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# Effect of the amount of excess oxides on the densification of α-SiAlON fabricated via a reaction-bonding process

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**Abstract** Y-α-SiAlONs with elongated grains were fabricated via a reaction-bonding process using starting compositions containing excess oxides in the form of $Y_2O_3$ and $SiO_2$. The density of post-sintered specimens reached a maximum value with compositions containing 2 mass% excess oxides, although conventionally sintered materials of this composition were not fully dense. However for compositions containing smaller amounts of excess oxides, the density of the specimen fabricated via a reaction-bonding process was lower than that via a conventional process. In these samples it is thought that liquid phase sintering was difficult to be achieve during the post-sintering process, since the amount of $SiO_2$ contained in the starting powder was lower and the $Al_2O_3$ in the starting composition was consumed for the production of β-SiAlON during nitridation. There was also a decrease in density of the reaction-bonded materials with further increases in the amounts of additional oxides. For these samples the compacts could not be densified uniformly, because of non-uniformity of the phase composition in the nitrided compacts. The dense reaction bonded α-SiAlON with elongated grains, fabricated from compositions with 2 mass% excess oxides exhibited both high fracture toughness and high hardness.

## Introduction

Among the Si-based nitrogen ceramics, α-SiAlONs have high hardness over 20 GPa, chemical inertness and reduced amount of grain boundary phase, which makes them a serious candidate for tribological materials. However, their use has been limited due to the low fracture toughness associated with the commonly observed equiaxed grain morphology.

In recent research work, several research groups have succeeded in fabricating single phase α-SiAlONs with elongated grain morphology [1–7]. Hwang et al. first reported elongated α-SiAlON grains containing Y, Sr and Ca as the interstitial metal cations [1]. Wang et al. similarly produced Ca-α-SiAlON ceramics with elongated grain morphology by adding excess CaO as a sintering additive [4]. Chen and Rosenflanz fabricated toughened α-SiAlONs with elongated grains by controlling the nucleation of the α-SiAlON grains using α-$Si_3N_4$ as the raw powder [5]. Shen et al. also reported the fabrication of toughened Yb-α-SiAlONs by the use of so-called spark plasma sintering (SPS) equipment [6]. Another example was given by Kurama et al., who formed elongated Y-α-SiAlON grains by adding extra $Y_2O_3$ to provide an excess liquid phase during sintering [7]. The interest in α-SiAlONs has increased due to the results of these works.

Silicon nitrides fabricated by nitridation of Si powder compacts followed by post-sintering are well-known as sintered reaction-bonded silicon nitrides. This process has the benefit that cheaper Si powder can be employed as the starting powder rather than the more expensive $Si_3N_4$ powder. In addition, since nitridation of Si powder compacts proceeds without

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dimensional change, shrinkages accompanied by post-sintering can be minimized [8, 9]. Recently we have fabricated elongated α-SiAlON with high hardness and fracture toughness via a reaction-bonding process [10]. However, an optimum composition for the fabrication of elongated α-SiAlON via the reaction-bonding process has not been investigated. In this work, we have investigated the effect of starting composition on the formation of α-SiAlON with elongated grains via a reaction-bonding process in comparison with the material produced via a conventional process using $Si_3N_4$ powder.

## Experimental procedures

Y-containing α-SiAlON with composition of $m = 1.1$, $n = 1.1$ in the chemical formula $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ was chosen for this study. In this composition, single-phase α-SiAlON should be produced within the lower amounts of the oxides ($Y_2O_3$, $SiO_2$ and $Al_2O_3$) in the starting composition. Therefore this composition could be advantage to investigate the effect of excess oxides to α-SiAlON composition. Excess oxides were added to the stoichiometric composition for α-SiAlON ($m = 1.1$, $n = 1.1$) in an effort to enhance densification and anisotropic grain growth. The excess oxides were composed of $Y_2O_3$ and $SiO_2$ with a molar ratio $Y_2O_3$:$SiO_2$ = 3:7, and total amounts of 1, 2, 3.5 and 5 mass%.

