Improvement of Mechanical Properties of Piezoelectric Ceramics by Incorporating Nano Particles

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SYNOPSIS

Lead zirconate titanate (PZT) based composites were prepared from commercially available PZT powder and a small amount (0.1 - 1.0 vol%) of nano-sized alumina or magnesia, and their mechanical and piezoelectric properties were evaluated. The fracture strength of the composites increased with increasing second phase content due to grain size reduction, particularly in the case of PZT/MgO composites, which showed a significant improvement in strength. The planar electromechanical coupling factor, Kp, of the composites remained unchanged. As a consequence, highly reliable PZT composites with high strength (140 MPa) and Kp (60%) have been fabricated.

KEY WORDS

PZT, nano composites, mechanical properties, microstructure, piezoelectric properties

1 Introduction

Because of their high piezoelectric properties, PZT and related materials are widely used for electromagnetic filters, resonators, actuators and so on. In the application of actuators, high reliability is especially important, because high stresses are applied from the large displacement of the PZT. However, PZT with suitable piezoelectric properties typically has poor mechanical properties, e.g., low Young’s modulus (60 – 80 GPa), fracture toughness (0.6 – 1.0 MPa m^(1/2)) and fracture strength (50 – 70 MPa). Several attempts to improve the mechanical strength of PZT based composite systems have been reported in the literature. In PZT/Ag [5], PZT/SiC [6] and PZT/ZrO₂ [7] systems, high strength ceramics have been successfully prepared. However, the piezoelectric properties, in particular, the planar electromechanical coupling factor, Kp, of the composites decreased to levels insufficient for their application as actuators. We have previously reported that microwave sintering and reinforcement by a small amount of second phase particles successfully maintain Kp and improve the mechanical properties of PZT based nanocomposites [8]. It was found that a little as 0.1 - 0.5 vol% of second phase is sufficient to improve the strength of PZT ceramics, and the reduction in Kp was minimal because the amount of second phase was small. However, as a result of using high purity and non-modified PZT (Pb(Zr₀.₅₂Ti₀.₄₈)O₃) with low Kp as the base material in these studies, the Kp of the composites was less than 40%, which is not large enough for high power actuators.

The purpose of this study is to obtain PZT based composites with high strength and suitable Kp for actuator applications. To achieve this target, commercially available hard PZT powder, which is expected to have a higher Kp, was selected as the matrix material. The effect of the small amount of second phases on the mechanical/piezoelectric properties and microstructure were investigated.

2 Experimental Procedures

The starting material for the matrix was commercially available PZT (PZTHQ, Sakai Chemical Industry Co. Ltd., Sakai, Japan). This PZT powder is modified to give a high mechanical quality factor (Qm; about 1500) and Kp (> 60%). The mean particle size of the PZT was 0.3 µm and the Zr:Ti atomic ratio was 50:50. As the second phase, Al₂O₃ (TMDA-R, Taimei Chemicals Co. Ltd., Nagano, Japan) and MgO (100A, Ube Chemical Industries Ltd., Ube, Japan), with average particle sizes of 100 nm and 15 nm respectively, were used in this study. The additive content of the second phase was between 0.1 and 1.0 vol% of the PZT matrix. The starting materials were mixed by wet ball-milling for 24 h in isopropyl alcohol using ZrO₂ balls. Disc shaped specimens (17 mm in diameter and 2.5 mm in thickness) were formed by uniaxial pressing at 5 MPa followed by cold isostatic pressing (CIP) at 196 MPa.
specimens were sintered at 1200 °C for 2 h in an alumina crucible under PbO atmosphere using a conventional electric furnace. For electrical measurements, sintered specimens were ground and lapped to 1 mm in thickness, and silver paste was printed on both sides of each disc, followed by firing at 600 °C for 10 min. Poling treatment was carried out in silicon oil at 120 °C for 30 min with an electric field of 3 kV/mm.

The bulk density was determined by Archimedes' method in water. The dielectric constant at 1 kHz was measured using an impedance analyzer (Model 4194A, Hewlett-Packard Co. Ltd., Tokyo, Japan). The planar electromechanical coupling factor, Kp, was calculated by the resonance method. The tetragonality (c/a) of the PZT phase was determined by XRD analysis using the (200) and (002) peaks of tetragonal PZT(JCPDS33-0784). The fracture strength of the unpoled disc-shaped samples (1.7 mm in thickness) was measured by the piston-on-ring biaxial flexure test. It has been confirmed that the strength value by this method is almost the same as the 4-point bending test using standard alumina specimens. Fracture toughness were measured by the indentation fracture (IF) method. Fracture surfaces and microstructure were observed with a scanning electron microscope (SEM). The average grain size of each composite was estimated from SEM micrographs by a linear intercept method.

