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# The effect of graphene on the properties of 8YSZ ceramics rapidly sintered by high-frequency induction heating

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Despite of many attractive properties, the low fracture toughness of 8YSZ ceramic limits its wide application. One of the most obvious tactics to improve the mechanical properties has been to add a reinforcing agent to formulate a nanostructured composite materials. In this respect, graphene was evaluated as the reinforcing agent of 8YSZ ceramics using high-frequency induction heated sintering (HFIHS). Highly dense alumina-graphene composites with a relative density were obtained within 2 min by HFIHS under a pressure of 80 MPa. The rapid consolidation method allowed the retainment of the nano-scale microstructure by inhibiting the grain growth. The grain size of 8YSZ was reduced significantly by the addition of graphene. The addition of graphene to 8YSZ improved the fracture toughness of 8YSZ-graphene composite.

Key words: Nano-materials, Sintering, Hardness, Fracture Toughness, Graphene.

# Introduction

Zirconia ceramics consist of three polymorphs; monoclinic, tetragonal and cubic. These phases can be obtained depending on temperature and compositional ranges under equilibrium conditions. Monoclinic zirconia is present below 1240 °C and is the stable room temperature phase of pure zirconia. Tetragonal zirconia is an intermediate phase, which lies between 1240 and 2370 °C. The retention of the tetragonal phase can be controlled as in the case of cubic zirconia by the addition of dopants. Y<sub>2</sub>O<sub>3</sub> additions yield an extremely fine grained microstructure known as tetragonal zirconia polycrystal which has excellent mechanical properties. Cubic zirconia is the highest temperature phase which is present in the temperature range of 2370 and 2680 °C. However, upon the addition of a few percent of stabilizers; such as CaO, MgO or Y<sub>2</sub>O<sub>3</sub>, the cubic phase can be obtained at lower temperatures [1, 2]. The hightemperature cubic phase can also be retained at room temperatures as a non-equilibrium phase by rapid cooling such that diffusive transformation does not occur. The cubic form of stabilized zirconia ceramics are of technological importance due to their high oxygen ionic conductivity at around 1000 °C. Their use as solid state electrolytes has allowed the creation of

novel application such as oxygen gas sensors, oxygen membrane separators and solid oxide fuel cells (SOFCs). 8 mol% yttria-stabilized zirconia (8YSZ) has been extensively used as an electrolyte in SOFCs from the standpoint of its high oxygen-ion and low electronic conductivity at high temperatures, desirable stability in both oxidizing and reducing atmospheres, and relatively economical cost [3-7]. However, as in the case of many ceramic materials, the current concern about this material focuses on their low fracture toughness below the ductilebrittle transition temperature. To improve its mechanical properties, the approach commonly utilized has been the addition of a second phase to form composites and to make nanostructured materials.

Nanocrystalline materials have received much attention advanced engineering materials with improved as physical and mechanical properties [8,9]. Since they possess a high strength and hardness as well as excellent ductility and toughness, they have garnered more attention recently [10, 11]. In recent days, nanocrystalline powders have been developed by the thermochemical and thermomechanical process named as the spray conversion process (SCP), co-precipitation and high energy milling [12-14]. The sintering temperature of high energy mechanically milled powder is lower than that of unmilled powder due to the increased reactivity, internal and surface energies, and surface area of the milled powder, which contribute to its so-called mechanical activation [15-17]. However, the grain size in sintered materials becomes much larger than that in pre-sintered powders due to rapid grain growth during

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a conventional sintering process. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 2  $\mu$ m or larger during conventional sintering [18]. So, controlling grain growth during the sintering process is one of the keys to the commercial success of nanostructured materials. In this regard, the high-frequency induction heated sintering (HFIHS) technique has been shown to be effective in the sintering of nanostructured materials in very short times (within 1 minute) [19-21].

