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Formation behavior, microstructure and mechanical properties of multi-cation α-sialons containing calcium and neodymium

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Abstract

Dual modifying cation (Ca + Nd) α-sialons were hot pressed for the $x = 1.0$ composition ($(Ca,Nd)_xSi_{12\text{-}3n}Al_{3n}O_nN_{16\text{-}n}$) with mixtures of CaO:$Nd_2O_3$ in the molar ratios of 0:1, 0.3:0.7, 0.5:0.5, 0.7:0.3 and 1:0. Experimental results showed that except for pure Nd- and Ca-α-silaon compositions, the main crystalline phase in samples hot-pressed at 1750°C for 1 h was α-sialon together with a small amount of melilite solid solution and AlN polytypoid. The higher CaO:Nd_2O_3 ratio in the starting composition, the higher α-sialon content and the lower melilite solid solution content in the final phase assembly. The α-sialon lattice also expanded with increasing substitution of Ca for Nd. Elongated grain morphology was observed in (Ca + Nd) α-sialon. EDS analysis revealed higher solubility of Ca than Nd in the α-sialon lattice and lower solubility of Ca than Nd in the intergranular phase. The hardness increased, ranging from 15.87 to 18.79 MPa, when the amount of α-sialon phase in the material became higher. The fracture toughness varied from 4.2 to 5.1 MP am$^{1/2}$ for (Ca + Nd) α-sialon compositions, in which the composition with CaO:Nd_2O_3 = 0.5:0.5 possessed the highest value. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanical properties; Microstructure-final; Phase development; Sialons

1. Introduction

α-Sialon, isostructural with α-Si_3N_4, has an overall composition expressed as $M_xSi_{12\text{-}(m+n)}Al_{(m+n)}O_nN_{16\text{-}n}$, where M generally falls into two categories, alkali and alkaline earth elements such as Li, Ca, Mg, or yttrium and most rare earth elements.[1]

It is noted that the extensive interest in yttrium and rare earth doped α-sialons has been raised for the past decade because of their highly refractory grain boundary phases. However, the results showing lack of thermal stability of some rare earth α-sialons, especially those with light modifying cations (such as Nd and Sm), have cast a shadow on their high temperature application.[2] On the other hand, Ca α-sialon has been found to possess excellent stability at elevated temperatures.[3] It is therefore desirable that partial replacement of CaO for Nd_2O_3 will improve the stability of the α-sialon structure without much loss of performance of Nd-α-sialon. Besides the consideration of higher stability, it is also of interest to investigate the formation behavior of dual cation α-sialons since previous studies have mostly concentrated on single-cation α-sialon and studies involving multi-cation α-sialons have shown some interesting results,[4–10] such as improved sinterability and selective solubility of cations in different phases.

The stabilization of Nd-α-sialon through calcia additions has been reported by one of the authors[11] and the results of phase formation, microstructure and mechanical properties of dual modifying cation (Ca + Nd) α-sialons ceramics will be described in this paper.

2. Experimental

The overall compositions investigated in this study are located on join line Si_3N_4–MO:3AlN (M = Ca, 2/3Nd) with the formula $(Ca,Nd)_xSi_{12\text{-}3n}Al_{3n}O_nN_{16\text{-}n}$ ($x = 2n/v$, v is the valency of the cation). Specifically, $x = 1.0$ was chosen with oxide mixtures of CaO:Nd_2O_3 in different molar ratios of 0:1, 0.3:0.7, 0.5:0.5, 0.7:0.3 and 1:0. The corresponding samples were respectively named as

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ND100, CN3070, CN5050, CN7030 and CA100. Starting powders were Si_3N_4 (UBE E-10, Japan, 2.0 wt.%O), AlN (1.3 wt.%O), $CaCO_3$ (99%) and Nd_2O_3 (99%). Powder mixtures were milled in an agate mortar in alcohol for 2 h. Pellets of dried powders (about 5 g) were hot-pressed at 1750°C for 1 h with an applied load of 20 MPa in a graphite resistance furnace under protective nitrogen atmosphere. Separate runs were also made on the $CaO:Nd_2O_3 = 0.5:0.5$ (CN5050) composition by hot pressing at intermediate temperatures ranging from 1350 to 1750°C to study the phase evolution. For each run, a dwell of 0.5 h was made at 1150°C for decomposition of $CaCO_3$ into CaO.