Powders of Si (>99 %, ca. <1 μm, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan), AlN (99%, containing 1.0% oxygen, type F, Tokuyama Corp., Tokyo, Japan), $Al_2O_3$ (>99.99%, AKP-50, Sumitomo Chemical Co., Ltd., Tokyo, Japan), $Y_2O_3$ (99.9%, RU-P, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) and $SiO_2$ (99.9%, HS-100, Hokko Chemical Industry Co., Ltd., Tokyo, Japan) were used as starting powders. In order to assess oxidation and loss of Si powder during the nitridation process, a compact composed of only silicon powder was nitrided, and the oxygen impurity and change in weight after nitridation were measured. It was revealed that the nitrided compact contained 1.2 mass% of impurity oxygen and that 5 mass% of Si was lost during nitridation [10]. Starting compositions were thus calculated based on the assumption that, during nitridation, 95 mass% of the Si powder is converted to $Si_3N_4$ containing 1.2 mass% oxygen. The oxygen content of the AlN powder was also taken into account in calculating the compositions. In addition, 0.3 mass% of $Fe_3O_4$ (99%, ca. 1 μm, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) based on the mass of Si was also added to promote Si nitridation [11, 12].

The starting powders were planetary milled in methanol using a silicon nitride pot and silicon nitride balls. The powder mixture was dried, and uniaxially pressed at 8 MPa before being cold isostatically pressed at a pressure of 300 MPa. For nitridation, compacts were located on BN powder inside a BN crucible. Nitridation was carried out in flowing $N_2$ gas (1.5 L/min) at 1375 °C for 4 h. The temperature was raised at 2 °C/min from room temperature to 1000 °C, and at 1 °C/min from 1000 °C to 1375 °C. The nitrided compacts were placed in a BN crucible and covered with a 70 wt% $Si_3N_4$:30 wt% BN powder bed, and post-sintered at 1900 °C for 3 h in a nitrogen atmosphere of 0.9 MPa with a heating rate of 12 °C/min. For the sake of comparison, α-SiAlON with the same composition was fabricated through the conventional method using mixtures of α-$Si_3N_4$ powder (E10, containing 1.2% oxygen, Ube Industries. Ltd., Yamaguchi, Japan), AlN, $Al_2O_3$, $Y_2O_3$ and $SiO_2$. The oxygen contents of the $Si_3N_4$ and AlN powders were also taken into account in calculating the compositions for these specimens.

The densities of the post-sintered samples were measured by the Archimedes' method. The phase composition was analyzed using X-ray diffraction (XRD, RINT2500, Rigaku Corp., Tokyo, Japan). The mass fractions of β-SiAlON phase in the nitrided were calculated from the method reported by Gazzara and Messier [13] using the α-SiAlON (101), (110), (200), (201), (102), (210) and (301) and the β-SiAlON (110), (200), (101) and (210) peak intensities. The $x$-value of the produced α-SiAlON (where $x = m/p$ for a $p^+$ stabilizing cation, i.e. $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$) was calculated using equations for lattice parameter determination i.e. $a$ (nm) = 0.775 + 0.0156$x$ and $c$ (nm) = 0.562 + 0.0162$x$ [14]. Similarly, the $z$-value of the β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$) in the formed material was calculated from $a = 0.7603 + 0.00296z$ and $c = 0.2907 + 0.00255z$ [15].

The changes in crystalline phases of the nitrided specimens with temperature were investigated by heating the specimens at temperatures of 1375–1900 °C for 30 min. This analysis was also carried out for green compacts from the conventional process. The relative peak intensities were determined from the intensities of the following diffraction peaks; α-$Si_3N_4$ (102), α-SiAlON (102), β-SiAlON (200), AlN (101), $YSiO_2N$ (200), $Y_4Si_2O_2N_7$ (031), $Y_2Si_3O_3N_4$ (211) and $Y_3Al_5O_{12}$ (420).

