

Effect of nano-sized TiO₂ powder on Ag-electrode in piezoelectric multilayer devices

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Abstract The objective of this study is to present sintering shrinkage behavior of Ag-Pd electrode powders with TiO₂ nano-particle addition and the matching characteristics to a piezoelectric ceramics, Pb(Zr,Ti)O₃. The densification of the nanoparticle TiO₂-added electrode paste followed the TiO₂ solid state diffusion-controlled mechanism upon sintering process. Reaction between ceramic and electrode layers with the TiO₂ nano-particle powder allows internal stress to be reduced and mechanical bonding strength to be increased. High adhesive strength and good electrical conductivity of more than 10⁴/Ω cm could be obtained in the multilayer ferroelectric structure. In order to understand the effectiveness of the nano-TiO₂ doped electrode for multilayer device, the multilayer ceramic actuators containing Ag-based electrode without and with nano-sized TiO₂ powder were fabricated and evaluated each other. Both the samples exhibited similar piezoelectric and dielectric properties.

Keywords Nano-sized TiO₂ particle · Ag-Pd electrode · Sintering · Adhesion · Electric conductivity

1 Introduction

Multilayer ferroelectric devices are fabricated by stacking ceramic and electrode layers followed by cofiring process. During the fabrication of multilayer devices, the electrode material can be tolerate in the cofiring process, keeping it at sintering temperatures of up to 1100–1400°C. Among sev-

eral electrode materials, Ag-Pd has been widely used as an electrode material available in heat treatment process above 960°C. Numerous studies have shown, however, that on the fabrication processes of multilayer devices various defects nucleate and grow at the interface between the electrode and ferroelectric multilayer structure because of formation of internal stress [1, 2]. In the cofiring process, the mismatch in the sintering properties of the two ceramic and electrode materials provides interfacial delamination, cracking and other defects [3, 4]. Such problems in the multilayer devices must be solved by modifying cofiring kinetics [5, 6]. One solution to the problem to be suggested in the present study, is adding small amount of ceramic powder to the metal electrode. This treatment allows the devices to be fabricated successfully by diminishing the amount of shrinkage difference between ceramic and electrode layers. The method offers the avoidance of cracks and delamination nearby interface between ceramic and electrode layers [7–9]. Also, the stronger adhesion between the ceramic and electrode layers in multilayer ferroelectric devices can be possible by controlling the interface reaction. The interface reaction occurs via diffusion of the particle to ceramic layer, along with the construction of a skeleton structure of ceramics within the electrode [10]. The skeleton structure formation gives rise to low electrical conductivity [10]. The deterioration in electric conductivity can be, however, avoided in a process that the modification of the ceramics distribution within metal electrode, i.e. from chain structure to unlinked agglomerate structure, can be achieved by controlling the sintering of nano-sized ceramics within electrode.

The objective of this study is to investigate the effect of nano-sized TiO₂ addition to Ag-Pd electrode. Nano particle TiO₂ was chosen in this study in that the material has higher adhesion and chemically stable to piezoelectric ceramics (typically PZT) among electric conductive oxide

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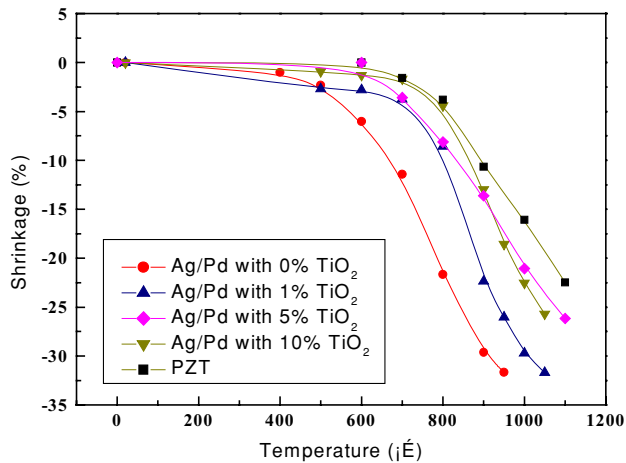


Fig. 1 Shrinkage as a function of sintering temperature for dried 70Ag-30Pd paste with TiO₂ powder addition

family, ZrO₂, TiO₂, SnO₂, Sb₂O₅, ZnO, In₂O₃ and MoO₃. This article describes the shrinkage characteristics of electrodes and microstructural modification. Besides, their mechanical adhesion to a PZT ceramic and electrical conductivity was evaluated.

