Grain Growth Analysis of ZnO in ZnO-Bi₂O₃-TiO₂ Ceramic

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The objective of this study is to clarify the grain growth behaviors of zinc-oxide varistor ceramics with Bi₂O₃ and TiO₂ additions. Zinc-oxide based ceramics have been widely used as transient surge suppressors for protecting electric equipment, because of their highly nonlinear voltage (V)-current (I) characteristics and excellent surge-withstanding capability. The electric properties of these ceramics are highly affected by the characteristics of the microstructures, such as ZnO grain size. A ZnO-6 mass% Bi₂O₃-0.55 mass% TiO₂ ceramic has been selected for investigating the ZnO grain growth behavior. The experimental results show that the samples consisted of equiaxed ZnO grains and a second phases with the Bi₂O₃ and spinel crystal structure. It also indicated that the grain growth behavior could be observed to follow a time law for grain size \( \omega \) of the form \( \omega = \omega_0\exp(-Q/RT) \cdot t \), where \( t \) is time and \( n \) is a kinetic exponent. The kinetic exponent for ZnO grain growth has been determined to be 1/2 for temperatures below 1303 K, but 1/5 above 1379 K. A convenient analysis technique for ZnO grain growth is also developed for their importance in terms of grain growth behaviors of ZnO varistors. A convenient grain growth model is directly determined by the number of ZnO grains per unit thickness in the device. Therefore, it is very important to clarify the microstructural evolution and to quantitatively evaluate the grain growth behaviors of ZnO in the varistor ceramics during sintering process.

1. Introduction

Zinc oxide (ZnO)-based ceramics containing small amounts of other oxide additives have been widely used as varistors for transient surge suppressors in both electric power systems and electronic circuits, because of their highly nonlinear current (I)-voltage (V) characteristics and excellent surge-withstanding capability. The electric properties of these varistor ceramics can be directly related to their microstructures.\(^1\),\(^2\) It is well-known that the nonlinear current (I)-voltage (V) characteristics are attributed to the grain boundary barriers.\(^3\)\(^-\)\(^5\) The two-phase microstructure, that consists of the ZnO grains and the grain boundaries, is essential for nonlinear ZnO-based ceramics. Namely, the varistor voltage is directly determined by the number of ZnO grains per unit thickness in the device. Therefore, it is very important to clarify the microstructural evolution and to quantitatively evaluate the grain growth behaviors of ZnO in the varistor ceramics during sintering process.

On the other hand, like Pr₂O₃, Bi₂O₃ is a primary component in virtually all of the ZnO varistor compositions, because it is essential for the liquid-phase sintering during the sintering process. Previous studies have investigated the ZnO grain growth in the case of several Bi₂O₃-containing systems.\(^3\)\(^-\)\(^5\) Also, it is well-known that small Zn₃Sn₂O₈ spinel particles formed at the grain boundaries suppress ZnO grain growth in the case of Sb₂O₃ additions.\(^6\) Similarly, it has been confirmed that ZnO grain growth was reduced by spinel particles such as ZnAl₂O₄ and Zn₃Nb₂O₇.\(^7\) It has been reported that sintered ZnO doped with alkali earth metal oxides, such as BaO, also exhibited nonlinear current (I)-voltage (V) behavior. The breakdown field for ZnO-BaO varistors was low due to the large grain size.\(^8\) The TiO₂ additions on the microstructure of ZnO-Bi₂O₃ varistors have also been reported significantly increase the grain size in spite of the Zn₂TiO₄ spinel formation.\(^9\)\(^-\)\(^1\) The grain growth behaviors of ZnO in the ZnO-Bi₂O₃ varistors with systematic TiO₂ additions have been investigated through the activation analysis of the ZnO grain growth phenomenon.\(^1\) However, the grain growth behaviors of the ZnO-Bi₂O₃ varistors with additions have not been fully clarified with respect to the various sintering conditions. Recently, the importance of analyzing the behaviors of ZnO grain growth for a rate controlled sintering has been reported.\(^1\)\(^2\) Computer simulation techniques for ordinary ceramics have begun to be developed for their importance in terms of grain growth analysis.\(^1\)\(^3\)\(^-\)\(^1\)\(^5\) Some models, such as Monte Carlo procedures, have been proposed, and good agreement between the experiments and the analysis results can be obtained. However, the treatment of multiphase problems is very complicated and the improvement of practical accuracies is now in progress. Hence, additional investigations into convenient analysis techniques for ZnO grain growth are also desirable for the ZnO varistors.