The polished surfaces of the post-sintered specimens were observed with a scanning electron microscope (SEM, JSM-6320FK, JEOL Ltd., Tokyo, Japan) in backscattered mode. In order to evaluate the mechanical properties of sintered specimens, hardness, fracture toughness and bending strength were measured. Hardness ($HV_{10}$) and indentation fracture toughness ($K_{1c}$) were measured using a Vickers hardness tester equipped with a diamond indenter on the polished surface under a load of 98 N. Specimens of 3 × 4× 40 mm were cut from the sintered bodies, and four-point bending tests were carried out with an inner span of 10 mm, an outer span of 30 mm and a cross-head speed of 0.5 mm/min.

## Results and discussion

Figure 1 shows the density of post-sintered reaction-bonding compacts and conventionally sintering specimens sintered at 1900 °C, as a function of the amount of excess oxides. For the conventional material, there was a sharp increase in density for the specimen sintered with only 1 mass% excess oxides and further slight increases with increasing amounts, reaching near theoretical density with an excess of 3.5 mass%. On the other hand, the increase in density of specimens via the reaction-bonding process was less pronounced at low excess amounts. These samples reached near theoretical density with 2 mass% oxides, however there was a decrease in density for compositions more than this amount.

Figure 2 shows the changes in the relative intensity of the XRD peaks as a function of temperature for the conventionally sintered samples. All of the samples in this figure contained 2 mass% excess oxides. For the conventional materials, $Y_3Al_5O_{12}$ (yttrium aluminum garnet YAG) was observed at temperatures between 1400 and 1700 °C. At lower temperature, since the dissolution of AlN and $Si_3N_4$ is very limited, a ternary eutectic oxide melt composed of $SiO_2$, $Al_2O_3$ and $Y_2O_3$ forms and tends to precipitate as YAG at 1340 °C [16]. The peak intensity of YAG showed a maximum at 1500 °C and decreased at higher temperatures, because AlN dissolves above 1420 °C and $Si_3N_4$ above 1470°C in the oxide melt [16]. The fraction of α-SiAlON phase increased steeply above 1500 °C and reached 100% at 1900 °C. Analysis of the XRD spectra showed that this α-SiAlON phase had an $x$-value of 0.4. The initial formation of α-SiAlON above 1500 °C was accompanied by the formation of transient $Y_2Si_3O_3N_4$, although this reached a maximum at a temperature of 1600 °C and was not observed in samples sintered at 1800 °C and above.

Figure 3 shows the XRD data of the nitirided compacts in the starting composition with 2 mass% excess oxides. In the compact nitrided at 1375 °C (Fig. 3a) α and β-phases, and $YSiO_2N$, $Y_4Si_2O_7N_2$ and AlN were observed. The $x$-value of the α-SiAlON was calculated at about 0.13 for the α-phase in the nitrided compact. Although, it has been shown that the minimum $x$-value of the α-SiAlON is about 0.3 for single phase materials [17, 18] an α-SiAlON composition with an $x$-value of 0.147 in the starting composition has been reported to result in α/β composite SiAlON materials with $x$-value of 0.24 for the α phase. The $z$-value of the β-SiAlON was also calculated at about 0.22 for the β-phase in the nitrided compact.