2 Experimental procedure

Pb(ZrTi)O₃ (hereafter, PZT) ferroelectric ceramic powders were prepared from approximate amounts of reagent-grade PbO (Cerac Incorporated, 325mesh, 99.9%, Japan), ZrO₂ (Cerac Incorporated, 325mesh, 99.7% Japan), TiO₂ (Cerac Incorporated, 325mesh, 99.9% Japan). The columbite method was used to synthesize the corresponding ceramic powders to eliminate the formation of a pyrochlore-type phase. The PZT powder with 5% Pb(MgNb)O₃ addition could be completely sintered by keeping at 1100°C for 2 h.

Titanate ceramic additives with a particle size of ~25 nm (Degussa, P25) was prepared. Then, this additive was uniformly dispersed in the 70Ag-30Pd alloy electrode paste at different ratios in an organic medium by attrition milling. The silver-palladium alloy pastes, which contained a mixture of Ag-Pd particles, an organic vehicle, and a glass-frit powder (BiO-SiO₂-PbO family), had a solid loading of 55%. The mean particle size of the silver-palladium alloy was 0.5–0.8 μm, as was determined by a line intercept method using scanning electron microscopy (SEM, Model S2700, Hitachi Co.).

Several cylindrical samples pressed under 1.5 kgf/cm² were used to measure the sintering densification characteristics as a function of sintering temperature in air at a heating rate of 5°C/min by a thermomechanical analyzer (TMA, 2940, Dupont Instrument.).

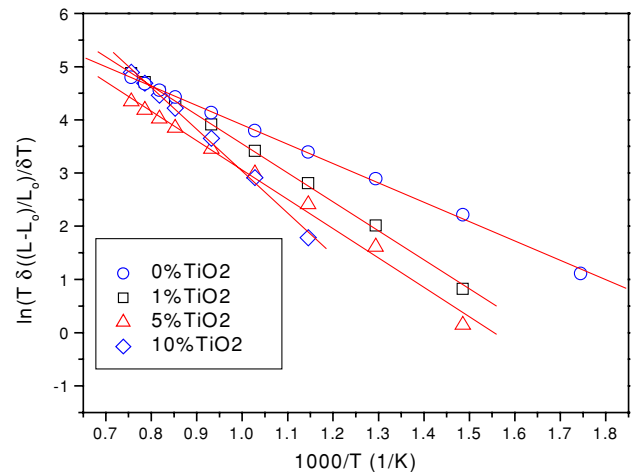


Fig. 2 Reconstructed curves showing kinetics for Ag-Pd electrode pastes without and with TiO₂ addition

Slurries for tape casting were made by mixing the calcinated powders with a solvent (an azeotropic mixture of Methyl ethyl ketone and ethanol), a dispersant (phosphate ester), a plasticizer (dibutyl phthalate), and a binder (polyvinyl butyral, PVB). The green tapes were produced using small-scaled caster with a doctor blade. The four types of Ag-Pd electrode pastes containing 0%, 1%, 5%, and 10% TiO₂ were printed on the tapes. Multilayer samples were fabricated by stacking process at 45°C under 2 MPa for 5 min to develop a good adhesion between the layers. Temperature dependence of dielectric constant, ϵ_{33}^T , and loss tangent, $\tan \delta$, of the samples were measured with an automated dielectric measurement system with a multi-frequency LCR meter (HP 4192A). Other piezoelectric properties were measured by the resonance–antiresonance method using an impedance analyzer.