In the present study, a convenient grain growth model based on activation analysis was investigated for analyzing the behaviors of ZnO grain growth in ZnO varistors. A ZnO–B₂O₉ ceramic with TiO₂ addition has been selected for experimental investigation of the ZnO grain growth behaviors. The ZnO grain growth behaviors during the sintering process were clarified. In particular, the effects of heating and cooling rates on the ZnO grain growth in the ZnO varistors were quantitatively evaluated.

2. Grain growth model

Activation analysis of the grain growth has been completed through the application of the phenomenon logical kinetic equation: \( \omega^m - \omega^o = K_0 \exp\left(-Q/RT\right) \cdot t \) \(^{16}\)

where \( \omega \) is the average grain growth size at temperature \( T \) and time \( t \), \( \omega_0 \) is the initial grain size, \( m \) is the kinetic grain growth model
growth exponent, $K_0$ is a preexponential constant, and $Q$ is the apparent activation energy for grain growth. When $\omega_1$ is significantly smaller than $\omega$, the assumption is general, then $\omega_1^m$ can be neglected relative to $\omega^n$.

Equation (1) can be simply written as follows.

$$\omega = k \cdot t^n$$

(2)

where $k$ is the grain growth rate constant and $n = (-1/m)$ is a reciprocal of the kinetic grain growth exponent. Namely, there is a tendency that the grain growth increases with increasing heating time. The grain growth exponent $n$ is readily determined as the inverse of the slope of a log $\omega$ vs. log $t$ plot.

Equation (2) shows that the grain growth follows an $n$ power time law. This equation is the basis of this study for analyzing the grain growth behaviors.

It is considered that the grain growth during heating and cooling during the sintering process is not negligibly small in the case of analyzing the experimental datum as shown in Fig. 1. This is particularly so during the heating process, because each grain size begins to grow before arriving at the sintering temperature. Namely, the grain sizes, $\omega_1$ and $\omega'$ cannot be neglected in comparison with the total grain size, such as $\omega_1$ and $\omega_2$. $\omega_0$ is the grain size during the heating process, and $\omega'$ is that during the transition to the cooling process as shown in Fig. 1. Then, the total grain sizes, $\omega_1$ and $\omega_2$ that correspond to $t_1$ and $t_2$ can be expressed as follows.

$$\omega_1 = \omega_0 - \omega' + k \cdot t_1^n$$

(3)

$$\omega_2 = \omega_0 - \omega' + k \cdot t_2^n$$

(4)

where $k$ is the rate constant of grain growth under the condition that the rate of heating and cooling is always constant.

Moreover, the rate constant of grain growth, $k$, is given by

$$k = \frac{(\omega_1 - \omega_2)}{(t_1^n - t_2^n)}$$

(5)

It is clear that Eq. (5) does not include $\omega_0$ and $\omega'$. Therefore, both $\omega_1$ and $\omega_2$ are considered to be negligible when calculating the rate constant, $k$, from experimental datum, in the case that the rate of heating and cooling is constant in experiments. On the basis of this result, the rate of heating and cooling during the sintering process was kept constant in the experiment. Figure 1 shows the technique for experimentally determining the rate constant, $k$, from a log $\omega$ vs. log $t$ plot. In practice, four datum points for holding time were used to determine it.

3. Materials and experimental details

A high-purity ZnO powder (Grade 911, St. Joe Zinc Co., 99.99%; average particle size of 0.11 $\mu$m) and reagent grade Bi$_2$O$_3$ and TiO$_2$ powders were prepared for sintering. To achieve a significant content of the Bi$_2$O$_3$-rich liquid phase during sintering, a ZnO-6 mass% Bi$_2$O$_3$-0.55 mass% TiO$_2$ composition was selected for this experiment. The composition is prepared by mixing with a mortar and pestle, then adding 3 mass% of Carbowax binder. The mixed powders are pressed at 140 MPa into disks 10 mm in diameter and 4 mm in thickness. Green densities obtained are about 60% of theoretical values. For sintering, the green compacts are first held in air at 773 K for 0.5 h to burn off the binder, and then sintered in air at 1173, 1235, 1303, 1379, 1465, 1562 and 1673 K for 0.5, 1.0, 2.0 and 4.0 h, respectively. The heating rate is kept constant at 0.014 K/s and the cooling rate is kept constant at 0.028 K/s during the sin-
For microstructural observation, the sintered specimens were cut into two parts and mounted in an acrylic resin. The polished cross section of each sample was lightly etched with dilute acetic acid (2 to 5%) for periods from 30 to 120 s. The average ZnO grain sizes were measured directly from photomicrographs of the etched samples, as shown in Fig. 2, by Mendelson's linear intercept method.

