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Electric and microstructural characteristics of bulk ZnO fabricated by underwater shock compaction

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Abstract

An underwater shock compaction of pure zinc oxide (ZnO) powder has been performed. This technique uses an underwater shock wave generated by detonation of an explosive. Shock pressure used in this work was about 10 GPa. The morphology and structure of shock-consolidated ZnO was investigated by X-ray diffraction (XRD) method and scanning electron microscopy (SEM). The density and impedance characteristics of shock-consolidated ZnO were measured by Archimedes method and Nyquist plot method, respectively. The shock-consolidated ZnO without visible cracks was successfully obtained. It was confirmed that the shock-consolidated ZnO had 99% of theoretical density without grain growth and high grain boundary resistivity in comparison with the commercial sintered ZnO.

Keywords: A. Grain growth; D. ZnO; Underwater shock compaction

1. Introduction

Recently, zinc oxide (ZnO) and related ceramic materials are extensively used in many fields such as flat panel display, solar cells, optical coating and varistors [1–3].

Thus, manufacturing technique of these ceramic materials has been widely studied by many different processes, such as spark plasma sintering [4], microwave sintering [5], dynamic compaction using gas gun [6].

However, in the case of sintering processes, using high temperature to obtain high density bulk materials, grain growth occurs easily due to prolonged heating. Especially, the properties of ZnO varistors used as voltage surge protection device are highly affected by grain boundaries and grain size [7–9]. Therefore, many researchers have been studying to obtain fine micro/nanostructured ceramic materials by reducing the grain growth [10–12].

A technique of underwater shock compaction was developed by Chiba et al. [13]. The technique uses the underwater shock wave generated by the detonation of an explosive [14,15]. During the pressurization and acceleration by the underwater shock wave, an intensive deformation of the powder surfaces is induced, and the powder surfaces undergo melting and solidifying process in the matter of microseconds. This technique is very advantageous to obtain fully dense materials without grain growth due to lack of heating and is further possible to obtain ultra-fine substructure by the passage of shock wave in the compacted sample [15]. However, the main problem in shock compaction is cracking of the compacts because residual stresses after shock loading become a source for creating cracks in the compacts [16]. Therefore, the shock-consolidated materials could not be used in commercial applications. Hokamoto et al. have investigated [16,17] a high temperature shock consolidation (HTSC) for hard ceramic powders, TiB_2 and c-BN in order to minimize the cracking problem by pre-heating the powders. They reported that the high temperature can induce a decrease of strength and hardness of powders as well as increase of ductility and enhancement of surface melting. However, the HTSC involves long time processing steps, such as Argon gas injection and setting the electrical furnace to pre-heat the powders. Therefore, a novel method is desired to remove the complicated processing steps. In this investigation, in order to obtain a good consolidation without

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cracks, we employed a residual temperature of copper (Cu) powder occurring after shock loading. When Cu powders are compacted by shock loading, a high temperature in the compressed Cu powders can be obtained in a very short time because of its low heat capacity. The high temperature can retard the rapid cooling of the compacts and allow relaxation of the residual stresses, minimizing the cracks formation in the compacts. Thus, the focus of this work is to fabricate crack-free bulk ZnO, using the residual temperature of shocked Cu powder and to investigate electrical properties of resulting shock-consolidated ZnO.

2. Experimental procedure

The powders used in this work were commercial ZnO powder (99.9% purity, under 5 μm particle size, Wako chemical Co. Ltd.) and Cu powder (99.9% purity, 45 μm particle size, Wako chemical Co. Ltd.). The shock compaction device is composed of several parts; explosive lens, explosive container, water container, powder container, powder capsule and cover plate as shown in Fig. 1. The explosive lens was used to create planar wave and was made using two types of high explosives: SEP and HABW explosives (both were provided by Asahi-Kasei Chemicals Corp., Japan; detonation velocity: 6.97 and 4.75 km/s, density: 1300 and 2200 kg/m^3, respectively). The explosive SEP (PETN 65% mass and paraffin 35% mass) was set in the explosive container as main explosive. The water container was filled with water to generate underwater shock wave. The water container was straight type, made by mild steel, and the dimensions were 10 mm in height and 70 mm in diameter.