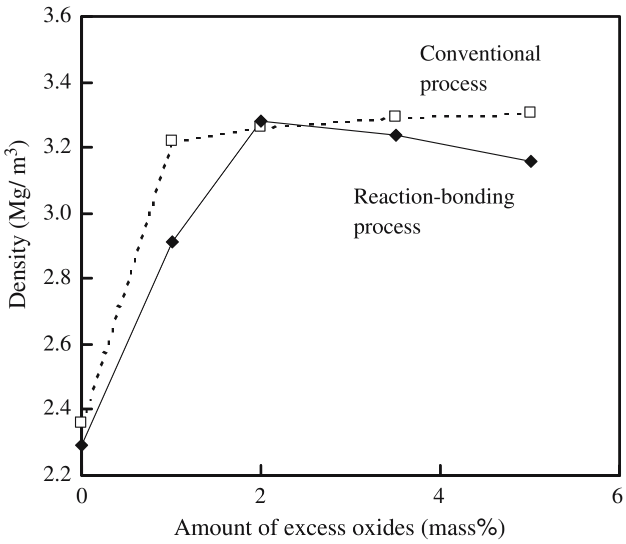

**Fig. 1** Relationship between density and the amount of excess oxides for specimens sintered at 1900 °C

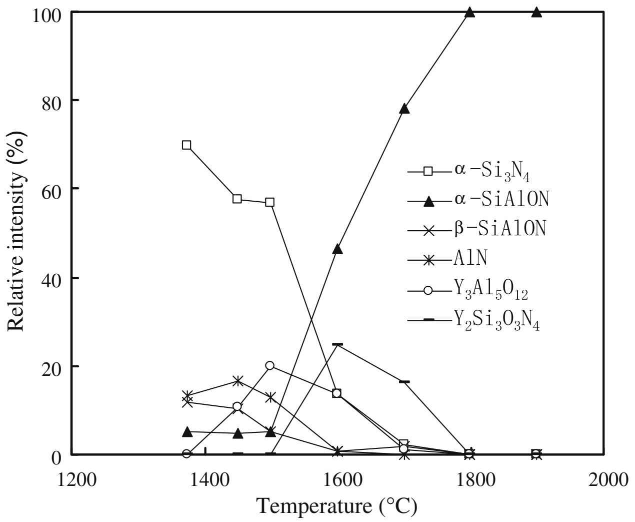

**Fig. 2** Relationship between relative intensity of XRD peaks and sintering temperature for samples containing 2 mass% excess oxides by conventional sintering

The change in phase assemblage with post-sintering temperature is shown in Fig. 3b. The fractions of the $x = 0.13$ α-SiAlON, β-SiAlON, $YSiO_2N$, $Y_4Si_2O_7N_2$ and AlN in the nitrided compacts decreased and α-SiAlON, with an $x$-value of about 0.37, increased above 1500 °C. Again this was accompanied initially with the formation of $Y_2Si_3O_3N_4$ although this decreased above 1600 °C, resulting in almost 100% α-SiAlON. Since the formation of both α- and β-SiAlON occurred during the nitridation process, the $Al_2O_3$ in starting powder is thought to react with the AlN, $SiO_2$, $Y_2O_3$ and nitrided Si in the compact, consequently producing the α-SiAlON and β-SiAlON. Since the $Al_2O_3$ was consumed in this way during the nitridation step, at temperatures above the 1375 °C used for nitridation the $Al_2O_3$ containing liquid phase could not be produced and the YAG phase produced by reaction between $Al_2O_3$ and $Y_2O_3$ was not detected. In these materials it is thought that the densification of α-SiAlON was promoted by the $SiO_2$ containing liquid phase. The lower density of the sintered specimens via the reaction-bonding process for compositions containing less than 2 mass% excess oxides indicates that in these materials the amount of liquid phase was too low to densify the compact.

