Thermal stability and mechanical performance of multiply heat-treated α-sialon ceramics densified with rare earth oxides

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Typical α-sialon starting compositions, of formula Ln0.33Si0.3Al2.7O1.7N14.3, were densified by hot-pressing using Ln2O3 as sintering additives, where Ln = Nd, Dy, and Yb. The as-sintered materials were heat-treated at 1450 °C for 96 hours and then re-sintered at 1800 °C for 1 hour to observe the overlapping effects of both Ln2O3 and multiple heat-treatment on thermal stability of the Ln-α-sialon phase and also the change in microstructure. The kinds of grain boundary phases which occurred also affected the results. The hardness, fracture toughness and flexural strength of the materials were evaluated using indentation and three-point bending tests, respectively. Mechanical tests and detailed microstructural analysis have led to the conclusion that a multiple-mechanism is involved, with debonding, crack deflection, crack bridging, and elongated grain pull-out all making a significant contribution towards improving the fracture toughness. Nd-containing specimens were tough with a highest indentation fracture toughness $K_{IC}$ of 7.0 MPa m$^{1/2}$. In contrast, Dy- and Yb-containing specimens were hard and brittle with a highest Vickers hardness $H_{V10}$ of 18.0 GPa. All re-sintered specimens underwent β→α transformation to some degree, leading to a degradation of mechanical properties as a consequence.


1. Introduction
Sialons, solid solutions of aluminum and oxygen in silicon nitride, have been widely studied for several decades as engineering ceramics, either in the α- or β-forms. From a preparative point of view, it is much easier to tailor the microstructure and properties of an α-sialon material, because of the wide solid solution range available for composition selection and also because of the possibility of α→β phase transformation. Concerning the mechanism of toughening as well as strengthening, in-situ reinforcement via elongated sialon grains has proved an effective intrinsic approach (by debonding, pull-out, crack bridging, and crack deflection) and has been suggested as a preferable alternative to extrinsic reinforcement (e.g. using platelets and whiskers), since it improves production economics, thermal stability, and environmental safety.

Isostructural with Si$_3$N$_4$, sialon has two forms, α-sialon (α’ and β-sialon (β’). The general formula of α-sialon is represented as M$_x$Si$_{12-x}$Al$_6$O$_6$N$_{16-x}$, where $x < 2$ and M cations Li, Mg, Ca, Y, La, and most rare earth ions (Ln) are incorporated into interstitial sites in the α’ network. However, the α’ structure can accommodate these M cations when available from liquid phase sintering additives, leaving a minimal compositional residue at grain boundaries in the final material, which is an important consideration in the development of fully dense sialon materials for use at elevated temperatures. On the other hand, the α’ phase usually forms as equiaxed grains which are therefore of low toughness due to the lack of the conventional pull-out toughening mechanism provided by elongated grains. However, α’ ceramics show unique hardness due to their intrinsically higher hardness compared with β’ phase. β-sialon, of formula Si$_6$C$_z$Al$_z$O$_z$N$_{14-z}$, is tougher by self-reinforcement because the final microstructure contains elongated grains. An additional important variable is that at the temperatures used to sinter and heat-treat sialon ceramics, rare earth α-sialons are unstable and transform to β’, thereby modifying the microstructure and hence the mechanical behaviour. Besides, heat treatment is an effective method for minimizing the grain boundary glass in nitrogen ceramics by converting it into refractory crystalline phase(s), thus improving the high temperature properties [1–6]. The present work is based on the idea of designing a series of sialon compositions.
of rare earth oxide-densified monolithic sialon ceramics with adequate thermal stability and enhancement not only of the hardness but also of the toughness by building up a mosaic assemblage of equiaxed and elongated grains by controlled in-situ $\alpha \rightarrow \beta$ sialon transformation. Previous studies have shown that $\alpha \rightarrow \beta$ transformation proceeds at different rates when different rare earth oxide densification additives are used [7–10], leading to the formation of different microstructures. There are therefore many parameters (e.g. starting composition, sintering additives, sintering methods, schedule of heat-treatment, and environment) which can be adjusted for property optimization. The aim of this work has been to determine the effects of various rare earth oxide additives, in order to reduce the extent of transformation by multiple heat-treatment to the modification of microstructure and the changes in mechanical properties.

For this purpose, light (Nd$_2$O$_3$), medium (Dy$_2$O$_3$), and heavy (Yb$_2$O$_3$) rare earth oxides were chosen as densifying additives to compare their effect on $\alpha$ thermal stability. The hot-pressed materials were not only heat treated at 1450 $^\circ$C for 96 hours but also re-sintered at 1800 $^\circ$C for 1 hour to figure out the overlapping effects of the two heat processing on $\alpha \rightarrow \beta$ transformation. That is one area of newness in this research. The effect of different cation size sintering additives on the thermal stability, microstructural characteristics and hence mechanical performance ($HV_{10}$, $K_Ic$, and $\sigma_f$) were evaluated.