The magnitude of shock pressure can be controlled by the height of water container, and the magnitude of shock pressure used in this work is about 10 GPa based on numerical simulation [18]. The measured pressure using manganin gauge developed by Mashimo and co-worker [19], also showed almost same value as with numerical calculation. The powders, both ZnO and Cu, were filled and pressed in the powder capsule (stainless steel) by using uniaxial press machine at 50 MPa. The powder capsule has an inner diameter of 30 mm, height of 50 mm, powder charging depth of 35 mm, and gas drain hole (1 mm) to allow the exhaust of air during compaction. The thickness of pressed ZnO and Cu powders was 15 and 19 mm, respectively. The cover plate was made of stainless steel plate which was 1 mm in thickness on top of the powders. The density of shock-consolidated ZnO was measured by the Archimedes method. The microstructure of shock-consolidated ZnO was observed by scanning electron microscopy (SEM) for the fracture surface, and crystal structure and the hardness of consolidated sample were examined by X-ray diffraction (XRD) and Vickers hardness measurements. In order to confirm the existence of impurities in the shock-consolidated ZnO, the surface analysis was investigated by means of XPS (Thermoelectron, SigmaProbe). The impedance characteristics of shock-consolidated ZnO and commercial sintered ZnO are investigated by the Nyquist plot method using commercial impedance analyzer (HIOKI 3532-80 Chemical Impedance Meter) with frequency ranging from 10 Hz to 1 MHz. The size of samples for each measurement was kept same, 4 mm × 4 mm × 2.5 mm.

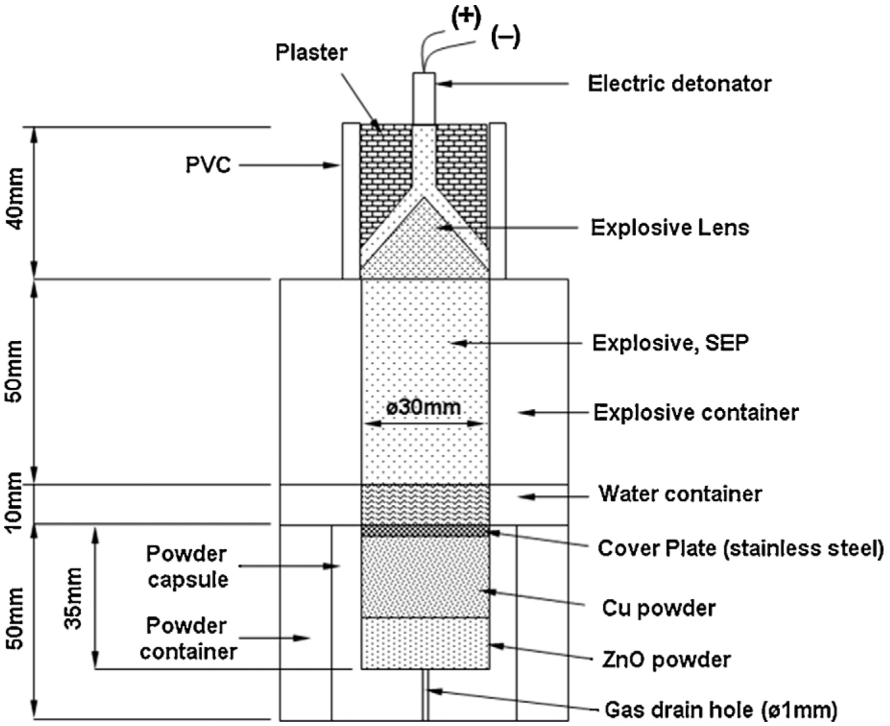

Fig. 1. Schematic illustration of underwater shock compaction device.