3 Results and Discussion

Table 1 shows some physical, dielectric, and piezoelectric properties of monolithic PZT and PZT composites. Almost fully dense bodies can be obtained by sintering at 1200 °C for 2 h. Addition of the second phases did not degrade the sinterability of the ceramics. The densities of composites containing Al2O3 or MgO were slightly higher than those of monolithic PZT. The dielectric constants of PZT/Al2O3 composites were higher than those of monolithic PZT; those of PZT/MgO composites increased initially up to 1710 with an addition of 0.1 vol% MgO, but thereafter decreased gradually with increasing MgO content. These differences in density and dielectric constant with second phase addition seem to be due to microstructural changes, such as a change in grain size of the composites. Fig. 1 shows the grain size dependence of the dielectric constants of monolithic PZT and PZT composites containing Al2O3 and MgO. As is evident from Fig. 1, the value of the dielectric constants depends significantly on the grain size of the specimens, and decreases as the grain size decreases, irrespective of the additive species. On the other hand, the reduction in Kp of the composites was not so significant, and it remained over 60% in all samples. It is well known that the Kp of PZT ceramics is easily altered by compositional modifications. If Al2O3 or MgO form a solid solution with Pb(Zr,Ti)O3, the Al3+ and Mg2+ ions should substitute for Zr4+ or Ti4+ in the perovskite crystal structure. Since substitution of lower valence ions produces oxygen vacancies to maintain charge neutrality, it also results in the reduction of the tetragonality and hence piezoelectric behavior of PZT ceramics. However, this was not found to be the case in the present study.

Fig. 2 shows the tetragonality (c/a) change with MgO and Al2O3 content of our PZT composites. There was no significant decrease in the tetragonality of the PZT/Al2O3 composites, while in the case of 0.1 vol% MgO, the tetragonality was actually a little bit higher than that of monolithic PZT. The small decrease of the tetragonality in 0.5 or 1.0 vol% MgO containing composites might be due to the grain size reduction, because the tetragonality slightly decreased on further addition of MgO. These results suggest that Al3+ or Mg2+ do not substitute for B-site atoms, and consequently, high Kp can be maintained even though non-ferroelectric particles such as Al2O3 or MgO are incorporated in the PZT matrix.

![Fig. 1. Grain size dependence of dielectric constants for PZT and PZT composites.](image-url)
The fracture strength of the composites increased with increasing second phase addition in all samples, as shown in Fig. 3. In the case of 0.5 and 1.0 vol% MgO containing composites, the strength was 140 MPa, which is much higher than that of monolithic PZT (93 MPa). This improvement in strength might be associated with the grain size reduction. In general, PZT ceramics with finer grain structure show higher fracture strength just as in other ceramic systems. Fig. 4 shows the fracture surface of the monolithic PZT and PZT composites. A completely intergranular fracture mode was observed in monolithic PZT, but it switched to intragranular fracture in the PZT composites. This change in fracture mode suggests that the grain boundaries of the composites are reinforced by the dispersoids. Second phase dispersoids can be found in both Al₂O₃ and MgO added composites. Fig. 5 shows the second phase particles in a PZT/Al₂O₃ composite. The secondary particles were dispersed at the grain boundary as well as inside of the PZT grain. As mentioned previously, although the grain size increased in Al₂O₃ containing composites, their strengths were slightly higher than that of monolithic PZT. It is assumed that grain boundary reinforcement and fracture toughness increase (Fig. 6) due to the secondary particles are responsible for the high strength. The fracture toughness increase in PZT/Al₂O₃ composites would be explained as an effect of crack deflection due to the enlarged grain size. Determination of

![Fig. 2](image) Tetragonality (c/a) of the PZT crystal lattice as a function of second phase content of PZT composites.

![Fig. 3](image) Flexural strength of PZT and PZT composites.

![Fig. 4](image) Fracture surfaces for (a) monolithic PZT, (b) PZT/0.5 vol% Al₂O₃ composite and (c) PZT/0.5 vol% MgO composite.
5 Acknowledgement

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References
8) ASTM Standard F393-78.


