Microstructural Observations of Cu_2O -Added BaTiO_3 Sintered under N_2 Flow

Chang Yeoul KIM, Tohru SEKINO, Tomohiko ADACHI, Yo YAMAMOTO and Koichi NIIHARA

Institute of Scientific and Industrial Research, Osaka University, 8-1, Mihogaoka, Ibaraki-shi, Osaka 567-0047

還元雰囲気焼結した Cu_2O 添加 BaTiO_3 の微細組織観察

金 昌烈・関野 徹・安達智彦・山本 陽・新原皓一

大阪大学産業科学研究所, 567-0047 大阪府茨木市美穂ヶ丘 8-1

BaTiO₃-Cu ferroelectric/metal composite was successfully fabricated by sintering a Cu_2O -added BaTiO_3 pellet using a 100 ml/min nitrogen gas flow rate. Abnormal grain growth was found to occur above 1280°C by scanning electron microscopy (SEM). Electron probe micro-analysis (EPMA) results indicated that crystalline spheres within abnormally grown grains were generated from excess titanium-contained BaTiO_3 and copper melt. Transmission electron microscopy (TEM) revealed that copper metal had twins and that BaTiO_3 had faceted boundaries.

[Received October 24, 2001; Accepted March 25, 2002]

Key-words: Barium titanate, Copper dispersion, Microstructure, Reductive atmosphere, Crystalline sphere, Abnormal grain growth, Grain boundary re-entrant edges, Liquid phase sintering

1. Introduction

Effects of dispersion of metallic phase into ferroelectric materials have been examined for various combinations, such as PZT/Ag,¹⁾ PZT/Pt,²⁾ and BaTiO_3/Ni ³⁾ systems. A small amount of metallic phase dispersed into ferroelectric ceramics has been known to improve the mechanical properties such as flexural strength and fatigue without degrading the electrical properties. The dispersed metallic phase can act as a bridge against crack propagation and increase fracture toughness and strength of the matrix. The advantage of dispersing metallic phase into ferroelectric ceramics is evident not only in the mechanical properties, but also in the electrical properties. The dispersed metallic phase increases the effective electrical field applied to the ferroelectric matrix while it also enhances dielectrical properties.^{4),5)} Also, silver metal in the PZT/Ag system was reported to improve PZT sinterability.⁶⁾

In the case of the BaTiO_3/Cu system, some difficulties in dispersion of metal into ceramics during sintering are expected. Since melting points or eutectic points of the Cu-O system are known to be 1065°C, far lower than the sintering temperature of BaTiO_3 , Cu metal becomes the liquid phase during sintering. Hennings et al.⁷⁾ reported that TiO_2 -excess BaTiO_3 sintering formed the eutectic melt and gave rise to pronounced discontinuous grain growth, that is, abnormal grain growth of BaTiO_3 . In the BaTiO_3/Cu system, abnormal grain growth might occur due to the formation of copper liquid. There have been some limited reports on the effects of copper oxide addition to BaTiO_3 on the sintering behavior and dielectric properties of the $\text{BaTiO}_3\text{-CuO}$ system.⁸⁾⁻¹³⁾ However, few investigations have explored microstructural observation or dispersion of Cu into BaTiO_3 . In our previous work,¹³⁾ reduction of Cu_2O to Cu in BaTiO_3 under 100 ml/min nitrogen flow was identified by XRD analysis; also, BaTiO_3/Cu composite was successfully fabricated by sintering under nitrogen flow. In this study, microstructural evolutions of BaTiO_3 were investigated during the fabrication of BaTiO_3/Cu by sintering Cu_2O -added BaTiO_3 in a nitrogen atmosphere. The formation mechanism of abnormal grains as well as microstructural characteristics of the present composite will be discussed in relation to Cu_2O addition.