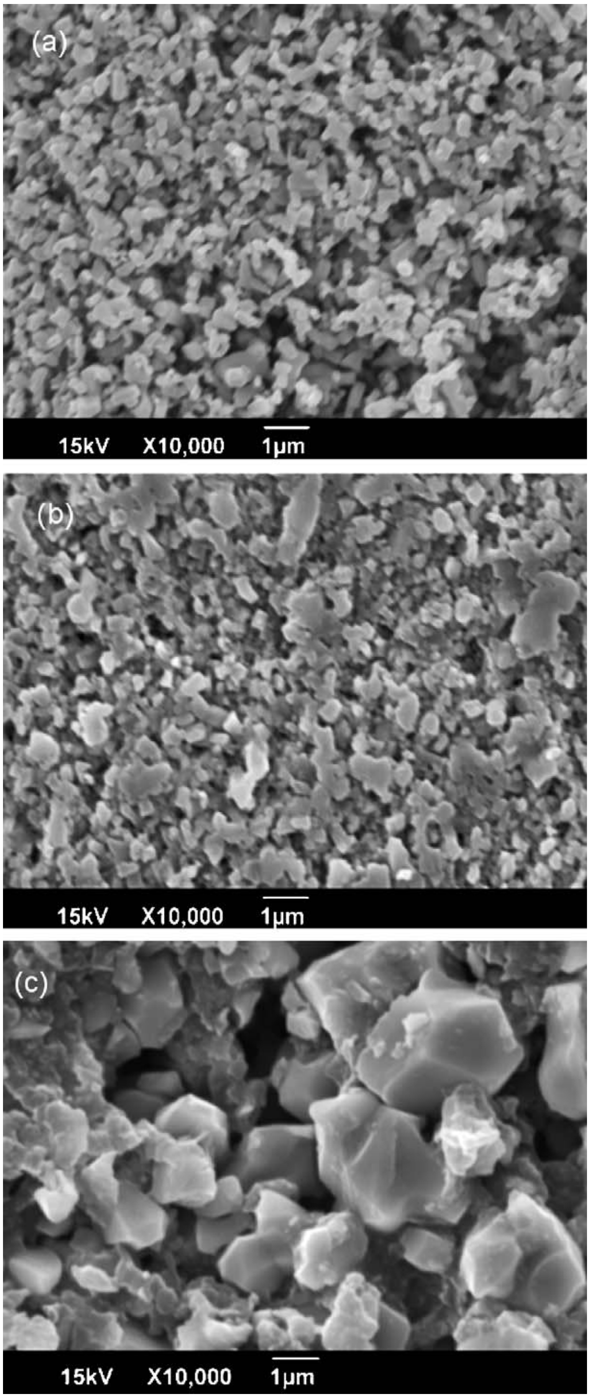

Fig. 2. SEM images of (a) starting ZnO powder, (b) fracture surface of shock-consolidated ZnO and (c) commercially sintered ZnO.

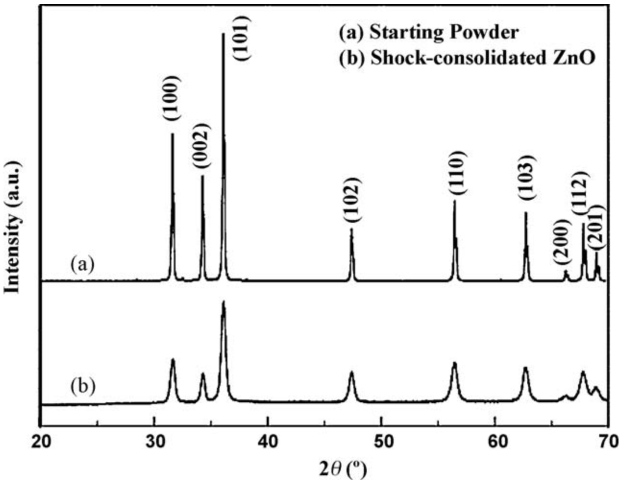

Fig. 3. XRD patterns of (a) starting ZnO powder and (b) consolidated ZnO.