3 Results and discussion

Four types of pastes were prepared from Ag-Pd electrodes containing 0%, 1%, 5%, 10% TiO₂ nano-particle. The pastes were dried and made into a disk shape and then sintered at temperatures from 600°C to 1100°C. The shrinkage of the disk was measured after the sinterings, in order to investigate if its shrinkage can tolerate to that of piezoelectric ceramic material, PZT.

Figure 1 shows the linear shrinkage profiles of dried 70Ag-30Pd pastes without and with 1%, 5%, 10% TiO₂ addition, and PZT ceramics. An apparent sintering mismatch mainly involves the following aspects: (i) the original sintering temperature, (ii) the initial and final sintering temperatures, (iii) the total shrinkage of the materials. The densification of the pure Ag-Pd alloy paste takes place in temperatures of 600°C to 950°C while the PZT ceramic material densifies at

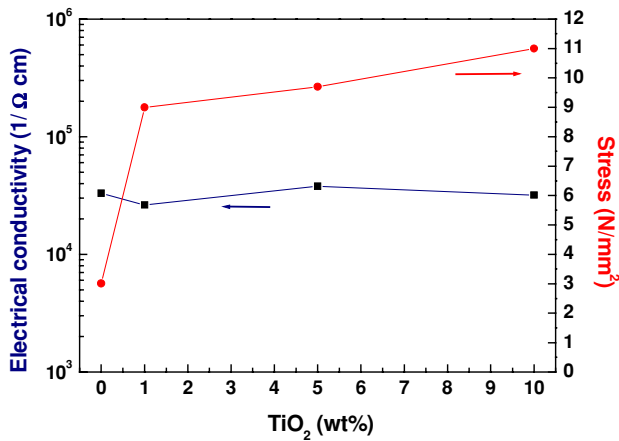


Fig. 3 Electrical conductivity and mechanical adhesion strength to PZT ceramics as function of TiO₂ amount for Ag-Pd electrode

700°C–1100°C. The different shrinkage behaviors also result in the formation of interfacial stress [11]. Adding nano-sized TiO₂ particles allows the sintering behavior of the electrode to be modified. The densification of the TiO₂-added elec-

trode proceeded in higher temperature ranges than that of the Ag-Pd electrode. The 10% TiO₂-added electrode specimen exhibited the shrinkage in the same temperature range, 700–1100°C, as the PZT ceramic. From the Fig. 1, it can be also mentioned that the starting point of shrinkage shifted to higher temperature as the TiO₂ amount increases. It is obvious that the shrinkage profiles for the electrodes are affected by the agglomeration and densification of oxide powder. The densification kinetics and mechanism are determined on the basis of kingery’s analysis for a ceramic-metal-glass composite. The shrinkage results obtained in Fig. 1 are analyzed using the following equation [12].

$$\ln[Td(\Delta L/L_0)/dT] = \ln(1/n K^{1/n}) - 1/n \ln \alpha - Q/(nRT) \tag{1}$$

where $\Delta L/L_0$ is the fractional shrinkage, T is the absolute temperature, n is the exponent, k is the heating rate, Q is the apparent activation energy of sintering and R is the gas constant. The n values are known to be in the range of 1.1–1.3