Bulk densities of the samples were measured according to the Archimedes principle. Crystalline phases present were identified with an RAX-10 diffractometer using CuK_α radiation. Semi-quantitative estimation of the crystalline phases was made based on the calibration curves. XRD patterns were also obtained in a Guinier-Hägg camera (Cu $K_{\alpha 1}$ radiation, $\lambda = 1.5405981$ Å) using Si as an internal standard. With the aid of a computer-linked scanner (LS-18) system and corresponding programs,[12,13] lattice parameters of α-sialon in each composition were precisely determined. Both polished and etched surfaces of prepared samples were used for microstructural observation on a KYKY-2000 scanning electron microscope (made in China) equipped with an energy dispersive spectrometer (LINK ISIS). Hardness and fracture toughness were measured on polished surfaces of hot-pressed samples at room temperature using a Vickers diamond indenter under a load of 98 N (10 kg).

3. Results and discussion

3.1. *Densification and phase assembly*

Table 1 lists the density and phase assemblage of dual cation (Ca + Nd)-α-sialons with different $CaO:Nd_2O_3$ ratios after hot pressing at 1750C. The general trend of decreasing bulk density with increasing Ca content in the composition indicated the effect of atomic number of the stabilizing cation. It was also found that the values of measured bulk densities of ND100 and CN3070 were very close. Because of the multiphase nature of the synthesized materials, as the phase assemblage of most samples consisted of multi-cation α-sialons, melilite solid solution ($Nd_2Si_{3-x}Al_xO_{3+x}N_{4-x}$, abbreviated as M′) and AlN polytypoid, it was difficult to estimate the theoretical density accurately. However, the closeness of the density values between ND100 (3.51 g/cm^3) and CN3070 (3.50 g/cm^3) and more amount of M’ phase, whose density is higher than the one of α′, occurred in the former sample than the latter one suggested that the dual cation (Ca + Nd) composition had the better densification behavior than the pure Nd composition.

As shown in Table 1, AlN polytypoid (12H($SiAl_5O_2N_5$) or 21R($SiAl_6O_2N_6$)) and M′ coexisted in the phase assemblage of most samples, α-sialon being the main crystalline phase. For the pure Ca composition(CA100) only α-sialon and AlN polytypoid remained, while for the pure Nd composition(ND100) nearly equal amount of α-sialon and M′ coexisted with very small amount of un-reacted AlN present. As it is known from the phase relationships in the systems Y,Si,Al/O,N and Ca–Si–Al–O–N,[14,15] the x = 1.0 composition is located within the α-sialon (entire region)-melilite compatibility region for the Y system[14] and within the α-sialon-AlN polytypoid compatibility region for the Ca system.[15] Although compatibility region of Si_3N_4–4/3AlN:Al_2O_3–NdN:3AlN (α-sialon plane) with M′ was not illustrated in subsolidus phase relationships in the systems Ln_2O_3–Si_3N_4–AlN–Al_2O_3 (Ln = Nd, Sm) reported by the previous work in our group,[16] the occurrence of M′ together with α′ in ND100 composition accounted for the similarity between Y- and Nd-containing systems for the compatibility region involving α′ plane phase and M′ however. The formation of M′ phase during the densification of Nd-α-sialon was also reported in literature[17] and our previous work.[18] The appearance of AlN in ND100 was resulted from un-reacted starting material. It was noted that the formation of M′ phase did consume Nd^{3+} of transient liquid during sintering, which resulted in a reduced amount of liquid phase and hindered the densification of ND100. Being different from ND100, the phase assemblage of CA100 composition contained much higher amount of α-sialon (91 wt.%) because of higher solubility limit of Ca^{2+} (1.4) in

Table 1
Bulk density and phase assemblage of (Ca + Nd)-α-sialons hot pressed at 1750°C/1 h, 20 MPa[a]

Sample no.	ND100	CN3070	CN5050	CN7030	CA100
$CaO:Nd_2O_3$ (mol%)	0:1	0.3:0.7	0.5:0.5	0.7:0.3	1:0
Density (g/cm^3)	3.51	3.50	3.42	3.36	3.21
Phases present	α′/m (49)	α/s (76)	α/s (78)	α/vs (89)	α/vs (91)
	M′/m (44)	M′/mw (17)	M′/mw (13)	M′/w (7)	
	AlN/w (7)	AlN′/w (7)	AlN′/w (9)	AlN′/vw (4)	AlN′/w (9)

[a] Note: M′ = nitrogen containing melilite solid solution; AlN′ = AlN polytypoid; s = strong; m = medium; w = weak; numbers in parentheses are weight percentages.