3. Results and discussion

Fig. 2 shows SEM images of starting ZnO powder, the fracture surface of the shock-consolidated ZnO and commercially sintered ZnO. In the case of the shock-consolidated ZnO as shown in Fig. 2(b), it was observed that the powders were substantially deformed to fill the voids and the powders after shock loading suggest slightly larger particles, which seem to be caused by joining original powders through surface melting. The result is consistent with the facts that the shock compaction leads to localized deformation and melting at only particle surfaces [20]. Also, the shock-consolidated ZnO had finer microstructure than the commercial sintered ZnO as shown in Fig. 2(c). Fig. 3 shows the XRD pattern of starting ZnO powder and shock-consolidated ZnO. We believe that the broadening peaks represent the decrease of crystalline size and/or crystalline dislocation in its substructure as reported for shock-consolidated powders earlier [21]. Since the peak pattern is similar for the two results, chemical reaction or phase change were not produced by the shock compaction, and according to the XPS analysis, as shown in Fig. 4, impurities do not exist in the shock-consolidated ZnO. Only the peaks of Zn, O and carbon (C) were detected. C is an element that is easily detected due to surface contamination of a sample. This result suggests that there is no penetration of impurities in underwater shock compaction technique. Fig. 5 shows the SEM image of interface layer (white line) between shock-consolidated bulk Cu and bulk ZnO and its photograph that they were joined to each

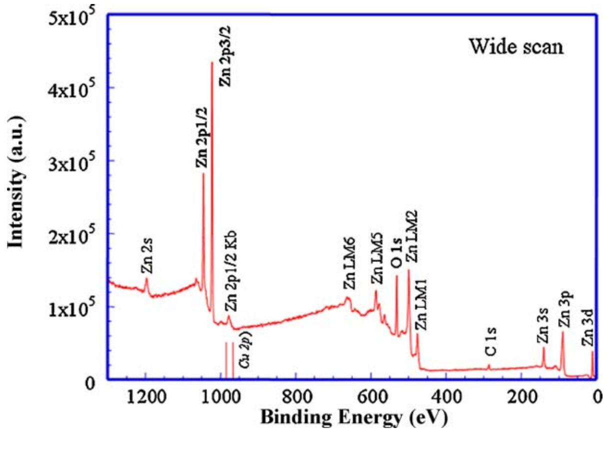

Fig. 4. XPS analysis of shock-consolidated ZnO.

