

MECHANICAL AND ELECTRICAL PROPERTIES OF ZnO/Ag
NANOCOMPOSITES*

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August 1998

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To be published in Proc. of "Ceramic Matrix Composites" Symp., American Ceramic Society Annual Mtg., Cincinnati, OH, May 3-6, 1998.

*Work supported by the U.S. Department of Energy, under Contract W-31-109-Eng-38.

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MECHANICAL AND ELECTRICAL PROPERTIES OF ZnO/Ag NANOCOMPOSITES

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ABSTRACT

Effects of Ag particle dispersions on microstructural development and some properties were investigated for ZnO/Ag nanocomposites. They were fabricated by Pulse Electric Current Sintering (PECS) Process to achieve finer and densified microstructure. ZnO/Ag nanocomposites with novel microstructure which were prepared by a reduction process using Ag_2O fine powders were compared with microcomposites prepared by mixing of Ag and ZnO powders. SEM observation indicated that fine Ag particles were homogeneously dispersed within the ZnO matrix grains and at the grain boundaries for ZnO/Ag nanocomposites prepared by the reduction process using Ag_2O fine powder. Hardness and fracture toughness increased with increasing the Ag volume fraction. Linear resistivity was decreased with increasing Ag volume fraction. However, the mechanical and electrical properties appeared to be significantly different for composites prepared by two different powder processes.

INTRODUCTION

Zinc oxide (ZnO) having wurtzite structure is a variable resistor and is used widely as a gas sensor, absorber of abnormal voltage, piezo-electric material, etc.. In these applications, ZnO is required to give better performances not only in electrical properties, but also in mechanical, chemical and electrical stability in special environments. However, ZnO displays poor mechanical properties. There are some material designs to strengthen and toughen ceramics by using composite techniques to incorporate particulate, whisker or platelet reinforcement.^{1,2} Recent investigations have shown that ceramic composites having nano-sized metal particulate dispersions show excellent mechanical properties like hardness, Young's

modulus, fracture strength and toughness even at high temperatures.³⁻⁷ In this study, therefore, the nanocomposite techniques were applied to improve the mechanical properties and electrical properties of ZnO. Ag particle was selected as a dispersion phase in this work, because Ag gives good sinterability⁸ and high electrical conductivity which gives to wide applications in high voltage regions to ZnO materials.

Recently, pulse electrical current process (PECS) has received much interest as a new process for sintering various kinds of powder materials.^{9,10} The process is a type of solid compression sintering process that is similar to hot-pressing (HP) because some pressure is applied during heating. In a special case, a process commercially called Spark Plasma Sintering (SPS) which enables us to sinter at considerably rapid heating rates.

The main effects for sintering enhancement in hot-pressing process are thermal diffusion and plastic flow due to high pressure. It is indicated in the PECS process that self-exothermic reactions due to electric discharge between particles at an early stage of ON-OFF d.c. pulse application enhances sintering processes, as well as effects of high pressure and rapid sintering. Recent reports support these advantages of the PECS process for obtaining highly densified and strengthened ceramic composites.^{11,12}

In this study, ZnO/Ag nanocomposites were fabricated by PECS Process to achieve finer microstructure with the high density. Effects of Ag particle dispersions on microstructural development and some properties were investigated. ZnO/Ag nanocomposites with a novel microstructure which were prepared by a reduction process using Ag₂O fine powder are compared with microcomposites prepared by mixing the Ag and ZnO powders. Furthermore, we attempted to understand the role of finer Ag dispersions on microstructure evolution, and electrical and mechanical property improvements for the ZnO/Ag nanocomposites from PECS method.

EXPERIMENTAL PROCEDURE

ZnO (Sakai Chemical Industry Co. Ltd., Osaka, Japan) was used as a matrix and Ag and Ag₂O (Kojundo Chemical Lab. Co. Ltd., Tokyo, Japan) as dispersion to fabricate the composite materials. Average particle size of ZnO is 0.28 μ m and Ag and Ag₂O are 3 μ m. the powder mixture was made by ball-milling ZnO and Ag powders in ethanol. Another powder mixture was prepared from ZnO and Ag₂O powders, and this composite powder was calcined in air atmosphere to get fine Ag after ball-milled in ethanol. ZnO/Ag₂O mixture powder were evaluated by thermogravimetry (TG) / differential thermal analysis (DTA) (DTG-50, Shimadzu Co., Kyoto, Japan) and high temperature X-ray diffraction (X1, Sintag Inc., USA) in order to select the calcination temperature required to decompose Ag₂O into Ag

