HIGH TEMPERATURE MECHANICAL LOSS OF NANOSTRUCTURED YTTRIA STABILIZED ZIRCONIA (3Y-TZP) REINFORCED WITH CARBON NANOTUBES

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ABSTRACT
High temperature mechanical spectroscopy measurements were conducted on carbon nanotube-reinforced fine-grained 3Y-TZP ceramics processed by conventional (CS, grain size ~ 350 nm) and spark plasma (SPS, grain size ~ 100 nm) sintering. The mechanical loss spectra are composed of a peak and an exponential background appearing at low frequencies or high temperatures. The SPS samples showed a much higher level of internal friction and lower creep resistance, which can be attributed to the easier grain boundary sliding in nanosize-grained specimens. The addition of carbon nanotubes resulted in a decrease in damping with respect to the high purity of zirconia powder and possibly in a reduction of creep.

INTRODUCTION
Toughness improvement of ceramics, even the more classical ones, is still nowadays a subject of interest1,2. Large increase in strength and fracture-toughness is frequently documented for ultra-fine ceramic/metallic structures; a phenomenon that is explained in part by small grain sizes using the well-known Hall–Petch relationship3. Grain refining is a promising route for simultaneous increase of mechanical strength and fracture toughness. Such improvement can be attributed to the fact that grain boundaries act as obstacles against deformation. For instance, application of two-step sintering method resulted in processing nanostructured cubic stabilized zirconia4, which exhibits up to ~ 96% increase in the fracture toughness (i.e. from 1.61 to 3.16 MPa m1/2), when the grain size is reduced from ~ 2.15 μm to ~ 295 nm. In addition to mechanical advantages, using nanopowder for fabrication of nanocrystalline parts, considerably, enhances sinter ability at lower temperatures rather than those of micrometric grains.

Spark Plasma Sintering (SPS) is a promising technique for production of nanostructured ceramics. SPS is a newly developed sintering process that combines the use of mechanical pressure and microscopic electric discharge between the particles. The enhanced densification in this process has been attributed to localized self-heat generation by the discharge, activation of the particle surfaces, and the high speed of mass and heat transfer during the sintering process5. As a result, samples can rapidly reach full density (in a few minutes) at relatively low temperatures. This process has been used to prepare a large variety of nanograined ceramics, including 3Y-TZP, Al2O3 and BaTiO3.

According to the above introduction, processing of nanostructured ceramics (instead of micrometric grains), can increase fracture toughness at room temperature. On the other hand, high temperature mechanical properties of ceramics and especially fine-grained 3 mol% yttria stabilized tetragonal zirconia polycrystals (3Y-TZP) depend highly on grain boundary (GB) properties6. GB sliding is an important mechanism of plastic deformation for fine-grained ceramics. It is mostly attributed to the fact that, when nanostructure is concerned, GB sliding can be activated at much lower temperatures than in the case of coarser grain size6,7. Hence, it seems that application of nano-structured ceramics at room temperature is reasonable. But, the domination of GB sliding at high temperature will deteriorate
creep resistance. According to the general equation of creep for ceramics, the creep rate ($\dot{\varepsilon}$) is inversely proportional to the grain size:

$$\dot{\varepsilon}(\sigma, T) = A \left(\frac{\sigma - \sigma_0}{G}\right)^n \left(\frac{\sigma}{G}\right)^p D$$

where $\sigma$ is the applied stress, $\sigma_0$ the threshold stress (which depends on the nature of the GBs, but is zero in many cases), $G$ the shear modulus, $n$ the stress exponent, $b$ is the Burger's vector, $d$ the grain size, $p$ the grain size exponent and $A$ a material constant. $D$ is the diffusion coefficient expressed as $D = D_0 \exp(Q/kT)$, with $D_0$ the pre-exponential factor, $Q$ the activation energy which accounts for the underlying controlling mechanism and $kT$ has the usual meaning.

In this work, CNTs were added to nanostructured zirconia samples in order to pin the grain boundaries and reduce GB sliding. As GB sliding is a source of energy dissipation, mechanical loss measurements are well suited to study such a mechanism. The mechanical loss spectrum of fine-grained 3Y-TZP reinforced with CNTs, processed by spark plasma sintering (SPS, grain size ~ 100 nm) and by conventional sintering (CS, grain size ~300 nm) are presented in the current investigation.

EXPERIMENTAL PROCEDURE

Pure commercial yttria-stabilized zirconia (3Y-TZP, Tosoh, Japan) and multiwall carbon nanotube (CNT, synthesized by chemical vapor deposition method) were used as raw materials. The powder with an amount of 3 wt% CNTs was first mixed by attrition milling for 24 h using zirconia grinding balls. Then the mixture was processed using two methods: conventional sintering and spark plasma sintering. Using the conventional method, the mixture was initially cold pressed under 100 MPa, followed by sintering at 1673 K for 3 h in Ar atmosphere. Spark plasma sintering was carried out in Stockholm University SPS apparatus at 1523 K for 5 min under the pressure of 50 MPa. The density of the sintered bodies was measured by Archimedes method in distilled water and using an accurate ($10^{-4}$ g) balance. For scanning electron microscopy (SEM, Philips XL30, Netherlands), the samples were cut, mechanically polished and thermally etched. The grain size of the sintered samples was determined by multiplying the average linear intercept by 1.56. For each specimen, 50 line segments were taken into account.

Mechanical spectroscopy measurements were carried out in an inverted forced torsion pendulum, working in a subresonant mode. Samples of the size 25 * 1 * 4 mm$^3$ were excited in torsion and the deformation of the sample was detected by an optical laser cell. The mechanical loss, tan ($\phi$), and the shear modulus, $G$, were measured from phase lag and the amplitude ratio between stress and strain signals, respectively. The measurements were performed under a 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$^{-1}$. The curves obtained are defined as mechanical loss spectra. Compressive creep tests were also preformed on parallelepiped samples (3 * 3 * 8 mm$^3$) under stress of 8 MPa at 1350 K.

