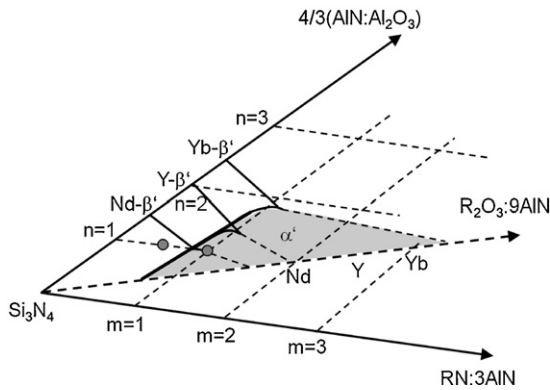

Fig. 1. Sample compositions with respect to homogeneity ranges of the α-SiAlONs.

of 1900 °C[4]; increasing the amount of sintering additives (thus increasing the amount of liquid at the sintering temperature) accelerates the anisotropic growth of α-SiAlON grains.[5–7]

- Use of mixed rare earth oxides and Ca results in more elongated grains.[3]
- β-Si$_3$N$_4$ as a starting powder for the synthesis of α-SiAlON ceramics results in retardation of α-SiAlON formation and therefore in an increase in the amount and period of existence of a transient liquid phase. The result is enhanced elongated grain growth.[8,9]
- Use of different sintering aids (CaO, SrO and Y$_2$O$_3$) simultaneously[10–12] and/or MgO and Y$_2$O$_3$[13] results in elongated grain growth.
- An excess of the cation R in comparison with the stoichiometric composition of α-SiAlON results in a small but stable R$_2$O$_3$-rich liquid and therefore also leads to reproducible densification and anisotropic grain growth of α-SiAlON.[14,15]

From the data it can be concluded that the formation of elongated α-SiAlON grains is mainly connected with the existence of a liquid phase with a high concentration of alkaline earth or rare earth elements during the whole sintering process. Successful use of this approach requires that the stability of the α-SiAlONs be taken into account.

Investigation of the stability region of α-SiAlON reveals that the maximum n value (oxygen content in the SiAlON) decreases with increasing rare earth cation size and decreasing

temperature.[9,16] The minimum amount of rare earth needed to stabilize the α-SiAlON (M$_x$Si$_{12-(m+n)}$Al$_{m+n}$O$_n$N$_{16-n}$) is thought to be equivalent to $x = 0.33$ and is nearly independent of temperature. The authors' investigations have shown that for low n values ($n = 0.6$–0.7) the m-value can be as low as 0.75 resulting in x-values as low as 0.25 for R = Y and Yb.[14,15,17] These results were based on the results of Rietveld analysis[15]. Similarly low values were obtained based on EDX measurements but with a much larger scattering of the x values.[18]. The Rietveld method allows precise determination of the amount of rare earth incorporated into the α-SiAlON structure and is therefore the method of choice for determination of the extent of rare earth incorporation.

As was shown previously the distribution of the rare earth between the α-SiAlON phase and the liquid is an important parameter affecting the grain growth behavior. There is no data available in the literature concerning the kinetics of incorporation of the rare earth into the α-SiAlON phase. Therefore the aim of this work was to investigate the kinetics of Nd, Y and Yb incorporation into the α-SiAlON with the nominal composition $n = 1$ and $m = 1$. Based on these results the densification and grain growth behavior of α-SiAlON materials are discussed.

2. Experimental procedure

Different compositions of α-SiAlON were prepared using the starting powders α-Si$_3$N$_4$ (UBE-10, containing 1.6% oxygen), AlN (Tokuyama, containing 1% oxygen), Al$_2$O$_3$ (99.99%, AKP50) and Y$_2$O$_3$, Yb$_2$O$_3$ and Nd$_2$O$_3$ (99.99%, HC Starck). The oxygen contents of the nitride powders were taken into account in the calculation of the compositions (Table 1). In the first series of additives α-SiAlONs with $m = 1$ and $n = 1$ and the same volume contents of excess Nd$_2$O$_3$, Yb$_2$O$_3$ and Y$_2$O$_3$ (in comparison with the α-SiAlON composition) were used. Additionally a composition with $n = 1$ and $m = 1.2$ with and without excess Y$_2$O$_3$ was prepared (Table 1).