and O_2 . The mixture was packed into carbon dies, and sintered at 700 to 900 °C under an applied pressure of 40 MPa for 1 to 20 minutes in vacuum by PECS (SPS-2080, Sumitomo Coal Mining Co., Tokyo, Japan). The heating rate is 200°C / min below 600°C and is 100°C / min at 600°C to sintering temperature in PECS method. Under these sintering conditions, the maximum current value was about 2500 A and the maximum voltage value was about 3.5V. The sintered disks, 30 mm in diameter and 4.0 mm in thickness, were cut ground and polished rectangular bars 2×3×25 mm in size. The phase composition of the powders and the sintered composites was examined by X-ray diffraction (RU-200B, Rigaku Co., Tokyo, Japan). The bulk density was measured by the Archimedes method in water. Fracture toughness was estimated by the indentation fracture (IF) method using Vickers diamond indenter. To evaluate linear resistivity, In-Ga electrode was printed on both sides of specimen. The linear resistivity was measured with a digital multi-meter (Model 7522, Yokogawa Electric Co., Tokyo, Japan). The microstructure was observed with field emission scanning electron microscopy (FE-SEM) (Model S-5000, Hitachi, Japan) and transmission electron microscopy (TEM) (Model H-8100, Hitachi, Japan).

RESULTS AND DISCUSSION

Reduction of Ag_2O

Ag_2O powder was subjected to thermogravimetry (TG) / differential thermal analysis (DTA) in order to know the reduction temperature for decomposing Ag_2O into Ag and O_2 in air. In TG/DTA, weight change (at 160°C to 240°C) represented an exothermic reaction with a corresponding decrease in weight. This weight change is due to Ag_2O decomposition forming Ag and O_2 . There is no reaction taking place at temperatures higher than 240°C. Fig. 1 shows high temperature X-ray diffraction (HT-XRD) patterns for the Ag_2O powder. Pt peaks come from a Pt HT-XRD stage. For powders reduced below 150°C, Ag peaks are not observed, and only Ag_2O peaks are clearly seen. However, broader and weaker Ag peaks for powders calcined at 200°C are observed in addition to Ag_2O peaks. For powders reduced over 250 °C, only Ag peaks are observed clearly. This observation suggests that decomposition of Ag_2O is completed at 300°C. Therefore, 300°C was selected as the reduction temperature to obtain the ZnO/Ag composite powder. Fig. 2 shows TEM images of reduction powder. After reduction treatment at 300 °C, Ag_2O particles were reduced to fine spherical Ag particles. The diameter of Ag particles was 30-70 nm.

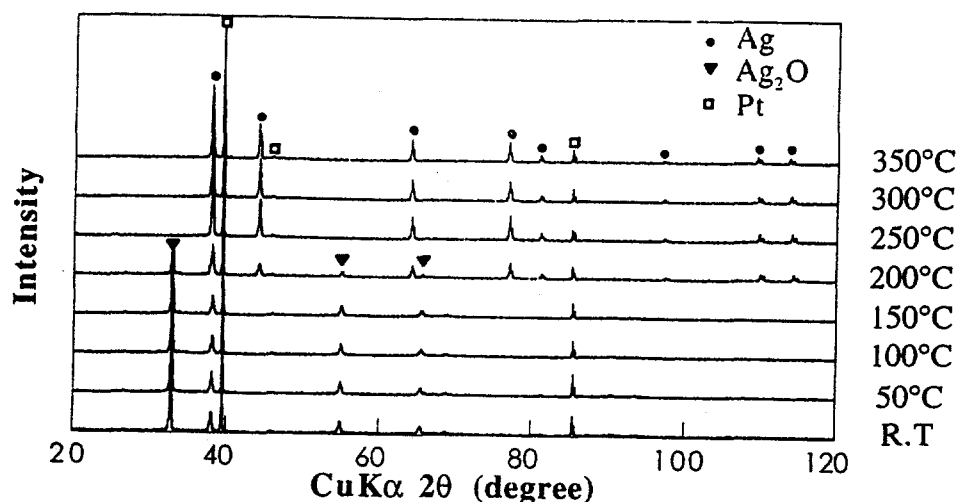


Fig.1 High temperature X-ray analysis of Ag_2O in air.