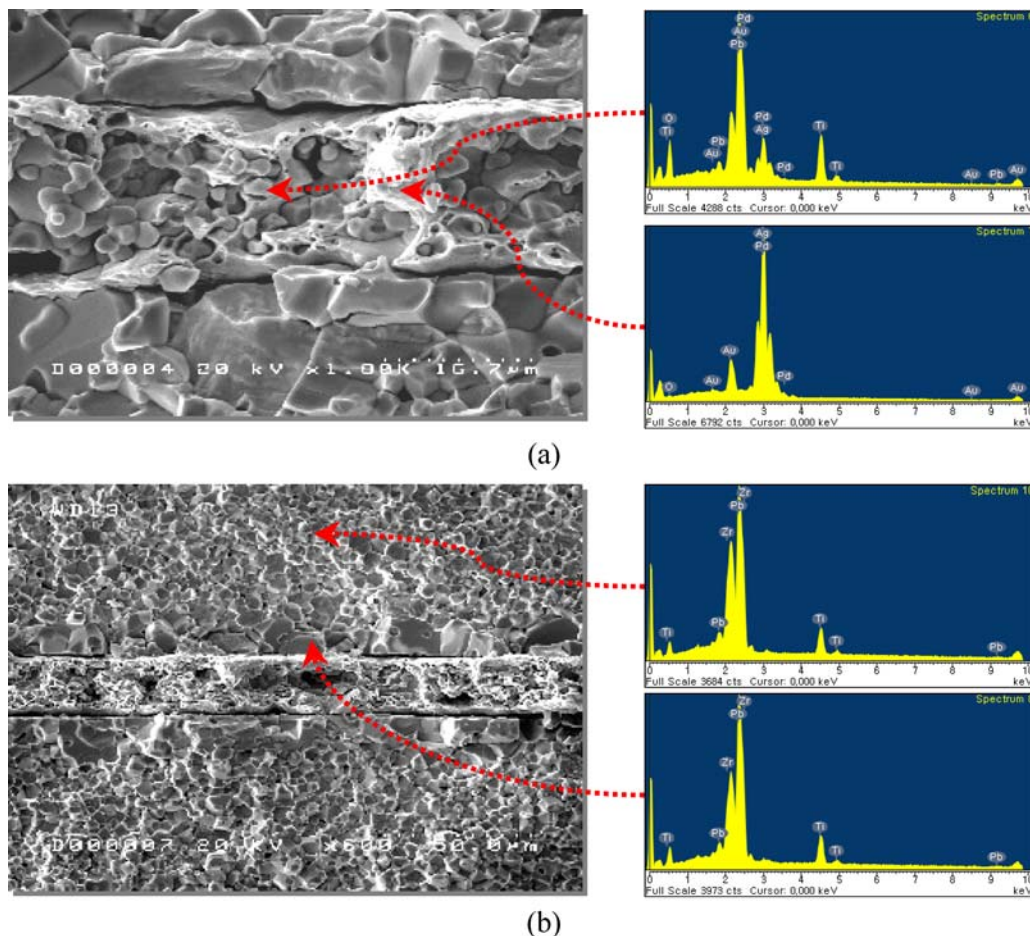


Fig. 4 Scanning electron micrographs showing fractured surfaces of electrode/PZT ceramics and dispersive X-ray spectroscopy analysis of some parts in electrodes/ceramics. (a) shows the existence of

TiO₂ agglomerates within electrode. (b) shows enlarged grains of PZT ceramics located nearby interface compared with inner PZT matrix grains

[13]. Given the n values, the apparent activation energy of densification for TiO_2 -added electrodes can be determined by reconstructing the data in Fig. 1 via Eq. (1) as $\ln [Td(\Delta L/L_0)/dT]$ vs. $1/T$, and the results are shown in Fig. 2. Straight lines are fitted and their slopes are used to determine the apparent activation energies. As the TiO_2 amount increases, the apparent activation energy increases from 30.5 kJ/mol for electrode without the ceramic addition to 85 kJ/mol for 10% TiO_2 added-electrode. The increase in the activation energy indicates that the sintering-related mechanism relies on a process involving the TiO_2 particle diffusion. That is, by adding the considerable amount of nano-sized TiO_2 powder the densification rate of the electrode is affected by the TiO_2 particle's agglomeration rate through diffusion. This TiO_2 contribution allows the shrinkage of the electrode to be closer to that of the PZT ceramic, leading improved level of interface match between electrode and ceramic layers.