A series of materials with compositions in the α/β-SiAlON phase region and with different excess amounts of Y$_2$O$_3$ were also produced.

The starting powders were weighed and milled in water-free isopropanol for 6 h in an agate jar using agate milling media. The wear of the milling media was less than 0.2 wt% and therefore was not taken into account. The mixed powders were dried and isostatically pressed at a pressure of 200 MPa. The size of the

Table 1
Composition of the SiAlON materials.

| Material name | R | m | n | Composition [wt%] | | | | | Theoretical density, g/cm^3 |
				Si$_3$N$_4$	AlN	Al$_2$O$_3$	R$_2$O$_3$	Excess R$_2$O$_3$	
Nd0101	Nd	1	1	75.742	13.011	0.334	10.913	2	3.37
Yb0101	Yb	1	1	74.036	12.718	0.326	12.920	2.8	3.45
Y0101	Y	1	1	78.439	13.474	0.346	7.741	1.5	3.28
Y1210	Y	1.2	1	76.112	15.019	0	8.919	1.5	3.31
Y1210a	Y	1.2	1	77.254	15.244	0	7.552		3.29
Y0609	Y	0.59	0.98	84.79	10.44	0.93	3.84	0	3.25
Y0609a	Y	0.59	0.98	83.43	10.27	0.915	5.38	1.6	3.28
Y0609b	Y	0.59	0.98	82.84	10.21	0.925	6.03	2.31	3.29
Y0609c	Y	0.59	0.98	81.83	10.08	0.926	7.16	3.48	3.29
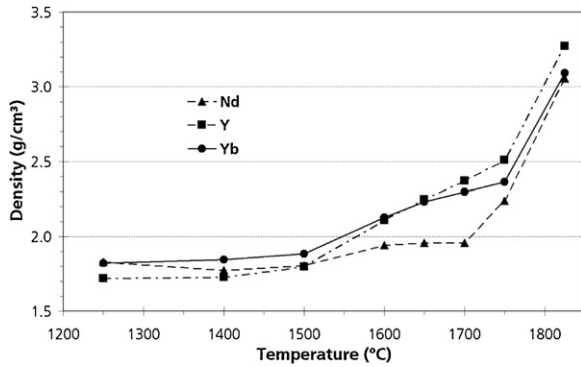
Fig. 2. Density as a function of temperature for the different α-SiAlONs.

samples used for the investigations was $10 \times 10 \times 10$ mm. The compositions are shown with respect to the homogeneity ranges of the α-SiAlONs in Fig. 1.

Sintering was carried out in a gas pressure sintering (GPS) furnace (DS1/150/2000, KCE) in a nitrogen atmosphere (up to 50 bar) at 1825 °C for 2 h.

Apart from being isothermally sintered, the samples were heated at a rate of 10 K/min to different temperatures (1250 °C, 1400 °C, 1500 °C, 1600 °C, 1650 °C, 1700 °C and 1750 °C) with a short dwell time of 5 min for temperature equilibration. The cooling rate was 100 K/min. This was carried out in a furnace with a W heater (11004080 W2, Thermal technology).

The materials Y1210 and Y1210a were hot pressed so that the composition without excess oxide additives could also be densified. Densification was carried out at 1800 °C for 30 min and the samples underwent an additional heat treatment at 1825 °C.

The effect of the excess of Y_2O_3 on density and phase content was investigated using α/β-SiAlON with $m = 0.59$ and $n = 0.98$ and sintered at 1850 °C for 2 h.