4. Results and discussion

4.1 Grain growth behaviors in experiments

Typical microstructures of the ZnO-6 mass% Bi₂O₃-0.55 mass% TiO₂ specimens after sintering at 1673 K for 0.5, 1.0, 2.0 and 4.0 h are shown in Fig. 2. It is clear that these specimens consist of equiaxed ZnO grains. Many pores of 1.0-5.0 μm in diameter remain at the triple-point junctions, but some smaller ones below 1.0 μm in diameter exist between and within individual ZnO grains. There is a tendency that the ZnO grain becomes slightly larger and clearer with increasing sintering time. This tendency is significant according to the evaluation by Mendelson’s linear intercept method. Also, although the number of pores reduces with increasing sintering time, the pore size becomes larger.

ZnO grain growth behaviors during the sintering of ZnO-6 mass% Bi₂O₃-0.55 mass% TiO₂ specimens are shown in Fig. 3. There is a tendency for the ZnO grain size to increase with increasing heating temperature and holding time. This is also confirmed by the representation of a log ω vs. log t plot in which the experimental datum of the ZnO grain growth follow approximately a linear relation. However, the slope of a log ω vs. log t plot can be divided into two parts according to sintering temperature. Since the slope of the log ω vs. log t plot is equal to the kinetic exponent as shown in Eq. (1), the kinetic exponent, n for ZnO grain growth, is determined to be about 1/2 for temperatures below 1303 K and about 1/5 above 1379 K.

It has been reported that TiO₂ rapidly dissolves in the Bi₂O₃-rich liquid phase, reacts with the Bi₂O₃ liquid, and forms the compound Bi₄Ti₃O₁₂.9), 10) The solid Bi₄Ti₃O₁₂ is then reported to decompose and react with the solid ZnO grains above 1323 K, according to the reaction of Eq. (7).10), 11)

\[ \text{Bi}_4\text{Ti}_3\text{O}_{12} \text{(solid)} + 6\text{ZnO} \text{(solid)} \rightarrow 2\text{Bi}_2\text{O}_3 \text{(liquid)} + 3\text{Zn}_2\text{TiO}_4 \text{(solid)} \] (7)

It can be considered that Bi₄Ti₃O₁₂ forms at lower sintering temperatures, then the Zn₂TiO₄ forms above 1323 K. Particles of both the Bi₄Ti₃O₁₂ and the Zn₂TiO₄ may affect the grain growth behaviors in each temperature range.9) It is thought that the inhibition effect of the ZnO grain growth exponent is different from that of spinel particles such as Bi₄Ti₃O₁₂ and Zn₂TiO₄. In other words, the inhibition effect of Zn₂TiO₄ particles is notable in comparison with that of the Bi₄Ti₃O₁₂ particles judging from the kinetic exponent value.

Figure 4 shows the datum below 1303 K in Fig. 3 replotted using t¹/₂ as a horizontal axis. Good linear relationships can be obtained for each test temperature. There is a tendency that the slope of the log ω vs. log t¹/₂ plot becomes steeper with increasing sintering temperature. The grain growth behaviors for ZnO-6 mass% Bi₂O₃-0.55 mass% TiO₂ below 1303 K are shown in Fig. 4. Below 1303 K, the grain growth follows a linear relationship, and above 1303 K, the grain growth follows a parabolic relationship. The grain growth behaviors for ZnO-6 mass% Bi₂O₃-0.55 mass% TiO₂ above 1379 K are shown in Fig. 5. Above 1379 K, the grain growth follows a parabolic relationship.

Fig. 3. Time dependency of grain growth behaviors for ZnO-6 mass% Bi₂O₃-0.55 mass% TiO₂.

Fig. 4. Grain growth behaviors for ZnO-6 mass% Bi₂O₃-0.55 mass% TiO₂ below 1303 K.

Fig. 5. Grain growth behaviors for ZnO-6 mass% Bi₂O₃-0.55 mass% TiO₂ above 1379 K.
size at $t^{1/2} = 0$, due to the grain growth during heating and cooling process of sintering, becomes slightly larger with increasing sintering temperature. The rate constant, $k$, of ZnO grain growth below 1303 K can be obtained from the slope of the log $\omega$ vs. log $t^{1/2}$ plot. In the same manner, Fig. 5 shows the datum above 1379 K in Fig. 3 replotted using $t^{1/5}$ as a parameter. It is clear that good linear relationships can be observed. The rate constant, $k$, of ZnO grain growth above 1379 K can also be obtained. It is clear from the experimental results that an Arrhenius-type temperature dependence for the rate constant of grain growth, $k$, was confirmed as shown in Figs. 6(a) and (b).