2. Experimental procedure

Cuprous oxide (Cu_2O , high purity chemical, 99%, about

3 μm) was mixed with BaTiO_3 powder (Sakai Chemical, hydrothermally synthesized powder, about 1 μm) by using wet ball milling in ethanol for 24 h. The powder mixture in ethanol was dried in an evaporator, pulverized, and then sieved with a 150 μm mesh. Contents of Cu_2O varied from 0 to 5 mass%. Mixed powders were compacted by a stainless steel mold with 10 MPa followed by cold-isostatic pressing (CIP) at 200 MPa for 3 min to fabricate a 10 mm diameter and 3 mm thick green mass. Sintering was conducted between 1200 and 1350°C at various nitrogen gas flow rates of which the heating and cooling rates were fixed to be 20°C/min. During sintering, oxygen partial pressure was measured to reflect the thermodynamic behavior of $\text{BaTiO}_3\text{-Cu}_2\text{O}$ sintering.

Dispersion of copper metal in BaTiO_3 matrix was observed using an optical microscope; size distribution and area ratio of the Cu to the matrix were analyzed using the Scion image analysis program. The $\text{BaTiO}_3\text{-Cu}_2\text{O}$ system microstructure was observed by FE-SEM (Model S-5000, Hitachi, Ltd., Tokyo) and TEM (H-8100T, 200 kV, Hitachi Ltd., Tokyo). The specimen for SEM observation was ground to about 1 mm thickness, polished with 0.5 μm alumina paste and then chemically etched in 5% HCl solution. The fracture surface was also observed. Constituent analysis of crystal phases was conducted by energy dispersive X-ray analysis (EDX; Horiba, Tokyo); electron probe micro-analysis (EPMA; JXA-8800R, JEOL, Osaka) was also undertaken to identify compositional distribution in the sintered specimen.

3. Results and discussion

3.1 Dispersion and size distribution of copper

Dispersed copper images of 1 and 5 mass% Cu_2O -added BaTiO_3 , sintered at 1280°C for 3 h under 100 ml/min N_2 flow, are shown in Fig. 1. Copper was dispersed homogeneously in barium titanate matrix and the phase of dispersed particles was identified as copper as in our previous report.¹³⁾ The remaining copper content was evaluated indirectly by analyzing the area ratio of copper to the matrix. It increased from 0.2%, for the 0.5 mass% Cu_2O addition, and to 2.3% for the 5 mass% Cu_2O addition (Table 1).

3.2 SEM observation and EDX analysis

Microstructures of the chemically etched surface (in 5 mol% of HCl) of samples sintered at 1250°C in 200 ml/

Fig. 1. Optical micrographs and the size distribution of copper for 1 mass% Cu₂O-added BaTiO₃ (a) and 5 mass% Cu₂O-added BaTiO₃ (b), sintered at 1280°C under 100 ml/min N₂ flow.

Table 1. Average Diameters (D_{ave}), Deviations (σ) and Area Ratio of the Dispersed Copper

Item \ Cu content / mass%	0.5	1	2	5
D_{ave} / μm	2.4	2.7	2.7	3.4
σ in D	1.3	1.9	1.6	2.2
Ratio of Cu area / %	0.2	0.65	0.95	2.3

min N₂ gas flow were observed by SEM (Fig. 2). Grain size of BaTiO₃ was about 1 μm and grain growth of BaTiO₃ was not observed. However, in the 1 mass% Cu₂O-added BaTiO₃ sintered at 1280°C under 100 ml/min N₂ flow, abnormal grain growth was clearly observed as shown in Fig. 3(a). The abnormal grain size was between 50 and 70 μm. When one abnormal grain was observed by magnification, it clearly contained small particles; some of those were identified as copper by EDX analysis in Fig. 3(c) while the others were not copper. The latter were identified as barium titanate by EDX analysis and were thought to be the same as the BaTiO₃ crystalline sphere in Fig. 3. A darker contrasted region around the copper particle was also observed in Fig. 3(d), which was thought to be the diffusion layer of copper.