For all samples the density was measured by the Archimedes method. Additionally, the theoretical densities of the samples are additionally given in Table 1. The values were calculated assuming that the sample has the equilibrium composition. The samples were cut in the middle and the formed cross sections were analysed to avoid the influence of the sintering skins. Phase composition was measured by X-ray diffraction. XRD measurements were carried out with the diffractometer XRD 7 (Seifert-FPM) using CuK_α radiation. The REFINE++ program (GE Inspection Technology) was used for quantitative XRD analysis and determination of the occupation factors. Details of the Rietveld analysis are given elsewhere[15]. The Rietveld analysis allows to determine the amount of α–β-Si_3N_4 and SiAlONs, and of the other crystalline grain boundary phases formed. The values given are the weight ratios of the crystalline phases. Additionally, the amount of rare earth ions incorporated into the α-SiAlON structure can be determined.[15]

The microstructure was characterized by FESEM (NVISION 40, Carl Zeiss SMT AG, Germany). The composition of the grain boundary phase was determined qualitatively using EDX. For a quantitative analysis the pockets were too small.

3. Results and discussion

The density and the phase composition as a function of temperature in the heating stage are given in Figs. 2 and 3. The α-SiAlON contents of the three compositions with $m = 1$ and $n = 1$

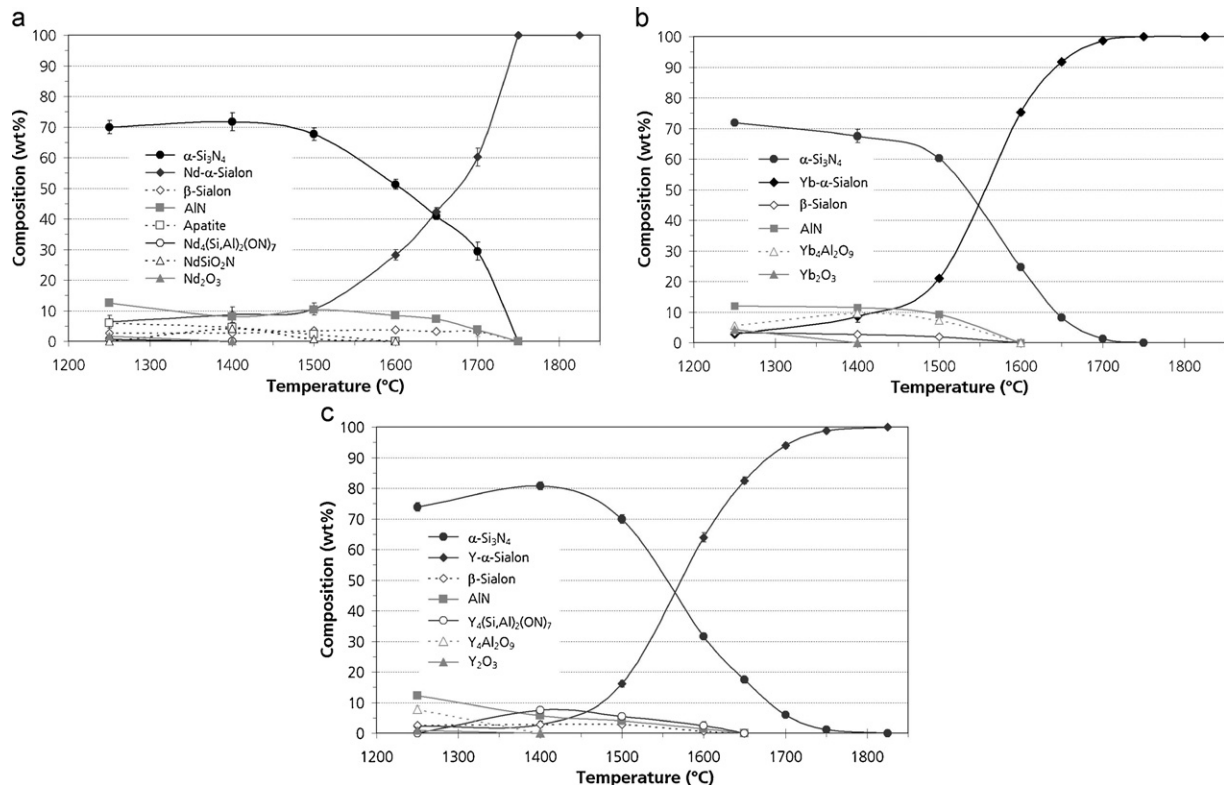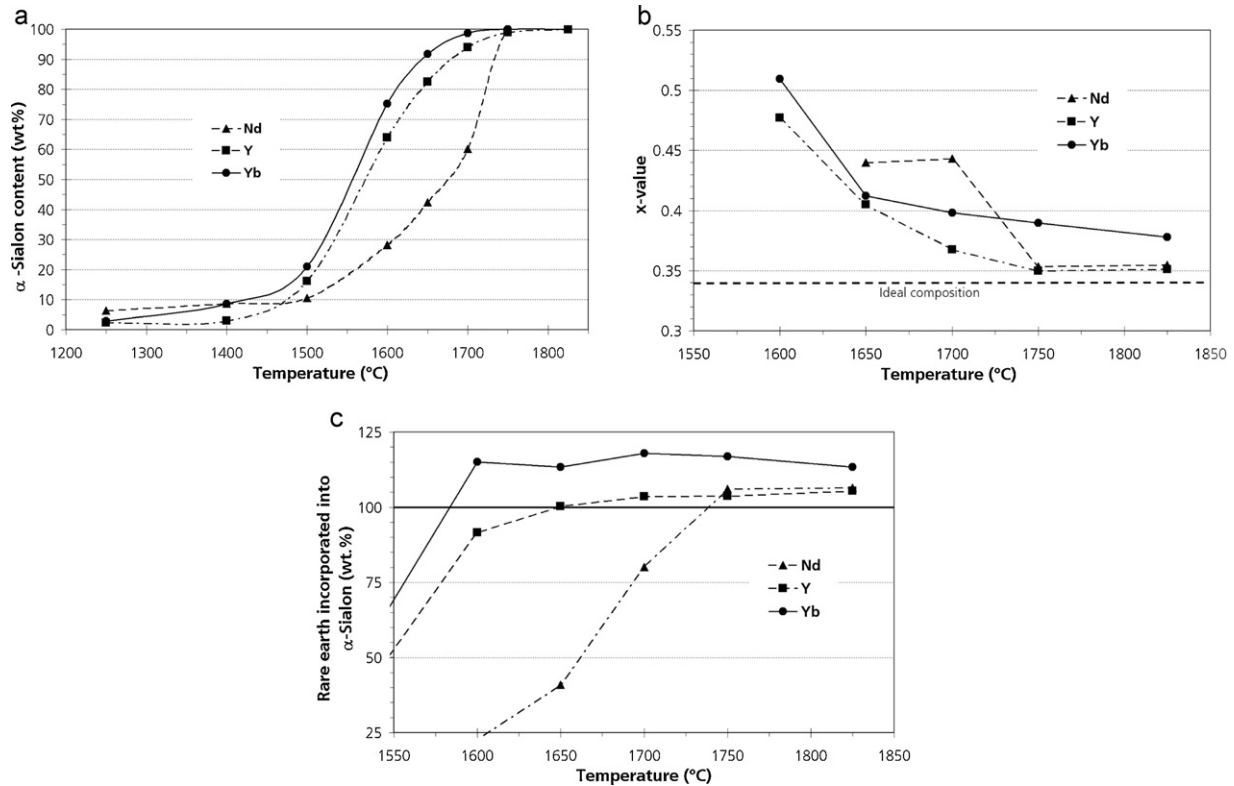Fig. 3. Phase composition as a function of temperature for the different α-SiAlONs: (a) Nd1010, (b) Yb1010 and (c) Y1010.

