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Effect of nano-sized TiO_2 powder addition on characteristics of silver–palladium electrodes

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Abstract This study presents the sintering behavior of silver/palladium electrode powders to which have been added TiO_2 nanoparticles, and the effect this additive has on the ability of the electrode to match the characteristics of piezoelectric ceramics, Pb(Zr, Ti)O_3. The densification (shrinkage) of the electrodes was investigated as a function of sintering temperature, and the reaction between the ceramic matrix and the electrodes was studied. The densification of the TiO_2-enhanced electrode paste during the sintering process was explained with reference to a solid-state diffusion mechanism which integrated the TiO_2 into the ceramic. Reactions occurred between the ceramic and electrode layers, resulting in reduced internal stress and enhanced mechanical adhesion. Based on these results, it is clear that high adhesive strength and good electrical conductivity of more than $10^4/\Omega$ cm can be obtained in multilayer ferroelectric devices composed of stacks of ceramic and electrode layers provided the contain these nanoparticles. In the sintering process, interfacial diffusion of TiO_2 occurred and, as a consequence, coarse grains of PZT were formed at the interface.

Introduction

Multilayer ferroelectric devices are usually fabricated using a process that involves coating a ceramic sheet with electrodes followed by a co-firing heat treatment process. During the fabrication of such multilayer devices, the electrode material must be able to tolerate the co-firing process, maintaining its integrity at sintering temperatures of up to 1100–1400°C. Silver/palladium (Ag–Pd) has been widely used as an electrode material in processes involving heat treatments above 960 °C. Numerous studies have shown, however, that during the fabrication of multilayer devices, various defects nucleate and grow at the interface between the electrode and the ferroelectric ceramic layers [1, 2]. This is of particular concern during the co-firing process, when a mismatch in the sintering of the two materials (the ceramic and the electrode) can cause interfacial de-lamination, cracking and other defects [3, 4]. One way of avoiding this problem and reducing interfacial defects [5, 6] in multilayer devices is by modifying the co-firing kinetics. This paper offers one possible solution to such problems which involves the addition of a small amount of ceramic powder to the metal electrode. This allows devices to be successfully fabricated by decreasing the difference between the amount of shrinking in the ceramic and electrode layers during co-firing. The method allows the avoidance of cracks and de-lamination at the interface between the ceramic and electrode layers [7–9]. In addition, it is possible to ensure strong adhesion between the ceramic and electrode layers in multilayer ferroelectric devices which are generated in this manner by permitting control of the interface reaction. This reaction, however, which

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occurs as a result of diffusion at the boundary, results in the construction of a skeleton structure of ceramic oxide within the electrode, which in turn results in low electrical conductivity [10]. Avoiding this outcome is, however, possible. By controlling the sintering of nanosized ceramics within the electrode, a modification of the geometric distribution of the ceramic powder in electrode matrix can be achieved, and good electrical conductivity maintained.

The objective of this study is to investigate the effect of the addition of nanosized TiO_2 to Ag–Pd electrodes on their properties and their sintering. TiO_2 was chosen because it has a high level of adhesion and chemical stability when bonded to piezoelectric ceramics (typically $Pb(Zr,Ti)O_3$, known hereafter as PZT), being a member of the (electrically conductive) oxide family: ZrO_2, TiO_2, SnO_2, Sb_2O_5, ZnO, In_2O_3 and MoO_3 [11]. The electrode to which the TiO_2 was added was coated onto a piezoelectric ceramic material and then subjected to the sintering process. This article describes the shrinkage characteristics and microstructural modification of the electrodes as a result of that process. Their electrical conductivity and mechanical adhesion to a piezoelectric ceramic sheet was evaluated, with special consideration being given to their microstructural evolution.

Experimental Procedure

PZT piezoelectric ceramic powders were prepared from approximate amounts of reagent-grade PbO (Cerac Incorporated, 325mesh, 99.9%, Japan), ZrO_2 (Cerac Incorporated, 325mesh, 99.7% Japan), and TiO_2 (Cerac Incorporated, 325mesh, 99.9% Japan). The columbite method was used to synthesize the ceramic powders in order to eliminate the formation of a pyrochlore-type phase. The PZT powder, with the addition of 5% $Pb(MgNb)O_3$, could be completely sintered by maintaining it at 1100 °C for 2 h.

