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High Temperature Mechanical Spectroscopy of α-SiAlON Ceramics with Different N/O Ratios

M. Mazaheri[1]*, D. Mari[1], R. Schaller[1], C. Yanbing[2], Z. Shen[2]

[1] Ecole Polytechnique Fédérale de Lausanne, Institut de Physique de la Matière Complexe, CH-1015 Lausanne, Switzerland

[2] Arrhenius Laboratory, Stockholm University, Stockholm SE-10691, Sweden

*e-mail : mehdi.mazaheri@epfl.ch

Abstract

High temperature mechanical properties of the silicon nitride based ceramics (such as SiAlON) depend highly on the formation of the grain boundary glassy phase obtained from sintering. In the present study, in order to investigate the effect of grain boundary chemistry and the N/O ratio on the chemical composition of α-SiAlON, the raw powders were hot-pressed for 4h at 2073 K under a pressure of 35 MPa, using two different sintering aids (Y^{3+} and Yb^{3+}), both with the oxygen rich (Y_2O_3 and Yb_2O_3) and the nitrogen rich (YN and YbN) compounds. The mechanical spectroscopy investigations of Y-SiAlON show a relaxation peak related to the glassy phase located on the triple-point junctions at around 1250 K. In the case of Yb-SiAlON, on the contrary, the absence of relaxation peaks stems from the very low content of glassy phase, together with the presence of elongated grains. In addition, the lower height of mechanical loss peaks in nitrogen rich Y-SiAlON samples versus oxygen rich ones is related to the substitution of oxygen by nitrogen in the [SiO_4] tetrahedral network that leads to a higher bond density in the glassy phase and high viscosity of the glassy phase at high temperatures.

Keywords: SiAlON, Glassy phase, Mechanical spectroscopy, Internal Friction, Sintering aids

WYSOKOTEMPERATUROWA SPEKTROSKOPIA MECHANICZNA CERAMIKI α-SIALON'OWEJ O RÓŻNEJ PROPORCJI N/O

Wysokotemperaturowe właściwości mechaniczne ceramiki bazującej na azotku krzemu (takiej jak SiAlON) bardzo zależą od fazy szklistej powstającej w granicach międzyziarnowych podczas spiekania. W prezentowanej pracy, aby zbadać wpływ chemii granicy międzyziarnowej i stosunku N/O na skład chemiczny α-SiAlON'u, surowe proszki prasowano na gorąco w temperaturze 2073 K przez 4 h pod ciśnieniem 35 MPa, wykorzystując dwa różne dodatki ułatwiające spiekanie: Y^{3+} i Yb^{3+}, obydwa w postaci związków albo bogatych w tlen (Y_2O_3 i Yb_2O_3), albo bogatych w azot (YN i YbN). Badania Y-SiAlON, wykonane z pomocą spektroskopii mechanicznej, pokazują pik relaksacyjny związany z fazą szklistą umiejscowioną w punktach potrójnych połączenia ziaren w temperaturze około 1250 K. W przypadku Yb-SiAlON'u absencja pików relaksacyjnych wynika z bardzo małej zawartości fazy szklistej razem z obecnością wydłużonych ziaren. Dodatkowo, mniejsza wysokość pików strat mechanicznych w próbkach Y-SiAlON bogatych w azot, w przeciwieństwie do próbek bogatych w tlen, związana jest z podstawieniem tlenu przez azot w sieci tetraedrów [SiO_4], co prowadzi do większej gęstości wiązań w fazie szklistej i większej lepkości tej fazy w wysokich temperaturach.

Słowa kluczowe: SiAlON, faza szklista, spektroskopia mechaniczna, tarcie wewnętrzne, dodatki ułatwiające spiekania

1. Introduction

According to the high covalent bonding character of the silicon nitride (Si_3N_4) crystal, this material cannot be sintered using the classical solid state sintering [1]. Full dense bodies can only be obtained through the liquid phase sintering. The most commonly used sintering aids are Al_2O_3, AlN, MgO, SiO_2 and Y_2O_3, which lead to the formation of an important volume fraction of the glassy phase located either between grains (glassy films) or at grain triple junctions (glassy pockets) [2]. This residual glassy phase after sintering is responsible for deterioration of mechanical properties at temperatures higher than 1000°C, due to the softening phenomenon [3]. Therefore, to improve the high temperature performance of Si_3N_4-based ceramics, efforts have been focused on controlling the characteristic of this glassy phase, such as quantity, viscosity, composition and glass transition temperature. For instance, other investigators reported that either by reducing the impurity of the glassy phase or by replacing more refractory glass oxides, such as Yb_2O_3 and Sc_2O_3 as sintering additives, the high temperature mechanical properties of SiAlON samples were improved [4].