Fig. 4. α-SiAlON contents (a), x values (b) and relative amounts of incorporated rare earth (c) for Nd1010, Yb1010 and Y1010 as a function of temperature.

are given in Fig. 4a. It can be seen that formation of α-SiAlON was very similar for the Y- and Yb-containing materials, but was strongly retarded in the Nd-containing material. This is in agreement with the results of Rosenflanz and was explained by the different composition of the liquid phase formed.[19] The x values of the formed α-SiAlONs ($M_x Si_{12-(m+n)} Al_{m+n} O_n N_{16-n}$) were also measured. The results are given in Fig. 4b. At low temperatures x values as high as 0.45 and 0.55 were found. These values were much higher than the value of x of 0.33 expected from the starting composition for compositions with all three investigated rare earth cations. The x value was found to decrease with increasing sintering temperature. Nevertheless, even after sintering at 1825 °C the amount of incorporated rare earth was higher than expected. The reason for the higher amount of rare earth incorporated into the α-SiAlON structure at low temperatures is not completely clear. The most probably explanation is connected with the composition of the liquid at low temperatures. In the temperature region below 1700 °C the dissolution of the α-Si_3N_4 proceeds relatively slowly, but all rare earth ions, alumina and AlN are solved in the liquid (see Fig. 3b, c). Therefore, a rare-earth-rich liquid is formed from which the α-SiAlONs with a higher rare earth content (higher x-values) crystallize. This is in agreement with the fact that a slower formation of the α-SiAlON was also observed for the Nd0101 sample which shows a slower dissolution of AlN. With increasing temperature the newly formed α-SiAlON precipitates on the existing rare-earth-rich α-SiAlON grains. The crystallization from the less rare-earth-rich liquid results in α-SiAlONs with lower x-values. To reach the equilibrium the

rare earth diffusion inside the grains or a complete dissolution precipitation of the grains has to occur. The solid diffusion is a slow process (Al gradients in α/β-SiAlONs were found by TEM[1]). A stable liquid has to exist at high temperatures for the dissolution precipitation process. The amount and composition of the liquid at different temperatures can be estimated using the amount of rare earth incorporated into the α-SiAlONs because only the remaining rare earth will be part of the liquid.

Fig. 4c shows the relative amounts of rare earth incorporated into the α-SiAlONs. This amount was calculated using the x-value and the total amount of formed α-SiAlON divided by the equilibrium amount of rare earth incorporated into the α-SiAlON ($x = 0.33$) for the given composition. The results showed that even at temperatures higher than 1600–1650 °C for the Y0101 and Yb0101 materials and above 1750 °C for Nd1010 the amount of rare earth elements incorporated into the α-SiAlON was greater than the stoichiometric amount expected from the starting composition (corresponding to 100%). As a consequence, without an excess of rare earth no rare earth would be left in the liquid at temperatures as low as 1600 °C to 1700 °C for Yb and Y and at 1750 °C for the Nd-containing materials. The highest amount of rare earth was found in the Yb-containing samples. This could be partially connected with the formation of Yb^{2+} ions; however, with the Rietveld method no distinction can be made between Yb^{2+} and Yb^{3+}.

