Characterization and Microstructure of PLZT RAINBOW Ceramics

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Abstract: A new type of large displacement actuating materials called RAINBOW (Reduced and Internally Biased Oxide Wafer) ceramics is fabricated by a chemical reduction of PLZT piezoelectric ceramics. It is found that PLZT is easily reduced and the thickness of reduced layer has a linear relationship with the reduction time. The optimal conditions for producing RAINBOW samples from PLZT are determined to be 950°C for 1-1.5 hours. SEM micrograph shows that the RAINBOW ceramics are composed of reduced and unreduced layer obviously. And the reduced layer is transgranularly fractured while the unreduced ceramic is intergranularly fractured. Metallic lead and refractor oxides (PbO, ZrO$_2$, ZrTiO$_4$, etc.) are found in the reduced layer by XRD analyses, however, the crystal structure of PLZT is not found. The analysis of the reduction mechanism is in good accordance with experimental data.

Key words: actuating material; RAINBOW; chemical reduction; piezoelectric ceramic; reduction mechanism

During the past several years, piezoelectric ceramics for actuators have received numerous investigations and undergone remarkable advances[1]. Traditional piezoelectric ceramics offer many advantages including quick response, high-induced stress, low energy consumption and low cost, which make them very attractive for a number of applications. However, the electric field-induced strains from piezoelectric ceramics are relatively small, which considerably limits their use. To achieve a higher displacement from the ceramics, a number of strain magnification mechanisms have been employed. Examples include the traditional unimorph and bimorph benders, and the "moonie" microstructures[2][5]. However, an increase of induced displacement is achieved at the expense of lowering generated stress significantly. The most recently developed strain amplifying method for piezoelectric ceramics which shows promise for meeting many applications is known as the RAINBOW technology[6,7]. This acronym denotes the basic active microstructure of the RAINBOW device, which is produced by a special high temperature chemical reduction process and stands for Reduced And Internally Biased Oxide Wafer. In their most basic sense, RAINBOW ceramics can be...
thought of as pre-stressed, monolithic and axial-mode benders. Because of their unique dome or saddle-like configuration, RAINBOW ceramics are able to produce much higher displacements and sustain significantly greater loads.

Since the excellent actuating properties of the RAINBOW actuators are dependent upon the physical properties of RAINBOW ceramics, a thorough investigation of the characterization and microstructure of reduced PLZT ceramics is significant for the application of RAINBOW ceramics in the nearly future. In this paper, the phase components and microstructure as well as the reduction mechanism of PLZT RAINBOWs are studied in detail.

1 Experimental Procedure

The RAINBOW samples used are prepared from PLZT (Pb0.98La0.01(Zr0.53Ti0.47)O3) ceramics. The ceramic wafers (Ø20 × 0.5) obtained from PLZT slugs are chemically reduced by placing them on a graphite block and heat treating in some conditions. After reduction, samples are quenched to room temperature in air, which makes samples have a highly stressed dome shape as seen in Fig. 1.

![Fig. 1 Schematic of RAINBOW ceramics](image)

Fractured and polished surfaces of the samples are used in both XRD and SEM analyses. For X-ray diffraction, the reduced side of the RAINBOWs are lapped off approximately 10μm and slightly expose the internal structures. This procedure is employed because a thin reoxidized layer is often formed on reduced surfaces during processing. Cross-sectional surfaces of RAINBOW samples are used for SEM analysis in this study. The fractured surfaces are obtained by breaking the RAINBOWs along their diameters. To prove the reduction mechanism put forward in this article, the SEM micrograph of the reduced layer’s porous structure and the change of element components of ceramics resulting from reduction are given. All of the X-ray diffraction experiments are performed on an X-ray diffratometer (D/MAX-rC) with Cu Kα radiation at a rate of 2° per minute, while a scanning electron microscope (JSM-6300) operating at an acceleration voltage of 15kV is used for the microstructure analyses.

2 Experimental Results

In order to operate properly, the reduced layer should have a suitable ratio to the unreduced PLZT. Temperature and reducing time are important factors in controlling the reduction process during fabrication of RAINBOW ceramics. The relations between reduced thickness and time at high temperature depend on the material itself.

Fig. 2(a) shows the reduced layer thickness of the PLZT ceramics as an appropriately linear function of reduction temperature for one hour. Fig. 2(b) shows the change of the reduced layer thickness with time at a constant temperature of 950°C for the PLZT sample. A nearly linear relationship

![Fig. 2 Variation of thickness of PLZT reduced layer with reduction conditions](image)
is also observed. Generally, at very high temperatures, the rapid reaction in PLZT ceramics leads to the loss of a large portion of lead phase from the reduced layer. However, a very low temperature implies impractical and long reduction time. It is found that the useful temperature range for the reduction is actually very narrow, approximately 920-1000°C. The optimal conditions for producing RAINBOW samples from PLZT ceramics in this study are determined to be 950°C for 1-1.5 h.