In this paper, to investigate the effect of glassy phase chemistry (N/O ratio)/quantity, mechanical pectroscopy experiments were performed as a powerful method to analyze the occurrence of anelastic relaxation (due to α-relaxation in glassy phase and grain-boundary relaxation at high temperature). The internal frictions (I.F.) of two grades of SiAlON ceramics with different sintering aids (Y^{3+} and Yb^{3+}), both with the oxygen rich (Y_2O_3 and Yb_2O_3) and the nitrogen rich (YN and YbN) compounds were also measured. The I.F. results are compared with the compressive deformation behavior of the SiAlON ceramics under a constant load in SPS apparatus.

2. Experimental

2.1. Processing and microstructure

Specimens were processed at Stockholm University using Si_3N_4, AlN, Y_2O_3/Yb_2O_3 (called oxygen rich) or YN/YbN (called nitrogen rich) as raw materials. Table 1 presents the starting powder and phase compositions of different SiAlON samples. The initial powders were mixed via ball milling in hexane for 1 h using Si_3N_4 grinding media and then dried in a vacuum furnace and moved quickly into an argon filled glove box. The mixtures were hot pressed in a steel die for 4 h at 1800°C, under nitrogen atmosphere and 35 MPa pressure.

Table 1. Starting powder and phase composition of samples.

Sample	Starting powders	Phases
N-rich RE-sialon, $RE_xSi_{12-3x}Al_{3x}N_{16}$,RE = Y, Yb; x = 0.4		
YN04	Si_3N_4, AlN, YN	α-sialon, β-sialon (trace)
YbN04	Si_3N_4, AlN, YbN	α-sialon
O-rich RE-sialon, $RE_xSi_{12-3x-1.5x}Al_{3x+1.5x}O_{1.5x}N_{16-1.5x}$, RE=Y, Yb; x=0.4		
YO04	Si_3N_4, AlN, Y_2O_3	α-sialon
YbO04	Si_3N_4, AlN, Yb_2O_3	α-sialon

Microstructural observations of polished and chemically etched surfaces were carried out using scanning electron microscopy (SEM, JEOL, Japan).

2.2. Mechanical spectroscopy

Mechanical spectroscopy measurements were carried out in an inverted forced torsion pendulum, working in a subresonant mode [5]. The mechanical loss, tanf, and the shear modulus, *G*, were measured from the phase lag and the amplitude ratio between stress and strain signals, respectively. The measurements were preformed under a high vacuum (10^{-3} Pa) as a function of temperature in the range of 300-1600 K and at a fixed frequency (*f* = 1).

3. Results and discussion

Fig. 1 demonstrates the typical spectrum (mechanical loss and shear modulus as a function of temperature) through heating and cooling of YO04 sample at a frequency of 1 Hz. During the heating stage, the mechanical spectrum is mainly composed of a mechanical loss peak that occurs around 1280 K, and this peak is superimposed on exponential increases in damping at higher temperatures and the modulus decreases. After heating up to 1450 K, upon cooling, the peak has disappeared and the level of I.F. background at high temperatures is low. Donzel [6] has compared the characteristic of this peak (activation energy and relaxation time limit) with anelastic relaxation of pure SiAlON glasses and interpreted this peak is due to the α-relaxation peak in the glassy phase pockets.

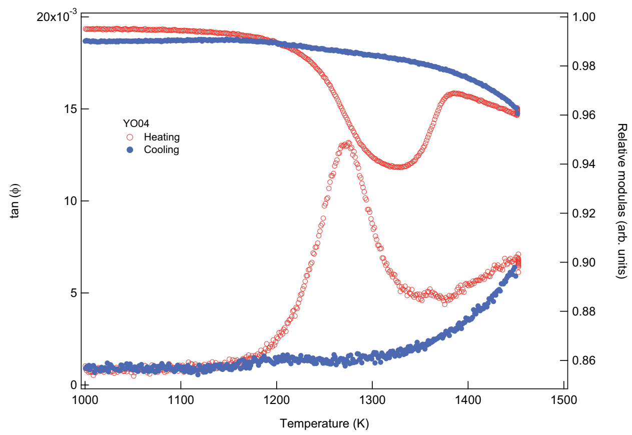


Fig. 1. Mechanical loss spectrum of YO04 during heating and after annealing at 1450 K.