Since the discovery of graphene using the simple scotch tape method [22], graphene has been considered as an ideal second phase to improve the mechanical, electrical and thermal properties of metals [23], ceramics [24] and polymers [25] due to its unique combination of electrical, thermal and mechanical properties [26-28]. We present here the results of the sintering of 8YSZ and 8YSZ-graphene composites by a high-frequency induction heated sintering with simultaneous application of induced current and high-pressure. The goal of this study was to produce dense and nanocrystalline 8YSZ and 8YSZ-graphene composites in very short sintering times (< 2 min). The effect of graphene on the mechanical properties, microstructures and relative densities of 8YSZ-graphene composites was also examined.

## **Experimental Procedures**

8YSZ powders with a grain size of <1 mm and 99.99% purity was supplied by Tosoh. Graphene (XG-Science. Graphene grade C-750) was used as the additive. Powders of three compositions corresponding to 8YSZ, 8YSZ-1wt.% graphene, and 8YSZ-3wt.% graphene were prepared by weighting and milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for 10 h. WC balls (9 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of balls-to-powder was 30 : 1. The grain size of the powders was calculated from the full width at half-maximum (FWHM) of the diffraction peak by Suryanarayana and Grant Norton's formula [29].

$$B_{r} (B_{crystalline} + B_{strain}) \cos\theta = k \lambda / L + \eta \sin\theta$$
(1)

where  $B_r$  is the full width at half-maximum (FWHM) of the diffraction peak after instrumental correction;  $B_{crystalline}$  and  $B_{strain}$  are FWHM caused by small grain size and internal stress, respectively; k is constant (with a value of 0.9);  $\lambda$  is wavelength of the X-ray radiation; L and ç are grain size and internal strain, respectively; and  $\theta$  is the Bragg angle. The parameters B and  $B_r$ follow Cauchy's form with the relationship:  $B = B_r + B_s$ , where B and  $B_s$  are the FWHM of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively.



Fig. 1. Schematic diagram of the apparatus for high-frequency induction heated sintering.

The milled powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the highfrequency induced heated sintering (HFIHS) system. A schematic diagram of this system is shown in Fig. 1. The HFIHS apparatus includes a 15 kW power supply which provides an induced current through the sample, and a 50 kN uniaxial press. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. An induced current was then activated and maintained until the densification rate was negligible, as indicated by the real-time output of the shrinkage of the sample. Sample shrinkage was measured in real time by a linear gauge measuring the vertical displacement. Temperature was measured by a pyrometer focused on the surface of the graphite die. A temperature gradient from the surface to the center of the sample is dependent on the heating rate, the electrical and thermal conductivities of the compact, and its relative density. The heating rates were approximately 1400 °K minute<sup>-1</sup> during the process. At the end of the process, the current was turned off and the sample was allowed to cool to room temperature. The entire process of densification using the HFIHS technique consists of four major control stages: chamber evacuation, pressure application, power application, and cooling off. The process was carried out under a vacuum of 5.33 Pa.

The relative densities of the sintered samples were measured by the Archimedes method. Microstructural information was obtained from fracture surface of product samples. Compositional and microstructural analyses of the samples were carried out through X-ray diffraction (XRD), and field-emission scanning electron microscopy (FE-SEM). Vickers hardness was measured by performing indentations at a load of 10 kg<sub>f</sub> with a

dwell time of 15 s.

# **Results and Discussion**

Fig. 2 shows the FE-SEM images of 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene powders after milling for 10 h. The powders show clusters of very fine particles. Fig. 3 shows X-ray diffraction pattern of the 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene powders after milling. The broadening of alumina peaks due to crystallite refinement and strain is evident. The milling process usually introduces impurities from the ball and/or container. However, in this study, peaks other than alumina could not be



Fig. 2. SEM images of 8YSZ powder + x wt.% graphene powder milled 10 h : (a) x = 0, (b) x = 1, (c) x = 3.