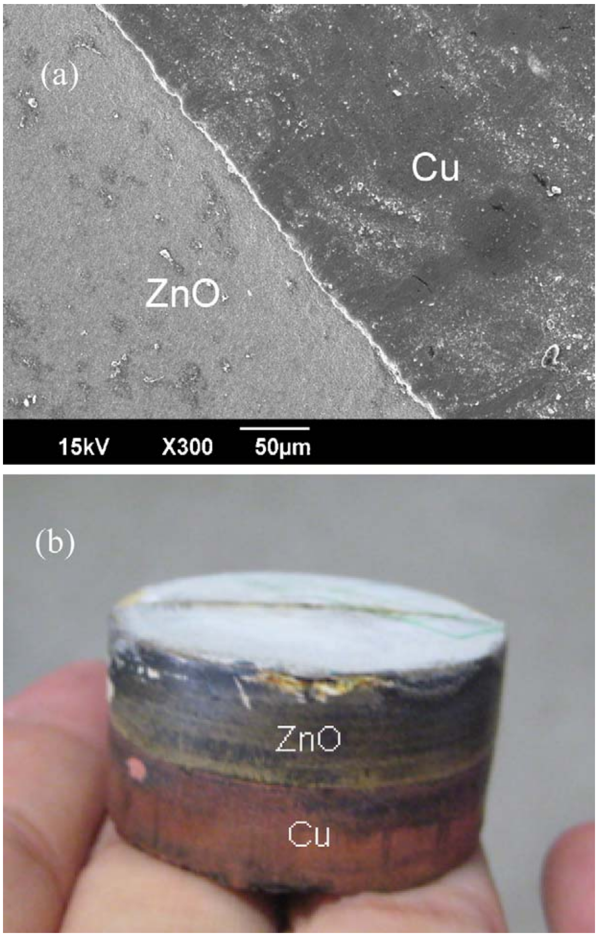

Fig. 5. (a) Micrograph of interface layer and (b) picture of joined shock-consolidated ZnO and Cu.

other. It was confirmed that both Cu powder and ZnO powder were completely consolidated and no cracks were observed in most of the areas. The residual heating in both consolidated Cu and ZnO areas may retard the cooling of the compact which is not inducing thermal cracks especially found at the boundary of the compacts. Also, it is possible to assist the sintering of the powders. As found in Fig. 5(b), the macroscopic appearance of the recovered sample is quite uniform and the result represents the effect of uniform shock wave pressurization. Fig. 6 shows the appearances of shock-consolidated ZnO. In the case of shock-consolidated ZnO without Cu powder, cracks occurred near the wall due to the rapid cooling process in the compacted material as shown in Fig. 6(a), whereas in the case of consolidated ZnO with Cu powder, we observed that the cracks were significantly reduced as shown in Fig. 6(b). This material has 30 mm in diameter, 8 mm in thickness without visible cracks. Its relative density measured was 99% (5.556×10^3 kg/m^3) of theoretical density (5.606×10^3 kg/m^3) and the hardness was 250–280 Hv under load 0.5 N. The value is higher than the commercial sintered ZnO at 200–220 Hv. The relative density of the commercial sintered ZnO was 95.7%. The difference in the density as well as the fine and strained substructure may cause such high hardness in the shock processed compact. Fig. 7 shows the Nyquist diagrams of shock-consolidated ZnO and commercial sintered ZnO. The linear parts are derived from resistivity of electrode. The semicircles are derived from grain boundary barrier and grain barrier. The diameter of the semicircle corresponds to the grain boundary resistivity, and sizes of those appeared in (a) and (b) are completely different. According to the experimental results, the grain boundary resistivity of shock-consolidated ZnO bulk was several hundred MΩ, whereas that of commercial sintered ZnO was several kΩ. In the case of shock-consolidated ZnO, it is considered that the large amount of grain boundaries generated by shock energy contribute to the extremely high impedance of bulk. Here, we suggest that shock-consolidated ZnO with high impedance is suitable for insulator, arrestor and especially varistor.

In recent literature, Wang et al. have mentioned [22] that an ideal varistor has minimal presence of mechanical defects such as voids, porosity and cracks. These features including grain refinement can be easily found in shock-consolidated materials because the shock energy generated by ultra-high pressure induces rapid and intense deformation