Abnormal grain growth is generally known to occur when particle shape is angular in liquid phase sintering.¹⁴⁾ This implies that abnormal grain growth could be observed when particle growth or dissolution is controlled by the interface reaction. Different sizes of angular-shaped particles in the liquid phase need a force more than the critical driving force, ΔG_c , to grow abnormally.¹⁵⁾ That value is calculated as

Fig. 2. SEM images of copper for 1 mass% Cu₂O-added BaTiO₃ (a) and 5 mass% Cu₂O-added BaTiO₃ (b), sintered at 1250°C under 100 ml/min N₂ flow (Bar is 1.8 μm).

$$\Delta G_c \leq 2\gamma V_m \left(\frac{1}{a^*} - \frac{1}{a} \right) \quad (1)$$

where a is the particle radius, a^* is critical radius, γ is surface energy of a particle, and V_m represents particle molar volume. Because only grains with a force greater than the critical driving force can grow, a^* must be smaller than a certain value and a must be larger than a^* . In this case, large

Fig. 3. SEM photographs of the etched surface and EDX mapping image of the 1 mass% Cu₂O-added BaTiO₃ sintered at 1280°C at 100 ml/min nitrogen flow. (a) abnormal grain of 1 mass% Cu₂O-added BaTiO₃, (b) magnified image of (a), (c) EDX mapping image of Cu within abnormal grain (left: SEM image, right: Cu image), (d) diffusion layer (DL) of copper into BaTiO₃ in abnormal grain.

grains having a force more than ΔG_c grow selectively, but other smaller grains can dissolve and disappear. As a result of DTA and TG analysis in our previous report,¹³⁾ melts of BaTiO₃-Cu or BaTiO₃-Cu₂O were found to appear between 900 and 1040°C,^{12,13)} which was consistent with the result in BaTiO₃-CuO sintering in air by Yang.⁸⁾ It is expected that the copper liquid phase or the eutectic melt would play an important role in densification and abnormal grain growth, or dissolution of particles. It is not certain, however, whether abnormal grain growth began to appear at 1280°C, higher than the 1040°C considered as the eutectic melting point.

Figure 4 shows the fracture surface of 1 mass% Cu₂O-added BaTiO₃ containing a number of BaTiO₃ crystals whose sizes vary from hundreds of nanometers to about 10 μm. And abnormal grains began to appear in the sintered sample at 1280°C under 100 ml/min N₂ flow, which contained polygonal and spheroidal crystals of BaTiO₃. Spheroidal crystals were also observed in areas where abnormal grains were extracted, that is, in the grain boundary of abnormal grains (Figs. 4(c) and 4(d)). Spheroidal crystals are considered to have formed from several grains fusing together, as seen in Fig. 4(d). When the sample was sintered at 1350°C under 100 ml/min N₂ flow, the number of abnormal grains increased and the abnormal grains were filled with many spheroidal crystals of a few microns to 10 microns in size as shown in Figs. 4(e) and 4(f). Figure 5 shows crystal spheres within abnormal grains of barium titanate and the EDX analysis result for 5 mass% Cu₂O-added BaTiO₃ sintered at 1350°C. Several spheroidal crystals were observed with copper attached to the surface; also, crystal growth planes were observed on the sphere surface. In EDX analysis, the spheroidal crystal had almost identical constituents of barium and titanium as that of the matrix, but it contained small amounts of copper as evident in Fig. 5(e). The attached crystal on the surface of the spheroidal crystal was identified as copper in Fig. 5(f). Therefore, it is inferred that copper played a role in forming spheroidal crystals within abnormal barium titanate grains.

For abnormal grains that contained a number of small BaTiO₃ crystals, it is believed that many drops of the liquid

Fig. 4. SEM micrographs of fractured surface of the 1 mass% Cu₂O-added BaTiO₃ showing (a) abnormal grain of the specimen sintered at 1280°C in 100 ml/min nitrogen gas flow, (b) polygonal crystal (marked by arrow) within abnormal grain, (c) BaTiO₃ crystal sphere in grain boundary between abnormal grain and matrix, (d) crystal sphere forming image, (e) fractured surface of 1 mass% Cu₂O-added BaTiO₃ sintered at 1350°C under 100 ml/min N₂ gas flow, (f) magnified image of (e).