Fig. 2 shows the microstructure of YO04 sample in the as-received condition after sintering, which is involved with a large amount of glassy phase at triple junctions. Annealing at high temperatures resulted in the crystallization of the glassy phase and consequently the peak disappearance (Fig. 1).

A relaxation peak is due to an anelastic strain, in which a restoring force limits this strain. In the case of Si_3N_4 based ceramics, this restoring force comes from the adjacent grains, which prevent mobility of the molecular glassy phase at temperatures higher than glass transition temperature [6, 7].

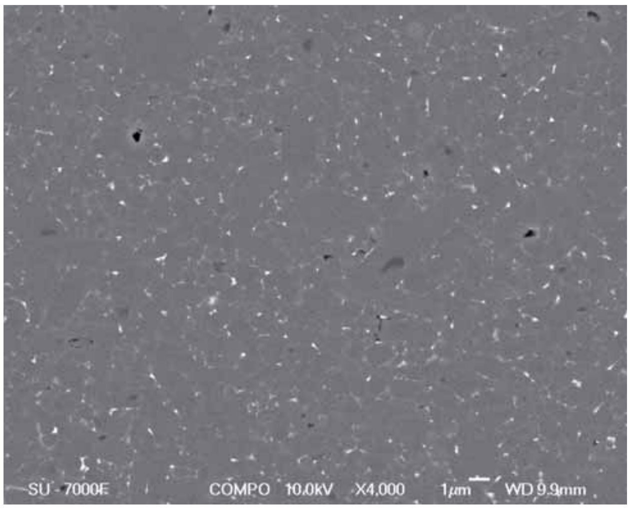


Fig. 2. Scanning electron microscopy of YO04. One observes the equiaxed grains and lot amount of glassy phase pockets, which located between the grains.

In contrast, it was found that pure SiAlON glass spectrum does not exhibit a relaxation peak, because there is no restoring force and anelastic strain increase without any limitation. It means that, three parameters are effective in characterization of the peak: composition of glassy phase (in position of the peak), the resorting force, and content of glassy phase (in amplitude of the peak) in silicon nitride base ceramics. For instance, Fig. 3 compares the mechanical spectrum of YO04 and YN04 as a function of temperature.

YN04 peak is located at temperature around 100 K lower than YO04 peak. The different composition of glassy phases in YN04 and YO04 allow the authors to interpret this behaviour as the effect of grain boundary chemistry and the