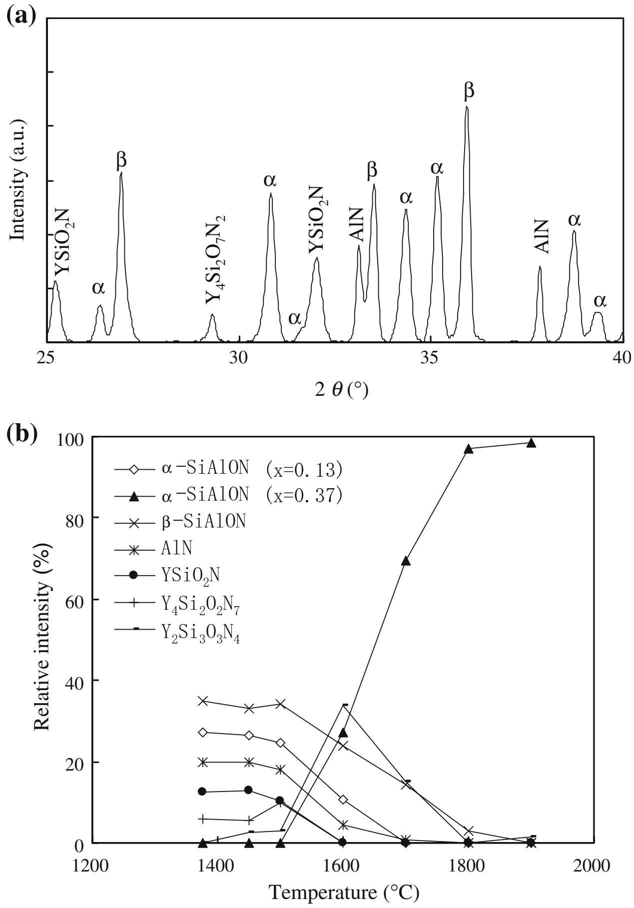

**Fig. 3** (**a**) XRD patterns of the sample nitrided at 1375 °C containing 2 mass% excess oxides, (**b**) Relationship between relative intensity of XRD peaks and sintering temperature for the post-sintered nitrided compact containing 2 mass% excess oxides

Figure 4 shows the fraction and $z$-value of β-SiAlON in nitrided compacts as a function of the amount of excess oxides. The fraction of β-SiAlON increased monotonically with the amount of excess oxides, indicating that the reaction to produce β-SiAlON occurred more easily during the nitiridation process with increasing amounts of excess oxides. It is thought that $SiO_2$ in the excess oxides enhances the formation of β-SiAlON during the nitridation process, through the reaction between Si, $Al_2O_3$, AlN, $SiO_2$ and $N_2$ gas. In addition, the $z$-value of the β-SiAlON also increased with the amount of excess oxides. The greater formation of β-SiAlON in the compositions containing larger amounts of excess oxides would result in the amount of liquid phase produced during the post-sintering process being lower since the $SiO_2$ and $Al_2O_3$ in the starting composition was used for production of the SiAlON during the nitridation.

Figure 5 shows the fraction of β-SiAlON at the surface and in the center of the nitrided compacts. The fraction of β-SiAlON was higher at the surface than at the center, attributed to exposure to the $N_2$ gas flow. Moreover, the difference in the β-SiAlON content between the center and the surface of the samples increased with increasing amount of excess oxides. As a result, the difference in the amount of liquid phase during post-sintering process would be greater between

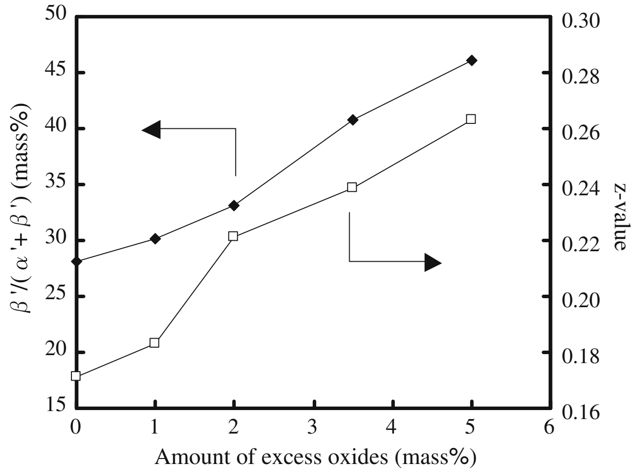

**Fig. 4** Relationship between the amount of excess oxides and the β-SiAlON content and $z$-value in $Si_{6-z}Al_zO_zN_{8-z}$ for the nitrided compacts