4.2 Estimation of grain growth behaviors

A typical experiment has previously been reported, in which the effect of post sintering process, including the cooling rate, for improving the degradation of ZnO varistor's characteristics was examined. The results show the importance of evaluating the ZnO grain growth during the transitional sintering process as well as during the constant heating process.

The rate equation for grain growth has been already reported as described by Eq. (2). According to Eq. (2), the
method of estimating grain growth during various heating processes can be described below.

Namely, from the differential of Eq. (2):
\[ \frac{d\omega}{dt} = k \cdot n \cdot (\omega/k)^{1-1/n} \]

Thus, Eq. (8) can be written as follows by integration
\[ \omega = \int [k \cdot n \cdot (\omega/k)^{1-1/n}] \, dt \]

Using the rate constants, \( k \), that are obtained by the experiments as shown in Fig. 6 (a) below 1303 K and in Fig. 6 (b) above 1379 K, it is possible to estimate the growth of grain size, \( \omega \), using Eq. (9). When the heating temperature changes with heating time, the ZnO grain growth behavior can be estimated by calculating Eq. (9).

The developed system flow for the grain growth analysis based on Eq. (9) is shown in Fig. 7. In this system, the grain growth analysis can be conducted with the input of initial datum, rate constant and temperature history. In Fig. 8, an example of ZnO grain growth behavior during the sintering process is shown. The temperature history of the sintering is also shown in the figure. The temperature dependencies of the rate constants used are shown in Figs. 6 (a) and (b). It is clear from these figures that the ZnO grain growth behavior changes from \( t^{1/2} \) power time law to \( t^{1/5} \) power time law. Also, it is confirmed that the grain growth during the heating and cooling processes cannot be neglected in comparison with the final grain size. The dotted line represents the ZnO grain growth subject only to the \( t^{1/2} \) power time law for reference. Next, identical analyses were conducted for changing the heating rate, the cooling rate and the holding time at temperature 1473 K. The obtained results for each parameter are shown in Fig. 9: (a) heating rate from 0 to 1473 K, (b) holding time at 1473 K and (c) cooling rate from 1473 to 0 K. It is a natural result that the grain size increases with increasing holding time at 1473 K. It becomes smaller with increasing heating rate. However, the effect on ZnO grain growth during the cooling process is small in comparison with the heating process. Finally, there is a tendency that the varistor voltage increases with decreasing the ZnO grain size. It is noteworthy that a change of 2–3 \( \mu \)m in grain size has a significant effect on the varistor voltage. Therefore, it is considered that ZnO grain growth as shown in Fig. 9 during the heating process cannot be neglected in practical sintering.

5. Conclusion

The nonohmic properties of ZnO-based ceramics are sensitive to variation in the sintering process, which is attributed to the number of ZnO grains per unit thickness in the device. ZnO–6 mass% Bi₂O₃–0.55 mass% TiO₂ was selected for experimental investigation of ZnO grain growth behaviors.

The experimental results show that there is a tendency for the grain size to increase with increasing heating temperature and heating time. The grain growth behaviors could be observed to follow a power time law for grain size \( \omega \) of the form \( \omega = k \cdot t^n \), where \( t \): time, \( k \): rate constant and \( n \): kinetic exponent. This is confirmed by the representation of a log \( \omega \) vs. log \( t \) plot in which the experimental data of the ZnO grain growth approximately follow a linear relation. Namely, the kinetic exponent, \( n \), for ZnO grain growth, which is the slope of the log \( \omega \) vs. log \( t \) plot, is determined to be about 1/2 for temperatures below 1303 K and about 1/5 above 1379 K. It was observed that Bi₄Ti₃O₁₂ forms at the lower sintering temperature, then Zn₂TiO₄ forms above 1323 K. It is considered that the inhibiting effect of Zn₂TiO₄
particles is significant in comparison with that of the \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) particles, judging from the kinetic exponent value. Also, it is clear from the experimental results that an Arrhenius-type temperature dependence for the rate constant of grain growth, \( k \), is confirmed.

A convenient computer-aided interactive system has been developed for analyzing ZnO grain growth behaviors in the ZnO–6 mass\%Bi₂O₃–0.55 mass\%TiO₂ sintered body. Using this system, it is clear that the ZnO grain growth during the heating and cooling processes could not be neglected in relation to the total ZnO grain growth. It is also clear that the effect of cooling process on ZnO grain growth was not significant in comparison with that of the heating process. Because a change of 2–3 μm in grain size has a significant effect on the varistor voltage, it is considered that the ZnO grain growth during the heating and cooling processes can not be ignored in practical sintering.

References