**Fig. 3.** XRD patterns of 8YSZ powder + x wt.% graphene powder milled 10 h : (a) x = 0, (b) x = 1, (c) x = 3.



**Fig. 4.** Plot of Br ( $B_{crystalline} + B_{strain}$ ) cos $\theta$  versus sin $\theta$  for 8YSZ in 8YSZ powder + x wt.% graphene powder milled 10 h : (a) x = 0, (b) x = 1, (c) x = 3.





1600

1400

1200

**Fig. 5.** Variations of temperature and shrinkage displacement with heating time during the sintering of 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene samples by HFIHS.



**Fig. 6.** XRD patterns of (a) 8YSZ, (b) 8YSZ-1 wt.% graphene, and (C) 8YSZ-3 wt.% graphene samples produced by HFIHS.

identified.

Fig. 4 shows plot of  $B_r$  ( $B_{crystalline} + B_{strain}$ ) cos $\theta$  versus sin $\theta$  in Suryanarayana and Grant Norton's formula [29] for particle size measurements. The average grain sizes of the 8YSZ in the 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene powders were calculated as about 10, 19 and 12 nm, respectively.

The shrinkage displacement-time (temperature) curve provides a useful information on the consolidation behavior. Fig. 5 shows the shrinkage record of 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene compacts. In all cases, the thermal expansion of the compacts occurs up to 1100 °C and then the shrinkage displacement rapidly increases above the temperature. The shrinkage curve suggests that the consolidation terminates in two minutes.



**Fig. 7.** Plot of Br ( $B_{crystalline} + B_{strain}$ ) cos $\theta$  versus sin $\theta$  for 8YSZ in 8YSZ powder + x wt.% graphene samples sintered : (a) x = 0, (b) x = 1, (c) x = 3.

Fig. 6 shows the XRD patterns of 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene after sintering. In all cases, only 8YSZ peaks are detected. Again, their particle sizes were calculated by the plot of  $B_r$  ( $B_{crystalline} + B_{strain}$ ) cos $\theta$  versus sin $\theta$  in Suryanarayana and Grant Norton's formula [29] as shown in Fig. 7. The average grain sizes were about 106, 68, and 50 nm for 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene, respectively. This means that the grain size of 8YSZ decreases as the graphene content increases. It is believed that graphene may block the grain growth of 8YSZ during sintering.

The grain refining effect of graphene can also be confirmed by the fracture surface. Fig. 8 shows the FE-SEM images of the fracture surfaces of the samples



**Fig. 8.** FE-SEM images of fracture surface of (a) 8YSZ, (b) 8YSZ-1 wt.% graphene, and (C) 8YSZ-3 wt.% graphene samples produced by HFIHS.

after sintering at about 1500 °C. It can be seen that the crack propagation mode for the 8YSZ, and 8YSZ-1 wt.% graphene samples is inter-granular as the cracks propagates along grain boundaries. In general, cracks propagate through the grain boundaries of ceramic materials because they are weaker than the grains. However, when the amount of graphene increased to 3 wt%, trans-granular type fracture appears to occur locally. Fig. 8(c) is the fracture surface of 8YSZ containing 8YSZ-3 wt.%. Obviously, the grain size is finer and the fracture surface appears to be the mixture of trans-granular and inter-granular type failure.

In any case, it should be mentioned that 8YSZ ceramics having nano structure could be obtained by HFIHS even for pure 8YSZ without graphene. This retention of fine grain structure can be attributed to the high heating rate and the relatively short exposure to the



**Fig. 9.** Vickers hardness indentation in (a) 8YSZ, (b) 8YSZ-1 wt.% graphene, and (C) 8YSZ-3 wt.% graphene samples produced by HFIHS.

high temperature. The composites were fairly dense and relative densities of 99.8, 99.1, and 98.9% were obtained for 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene, respectively. It is clearly demonstrated that the method is effective to consolidate nano-structured 8YSZ and 8YSZ-graphene composites. The role of the current in sintering and/or synthesis has been the focus of several attempts to provide an explanation for the observed sintering enhancement and the improved characteristics of the products. The role played by the current has been variously interpreted. The effect has been explained by fast heating due to Joule heating at contacts points, the presence of plasma in pores separating powder particles, and the intrinsic contribution of the current to mass transport [30-34].