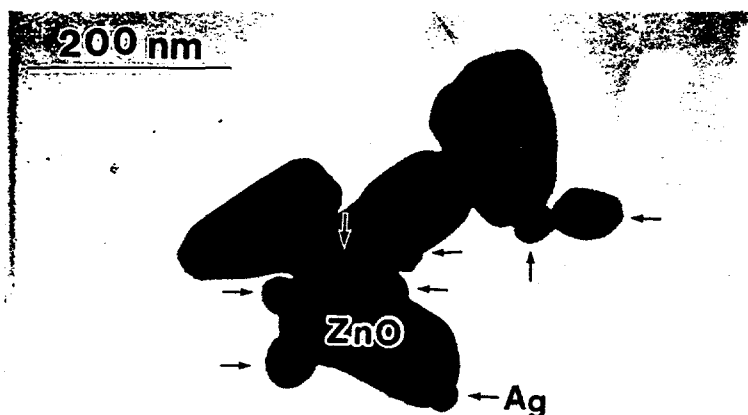


Fig.2 TEM image of ZnO/5vol% Ag reduction powder.

Microstructure of ZnO/Ag composites

Fig. 3 shows SEM micrographs of ZnO/Ag composites with varying Ag contents. The Ag particles are spherical in shape, and are mainly dispersed homogeneously at grain boundaries and triple grain junctions. It suggests that Ag particles migrated during sintering and grain growth with moving grain boundaries. It can also be seen that the Ag particle size increased with increasing Ag contents. Similar observations were also made for PZT/Ag composites.⁸ It is believed that the Ag particles become soft and then agglomerates to form large particles at higher

Ag content. The matrix grain size decreases with increasing Ag content as observed in Fig. 3. Micrographs in Fig.4 show the effect of the source of Ag (Ag powder or Ag_2O powder) addition on microstructure development. It was observed that composites from the Ag_2O powder and its reduction had Ag particles primarily less than $0.3\ \mu\text{m}$, dispersed in the ZnO matrix, while the Ag particles were larger than $30\ \mu\text{m}$ in composites fabricated from Ag powders. These large Ag dispersions are attributed to agglomeration during ball milling due to high ductility of Ag and to poor dispersibility due to the density differences between ZnO and Ag.

Average grain size of the ZnO matrix in ZnO/5 vol% Ag composites prepared using Ag_2O and reduction process is smaller than that of ZnO/5 vol% Ag composites prepared by conventional mixing. This is attributed to the stronger pinning effect of Ag particles on the grain boundary migration of ZnO by dispersing larger number of Ag Particles with the smaller particle size, Ag particle. Also, as expected, both families of composites showed increase in grain size with increasing sintering temperature. It can be also seen that the Ag particle size increased with increasing sintering temperature. It is believed that the Ag particles become softer at higher sintering temperatures and form large particles.

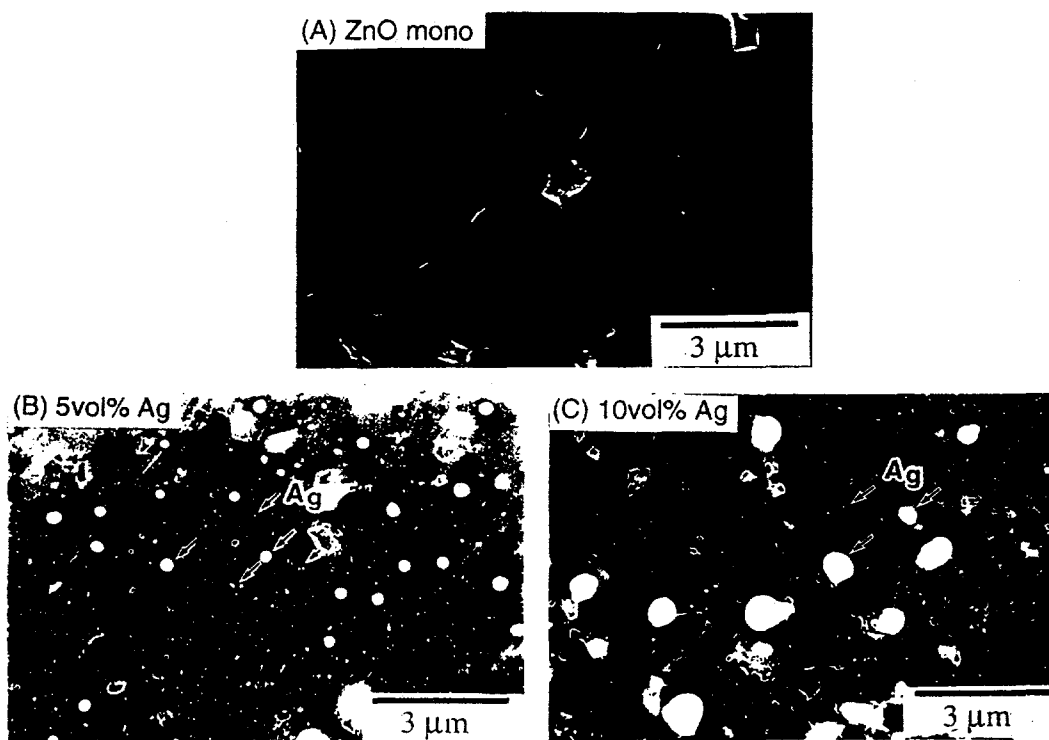


Fig.3 SEM micrographs of ZnO/ Ag composites with varying Ag contents. These composites were sintered at 800°C for 5 min in vacuum.

