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Evaluation of Mechanical Properties of $Pb(Zr,Ti)O_3$ Ceramics Prepared by Aerosol Deposition

Tetsu Miyoshi

FUJIFILM Corporation, Ashigarakami, Kanagawa 258-8577, Japan
Fax: 81-0465-86-1016, e-mail: tetsu_miyoshi@fujifilm.co.jp

In our previous study, a comparative investigation of the sintering behavior of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) ceramics prepared by aerosol deposition (AD) and conventional solid-state sintering (CV) was performed. As a result, despite the small grain size of 0.42 μm, AD-processed PZT ceramics fired at 1000°C showed good electrical properties comparable to those of bulk PZT ceramics with a large grain size (> 1 μm) prepared by CV at 1100 to 1200°C. In this study, Vickers hardness of AD-processed PZT ceramics was evaluated as a function of firing temperature and compared with those of CV-processed specimens. As a result, higher hardness was obtained in AD due to the smaller grain size, which is indicating that piezoelectric ceramics with higher mechanical properties can be prepared by AD without any sacrifice in electrical properties.

Key words: aerosol deposition, PZT, bulk ceramics, Vickers hardness, Hall-Petch

1. INTRODUCTION

Aerosol deposition (AD) developed by Akedo et al. is a technique to prepare high density ceramic thick-film with thickness from 1 to 100 μm by ejecting the aerosol consisting of a mixture of ceramics powder and gas from the nozzle to the substrate [1]. It was reported that mechanical properties of Al_2O_3 films prepared by AD are comparable to those of bulk Al_2O_3 ceramics prepared by conventional solid-state sintering (CV) [2]. In contrast, as for a piezoelectric material such as $Pb(Zr,Ti)O_3$ (PZT), there was few report of having achieved the electrical properties comparable to those of bulk ceramics. When PZT is prepared by AD, it is possible to improve the electrical properties by post-deposition firing treatment accompanied by an increase in the grain size, even though grain size is very small (< 0.1 μm) and electric properties are very poor in the as-deposited state [3]. However, there is an upper limit in the firing temperature for the chemical reaction in the interface between the PZT layer and the substrate [3, 4]. Thus, it is difficult to increase the grain size equally to the bulk ceramics prepared by CV. In addition, it is thought that stress from the substrate might also decrease the electrical properties. Akedo and Lebedev reported the relationship between the piezoelectric constant and clamping from the substrate [5]. They indicated that the piezoelectric constant of PZT film released from the substrate was almost two times that of film clamped from the substrate. Similar effect of substrate clamping is reported for PZT thick-films prepared by the printing method [6]. Therefore, a reduction in the electrical properties for piezoelectric films prepared by AD is attributed to small grain size and stress from the substrate.

In our previous study, to exclude the influences of substrate mentioned above, the substrate was removed from the AD-processed PZT ceramics by a chemical dissolution, followed by firing at various temperatures from 800 to 1200°C [7, 8]. As a result, despite the small grain size of 0.42 μm, AD-processed PZT ceramics fired at 1000°C showed equivalent electrical properties compared to bulk PZT ceramics with a large grain size (> 1 μm) prepared by CV at 1100 to 1200°C.

In this study, Vickers hardness of AD-processed PZT ceramics were evaluated as a function of firing temperature and compared with those of CV-processed specimens on the assumption that piezoelectric ceramics with higher mechanical properties can be prepared by AD without any sacrifice in electrical properties.

2. EXPERIMENTAL

2.1 Sample preparation

PZT thick-films with thickness of 300 μm were deposited on $Pt/TiO_2/SUS430$ substrate by AD at 600°C. Commercially available PZT (Zr/Ti = 52/48) powder (Sakai Chemical) with an average primary particle size of 0.3 μm was used as starting powder. Then, bulk PZT ceramics were obtained by dissolving the substrate with $FeCl_3$ solution at 50°C, followed by firing at various temperatures from 800 to 1200°C for 3 h in air. Table I shows typical parameters of the deposition conditions for AD. For comparison with AD, bulk PZT ceramics were prepared by CV from the same starting powder. Using poly(vinyl alcohol) as a binder, the starting powders were uniaxially pressed into green bodies with diameter of 25 mm and with thickness of 2.5 mm under a pressure of 100 MPa, followed by firing at various temperatures from 800 to 1200°C for 3 h in air.

