

# Plasma-Sprayed Lead Zirconate Titanate-Glass Composites

Stewart Sherrit, Chris R. Savin, Harvey D. Wiederick, and Binu K. Mukherjee\*

Department of Physics, Royal Military College of Canada, Kingston, Ontario K7K 5L0, Canada

S. Eswar Prasad\*

Sensor Technology, Ltd., Collingwood, Ontario L9Y 3Z4, Canada

A plasma-spray process was used to produce piezoelectric lead zirconate titanate (PZT)-glass composite thick films. The films were found to have the same crystal structure as the PZT (Navy-type V) and lead-based glass starting powder mixture. The films showed good adhesion to stainless steel and silver-coated glass slides and poor adhesion to aluminum substrates. The dielectric constant of the films varied between 58 and 20 with dissipations between 0.019 and 0.032. The films were poled, and their piezoelectric charge coefficient,  $d_{33}$ , was 1.1 pC/N.

## I. Introduction

THE use of plasma spraying to deposit thick films of wear-resistant materials, including ceramics, is a well-established process.<sup>1</sup> Plasma spraying allows the coating of complex shapes to be easily automated. This led Malric *et al.*<sup>2</sup> to attempt plasma spraying as a method of producing piezoelectric lead zirconate titanate (PZT) thick films for use in transducers. Although their films showed the proper crystal structure, no piezoelectric activity was detected. They concluded that the films might have to be annealed at the usual sintering temperatures of 1280° to 1300°C for them to exhibit piezoelectricity.

In other work,<sup>3</sup> the parameters affecting the plasma spraying of PZT have been investigated. It has been shown that the PZT powder in the plasma is subjected to temperatures exceeding the solidus at 1350°C.<sup>4</sup> The particles begin to melt from the outside inward, and, since the time of flight in the plasma is relatively constant, the degree of melting is dependent on the particle size. During the melting stage, the more-volatile PbO is lost, ZrO<sub>2</sub> is formed, and the melted portion of the powder contains a PbTiO<sub>3</sub>-enriched PZT. The incongruently melted powder is quenched on impact with the substrate. The resultant film consists of stoichiometric PZT (unmelted portion of powder) and nonstoichiometric PZT and ZrO<sub>2</sub>. This is evident from X-ray diffractograms of untreated, plasma-sprayed PZT films, which show doublets where one would expect a single PZT peak and peaks corresponding to ZrO<sub>2</sub>.<sup>2,3</sup> Other problems associated with these films are their porosity and surface roughness, which make poling difficult.

To circumvent the above problems, this work investigated the plasma spraying of PZT-glass composites, similar in composition to the bulk PZT-glass composites reported earlier.<sup>5</sup> The melting temperature of the glass is much lower than the solidus temperature of the PZT, so that the glass melts prior to the PZT. The melted glass then increases the partial pressure of PbO and acts as a glue for the PZT particles. In essence, the films, as

deposited, are a three-phase composite of pores, glass, and PZT of unknown connectivity, as defined by Newnham *et al.*<sup>6</sup>

## II. Processing

The starting powders consisted of mixtures of PZT (Navy-type V) and lead aluminosilicate glass (BM1085, Sensor Technology, dielectric constant = 9 and  $\tan \delta = 0.001$  at 1 kHz) which were characterized by their PZT contents of 92, 85, and 77 vol%. The powders were wet milled in methanol for 1 h and calcined at 500° to 700°C. The powders were then remilled and used for the plasma spraying. The particle sizes in the powder varied between 1 and 3  $\mu\text{m}$ . For purposes of comparison, a few disks were pressed at 10 000 kPa with a poly(vinyl alcohol) binder and fired at 750°C. The disk samples were electroded and poled at 50 kV/cm at 120°C for 1 h.

The plasma gases used were argon (at a pressure of 690 kPa (100 psi) and a flow rate of 1.4 m<sup>3</sup>/h (50 ft<sup>3</sup>/h)) and hydrogen (345 kPa (50 psi) and 0.42 m<sup>3</sup>/h (15 ft<sup>3</sup>/h)). The plasma gun was set at 500 A and 80 V with a barrier gas of argon at 1.1 m<sup>3</sup>/h (40 ft<sup>3</sup>/h). The powder flow rate was 1.1 kg/h (2.5 lb/h). The gun to work piece distance was between 10.0 and 10.6 cm. The substrate was initially at room temperature, and the temperature was not controlled.

## III. Results

The films were sprayed on three different types of substrates to assess the adhesion to different substrate materials. For small-area samples, steel, aluminum, and silver-coated glass showed good adhesion. For large-area films, however, the aluminum substrate gave poor adhesion. The film thickness ranged from 0.08 to 0.25 mm. The film densities were measured by lifting square sections from the aluminum substrate, measuring the mass and determining the volume from the dimensions. The densities ranged from 2500 to 3700 kg/m<sup>3</sup>. These values are slightly lower than the actual film densities due to the surface roughness of the films. The low film densities suggested that the volume occupied by pores is of the order of 30% to 40%. To avoid confusion, films are identified by the composition of the starting powders. However, the actual PZT and glass percentages by volume for the films are much lower due to the pores in the films.

Photomicrographs of the films are shown in Fig. 1. The film surface is rough, and hot spots—where the powder has melted—are visible. These hot spots may be due to the plasma gun arcing to the substrate. The X-ray diffractograms for the 92 vol% starting powder and the resultant plasma-sprayed sample on a silver-coated glass substrate are shown in Fig. 2. The X-ray spectrum for the powder has been shifted approximately 0.5° to account for an error in the initial setup. The peaks match both in spacing and relative intensity. The small broad peak at  $2\theta = 28^\circ$  corresponds to PbO. The small peak on the side of the primary PZT line at  $2\theta = 30^\circ$  corresponds to the pyrochlore phase of PZT.