The absence of the rare earth in the liquid would result in the formation of polytypes and β-SiAlON strongly reducing the amount of liquid phases left. Reduced densification and grain growth are the consequences. These conclusions were proved
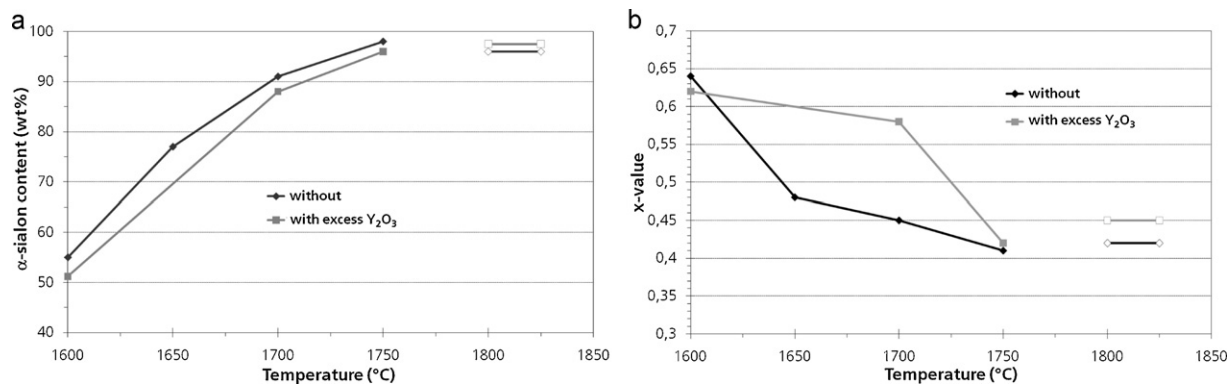
Fig. 5. α-SiAlON content (a) and *x* values (b) of the materials Y1210 and Y1210a as a function of temperature.

comparing two samples – Y1210 and Y1210a – with and without excess of Y_2O_3 and the same *n*- and *m*-values. The results (Fig. 5) showed the same situation. Nearly independently of the excess of Y_2O_3, α-SiAlON with high *x*-values was formed at the beginning of sintering. The *x*-values for the sample without an excess of Y_2O_3 (Y1210a) were slightly lower than the values for the material with an excess of Y_2O_3, indicating the influence of the concentration of the rare earth in the liquid on the formed α-SiAlON composition. Even after hot pressing and heat treatment the *x*-values of the formed α-SiAlON were higher than the expected ones ($x = 0.40$). The consequence of this high amount of Y_2O_3 incorporated in the α-SiAlON was that polytypes, in addition to α-SiAlON, were formed in the Y1210a sample without the excess of Y_2O_3 (Fig. 6b). In the opposite no polytypes were found in the Y1210 sample with an excess of Y_2O_3 (Fig. 6a). This is in agreement with the explanation given above.