2.2 Characterization

For mechanical measurement, the specimens were polished into mirror faces and Vickers hardness was measured using a micro-hardness tester (Shimadzu, DUH-W201) with a Vickers indenter. Seven dots were measured, and the average of five dots, omitting the maximum and minimum values, was estimated.

Table I. Deposition Conditions for PZT by AD

Starting powder	PZT (Zr/Ti = 52/48)
Substrate	SUS430
Substrate temperature (°C)	600
Carrier gas	O_2
Consumption of carrier gas (L/min)	6
Orifice size of the nozzle (mm x mm)	7.5 x 0.3
Scanning rate (mm/s)	0.5
Deposition area (mm x mm)	7.5 x 10
Film thickness (μm)	300
Pressure in the deposition chamber (Pa)	50
Pressure in the aerosol chamber (kPa)	70

3. RESULTS AND DISCUSSION

Figure 1 shows the Vickers hardness as a function of firing temperature. Figure 2 shows the Vickers hardness as a function of grain size [7]. Relatively high hardness was achieved in AD as compared with CV over the whole grain size range. Hardness simply decreased with increasing grain size in AD. In contrast, hardness increased with increasing grain size up to 1.0 μm in CV, above which it decreased with increasing grain size.

Dependence of strength or hardness of conventional polycrystalline materials on grain size (d) is usually described by the Hall-Petch relationship as follows:

$$H_v = H_{v0} + kd^{-1/2} \quad (1)$$

where H_{v0} and k are constant [9, 10]. This relationship has been confirmed in both theory and practice in many metallic materials with average grain size of 100 nm or larger. Here pile-up of dislocations at grain boundaries is envisioned as a key mechanistic process underlying an enhanced resistance to plastic flow from grain refinement.

Figure 3 shows the relationship between Vickers hardness and inverse of the square root of grain size. It was found that the Hall-Petch relationship was obeyed in AD over the almost whole grain size range above 100 nm, while the relationship was obeyed in CV only above 1.0 μm. The result can be explained considering the difference in microstructures between AD and CV, as shown in Fig. 4 [7]. Namely, only grain size could be the determining factor of hardness in AD, since density is almost constant against grain size. In contrast, density could be the major factor determining hardness up to the critical grain size of 1.0 μm where densification is almost accomplished in CV.

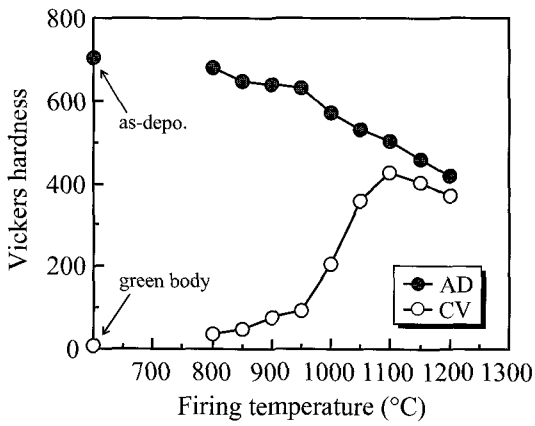

Fig.1 Vickers hardness as a function of firing temperature.

It is expected that slight softening (the deviation from the Hall-Petch relationship) in AD below the grain size of 100 nm is attributed to so-called inverse Hall-Petch effect (grain boundary sliding and/or Coble creep) [11, 12] or lattice distortion in the as-deposited state, and that drastic softening in CV below the grain size of 1.0 μm is simply attributed to the presence of porosity.