2.1 Reduced Layer of RAINBOW Ceramics Samples

Fig. 3 shows the X-ray diffraction patterns from the surface of the reduced layer of RAINBOW samples. It is found that the strongest peak in the diffraction patterns is produced by the metallic lead phase. The remaining weaker peaks are oxide phases formed during the reduction process. As is indicated in the figure, the oxide phases identified include PbO, ZrO₂, LaTiO₃ and ZrTiO₄. In addition, a micrograph of higher magnification on the reduced region surface, which is given in Fig. 4, indicates that the layer is composed of various fine-grained particles. These small uniformly distributed particles are believed to be Pb grains, which account for the good conductivity of reduced layer of the RAINBOW.

2.2 Cross section of RAINBOW ceramics samples

Fig. 5 shows the SEM micrograph of the fractured cross-section of the RAINBOW. The left portion of the micrograph shows the reduced layer, and the right portion is the unreduced layer. Two layers are separated by an interface where both the unreduced and reduced phases are revealed. From the reduced layer to the unreduced layer, as seen in Fig. 6, the transgranular fracture is replaced by the intergranular fractured step by step. The difference of the fracture behavior is believed to be the result of an initial modification of the grain boundaries in the form of lead oxide’s loss and the reduction from the grain boundaries. This process is the first stage of the reduction process, with the second stage being the full reduction of the PLZT grains.

![Fig. 3 X-ray diffraction patterns of the reduced layer](image)

![Fig. 4 SEM micrograph of the reduced layer](image)

![Fig. 5 SEM micrograph of the RAINBOW ceramics cross section](image)
3 Reduction mechanism

The thickness of reduced layer is determined by the thermodynamics and kinetics of the reduction process. It is found that, in the case of oxidation of metals or reduction of oxide solids, the reaction kinetics is controlled by surface and interface reaction at initial stage of reaction processed when the reduced layer is less than 5µm thick\(^8\). The reaction rate is then independent of reduction layer thickness. If the reaction product is porous or with channel microstructure through which gaseous species can easily pass, the interface reaction will be the rate-controlling process and thus a linear relationship between thickness and time can be obtained. However, if the formed layer has a dense microstructure, diffusion of reaction species through the product layer may become the rate-controlling process, and in this case a parabolic law is followed\(^9\). In this study, the reduced layer of RAINBOW samples has a micro-channel and porous structure as seen in Fig. 7, which accounts for PLZT’s linear reduction behavior depicted in Fig. 6.

Fig. 6 SEM micrograph of the fracture of the RAINBOW ceramics

Fig. 7 SEM micrograph of the reduced layer’s porous structure

Fig. 8 schematically shows the general chemical reactions occurring in the fabrication for the RAINBOW ceramics. Obviously, the liberation of oxygen results in the formation and diffusion of oxygen vacancies. As reduction reaction proceeds at elevated temperatures, more and more oxygen will be consumed. Some PLZT ceramics will become semiconducting due to the loss of oxygen and the formation of weakly trapped electrons\(^10\). Some PLZT ceramics will be decomposed to mixture of oxides such as PbO, ZrO\(_2\) and so on. Some metal Pb will be formed and located intergranularly in reduced layer. This leads to the metallic conduction behavior and the transgranular fracture type of reduced layer. Deduction above can be testified by the change of the element components of ceramics during the reduction. Table 1 offers the element components of the RAINBW sample’s surface, from which it is found that the reduced layer has fewer Pb and O but more Ti and Zr as compared with the unreduced layer. This experimental outcome is in good accordance with the chemical reactions during the reduction of the RAINBOW listed in Fig. 8.

Fig. 8 Chemical reactions occurring in the fabrication of the RAINBOW ceramics
Table 1  The main element components of the RAINBOW
ceramics sample’s surface

<table>
<thead>
<tr>
<th>Surface</th>
<th>Element atomic ratio/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Reduced layer</td>
<td>32.92</td>
</tr>
<tr>
<td>Unreduced layer</td>
<td>48.93</td>
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</tbody>
</table>

4 Conclusions

In summary, PLZT is easily reduced piezoelectric ceramics whose reduced layer thickness has a linear relationship with the reduction time. The optimal conditions for producing RAINBOW samples from PLZT ceramics are determined to be 950°C for 1-1.5 hours. A number of different phases have been found in the reduced layer of RAINBOW ceramics by XRD analyses. The phases found include metallic lead and other oxide phases, such as PbO, ZrO₂ and ZrTiO₄. The original PLZT phase is not observed. It is shown that the Pb grains (about 0.2μm) constitute a continuous phase in the reduced layer, which is consistent with its good electrical conductivity. The reduced layer is transgranularly fractured while the unreduced ceramic is intergranularly fractured. Two kinds of fracture types can be seen in interface, which denotes the different degrees of reduction.

References


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