Figure 3 is the plot of electrical conductivity versus the ceramic additive TiO_2 amount for the electrodes. A considerable amount (here, 10%) of the ceramic additive did not show to a measurable extent the change in the electric conductivity of the electrode. According to an investigation [10] describing the effect of 0.76 μm BaTiO_2 and PbO ceramic powders to the Ag-Pd electrode materials, it was shown that the electric conductivity significantly decreased with increasing the amount of ceramic additives. The conductivity was below $10 \Omega^{-1} \text{cm}^{-1}$, which is the lowest value possible for use in electrode. However, when TiO_2 with a particle size of 25 nm is added to electrode, the conductivity of electrode remains unchanged in the electrode investigated in this study. The observation of constant electrical conductivity, regardless of the TiO_2 addition, may be related to the microstructure of the TiO_2 particle distribution in Ag-Pd matrix. It was also shown in Fig. 2 that adhesion between the electrode and piezoelectric ceramics increased with the amount of ceramic additive.

The changes in electrical conductivity and bonding strength of material are related to its microstructure, and in the present study is explained by viewing the TiO_2 particle distribution within the Ag-Pd matrix and at interface between the electrode and ceramic layers. Figure 4 shows microstructures of TiO_2 particles within matrix Ag-Pd electrodes. In the electrodes containing 10% TiO_2 , the significant amounts of TiO_2 particles were observed within the matrix. The particles of the oxide grow up to 3–4 μm , and the unlinked agglomerates of TiO_2 could be found within the matrix. Their presence attributes to improved electric conductivity in TiO_2 -added electrode. It was also seen that the interfacial chemical reaction occurs via the diffusion of TiO_2 into the ceramics. Accordingly, TiO_2 -riched PZT grains grow at the interface, evidenced by the energy dispersive X-ray spectroscopy results (see Fig. 4 and Table 1) that TiO_2 concentration is 43.76 at% in a grain near the interface and 30.16 at% in a grain

Table 1 Chemical composition of PZT ceramic grains located near by the interface and inner matrix

Element	Atomic%	
	Inner matrix	Nearby the interface
Ti	30.16	43.76
Zr	16.68	9.99
Pb	53.17	46.25

Table 2 Piezoelectric and dielectric properties of the piezoelectric multilayer devices containing Ag-Pd electrode (a) without additional oxide powder and (b) with TiO_2 powder

	Without TiO_2	With TiO_2
$\epsilon_{33}^T/\epsilon_0$	1716.5	1772.5
$\tan \delta$	0.025	0.03
$K_t(\%)$	49	49.2
$d_{33}(\text{pC/N})$	520	521
$S_{11}^E (10^{-12} \text{m}^2/\text{N})$	7.47	7.21

within matrix, respectively. The chemical reaction resulted in the improved mechanical adhesion obtained in Fig. 3 by employing the pull-off (shear stress) test.

The Piezoelectric and dielectric properties of the piezoelectric multilayer devices, containing Ag-Pd electrode without additional oxide powder and with 10% TiO_2 powder, were listed in Table 2. Both the samples exhibited similar piezoelectric and dielectric properties.

4 Conclusion

Addition of TiO_2 nano-particle allows the sintering behaviors to take place in higher temperatures than Ag-Pd electrode and followed in TiO_2 solid state diffusion, resulting in improved sintering mismatch between electrode to PZT ceramics. The start and final points become shifted to higher temperature range than those of pure Ag-Pd electrode. The formation of TiO_2 agglomerates within electrode is related to the change in electrical conductivity, keeping unchanged irrespective of the oxide amount. In addition, the reaction of some TiO_2 with a PZT ceramic gives rise to high adhesion of electrode to the ceramics. To evaluate the electrode with TiO_2 nano-particle, multilayer piezoelectric devices were fabricated, and their properties were measured. The multilayer device containing nano-particle TiO_2 -added electrode showed the excellent piezoelectric properties, comparable to device containing pure metal electrode without the oxide particle.

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