α-sialon.[15] Overall, it can be seen from Table 1 that the α-sialon content increases and the amount of M′ phase decreases in the final phase assembly drastically with increase in the molar ratio of CaO to Nd_2O_3 in the designed compositions. Thus the use of dual modifying cations has its advantage in suppressing the formation of M′ phase and accordingly enhancing the yield of α-sialon and densification.

A general trend of the densification behavior and reaction sequence of the dual cation ($0.5CaO+0.5Nd_2O_3$) α-sialon composition can be derived from Figs. 1 and 2, respectively. As shown in Fig. 1, the densities increased with increasing sintering temperatures, and an obvious increment in density occurred at temperature ranging from 1450 to 1650°C. When the temperature was higher than 1650°C, the variation of densities became smaller and the density values reached a stable level. According to the reaction sequence of CN5050 shown in Fig. 2, it was found that a small amount of M′ phase was already formed even at such a low temperature as 1300°C. With increasing temperature, the amount of liquid phase increases and more Si_3N_4 and AlN dissolve into the liquid phase. At 1450°C, a very small amount of α-sialon and AlN polytypoid were formed. The α-sialon content increases obviously from 1450 to 1650°C, which reflected the similar trend as the densification behavior of the material. On the other hand, the amount of AlN polytypoid remained around 10 wt.% at all temperatures higher than 1450°C, whereas M′ content changed with sintering temperature. The maximum amount of M′ phase at 1650°C may be caused by fully dissolution of α-Si_3N_4 into liquid phase at that temperature. The presence of M′ phase at 1750°C may be partly resulted from devitrification of grain boundary glassy phase.

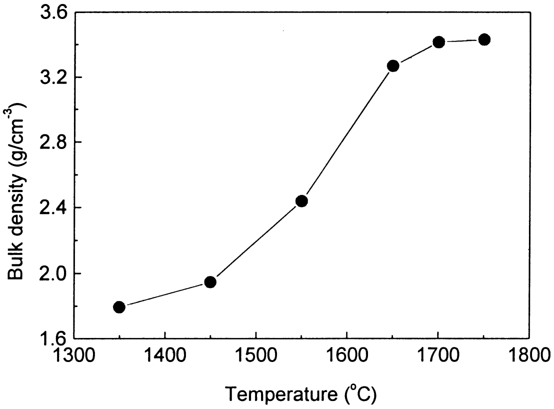

Fig. 1. Densification of (0.5Ca + 0.5Nd)-α-sialon composition hot pressed at different temperatures.

Our previous work on Nd-α-sialon ($x=0.5$)[18] showed that the densification of the material was completed at 1700°C, whereas the final products at 1800°C still contained a small amount of un-reacted Si_3N_4 besides α-sialon, melilite and β-sialon phases. This indicated that the completeness of densification of Nd-α-sialon ($x=0.5$) was prior to the reaction sequence. On the other hand, the densification process of CN5050 was almost synchronous with its reaction sequence as shown in Figs. 1 and 2. Therefore, the advantage by using dual cations to stabilize α-sialon structure is not only to reduce the eutectic point of system, but also to promote the reaction process.

It was found that the major difference in reaction sequence between CN5050 and single-cation Ca-α-sialon ($x=1.0$)[19] was the intermediate phase. For Ca-α-sialon composition, $Ca_2Al_2SiO_7$ was the unique intermediate phase and dissolved completely in the liquid phase while temperature was above 1600°C. For CN5050 composition, Nd-M′ phase, instead of $Ca_2Al_2SiO_7$, was identified from XRD pattern as an intermediate phase in the whole reaction sequence. This implied stronger formation ability of Nd-M′ than the one of $Ca_2Al_2SiO_7$ phase in multi-cation (Ca + Nd)-α-siloans.