Vickers hardness measurements were performed on polished sections of 8YSZ, 8YSZ-1 wt.% graphene,



Fig. 10. Crack propagation in 8YSZ-3 wt.% graphene samples produced by HFIHS.

and 8YSZ-3 wt.% grapheme samples using a 10 kg<sub>f</sub> load and 15 s dwell time. Indentions with  $10kg_f$  load produced median cracks around the indentation from which fracture toughness can be calculated. The lengths of these cracks permit the estimation of fracture toughness of the materials by means of the expression [35]:

$$K_{IC} = 0.203(c / a)^{-3/2} \cdot H_v \cdot a^{1/2}$$
(2)

where c is the trace length of the crack measured from the center of the indentation, a is one half of the average length of the two indent diagonals, and  $H_v$  is the hardness.

The Vickers hardness and the fracture toughness values of the 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene samples were 1263 kg/mm<sup>2</sup>, 3 MPam<sup>1/2</sup>, and 1245 kg/mm<sup>2</sup>, 3.5 MPam<sup>1/2</sup> and 1087 kg/mm<sup>2</sup>, 4 MPam<sup>1/2</sup>, respectively. All values represent the average of five measurements. The results suggest that fracture toughness increased with increase in grapheme and hardness is reversed. To understand the effect of graphene on the mechanical properties, two factors may be considered. One is the effect of grain refinement of 8YSZ. The other would be the role of graphene on the crack propagation to affect the toughness. This may be the case since the addition of graphene refined the grain size of 8YSZ significantly in this study. Vickers hardness indentations in the samples are shown in Fig. 9. They show typically one to three additional cracks propagating radially from the indentation.

The toughness of 8YSZ-graphen composite may be that the graphene network may deter the crack propagation. Fig. 10 shows a crack propagated in a deflective manner ( $\uparrow$ ) in 8YSZ-3 wt.% graphene composite. The enhanced fracture toughness of 8YSZ-3 wt.% graphene composite is believed that graphene in the composite may deter the crack propagation. In this study, the hardness decreased with decrease in grain size. This is not easy to understand when one considers the Hall-Petch type relationship between the grain size and hardness:

$$\sigma = \sigma_0 + k d^{-1/2} \tag{3}$$

where,  $\sigma_0$  is the lattice friction stress required to move individual dislocations, k is a material-dependent constant known as the Hall-Petch slope, and d is the average grain size. There appears to be a range of grain sizes at which the relationship holds. It is known that when the grain size is less than 100 nm, k value often becomes negative (inverse H-P relation) [36]. This relation may explain why the hardnesses of nanostructured 8YSZ-graphene composites were lower than those of the 8YSZ.

### Conclusions

Using high-frequency induction heated sintering (HFIHS), the rapid consolidation of the 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene samples was accomplished successfully. Near full-density nanostructured 8YSZ-graphene composites could be obtained within 2 min. The grain size of 8YSZ was reduced remarkably by the addition of graphene. The average grain sizes of the 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene were about 106, 68, and 50 nm, respectively. The Vickers hardness and the fracture toughness values of the 8YSZ, 8YSZ-1 wt.% graphene, and 8YSZ-3 wt.% graphene samples were 1263 kg/mm<sup>2</sup>, 3 MPa  $\cdot$  m<sup>1/2</sup>, and 1245 kg/mm<sup>2</sup>, 3.5 MPa  $\cdot$  m<sup>1/2</sup> and 1087 kg/mm<sup>2</sup>, 4 MPa  $\cdot$  m<sup>1/2</sup>, respectively. The addition of graphene to 8YSZ improved the fracture toughness in 8YSZ-graphene composite and the hardness was reversed. This study demonstrates that the graphene can be an effective reinforcing agent for improved fracture toughness of 8YSZ composites.

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