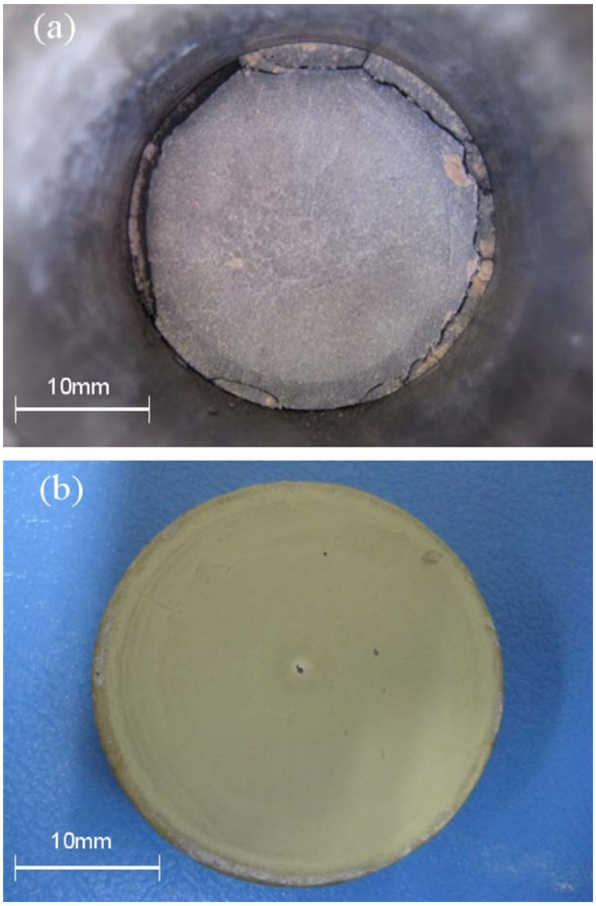

Fig. 6. Appearances of shock-consolidated ZnO; (a) consolidated ZnO without Cu powder in the powder capsule and (b) consolidated ZnO with Cu powder.

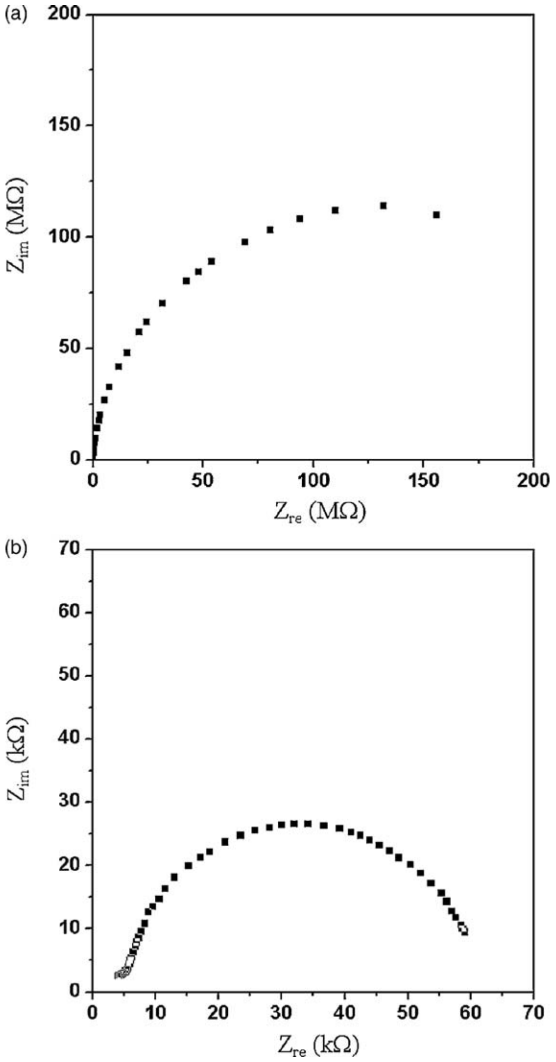

Fig. 7. Nyquist diagrams; (a) is the shock-consolidated ZnO and (b) is the commercial sintered ZnO.

at powder particle, and also the strong impact can lead to slight grain refinement [23]. This is advantageous to obtaining a varistor which exhibits high grain boundary resistivity.

4. Conclusions

Underwater shock compaction for ZnO powder has been performed and the characteristics of shock-consolidated ZnO were investigated. Fully densified ZnO compact without cracks was recovered successfully. A high density, 99%, and hardness, 250–280 Hv, were measured for the compact as well as the broadening of XRD peaks which suggest ultra-fine or highly strained substructure. The authors believe that the use of Cu powder layer to enhance the effect of heating may improve the quality of interparticle bonding between the ZnO powders but the effect does not significantly change the crystalline structure as measure by XRD measurement; the shock compaction technique is effective to fabricate ZnO varistors with high grain boundary resistivity. The authors also expect that commercial applications for ceramic target materials may be achieved by solving the cracking problem.

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