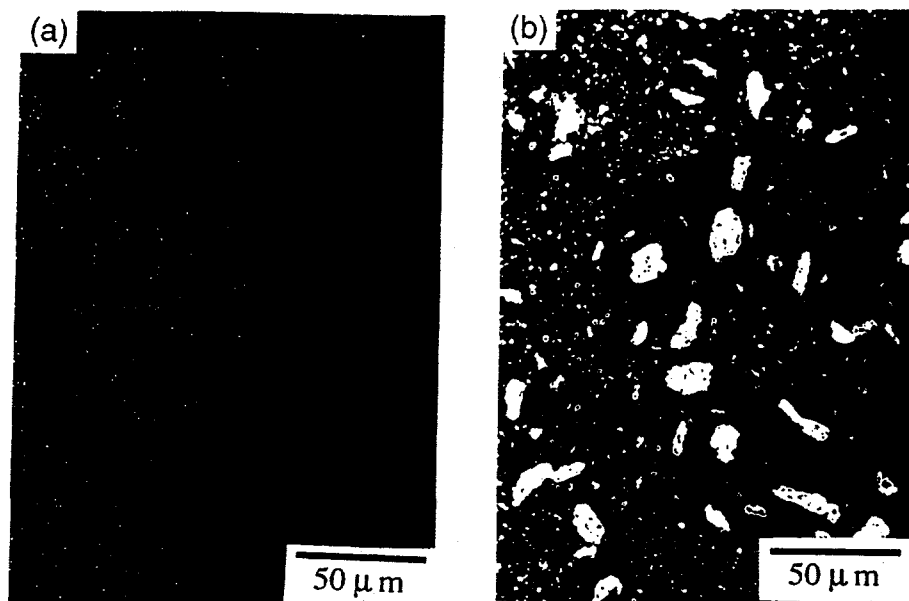


Fig.4 SEM images for ZnO/ 5vol%Ag composites prepared from Ag_2O (a) and Ag (b) starting powders. These composites were sintered at 800°C for 5 min in vacuum.

Mechanical Properties

In general, mechanical properties of ceramics and composites are greatly controlled by their microstructure. Ceramic/metal composites have been observed to display big improvements in mechanical properties.^{3-6,8,13} The metal particulate dispersed composites also derive their toughness from the plasticity of metal particles.

A measured variation of fracture toughness with Ag content is shown in Fig. 5. The fracture toughness of ZnO with 10 vol% Ag additions increased to a value of $\sim 2.77 \text{ MPa}\sqrt{\text{m}}$ from a value of $\sim 0.95 \text{ MPa}\sqrt{\text{m}}$ for monolithic ZnO. This represents an approximately three-folds increase in fracture toughness due to 10 vol% Ag additions. This increase in fracture toughness is believed to be results from crack deflection and bridging provided by Ag particle dispersions.

Fig. 6 shows the dependence of hardness on Ag content. As shown in this figure, the hardness increased with increasing Ag content. In general, the hardness of ceramics and composites is affected by density, grain size, grain boundary and second phase additions. In the present ZnO/Ag composites, the second phase Ag has high ductility and high malleability. In ZnO/Ag composites, the density increased with increasing Ag content and grain size decreased with increasing Ag content. Therefore, it is believed that the increase in hardness of ZnO/Ag composites is a result of the increasing density and the decreasing matrix grain size.

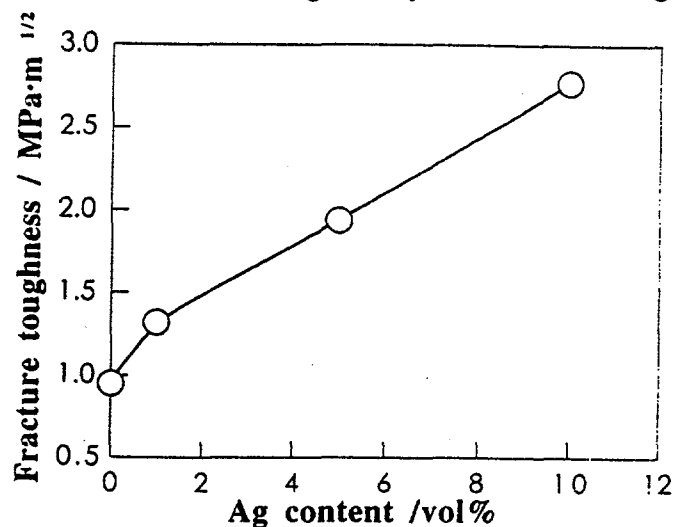


Fig.5 Variation of fracture toughness as a function of Ag content for ZnO and ZnO/Ag composites.

