HIGH TEMPERATURE MECHANICAL PROPERTIES OF NITROGEN-RICH Ca-α-SIALON CERAMICS

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Nitrogen-rich Ca-α-SiAlON ceramics with different starting powder compositions have been studied by high temperature mechanical spectroscopy in parallel with compressive deformation in a spark plasma sintering equipment. The mechanical loss spectra measured upon heating show a relaxation peak at about 1150 K and a high temperature exponential background at higher temperatures (>1400 K), which originate from the α-relaxation in the glassy phase and grain boundary sliding, respectively. The intensity of the peak is not only affected by the glassy phase quantity but also depends on the restoring force due to grain elasticity. Moreover, the peak amplitude can be used to predict the compression creep of silicon nitride based ceramics.

INTRODUCTION

Among current structural ceramics, silicon nitride based ceramics (SiAlONs) exhibit excellent mechanical properties at both room and high temperatures \([1,2]\). Due to the low atomic diffusion of high covalent bonding character silicon nitride ceramics cannot be densified using classical solid state sintering techniques \([3]\). Full dense bodies can only be obtained through liquid phase sintering \([2]\). The most used sintering aids are Al\textsubscript{2}O\textsubscript{3}, AlN, MgO, SiO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3}, which produce an oxynitride liquid during sintering and lead to the formation of a residual glassy phase during cooling.

Mechanical spectroscopy is a non-destructive and sensitive method to obtain information about defect mobility and phase transformations \([4]\). In the case of SiAlON ceramics, several articles \([5-7]\) have reported the occurrence of an anelastic relaxation peak, superimposed on an exponential background due to grain boundary relaxation at a temperature of 1270 K. Lakki et al. \([6]\) have shown that the peak can be attributed to the presence of an intergranular glassy phase. In this paper, mechanical spectroscopy was used in order to characterize residual glassy phase of a series of nitrogen-rich Ca-α-SiAlON samples. Different primary compositions located along the tie-line Si\textsubscript{3}N\textsubscript{4}-1/2Ca\textsubscript{3}N\textsubscript{2}·3AlN allows an analysis of the effect of microstructure, \textit{i.e.} equiaxed versus elongated grains, and of the quantity of glassy phase on the height of the relaxation peak. In order to obtain a relation between the anelastic deformation determined by mechanical spectroscopy measurements and
plastic deformation, compressive deformation tests were conducted in a Spark Plasma Sintering (SPS) apparatus as a function of temperature.

**EXPERIMENTAL TECHNIQUES**

Si$_3$N$_4$, AlN and CaH$_2$ powders were mixed in a planetary mill with hexane for 1 h. The general formula of Ca$_x$Si$_{12-2x}$Al$_{2x}$N$_{16}$, with $x = 0.2, 0.4, 0.8$ and $1.6$, represents the designed overall compositions of the samples, henceforth labeled Ca2N, Ca4N, Ca8N and Ca16N respectively. Pellets of the mixtures were hot pressed in BN-coated graphite dies in nitrogen atmosphere in a graphite resistance furnace at 2073 K for 4 h under 35 MPa uniaxial pressure. Details of the sintering process, phase assemblages after sintering and thermal stability of the phases are presented elsewhere [8-10].

Mechanical spectroscopy measurements were carried out in an inverted forced torsion pendulum, working in subresonant mode [11]. Samples of the size $25 \times 1 \times 4$ mm$^3$ were excited in torsion. The mechanical loss, $\tan(\phi)$, and the shear modulus, $G$, were measured from phase lag and from the amplitude ratio between stress and strain, respectively. The measurements were performed under high vacuum ($10^{-3}$ Pa) as a function of temperature (at a fixed frequency of 1 Hz) in the range of 300-1600 K with a heating rate of 1 K min$^{-1}$ or as a function of frequency (between $10^4$ and 10 Hz) at fixed temperatures.

Compressive plastic deformation tests under a constant load and as a function of temperature were performed in a spark plasma sintering apparatus, Dr. Sinter 2050, Tokyo, Japan. The initial applied load corresponds to a compressive stress of 40 MPa. The temperature was increased in a ramp of 1 K min$^{-1}$.

**RESULTS AND DISCUSSION**

Figure 1a shows the mechanical loss and shear modulus spectra as a function of temperature, upon heating and cooling of the Ca2N sample. Upon heating, the mechanical loss spectrum is composed of a peak superimposed on an exponential increase (background) in damping. The peak appears at a temperature of 1110 K for the frequency of 1 Hz and is accompanied by a modulus drop of about 6%. Above the peak, between 1210 and 1290 K, a modulus recovery is observed that practically compensates the entire drop observed at the peak. The peak shifts in frequency when the temperature of isothermal measurements is changed. This means that this peak is due to a thermally activated relaxation. The activation energy was $Q = 810$ kJ mol$^{-1}$ and the relaxation limit time was $\tau_0 = 2 \times 10^{-40}$ s. These values are rather unusual and they have to be considered as apparent values [5-6].

Upon cooling, after dwelling for 1 h at 1600 K, one can observe that the mechanical loss peak and the modulus anomaly disappear while the high temperature mechanical loss background is lower than in the as-sintered sample. The features observed in the first heating are irreversibly lost in the next heating cycle. A stable and reversible exponential background and the corresponding decrease in shear modulus are then observed above 1300 K. Mechanical spectroscopy results of as-sintered samples with different compositions are compared in Fig. 1b. The height of the peak increases in samples Ca2N-Ca8N with increasing Ca doping while in sample Ca16N, the peak is lower.

Figure 2 represents the compressive plastic deformation curves obtained during
temperature scans in SPS of the samples Ca4N, Ca8N and Ca16N recorded up to 2030 K. As shown, the onset deformation temperature for these three samples is very close to each other at about 1800 K. However, sample Ca4N starts to deform at higher temperatures in comparison with the other samples. At 1973 K, the deformation strain of the samples Ca4N, Ca8N and Ca16N have been found to be 18, 27 and 23%, respectively. There is a trend similarity between the height of the peak in mechanical loss measurements and deformation at high temperatures: the higher the peak, the lower the deformation start temperature.

FIGURE 1: a) Mechanical loss spectrum of sample Ca2N measured as a function of temperature at 1 Hz. The relative shear modulus variations are also reported. b) The amplitude of the peak is reported for Ca2N-Ca16N.

As documented in several articles, the presence of a glass phase at the boundaries of SiAlON grains is at the origin of the mechanical loss peak found in the present materials [5-7]. The peak appears on first heating cycle and it disappears after passing 1200 K where the recrystallization of the glass phase starts. The presence of such a phase is also responsible for creep at high temperature. However, the grain morphology has to be taken into account as well. Figure 3 shows the fracture surfaces of two representative samples. Sample Ca4N shows a fine equiaxed structure while sample Ca16N shows more elongated \( \alpha \)-Si\(_3\)N\(_4\) grains. This means that increasing the Ca content two parameters vary: the quantity of glassy phase between grains and the quantity of elongated grains. Creep is hindered by the restoring force due to elongated grains.

A rheological model of the system made of a viscous element in parallel with the restoring force due to adjacent grains justifies the trend observed in the amplitude of the mechanical loss peak. The increasing amplitude of the peak observed in samples Ca2N, Ca4N and Ca8N is due to an increase of the quantity of the glass phase.
Instead, sample Ca16N shows a lower peak despite a higher glass phase content due to a higher restoring force of elongated grains.

FIGURE 3: Scanning electron micrographs showing fracture surface of a) sample Ca4N and b) sample Ca16N.

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REFERENCE LIST