phase seemed to be formed and captured due to very fast abnormal grain growth. Some liquid-phase drops greater than the critical size grew or united with one another, creating visible crystal-growth planes. Copper metal was attached to some crystal-growth planes, implying that copper metal may be reprecipitated on the crystal-growth plane during cooling down. But small liquid drops may be dissolved into the abnormal grain so that it becomes smaller than the original particle size. Choi et al.¹⁵⁾ observed captive crystals within abnormal grains during liquid-phase sintering of TaC-TiC-Ni cermets. In their system, Ti would diffuse to the TaC side and reprecipitate as (Ta, Ti)C. In this case, the driving force for grain coarsening can be given as Eq. (2),

$$\Delta G_{\text{tot}} = \Delta G_v + \Delta G_{\text{chem}} \quad (2)$$

where ΔG_v is the free energy change with coarsening for grain size a , and ΔG_{chem} represents free energy change with formation of solid solution. Such an increased driving force may explain the formation of exceptionally large grains. In this case, the coarsening rate is accelerated when grain boundary re-entrant edges (GBRE), formed by coalescence, are present. Entrapment of small grains into abnormally large grains is believed to be a consequence of the GBRE process.

In the case of Cu₂O-added BaTiO₃ sintering, the mechanism of entrapped grains is thought to be the same as in the TaC-TiC-Ni system. During liquid-phase sintering of Cu₂O-

Fig. 5. SEM micrographs and EDX analysis of fractured surfaces of Cu_2O -added BaTiO_3 abnormal grain, which contained many BaTiO_3 single crystals with Cu attached when the specimen was sintered at 1350°C under 100 ml/min N_2 flow. (a) spheroidal crystals, (b) single crystal sphere with copper attached, (c) magnified image of crystal growth planes of crystal sphere, (d) EDX analysis of BaTiO_3 matrix, (e) EDX analysis of spheroidal crystal in (b), (f) EDX analysis of copper attached on crystal sphere in (b).

Fig. 6. Electron probe microanalysis of Cu_2O -added BaTiO_3 crystal sphere within abnormal grain. (a) SEM image, white solid line: electron scanning line, (b) relative intensity of constituents along the scan line. dotted line: equivalent region of scan line in (a).

added BaTiO_3 under N_2 flow, copper diffused into barium titanate and reprecipitated to $(\text{Ba}, \text{Cu})\text{TiO}_3$ so that the driving force of grain coarsening due to the chemical composition difference could appear and accelerate abnormal grain growth. The solid solution of Cu_2O - BaTiO_3 was also confirmed by SEM image, EDX analysis, and EPMA analysis data (Figs. 3, 5, and Fig. 6). A possible explanation is that the GBRE between abnormal grains and small grains accelerated grain coarsening to the extent that small BaTiO_3 grains and the eutectic melt of Cu_2O - BaTiO_3 were entrapped by abnormal grains; copper was then reprecipitated on the barium titanate crystal-sphere surface and within abnormal grains.

3.3 EPMA

In results of EPMA in Fig. 6, BaTiO_3 crystal spheres, with some copper attached to the surface showed a strong copper peak and weak Ba, Ti, and O peaks. There is another region (B region) in which Ba and O peak intensities were relatively lower than those without crystal spheres, but Ti intensity was almost identical inside and outside the BaTiO_3

crystalline sphere. This means that the crystal sphere has excess Ti over that of the matrix. The BaTiO_3 crystal sphere contained small amounts of copper, even though the matrix had no copper content, as evident in Fig. 6(b). Therefore, we infer that crystal spheres consisted of TiO_2 -excess BaTiO_3 with traces of copper to form the solid solution of $(\text{Ba}, \text{Cu})\text{TiO}_3$. Above the eutectic temperature of 1332°C , abnormal grain growth of TiO_2 -excess BaTiO_3 was thought to result from rapid precipitation of the material through a thin Ti-rich liquid film at grain boundaries. In EPMA of a crystal sphere, it is believed that a crystal sphere could be formed of TiO_2 -excess BaTiO_3 liquid containing copper.

3.4 TEM observations

As is evident in Fig. 7(a), copper grain has slip bands or twins. In electron diffraction pattern analysis results, its zone axis was $[011]$; the (200) and (111) planes were consistent with its twin planes by rotating 180° along the twin planes (arrow in Fig. 7(b)). A typical grain boundary between BaTiO_3 grains is shown in Fig. 7(c) where the boun-