It has been reported in our previous work on Ca α-sialon[19] that the lattice parameters of Ca α-sialon phase increased with the increase of x values in nominal compositions. Fig. 3 shows the variation in unit cell dimensions of

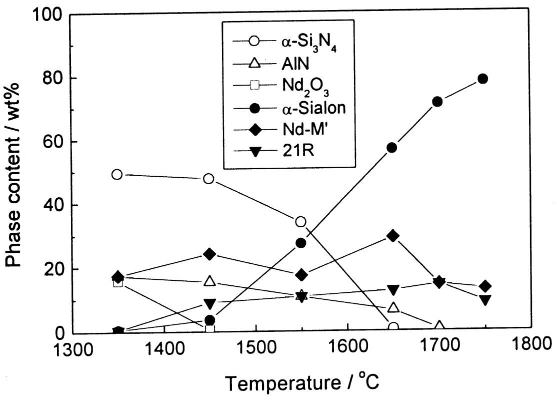

Fig. 2. Phase assembly of (CN5050) composition hot-pressed at different temperatures.

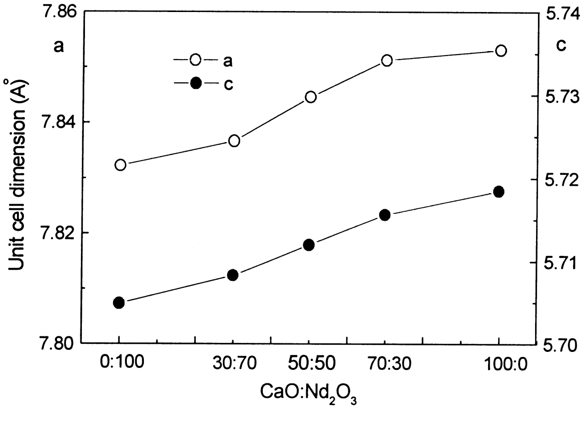

Fig. 3. The variation in unit cell dimensions of α-sialon in hot-pressed samples with different Ca/Nd ratios.

multi-cation (Ca + Nd) α-sialons, in which x value of the compositions was fixed as a constant 1.0. As seen from Fig. 3, the present results have also revealed an expansion of the α-sialon lattice in both a and c dimensions with increasing substitution of Ca for Nd, which might be correlated with the much higher solubility of Ca than Nd in α-sialon lattice. Ca is known to be a good α-sialon stabilizer, while Nd does not perform well as a modifying cation mainly due to the formation of melilite, which uses up excessive quantities of Nd. It is therefore proposed that the solubility of the "active modifying cation" was enhanced by the "less active", which is similar to the case of multi cation (Ca + Mg)- and (Nd + Y/Yb)-α-sialon as reported in our previous work.[7,9,10]

3.2. Microstructural observation and mechanical properties

Fig. 4(a)–(e) shows SEM micrographs [(a)–(d) taken from back scatter image, (e) taken from secondary electron image] of the polished surface of hot-pressed (Ca + Nd) α-sialon compositions with the different molar ratios of Ca to Nd. The white, gray and black in the photos represent grain boundary, α-sialon and AlN polytypoid phase respectively. It is seen that with the increase in the ratio of Ca to Nd in the compositions, white color regions are reduced. This trend is consistent with the results of phase analysis of (Ca + Nd)-α-sialon compositions. Fig. 5 is a typical micrograph of the etched surface

