HIGH TEMPERATURE MECHANICAL PROPERTIES OF NANOSTRUCTURED ZIRCONIA REINFORCED WITH CARBON NANOTUBES PROCESSED BY SPS

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New zirconia – carbon nanotube composites were fabricated by spark plasma sintering method. Various amounts of carbon nanotubes (ZrO₂ + X wt% CNT, X = 0, 0.5, 1.5 3 and 5) were added as reinforcement. Microscopic analysis proves that carbon nanotubes (CNTs) are well dispersed and embedded in grain boundaries of the sintered body. High temperature mechanical properties are investigated using mechanical spectroscopy and low stress (8MPa) creep at 1600 K. Our results have shown that the mechanical loss and creep rate drastically decrease with CNTs addition. We suppose that CNT can hinder grain boundary sliding at high temperatures, resulting to the creep resistance improvement.

INTRODUCTION

Over the past decade there has been growing interest in composites of ceramics and carbon nanotubes (CNTs) [1]. This attraction is due to interesting physical and mechanical properties of CNTs, such as high elastic modulus, high electrical and thermal conductivity, high strength and aspect ratio. For instance, Curtin et al. [2] have shown that the addition of CNTs into a ceramic matrix improves the fracture toughness, the hardness, and the Young modulus.

While desired applications of ceramics and their composites are mainly dedicated to high temperature applications, only a few reports are available in the literature on high temperature mechanical properties of CNT/ ceramics [3-5]. It is well know that grain boundaries play a crucial role on the high temperature deformation of polycrystalline ceramics. Hence, the presence of CNTs in the boundaries may improve the creep resistance. This is why CNT-alumina polycrystalline nanocomposite showed a two orders of magnitude reduction of creep rate compared to a monolithic alumina with same grain size [3]. In CNTs reinforced yttria stabilized zirconia (3Y-TZP), the same trend was illustrated [4, 5].

Despite the abovementioned results, there has not been an enlightening investigation describing the probable mechanisms for pinning effect of nanotubes located in the ceramic grain boundaries. Therefore, the objective of this work is to study the unique creep behavior of spark plasma sintered CNT-reinforced 3Y-TZP composites using mechanical spectroscopy. As grain boundary sliding is a source of energy dissipation in materials, mechanical loss
measurements are well adapted to study such a mechanism. In parallel, creep measurements at low stress regime (6 MPa) were conducted.

**MATERIALS AND TECHNIQUES**

Commercially available high purity yttria stabilized zirconia 3Y-TZP powder (Tosoh Co., Japan) and multi walled carbon nanotubes (Arkema, France) were selected as starting powders. Scanning electron microscopy (SEM, XLF-30, Philips, Netherlands) examinations show that the raw powder (covered with a thin layer of carbon) is constituted of spherical nanopowders having an average diameter of about 70 nm. The CNTs were synthesized by catalytic chemical vapor deposition. They have a length of around 5-20 μm and a diameter of about 10-20 nm.

3Y-TZP powder with 0, 0.5, 1.5, 3 and 5 wt% CNTs, were mixed by attrition milling with zirconia balls for 24 hours. In order to obtain full dense nanocomposites (> 98% of theoretical density TD), to retain the zirconia grains in nano-scale and avoid damage of nanotubes, the samples were processed by Spark Plasma Sintering (SPS, FCT Gmbh, Germany) under vacuum.

Mechanical spectroscopy measurements were carried out in an inverted forced torsion pendulum, working at subresonant frequency. Samples of the size 25 × 1 × 4 mm³ are excited in torsion and the deformation of the samples was detected by an optical cell. The measurements were performed under a high vacuum (10⁻³ Pa) as a function of frequency at 1600 K. Conventional compressive creep tests were performed on specimens with size 3 × 3 × 8 mm³ under vacuum and at constant stress of 6 MPa at 1600 K.

**RESULTS**

TEM images of 3Y-TZP with 5wt% CNTs are presented in Figures 1a and b. Some interesting features can be highlighted: (1) CNT clearly surround the zirconia grains. (2) Most of zirconia grains remained smaller than 100 nm, confirming that CNTs lead to grain refinement. (3) CNTs are homogeneously dispersed in the matrix, even at high volume percentages of nanotubes. (4) The nanotubes were not damaged both during the powders blending, and upon spark plasma sintering. (5) CNTs pull-out can be observed.

FIGURE 1: HR-SEM (a) and TEM (b) micrograph of spark plasma sintered 3Y-TZP reinforced with 5wt% CNTs.
The creep strain rate of monolithic and composites with different amount of CNTs is represented in Figure 2 as a function of creep strain. One can observe the creep rate decreases with increasing nanotubes percentage. This result is in line with previous findings reported by Zapata-Solvas [3] for alumina-CNT composites. Almost steady state creep was obtained, only for 3Y-TZP and for 3Y-TZP reinforced with 0.5 wt%CNT. However, the creep rate for the reinforced specimen was less than that of monolithic zirconia. For the other composites with higher amounts of reinforcement (1.5, 3 and 5 wt%) after a transient decreasing creep, the creep rate dropped to almost zero. For instance in 3Y-TZP reinforced with 5 wt% CNTs, the creep rate decreased three orders of magnitudes after a strain of only 0.07.

FIGURE 2: Creep rate as a function of creep strain measured at 1600 K for composites with different amount of CNTs in comparison with monolithic zirconia.

Figures 3a and b show the variation of mechanical loss tan(ϕ) and shear modulus as a function of frequency at 1600 K for composites with different amounts of CNT in comparison with monolithic zirconia.

FIGURE 3: Mechanical loss (a) and elastic shear modulus (b) measured at 1600 K as a function of frequency for composites with different amount of CNTs.
The typical spectrum of 3Y-TZP was already analyzed by [6] showing a mechanical loss peak at a frequency of about 0.1 Hz superimposed on an exponential increase at low frequency. With an increasing content of CNTs, a better resolved peak and a lower mechanical loss background are observed at low frequency. Despite a general modulus decrease at low frequency to be associated with the background, the relative shear modulus of the reinforced specimens increases with increasing CNTs regardless of the value of frequency.

**DISCUSSION**

A theoretical model has been developed by Lakki et al. [6] to explain the mechanical loss spectrum of zirconia by sliding of the grains that are separated by an intergranular viscous layer. The model accounts for a relaxation peak. However, the experimental results did not show a well-marked peak but only an exponential increase in damping at low frequency (Fig. 3a). The absence of a well-marked peak was justified considering that the restoring force at triple junctions due to neighboring grains strongly reduces at low frequency or high temperatures. Therefore, the strain is no more limited and consequently the mechanical loss increases exponentially. Such an exponential increase in damping can be correlated to macroscopic creep. The present experiments show that an additional restoring force is provided by the presence of the nanotubes which is marked by a well defined mechanical loss peak. Moreover, the low frequency background is decreased which proves that beyond the anelastic limit the CNT still limit the grain boundary sliding.

On the other hand, as observed in Figure 3b, the elastic modulus of the samples is considerably increased by the presence of the nanotubes even if they are multiwall. This a new feature is probably due to good imbedding of the CNT in the grain boundaries. From the microscopic point of view, CNTs seem to form an interwoven network around zirconia grains. In the beginning stage of creep, the grains may slightly rearrange to reach a relaxed status which results in a higher creep rate in the beginning (Fig. 2). As strain increases, the CNTs entangle and the creep rate decreases strongly to almost zero.

**REFERENCE LIST**