Titanate ceramic additives with a particle size of ~25 nm (Degussa, P25, Japan) were also prepared. This additive was uniformly dispersed in the 70Ag–30Pd alloy electrode paste in different ratios by attrition milling. The silver–palladium alloy pastes, which contained a mixture of silver/palladium alloy particles, an organic vehicle, and a glass-frit powder (BiO–SiO_2–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 were pressed under 1.5 kgf/cm^2 and used to measure the sintering densification characteristics as a function of sintering temperature. The characteristics were measured in air at a heating rate of 5 °C/min using a thermomechanical analyzer (TMA, 2940, Dupont Instrument.).

Slurries for tape casting were made by mixing the calcinated powders with the 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 a small-scale caster with a doctor blade. The four types of silver/palladium electrode pastes, containing 0%, 1%, 5%, and 10% TiO_2, respectively, were deposited on these tapes. The sintered samples were used to observe the inner and interfacial microstructures.

An X-ray diffractometer (XRD, 200 Philips Co.) which utilised CuK$_\alpha$ radiation was used to identify the chemical reactions between the silver/palladium and the ceramic additive. The electric properties of the electrode samples containing the additive were determined using an analysis based on a modified version of Ohm's Law. The grain morphology and interfacial microstructure of the samples sintered at 1100 °C were observed using scanning electron microscopy (SEM, S2700, Hitachi).

Results and discussion

Four types of pastes were prepared from which the electrodes were formed. They were made by adding 0%, 1%, 5% and 10% TiO_2 nanoparticles, respectively, to Ag–Pd. The pastes were dried and formed into a disk shape, and then sintered at temperatures from 600 °C to 1100 °C. The shrinkage of the disk was measured after the sintering, in order to investigate whether the amount of shrinkage would be compatible with that of a piezoelectric ceramic material, PZT.

Figure 1 shows the linear shrinkage profiles of the dried Ag/Pd pastes with 0%, 1%, 5%, and 10% TiO_2, respectively, and the profile for the PZT ceramic. There are three important aspects of the sintering process which need to be considered when investigating the possibility of a sintering mismatch between the electrodes and the ceramic on which they are being deposited. These are (i) the original sintering temperature, (ii) the initial and final sintering temperatures, (iii) the total shrinkage of the material during sintering. The densification of the pure silver/palladium alloy paste takes place at temperatures from 600 to 950 °C, while the PZT ceramic material

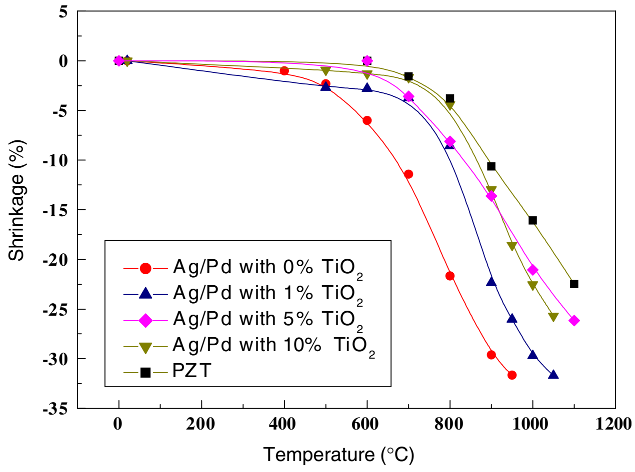


Fig. 1 Shrinkage as a function of sintering temperature for dried 70 Ag/30Pd paste with various quantities of TiO_2 powder added

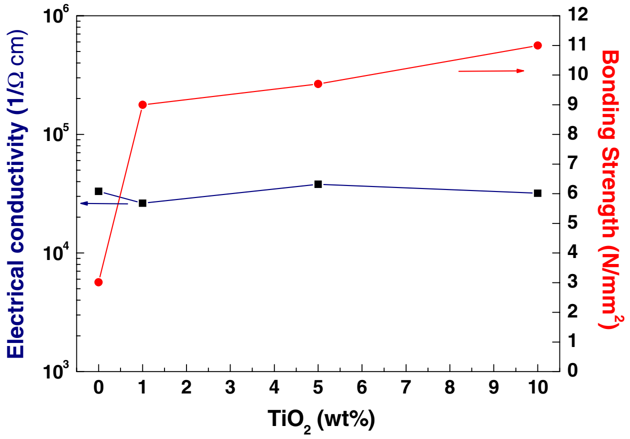


Fig. 2 Electrical conductivity and mechanical adhesion to PZT ceramics as a function of TiO_2 amount for a 70%Ag/30%Pd electrode