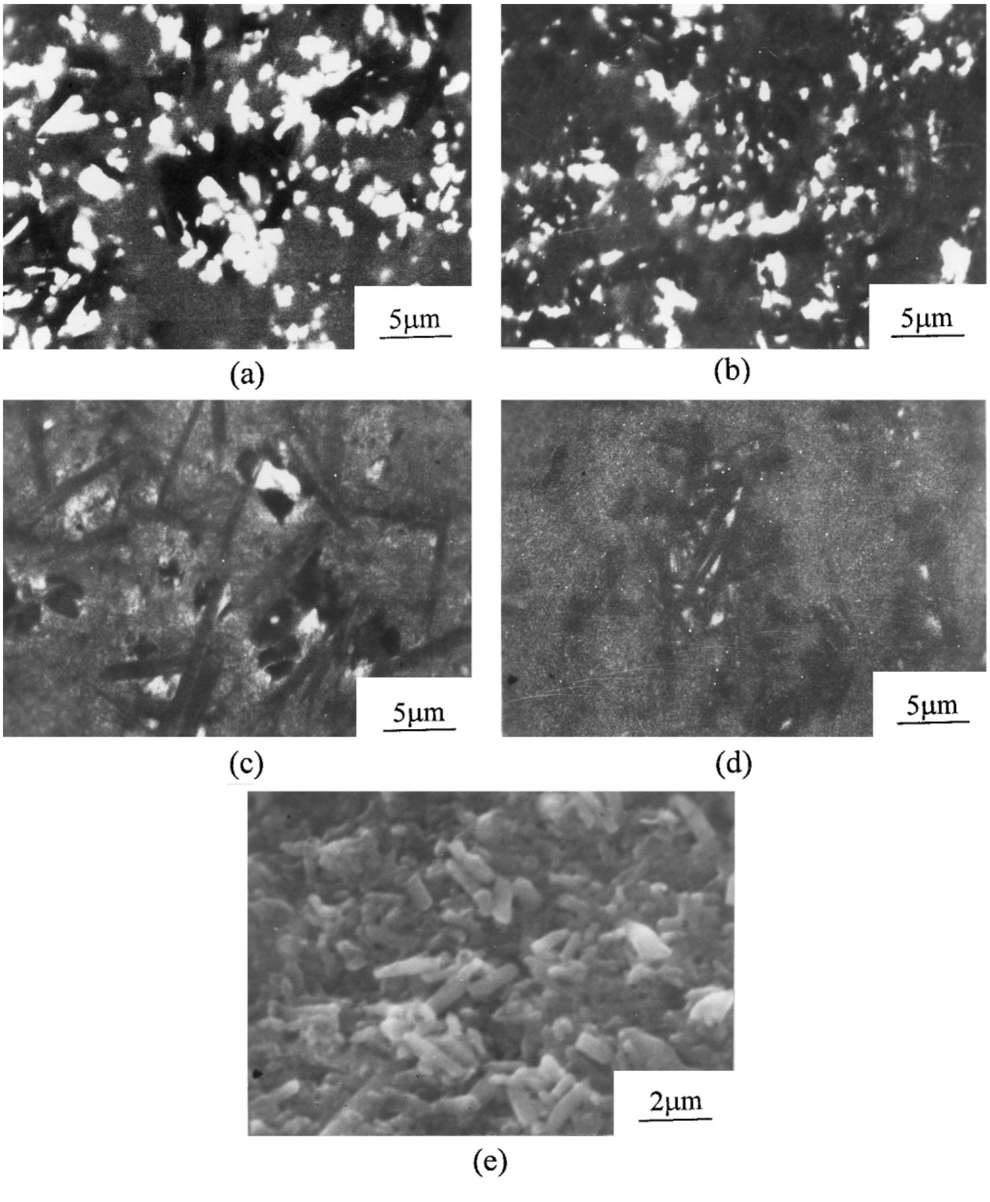

Fig. 4. SEM micrograph of polished surface of hot-pressed (Ca + Nd)-α-sialon compositions. (a) ND100; (b) CN3070; (c) CN5050; (d) CN7030; (e) CA100. Note: (a)–(d) taken from back scatter image, (e) taken from secondary electron image.

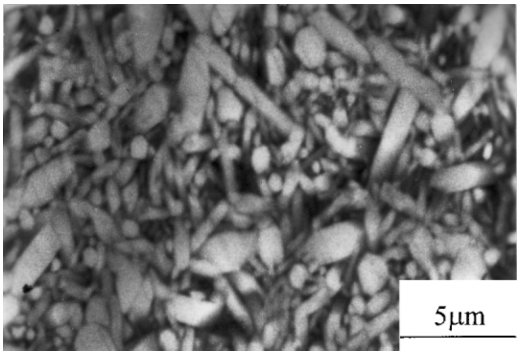

Fig. 5. SEM micrograph of etched surface of hot-pressed CN5050 composition.

of hot pressed (Ca + Nd)-α-sialon sample (CN5050). Both equi-axed and elongated shapes are found for α-sialon grains. The occurrence of elongated α-sialon in the investigated material should come as no surprise since recent studies have shown that the anisotropic growth of α-sialon grains could be promoted in both Ca and light rare earth doped system with high x values.[20,21] Semi-quantitative EDS analysis was made to investigate the solubility of Ca and Nd in the α-sialon grain (Fig. 5), and in the intergranular phase [Fig. 4(c)]. The elongated α-sialon grains contained both Ca and Nd in its lattice, but the Ca solubility was much higher than that of Nd [Fig. 6(a)] although the designed composition had the same CaO and Nd_2O_3 molar amount. On the other hand, much higher amount of Nd than that of Ca was found in intergranular region [Fig. 6(b)]. Therefore, Ca was mostly responsible for α-sialon formation while most of Nd contributed to the intergranular phase formation in multi-cation (Ca + Nd) α-sialons.