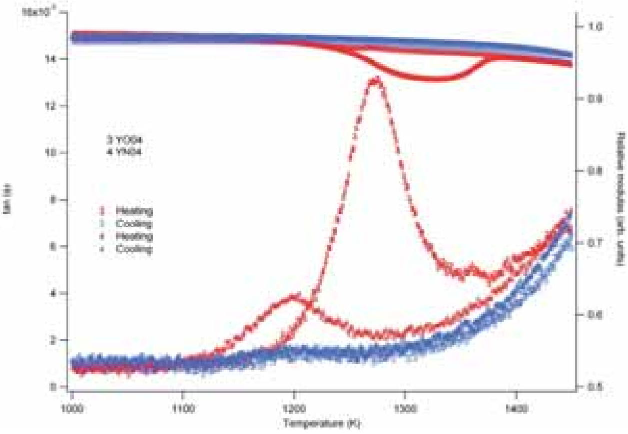
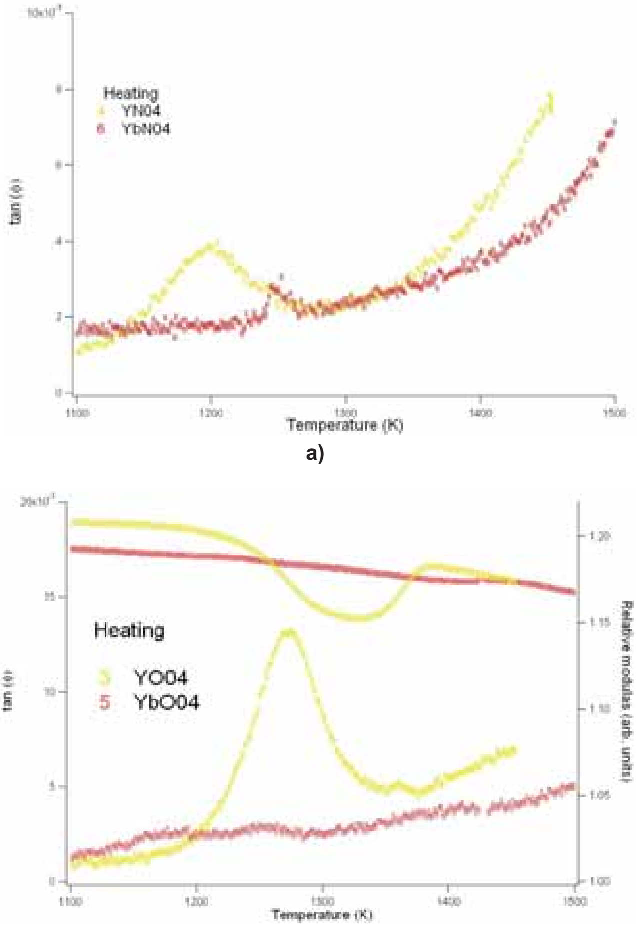


Fig. 3. Mechanical loss spectrum of YO04 and YN04 during cooling and after annealing at 1450 K. The position and height of the peak are related to chemistry of glassy phase and quantity of glassy phase.



a)

b)

Fig. 4. The mechanical loss spectra: a) YN04, YBN04 and b) YO04, YbO04.

N/O ratio on the chemical composition of α-SiAlON glass. According to the literature, substitution of oxygen by nitrogen in the [SiO_4] tetrahedral network results in a higher bonding density per unit volume of the glass, thus improving the glass properties [2]. The lower height of the peak in the case of YN04 can be attributed to the lower quantity of glassy phase in the microstructure.

Figs. 4a and 4b represent the mechanical loss spectrum of Yb_2O_3 and YbN, compared to Y_2O_3 and YN, respectively. As observed in this figure, the spectrum of samples with Yb additive, for both oxygen and nitrogen rich states, exposes no significant peaks. The level of high temperature background in Yb_2O_3/YbN samples is less than of Y_2O_3/YN ones. Such a behavior is related to the very low content of the glassy phase, together with the presence of elongated grains. Also, according to the literature, a powerful strategy to improve the high temperature performance of silicon nitride based ceramics is replacing glass-forming refractory oxides, such as Yb_2O_3 as sintering aids. The results of the high temperature compressive deformation (in SPS apparatus) of Yb_2O_3/YbN and Y_2O_3/YN samples show a similar trend. The onset of deformation for Yb_2O_3/YbN is reported to be at 1580/1594°C, while this value for Y_2O_3/YN is 1543/1576°C.

4. Conclusions

In the current investigation, mechanical spectroscopy experiments were performed as a powerful method to analyze anelastic relaxation (due to α-relaxation in the glassy phase and the grain-boundary relaxation at high temperatures). The internal frictions (I.F.) of two grades of SiAlON ceramics with different sintering aids (Y^{3+} and Yb^{3+}), both with the oxygen rich (Y_2O_3 and Yb_2O_3) and the nitrogen rich (YN and YbN) compounds were measured. The results indicate that the mechanical spectroscopy investigations of Y-SiAlON demonstrates a relaxation peak related to the glassy phase located in the grain-boundaries and triple-point junctions at around 1250 K and high temperature exponential background at temperatures higher than 1400 K. In case of Yb-SiAlON, on the contrary, no peak is observed, which is related to the very low content of glassy phase, together with the presence of elongated grains. In addition, the lower height of the mechanical loss peak in the nitrogen rich Y-SiAlON samples versus the oxygen rich ones refers to the substitution of oxygen by nitrogen in the [SiO_4] tetrahedral network, which leads to a higher bond density in the glassy phase and high viscosity of glassy phase at high temperatures.

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