densifies at 700–1100 °C. There is also a shrinkage mismatch between the two materials, which results in the formation of interfacial stresses and warping deformations [12]. If TiO_2 with a particle size of 25 nm is added to the electrode material, however, it can be seen that the sintering behavior of the electrode is modified. The densification of the TiO_2-enriched electrodes proceeded in higher temperature ranges than that of the pure silver/palladium electrode. The specimen containing 10% TiO_2 exhibited shrinkage in the same temperature range (700–1100 °C) as the PZT ceramic. A closer investigation of Fig. 1 makes it clear that the starting point for the shrinkage shifted to higher temperatures as the quantity of TiO_2 was increased. It is apparent from this that the shrinkage profile of the TiO_2–silver/palladium mixture was affected by the agglomeration and densification of oxide powder. That is, the addition of the ceramic powder to the Ag–Pd retarded the shrinkage of the electrode, which should result in a better sintering match between the electrode and the PZT ceramics.

Figure 2 shows a plot of electrical conductivity versus the amount of ceramic additive in the electrodes. A small amount of the TiO_2 (here, up to 10%) did not make any measurable difference to the electric conductivity of the electrode. The fact that the electrical conductivity was constant, regardless of the addition of TiO_2 to the electrodes, may be related to the microstructure of the TiO_2 particle distribution in Ag–Pd matrix. This possibility is investigated further below. Figure 2 also shows the result of a test which measured the adhesive force between the electrode and piezoelectric ceramics. In this case, it is clear that the bonding strength increases with the amount of TiO_2 added.

To understand the shrinkage, and electrical and mechanical characteristics observed electrode material enriched with nanosized TiO_2 particles, the densification mechanisms and microstructural evolution of the electrodes were next investigated.

The densification mechanism and kinetics were determined on the basis of Kingery's analysis for a ceramic–metal–glass composite. The shrinkage results obtained in Fig. 1 were analyzed with reference to the following equation [13].

$$\ln[T\,d(\Delta L/L_0)/\mathrm{d}T]=\ln(1/nK^{1/n})-1/n\ln\alpha-Q/(nRT) \qquad (1)$$

where $\Delta L/L_0$ is the fractional shrinkage, T the absolute temperature, n the exponent, K the heating rate, Q the apparent activation energy of sintering and R the gas constant. The n values for these substances are known to be in the range of 1.1–1.3 [14]. Given these, the apparent activation energy of densification for the TiO_2-enriched electrodes can be determined by re-plotting the data from Fig. 1 in the form ln $[T\ \mathrm{d}(\Delta L/L_0)/\mathrm{d}T]$ versus $1/T$. The results are shown in Fig. 3. Straight lines were fitted to the data sets, and their slopes were used to determine the apparent activation energies (Q). The pure silver/palladium electrode shows Q = 30.5 kJ/mol, a value which increased to Q = 85 kJ/mol for the 10% TiO_2-enriched electrode specimen. This increase in the activation energy indicates that the densification which occurs during sintering changes from a process which relies on Ag–Pd metal solid-state diffusion to one which is controlled by the rate of TiO_2 particle diffusion. That is, by adding a considerable amount of nanosized TiO_2 particles (in this case 10%) the rate of densification of

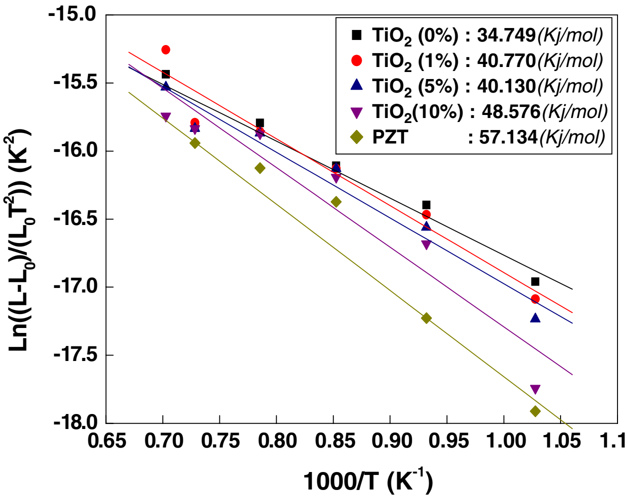


Fig. 3 Kinetic behaviour of silver/palladium electrode pastes with and without added TiO_2

the electrode begins to be controlled by the agglomeration rate of the TiO_2 particles. As a consequence, the shrinkage of the electrode becomes much closer to the shrinkage which occurs during sintering of the PZT ceramic. This in turn leads to an improved level of matching between the electrode and ceramic interfaces compared to that which usually occurs.