The micrographs of the Y1210 material with an excess of Y_2O_3 show a grain boundary phase containing the remaining Y (bright phase in Fig. 6a; confirmed by EDX). The micrographs also proved the absence of a rare earth-containing liquid in the sample without excess Y_2O_3 (no bright phase in Fig. 6b). Additional heat treatment resulted in a pronounced elongated grain growth in the material with excess Y_2O_3 and much less grain growth in the sample with the stoichiometric composition (Y1210a). This proves the decisive role of a rare-earth-containing liquid phase existing at high sintering temperatures for elongated grain growth.
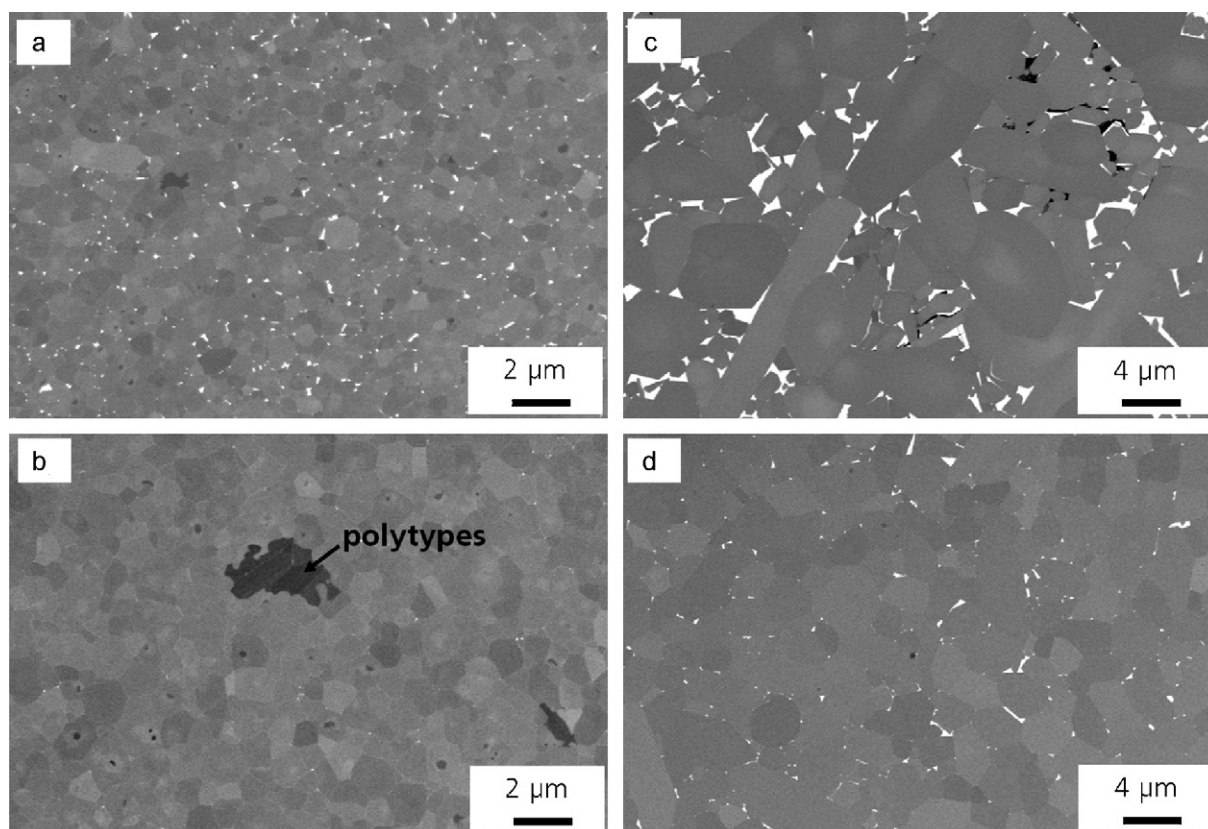

Fig. 6. Microstructures of the materials Y1210 (a, c) and Y1210a (b, d) after hot pressing (a, b) and after additional heat treatment (b, d).
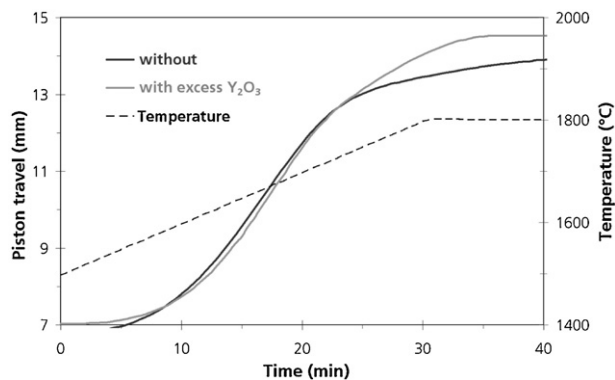
Fig. 7. Densification curves during hot pressing of Y-α-SiAlON ($m = 1.2$; $n = 1$) with and without additional Y_2O_3 (1.4 wt%; Y1210 and Y1210a).

In the Y1010a sample without an excess of rare earth small amounts of Y_2O_3 released from the α-SiAlON during Ostwald ripening formed a small amount of additional Y-containing liquid (Fig. 6d). But this liquid was not enough for a pronounced grain growth. Also the grains are nearly equiaxed. Additionally the polytypes were not completely dissolved in the very low amount of liquid phase. This is simply referred to kinetic reasons and the low amount of the formed liquid at heat treatment temperature.