2. Experimental procedure

The starting compositions were very similar and corresponded to compositions at the low- $\alpha$-sialon boundary of the type $\text{Ln}_{3.3}\text{Si}_{9.3}\text{Al}_{2.3}\text{O}_{17}$, with $\text{Ln} = \text{Nd, Dy, and Yb}$. Sialon starting powders (i.e. $\text{Si}_3\text{N}_4$, $\text{Al}_2\text{O}_3$, $\text{Nd}_2\text{O}_3$, $\text{Dy}_2\text{O}_3$, and $\text{Yb}_2\text{O}_3$) were ball milled using $\text{Si}_3\text{N}_4$ balls in isopropanol for one day to prepare a suspension. The fresh suspension was processed by magnetic stirring, drying, and then sieving. The resulting powders were hot-pressed in BN-coated graphite dies at 1800 $^\circ$C for one hour at a pressure of 30 MPa. As-sintered samples were heat-treated in an alumina tube furnace in flowing nitrogen at 1450 $^\circ$C for 96 hours, and re-sintered in a carbon resistance furnace at 1800 $^\circ$C for 1 hour under a protective nitrogen atmosphere, and then the furnace was cooled at a rate of 50 $^\circ$C min$^{-1}$ from 1800 to 1200 $^\circ$C to modify the microstructure and change the $\alpha / \beta$ ratio. Before being heat-treated and re-sintered, the specimens were embedded in micron-sized boron nitride powder in graphite crucibles. Densities of the samples were measured with a mercury displacement balance using Archimedes’ principle. Phase identification was carried out by x-ray diffraction using a Hagen-Guinier focusing camera with Cu K$_{α1}$ radiation, and using the intensities of the (102) and (210) peaks of the $\alpha$-sialon phase and the (101) and (210) peaks of the $\beta$-sialon phase for quantitative estimation of the $\alpha / \beta$ sialon ratio. The Vickers hardness as well as indentation fracture toughness were determined at room temperature by indentation using a Vickers diamond indenter and a load of 98 N for 10 minutes. The hardness and fracture toughness were evaluated according to the method of Evans and Charles [11]. The flexural strength of samples (30 $\times$ 3.5 $\times$ 5.5 mm) was measured at a constant cross-head speed of 0.2 mm/min using a three-point bending equipment (C100D-testing Machine, R. D. P. Howden) with an outer span of 20 mm. The measured strength values were used to provide reference data because only 2–3 bars for each sample were available for testing due to the limitation of sample size. All samples for mechanical property measurements were ground and polished with diamond pastes of size 45 $\mu$m, 25 $\mu$m, 14 $\mu$m, 6 $\mu$m, and 1 $\mu$m. SEM microstructural studies were carried out using a HITACHI SEM (S-2400) instrument.

3. Results and discussion

3.1. Thermal stability and reversible $\alpha \leftrightarrow \beta$ transformation of Ln-$\alpha$-sialons

X-ray analysis of Ln-$\alpha'$ phase content in samples hot-pressed at 1800 $^\circ$C, heat-treated at 1450 $^\circ$C, and re-sintered at 1800 $^\circ$C is illustrated in Fig. 1. The levels of $\alpha'$ phase formation were quite different in the Nd-, Dy-, and Yb-system. Whereas the as-sintered samples, originally designed to give pure Nd-$\alpha'$, now contained some $\beta'$ phase (about 30%), but the original Dy- and Yb-$\alpha'$ samples were still almost pure $\alpha'$ phase. The $\alpha$-sialon stability was highly marked in the case of samples densified with higher atomic number rare earth oxides, and arises mainly because of the larger homogeneity range of the heavy rare earth $\alpha$-sialon phase [12, 13]. This is also obviously apparent from SEM micrographs shown in Fig. 2. Fig. 2 shows the microstructural changes in Nd-containing samples before and after post-heat-treatment. Back-scattered electron micrographs give a sharp contrast between the various phases: $\beta'$ grains without rare earth element are black and more elongated, whereas the $\alpha'$ grains accommodating rare earth cations are gray and more equiaxed, whilst Nd-rich crystalline or glassy phase is white.

To study the effects of temperature on the thermal stability of Ln-$\alpha$-sialon in more detail, the hot-pressed samples were heat-treated at 1450 $^\circ$C for 96 h. The thermal stability of the $\alpha$' phase was obviously dependent on the kind of additive, i.e. Nd$_2$O$_3$, Dy$_2$O$_3$, or Yb$_2$O$_3$.

![Figure 1](image-url) XRD analysis of $\alpha$-sialon phase contents in Ln-added samples before and after post-heat-treatment.