Figure 4 shows the X-ray diffraction patterns from as-dried, 600 °C and 1100 °C sintered 70Ag/30Pd paste specimens with 10% TiO_2. All specimens exhibited diffraction peaks characteristic of TiO_2. In fact, the diffraction pattern from the as-dried specimen showed evidence of two forms (rutile and anatase) of this crystal. After 1100 °C sintering, however, only peaks characteristic of the rutile phase were observed. This implies that a phase transition occurred during the heat treatment of the electrodes. The TiO_2 experiences sintering behavior and is transformed into one stable phase, which has a rutile structure. Similarly, while in the case of the as-dried specimen peaks characteristic of Ag, Pd and of the Ag–Pd alloy were observed, after 1100 °C sintering only the silver/ palladium alloy peaks were evident [15–17].

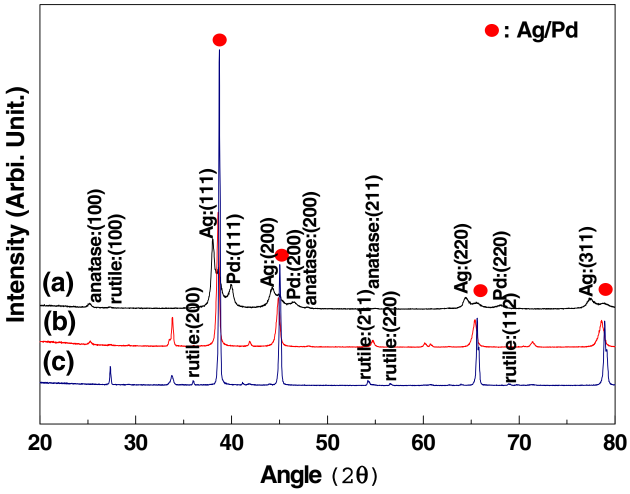
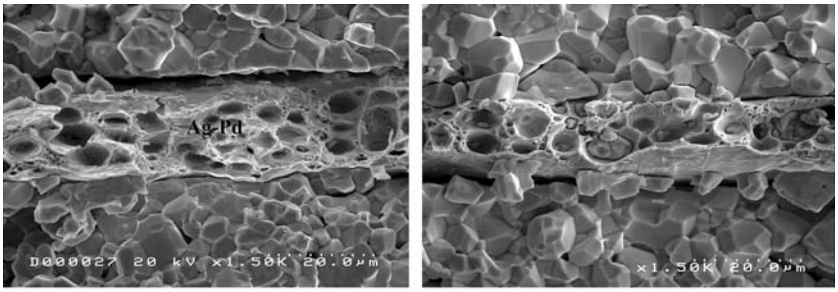


Fig. 4 X-ray diffraction patterns of (**a**) 25 °C dried, (**b**) 600 °C sintered and (**c**) 1100 °C sintered 70 Ag–30Pd pastes with 10% TiO_2

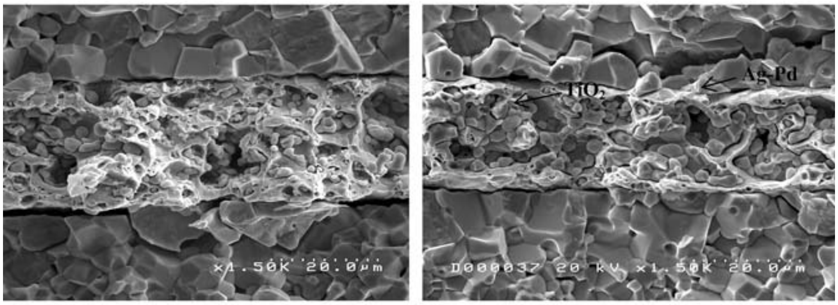
Changes in the electrical conductivity and bonding strength of any material are strongly related to its microstructure, and in this case provides evidence of the TiO_2 particle distribution within the Ag–Pd matrix and at the interface between the electrode and the ceramics. Figure 5 shows various TiO_2 particle microstructures within the matrix of the Ag–Pd electrodes. Figure 5a–d show the scanning electron micrographs for 0%, 1%, 5% and 10% TiO_2-enriched Ag/Pd electrodes. In the 0% electrode specimen, many voids were observed in the electrode matrix due to the difference in the rate of shrinkage between the electrode and PZT ceramic. The 1% TiO_2-enriched specimen (Fig. 5b shows evidence of TiO_2 particles in a few places. The specimens with 5% and 10% TiO_2 can be seen to have a significant number of TiO_2 particles within the matrix. Their unlinked agglomerates are also visible (see Fig. 5c, d), and have a particle size of 3–4 μm. That is, TiO_2 particles with an agglomerate structure were found within the matrix. Their presence contributed to the improved level of electric conductivity in the TiO_2-enriched electrode.