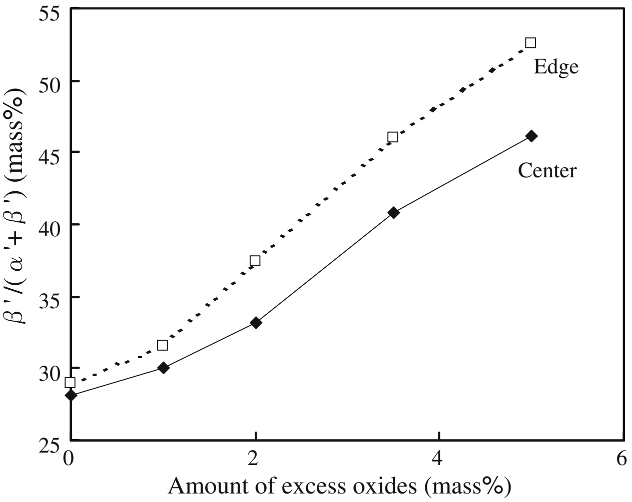

**Fig. 5** Difference in the amount of $\beta$-SiAlON between the center and edge of the nitrided compacts with amount of excess oxides

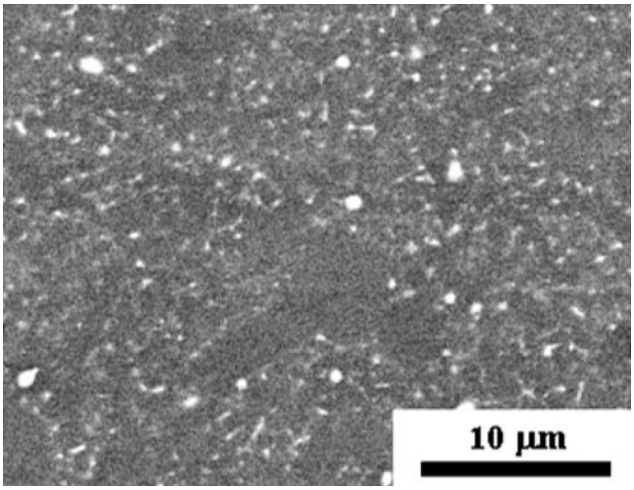

**Fig. 6** Back-scattered SEM micrograph of the polished surface of the reaction-bonded sample with 2 mass% excess oxides post-sintered at 1900 °C

the center and edges in the compacts with increasing amounts of excess oxides. This non-uniformity is thought to be the reason for the reduced density in the compositions containing 3.5 and 5 mass% excess oxides, as was shown in Fig. 1.

For the composition containing 2 mass% excess oxides, the specimen produced via the reaction-bonding process was dense, as was shown in Fig. 1. The amount of $SiO_2$ in the starting composition was sufficient to produce an adequate amount of liquid phase and achieve densification of the compacts during the post-sintering process. In addition, the difference in the amount of $\beta$-SiAlON between the center and the edges in the nitrided compacts with 2 mass% excess oxides was smaller than with greater amounts of excess oxides, as was shown in Fig. 5. The density of this specimen was slightly higher than that of the conventionally sintered specimen with the same amount of excess oxides. This may be due to the higher relative density of the pre-sintered compact, which increased from about 57% to 70% with nitridation treatment compared with a green body density of 53 % for the conventionally sintered material. The higher density of the pre-sintered body may be one possible reason for the higher density of $\alpha$-SiAlON via the reaction-bonding process. In addition, the differences in liquid phases formed between the two processes as was shown in Fig. 2 and Fig. 3b, may also affect densification of the specimens.