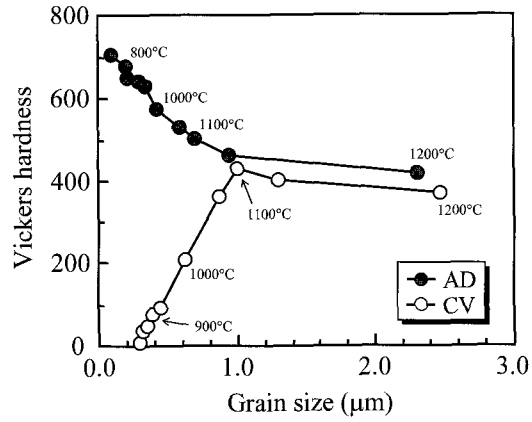

Fig.2 Vickers hardness as a function of grain size.

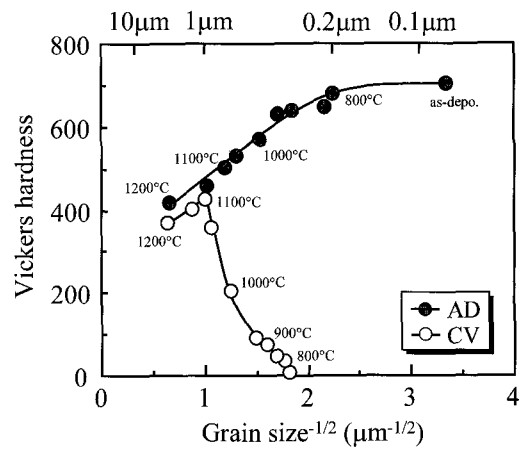

Fig.3 Relationship between Vickers hardness and inverse of the square root of grain size.

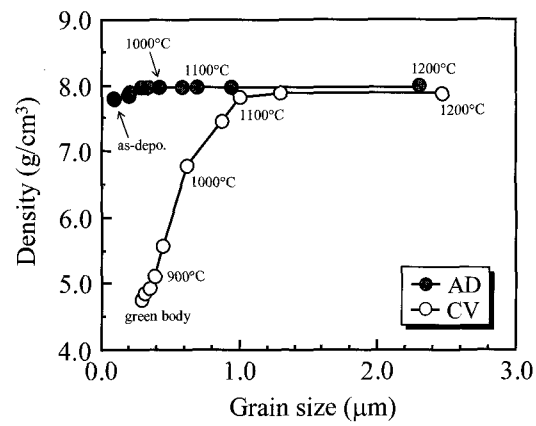

Fig.4 Density as a function of grain size.

4. CONCLUSIONS

In this study, Vickers hardness of AD-processed PZT ceramics were evaluated as a function of firing temperature and compared with those of CV-processed specimens. As a result, higher hardness was obtained in AD due to higher densification and finer grain size. Therefore, it is confirmed that piezoelectric ceramics with higher mechanical properties can be prepared by AD without any sacrifice in electrical properties, as shown in Fig.5 [7].

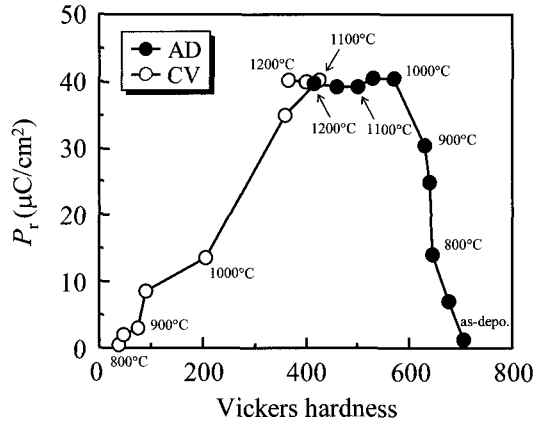

Fig.5 Relationship between Vickers hardness and P_r.

5. REFERENCES

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