It was also found that microstructural modification occurs at interface between the electrode and the ceramic due to interfacial diffusion of the elements Ti, Ag and Pb. The energy dispersive X-ray spectrum intensity was measured at the interface for two specimens which had been sintered at 1100 °C. For each specimen, one of which had TiO_2 added to the electrodes while the other did not, the intensity ratio of the TiKα line relative to (PbMα + TiKα + ZrLα) was calculated. The ratio Ag:Ag_{max} was also calculated for each specimen, and the results compared (see Fig. 6). From this figure, it can be seen that in the specimen which contained additional TiO_2, the intensity ratio of the TiKα line at a point 10 μm from the interface was approximately 0.28. The value when measured far from the interface was less than 0.25. In contrast, the specimen without TiO_2 had an intensity ratio for the Ti line which was almost constant in all areas of the PZT ceramic. It is suggested that these results can best be understood by assuming that a chemical reaction occurs between the electrode and the PZT due to Ti diffusion.

Fig. 5 Fracture image of 1100 °C sintered PZT ceramics and 70Ag–30Pd electrodes containing (**a**) 0% TiO_2 (**b**) 1% TiO_2 (**c**) 5% TiO_2 and (**d**) 10% TiO_2



(**a**) 0 % TiO_2 (**b**) 1 % TiO_2



(**c**) 5 % TiO_2 (**d**) 10 % TiO_2

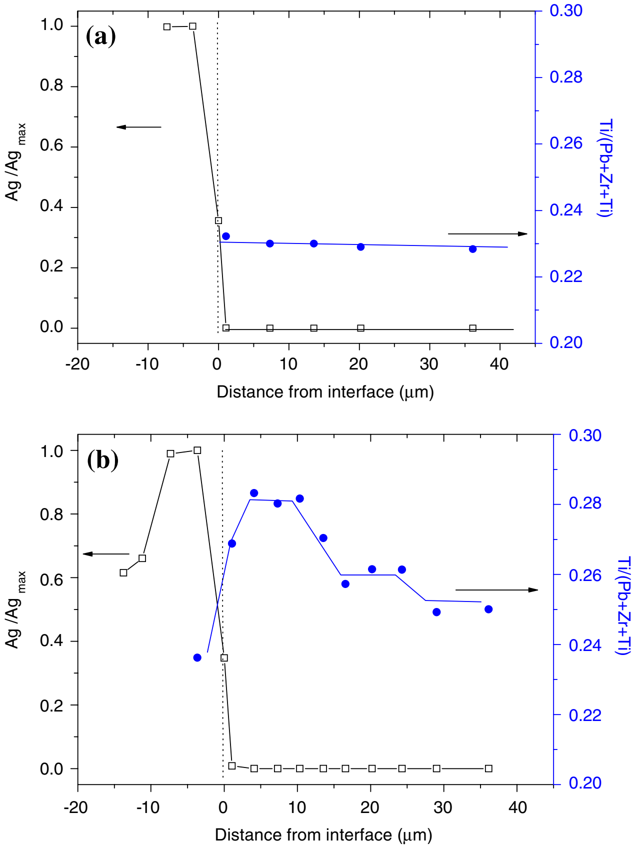
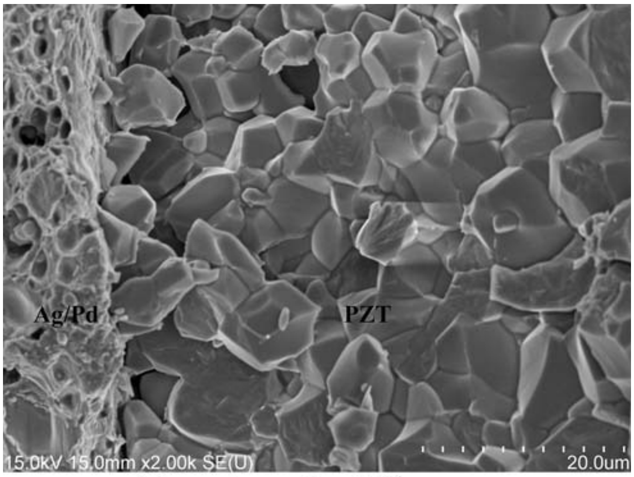