Figure 6 shows the microstructure of $\alpha$-SiAlON fabricated via reaction-bonding for the composition containing 2 mass% excess oxides. An elongated grain morphology was observed when using the starting compositions containing the excess oxides. However, for this composition only a small amount of grain boundary phase was observed. Assessment of the mechanical properties of this sample showed that the hardness was 1820 ($HV_{10}$), whilst the hardness of the conventionally sintered $\alpha$-SiAlON was 1680 ($HV_{10}$) possibly because of the lower density of the specimen. For the reaction-bonded material, the fracture toughness was 4.9 $MPam^{1/2}$ and the bending strength was 582 MPa. In order to achieve similar mechanical properties by conventional sintering, starting compositions with more than 3.5 mass% excess oxides were required.

## Conclusions

The effect of the amount of excess oxides on the densification of $\alpha$-SiAlON with elongated grains fabricated via a reaction-bonding process was investigated by using a starting composition, $m = 1.1$, $n = 1.1$, in the chemical formula $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ and the addition of excess oxides composed of $Y_2O_3$ and $SiO_2$ with a molar ratio of 3:7. The density of post-sintered specimens had a maximum value with additions of 2 mass% excess oxides although similar specimens conventionally sintered could be not densified.

However, for compositions containing lower amounts of excess oxides, the density of the specimen fabricated via the reaction-bonding process was lower than that via the conventional process. The reason for this lower densification is thought to be a decrease in the amount of liquid phase since $Al_2O_3$ in the starting composition was consumed through the production of $\beta$-SiAlON during the nitridation process. In addition the amount of $SiO_2$ contained in the starting powder was lower in the nitrided sample. Moreover, with adding larger amounts of excess oxides, the density of the specimens fabricated by reaction-bonding process was decreased since the phase composition of the nitrided compacts was non-uniform.

The $\alpha$-SiAlON fabricated via a reaction-bonding process with a composition containing 2 mass% excess oxides, which reached near theoretical density, had both a high fracture toughness of 4.9 $MPam^{1/2}$ and high hardness of 1820 ($HV_{10}$). Such properties could not be achieved in the conventional materials without the addition of larger amounts of excess oxides.

## References

1. Hwang CJ, Susintzky DW, Beaman DR (1995) J Am Ceram Soc 78:588
2. Huang ZK, Jiang YZ, Tien TY (1996) J Mater Sci Lett 16:747
3. Nordberg L-O, Shen Z, Nygren M, Ekstrom T (1995) J Eur Ceram Soc 17:575
4. Wang H, Cheng Y-B, Muddle BC, Gao L, Yen TS (1996) J Mater Sci Lett 15:1447
5. Chen I-W, Rosenflanz A (1997) Nature (London) 389:701
6. Shen Z, Zhao Z, Peng H, Nygren M (2002) Nature (London) 417:266
7. Kurama S, Herrmann M, Mandal H (2002) J Eur Ceram Soc 22:109
8. Mangels JA, Tennenhouse GJ (1980) Am Ceram Soc Bull 59:1216
9. Ziegler G, Heinrich J, Wötting G (1987) J Mater Sci, 22:3041
10. Kaga Y, Jones MI, Hirao K, Kanzaki S (2004) J Am Ceram Soc 87:956
11. Mitomo M (1977) J Mater Sci 12:273
12. Pavarajarn V, Kimura S (2001) J Am Ceram Soc 84:1669
13. Gazzara CP, Messier DR (1977) Am Ceram Soc Bull 56:777
14. Shen Z, Ekström T, Nygren M (1996) J Am Ceram Soc 79:721
15. Ekström T, Käll PO, Nygren M, Olsson PO (1989) J Mater Sci 24:1853
16. Hwang S-L, Chen I-W (1994) J Am Ceram Soc 77:165
17. Huang ZK, Tien TY, Yen TS (1986) J Am Ceram Soc 69:C241
18. Sun WY, Tien TY, Yen TS (1991) J Am Ceram Soc 74:2547