RESULTS AND DISCUSSION

A typical mechanical loss and shear modulus spectrum of a high purity nanostructured 3Y-TZP, processed by SPS, is shown in Figure 1 as a function of temperature. In the measured domain, two regions of special interest may be observed:

a) At about 400 K, a mechanical loss peak is observed, which is associated with a decrease in the shear modulus. The peak has been interpreted as due to the reorientation of elastic dipoles of the type "oxygen vacancy – yttrium cations" under the influence of the applied stress. 
b) At higher temperatures (>1200 K), the spectrum consists of a monotonic increase of the high temperature damping background and a steep decrease in the material stiffness. The amplitude of the applied cyclic stress during measurements was of the order of 8 MPa. High temperature plastic deformation of polycrystalline ZrO₂ is related to grain boundary (G.B.) sliding, and consequently it seems reasonable to link the mechanical loss spectrum with G.B. sliding as a source of energy dissipation. Lakki⁶,⁷ has developed a theoretical model in order to interpret the high temperature mechanical loss of 3Y-TZP due to the relative sliding of hexagonal grains separated by an intergranular glassy phase (viscous layer). A dissipative force related to the viscosity of the layer and a restoring force corresponding to the elasticity of the neighboring grains (which limits the sliding at the triple point junctions) are two forces playing a key role in the relaxation process. In the spectrum shown in Figure 1, at temperatures higher than 1200 K, no peak but an exponential increase in the mechanical loss is observed, while, the abovementioned model (Lakki’s model⁶,⁷) accounts for a Debye peak. This behavior can be explained by considering that the restoring force in triple junction is decreasing drastically with temperature, due to large relative movement of grains (creep). When the restoring force vanishes, grain boundary sliding is no more limited. Consequently, the mechanical loss increases exponentially with temperature and one can consider this exponential background in the spectrum as the signature of creep.

![Graph](image)

**Figure 1.** Mechanical loss and shear modulus spectra as function of temperature through the heating of a high purity 3Y-TZP processed via SPS.

Figure 2 shows the mechanical loss spectrum and the relative shear modulus of pure zirconia sintered conventionally in furnace and in spark plasma sintering apparatus. SEM micrographs of both grades of 3Y-TZP are presented in Figure 3 (a) and (b). The grain size of the samples sintered in SPS is about 3 times less than in the conventionally sintered ones (~100 nm for SPS versus ~ 350 nm for
conventionally sintered sample). As a consequence, grain sliding in SPS sample starts at lower temperatures, and increases faster than in conventionally sintered samples. In addition, the shear modulus drops at temperature around 1100 K for SPS sample, while this temperature for conventionally sintered sample was observed at ~ 1300 K. It can be attributed to the easier grain boundary sliding in nanosize-grained specimens.

![Figure 2](image2.png)

Figure 2. Mechanical loss spectra (a) and relative shear modulus (b) of high purity 3Y-TZP samples sintered via SPS and conventional methods.

![Figure 3](image3.png)

Figure 3. SEM micrographs of pure 3Y-TZP specimens sintered by conventional sintering (a) and spark plasma sintering (b).

For comparison, creep measurements at low stress regime (8 MPa) and 1350 K were carried out in SPS and CS samples. Figure 4 shows that the creep strain in SPS sample is much higher than in CS one. This result is in agreement with mechanical spectroscopy (Fig. 2) and also with the power law creep equation (Eq. 1). A higher level of the mechanical loss at high temperature for SPS specimen can be interpreted by a worse creep resistance of nanosized grain sample.

![Figure 5](image5.png)

Figure 5 compares the mechanical loss spectrum of pure (un-doped) and 3wt % CNTs doped 3Y-TZP both processed via SPS, with a mean grain size in the range of 100 nm. Doping the grain boundaries with carbon nanotubes results in a decrease in damping with respect to high purity zirconia. Daraktchiev et al.\textsuperscript{10} have interpreted the decrease in damping at high temperature as due to the presence of carbon nanotubes (CNT) on the grain boundaries, which would reduce the grain boundary...
sliding process drastically. Ionascu et al.\textsuperscript{11} have also shown that 3Y-TZP reinforced with CNTs or SiC exhibits a lower exponential background in the mechanical loss spectrum and a lower creep strain than pure zirconia. In these new composites, grain boundary sliding is more difficult and consequently a better creep resistance is observed. In other words, addition of CNTs can provide pinning centers on the grain boundaries, which are stable at high temperature. The mechanical loss spectrum of a 30 h annealed sample (reinforced 3Y-TZP) at 1600 K is added to Figure 3. In this case, the decrease in the level of mechanical loss is probably due to grain growth during annealing at 1600 K.

![Figure 4. True strain as a function of time during creep test for pure and CNTs doped 3Y-TZP at 1350 K and stress of 8 MPa.](image)

![Figure 5. Mechanical loss spectra of high purity, CNTs doped 3Y-TZP, and annealed for 30 h at 1600 K.](image)
CONCLUSION

In the present study, high temperature mechanical spectroscopy measurements were performed in zirconia: pure 3Y-TZP and 3Y-TZP reinforced with carbon nanotubes. Two types of samples with different grain size of 100 and 350 nm were processed via conventional and spark plasma sintering methods, respectively. SPS sample showed a much higher level of internal friction, which can be attributed to the easier grain boundary sliding in nanosize-grained specimens. The addition of carbon nanotubes resulted in a decrease in damping with respect to the un-doped zirconia which can be interpreted as a better resistance to creep of doped specimens.

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REFERENCES