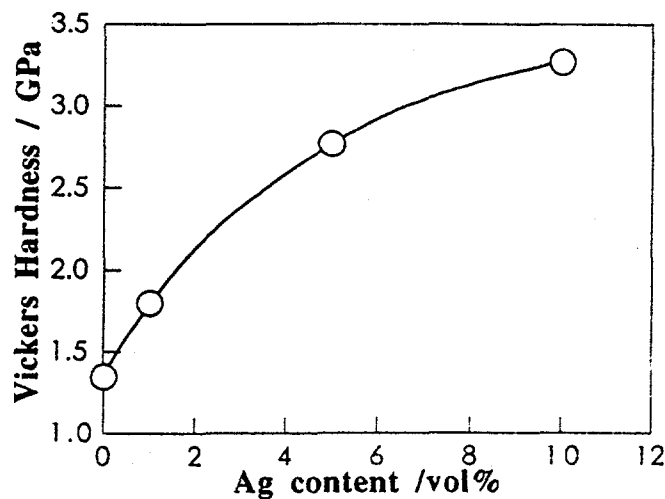


Fig.6 Variation of Vickers hardness as a function of Ag content for ZnO and ZnO/Ag composites.

Linear resistivity

Fig. 7 shows the dependence of linear resistivity on Ag content for ZnO/Ag composites. As shown in this figure, the linear resistivity decreased with increasing Ag content. The linear resistivity of the ZnO/Ag composites prepared using Ag_2O and reduction process is smaller than that of conventionally prepared. This change of linear resistivity can be explained by the effects of size and volume of dispersed Ag particles as well by an effective medium theory and percolation theory.^{14,15}

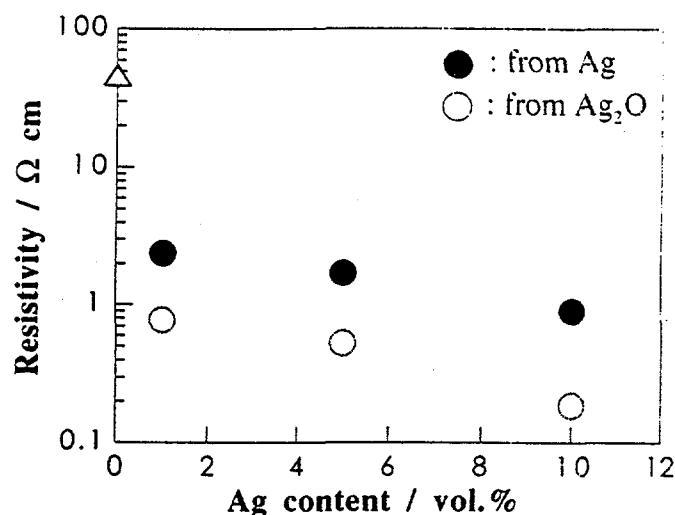


Fig.7 Variation of resistivity as a function of Ag content for ZnO and ZnO/Ag composites. These composites were sintered at 800°C for 5 min in vacuum.

SUMMARY

Two types of ZnO-based composites incorporating Ag particles were fabricated by Pulse Electric Current Sintering (PECS) method. Homogeneous dispersion of fine Ag particles was achieved using Ag_2O and reduction process. The uniform dispersion of Ag in ZnO matrix resulted in the microstructural refinement. The Ag particles were uniformly dispersed along the matrix grains and the matrix grain size decreased from $\sim 3 \mu\text{m}$ for monolithic ZnO to $\sim 300 \text{ nm}$ for ZnO/ 10vol% Ag composites. The uniform distribution of Ag particles resulted in a two-fold increase in fracture toughness. In addition, a 2.5-folds increase in Vickers hardness for ZnO was observed with 10 vol% Ag addition. The improvement in toughness was mainly caused from the crack deflection and bridging provided by Ag particles, and the increment in Vickers hardness was believed to cause from the matrix grain refinement by the fine metal particle dispersion. Also, ZnO/Ag composite resulted in substantial increase in linear resistivity with increasing Ag content.

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