The disappearance of the liquid phase was also clearly demonstrated by the kinetics of hot pressing (Fig. 7). Up to 1700 °C the densification behavior of both samples was nearly identical due to the fact that the small excess amount of Y_2O_3 did not significantly change the amount of transient liquid. After the transient liquid was consumed the excess of Y_2O_3 resulted in much faster densification than was the case in the sample with a stoichiometric amount of additives.

The effect of the amount of additional Y_2O_3 on densification and α-SiAlON formation during gas pressure sintering is shown in Fig. 8. The same influence of the excess of Y_2O_3 on densification was observed. The material without or with a small amount of additional Y_2O_3 could not be fully densified under these conditions. Full densification was observed for materials with a higher content of Y_2O_3.

The amount of α-SiAlON changed remarkably. For the samples with a high excess of Y_2O_3 nearly 100% α-SiAlON was
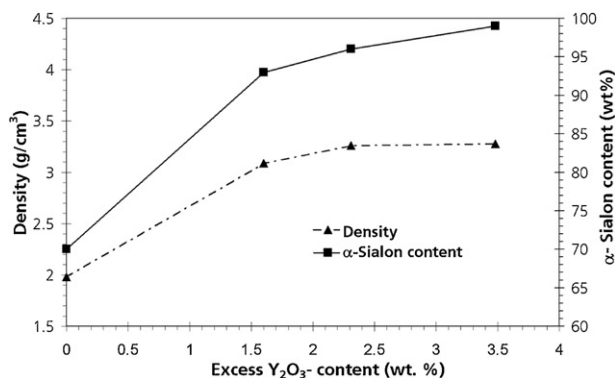

Fig. 8. Density and α-SiAlON content of Y-α-SiAlON ($m = 0.6$; $n = 1$) as a function of excess Y_2O_3.

observed. There are two reasons for this: The sample without excess Y_2O_3 had a higher x value than the expected equilibrium one. Hence the α/β-SiAlON ratio was shifted towards β-SiAlON because rare earth is not enough available in the liquid (see explanation above). The second reason is connected with the formation of the grain boundary phase. The grain boundary did not solely contain the excess rare earth but SiO_2 and Al_2O_3 were also dissolved in the liquid phase formed during sintering. If the liquid is more oxide rich in comparison to the overall composition, than by the rule of mixture in the remaining will be more nitride rich. This resulted in the formation of more α-SiAlON (see also Ref. 14). The results clearly demonstrated that the excess of the rare earth strongly influenced the α/β-SiAlON content in the materials.

4. Conclusions

Regarding microstructure formation it can be concluded that the formation of elongated α-SiAlON grains was mainly connected with the existence of enough liquid phase with a high concentration of alkaline earth or rare earth elements over the entire sintering process. A successful approach for obtaining α-SiAlON-rich materials with elongated grains and high fracture toughness is the use of an excess of rare earth cations in comparison with the stoichiometric α-SiAlON structure ($M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$). Gaining knowledge of the kinetics of rare earth incorporation into the α-SiAlON is important for understanding these processes. The method of choice for the precise determination of the amount of rare earth incorporated into the α-SiAlON is the Rietveld method. Use of this method revealed the following:

- A rare earth cation content of less than $x = 0.33$ (amount stated in the literature) could stabilize the α-SiAlON structure.
- In the early stages of sintering more rare earth cations were incorporated into the α-SiAlON structure than would be expected from the stoichiometric composition.

The observed incorporation of the rare earth was associated with nearly complete consumption of the rare earth even if the formation of α-SiAlON was not completely finished, resulting in the additional formation of polytypes which only very slowly dissolved during further heat treatment. The excess of rare earth oxides compensated this process and resulted in a stable rare earth-rich liquid which enabled anisotropic grain growth of the α-SiAlON. The detailed growth mechanism of α-SiAlON is still not clear, but based on the data concerning β-Si_3N_4 and β-SiAlON[20] grain growth, which indicates the decisive role of the rare earth in anisotropic grain growth, it can be expected that a similar mechanism takes place for α-SiAlONs.

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