Table 2 lists the hardness and fracture toughness of (Ca + Nd)-α-sialon compositions with the different molar ratio of Ca to Nd. It was found that the hardness became higher with the increase in substitution of Nd for Ca. Since the amount of α-sialon phase increases with increasing molar ratio of Ca to Nd, this trend does reflect the contribution of α-sialon phase to hardness of the material. It is noted that the hardness of CA100 has a slightly lower value than the one of CN7030, although the amount of α-sialon in the former sample is somewhat higher than in the latter one. It is known that the presence of glassy phase on grain boundaries could reduce hardness of materials.[22] For CA100 composition, the final phases consist of α-sialon and AlN polytypoid. Considering the reaction sequence of CN5050, the M′ phase in final products of CN7030 could be formed due to partial devitrification of grain boundary glassy phase. This may cause the decrease in the amount of the latter and thus enhance the hardness of CN7030.

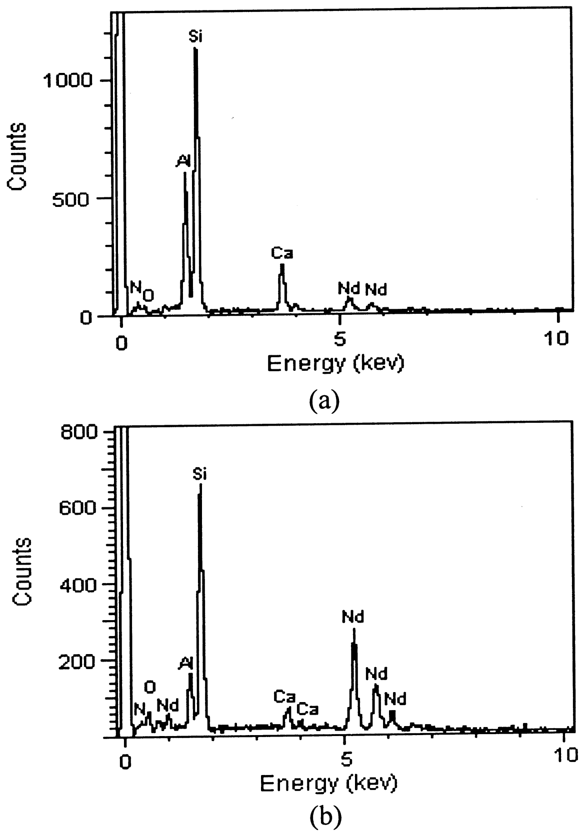

Fig. 6. EDS spectra from (a) the α-sialon grain and (b) the intergranular phase of CN5050 composition.

Table 2
Mechanical properties of hot-pressed (Ca + Nd)-α-sialons

Sample no.	ND100	CN3070	CN5050	CN7030	CA100
H_{v10} (GPa)	15.87	16.36	16.90	18.79	18.21
K_{1c} (MPa m$^{1/2}$)	4.2	4.6	5.1	4.8	4.9

The fracture toughness of (Ca + Nd)-α-sialon compositions varies from 4.2 to 5.1 MPa m$^{1/2}$ as shown in Table 2, in which CN5050 has the highest value. The elongated morphology of α-sialon grains is of benefit for the fracture toughness enhancement. It was also known that the fracture toughness of α-sialon material was affected by the interface association between grain and intergranular phase.[23,24] The difference in amount and component of intergranular phase resulted from the different ratios of Ca/Nd in the starting compositions could cause the different interface association situations and thus result in the change of fracture toughness. It is possible to tailor the mechanical properties of α-sialon by adjusting the ratio of dual stabilizer in multi-cation α-sialons materials.

4. Conclusion

The phase formation in (Ca + Nd) α-sialon compositions is different from that in either Ca- or Nd-doped α-sialon compositions. The advantage of partial substituting Nd with Ca as a modifying cation is that the formation of melilite has been suppressed and hence the yield of α-sialon has been enhanced. Moreover, more amount of Ca than that of Nd are incorporated into α-sialon structure and most of the added Nd are kept in the intergranular phase. It is also expected that the mechanical properties of the dual cation (Ca + Nd)-α-sialons can be tailored through the adjustment of CaO:Nd_2O_3 ratio in the starting compositions.

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