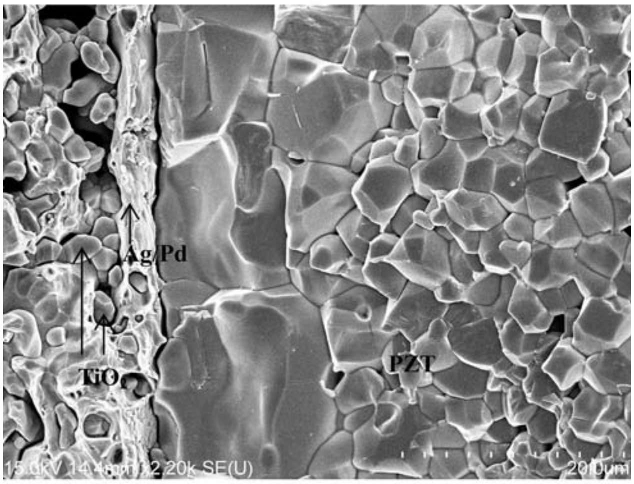
Fig. 6 Spatial variation in the relative intensity of Ag/Ag_{max} ratio (□) and Ti/(Pb + Zr + Ti) ratio (•) in the specimen (**a**) without TiO_2 and (**b**) with TiO_2

In addition, the specimens containing TiO_2 were observed to have coarser PZT grains (grain size over 20 µm) at the interface than that in the PZT matrix (grain size of 5 µm). This is demonstrated in Fig. 7, which shows scanning electron micrographs of the interface for two specimens, only one of which had TiO_2 added to the electrodes. It is obvious from this that the interfacial diffusion of TiO_2 enhances the PZT grain growth at the interface and thus its bonding strength. The effect of Pb and Ag diffusion at the interface was also examined. Considering the fact that the intensity of Pb and Ag at the interface is almost the same as the intensities for these species in the electrode and in the PZT matrix, it is thought that diffusion of these two elements do not occur to a significant extent.

It has been reported in a previous investigation [10] that the formation of an additive ceramic skeleton structure resulted in a decrease in the electrical conductivity and an increase in the mechanical bonding between interfaces similar to those investigated here. In that study, the effect of mixing 0.76 µm $BaTiO_2$ and PbO ceramic powders with Ag/Pd to form new electrode materials was explored, and it was shown that the electric conductivity significantly decreased as the amount of ceramic in the electrode increased. In fact, the conductivity dropped below $10^{-4}\ \Omega^{-1}\ cm^{-1}$, which is the minimum value possible for use in a material which is acting as an electrode. In the present study, however, enhancement in both the conductivity



(a) specimen without TiO_2



(b) specimen with TiO_2

Fig. 7 Scanning electron micrographs showing fractured surfaces of electrode/PZT ceramics for specimens (**a**) without and (**b**) with TiO_2

and strength of the mechanical bonding was observed. This difference, especially the difference in the conductivity, implies that the microstructure in the case of the addition of nanosized ceramic particles is different to that of electrodes containing submicron-sized additives. The microstructural variation is affected by the sintering behavior of the electrode and the resultant densification process. This investigation into the addition of nanosized TiO_2 suggests that the electrical and mechanical characteristics of the electrode can be controlled by manipulating the sintering behavior and geometric distribution of TiO_2 in the electrode.

Conclusion

The addition of nanometer sized particles of TiO_2 to Ag–Pd allows the sintering behaviors of this electrode material to take place at higher temperatures than for Ag–Pd alone, and results in the diffusion of TiO_2 across the interface between the electrode and the (PZT) ceramic on which it is deposited. This diffusion results in an improved sintering match between the electrode and the PZT ceramics. The initial and final sintering temperatures were shifted to a higher temperature range than that typical of the pure Ag–Pd electrode case. The formation of TiO_2 agglomerates within the electrode have an influence on the electrical conductivity of the specimen, regardless of the amount of oxide added. In addition, the reaction of some of the TiO_2 particles with the PZT ceramic itself gives rise to enhanced adhesion of the electrode to the ceramic.

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