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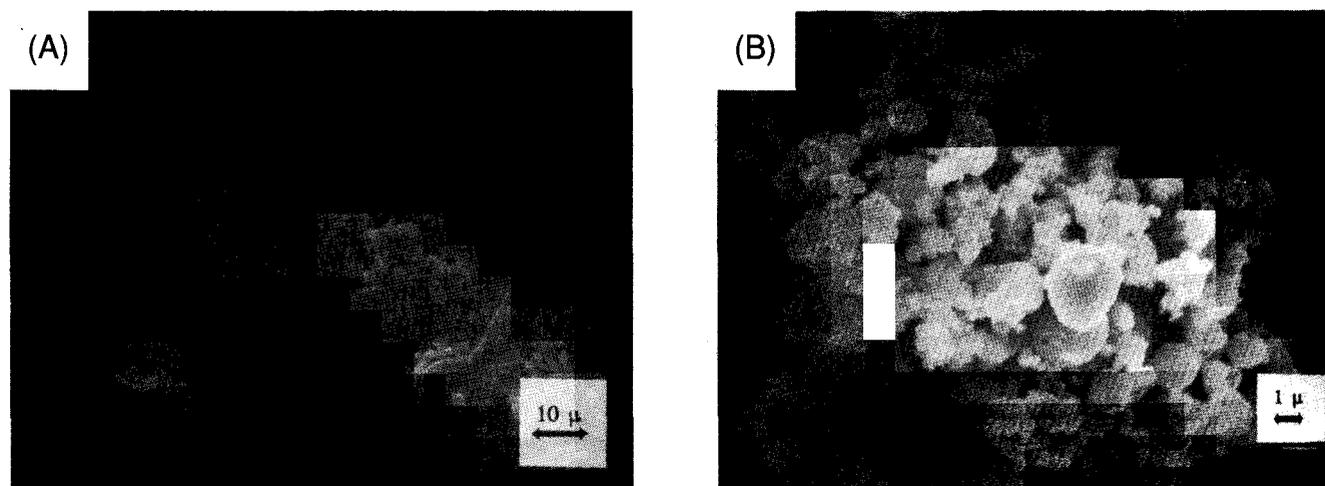


Fig. 1. SEM micrographs of plasma-sprayed surface: (A) 92 vol% sample (note melted section in lower-right corner) and (B) 92 vol% sample (note high porosity).

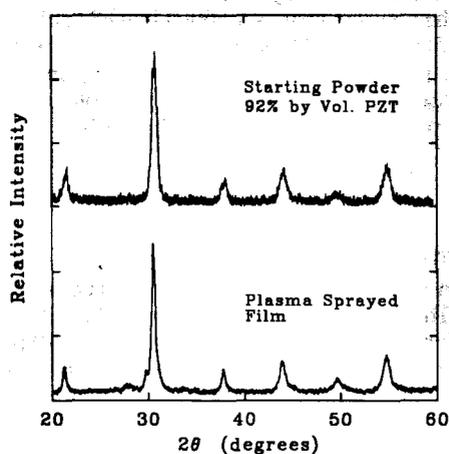


Fig. 2. X-ray diffractograms of plasma-sprayed film and starting powder (92 vol% PZT) (radiation is  $\text{CuK}\alpha$ ).

The dielectric properties at 1 kHz of the plasma-sprayed films and of the sintered disks were measured using an impedance analyzer (HP4192A, Hewlett-Packard Co., Palo Alto, CA) and are shown in Table I. A 1.8-cm-diameter disk of conductive silver paint (Demetron 200) was used as the top electrode, and the substrate was used as a bottom electrode. The dielectric properties of the 92 and 77 vol% films were measured after poling for 2 h with an electric field of 80 kV/cm at 100°C. The 85 vol% films were too thin to pole, and the dielectric constant and dissipation for these films were measured prior to poling.

Table I shows that the dielectric constant of the plasma-sprayed films is much lower than the range of values found for the sintered disks. This is likely to be due to the porosity of the films. Pores with an effective dielectric constant of 1 act as a third phase, reducing the area of PZT that is directly connected

between the electrodes. The pores are electrically in series with the PZT-glass mixture, and the effective dielectric constant is governed by a series connectivity. For the 92 vol% samples, the dielectric constant of the composite disks is a factor of 3 smaller than the value for bulk PZT, whereas the dielectric constant of the plasma-sprayed samples is a factor of 60 smaller than the value for the bulk PZT. This strongly suggests that the dielectric properties are controlled by the porosity rather than by the glass content.

The first evidence of piezoelectricity in the films was found when the application of an alternating voltage of 10 V with a frequency between 7 and 11 kHz resulted in an audible sound whose frequency varied as the applied frequency was changed. The piezoelectric charge coefficients of the samples were then measured using a Berlincourt-type  $d_{33}$  meter, and the results are shown in Table II.

The piezoelectric charge coefficient also has been measured using a ramped stress technique which has been described elsewhere.<sup>7</sup> Figure 3 shows the piezoelectric voltage generated as a function of the applied uniaxial stress for the 77 vol% film. The stress is applied in the 3 direction. The  $d_{33}$  value is calculated by noting that the induced dielectric displacement  $D$  is related to the applied stress  $T$  by

$$D = d_{33}T \quad (1)$$

Since  $DA = Q = CV$  and  $TA = F$ —where  $A$  is the area of the electrode,  $Q$  the induced charge on the sample,  $C$  the sample capacitance,  $V$  the induced voltage, and  $F$  the uniaxial force on the sample—we may write

$$V = \frac{d_{33}F}{C} \quad (2)$$

$$d_{33} = C \frac{dV}{dF} \quad (3)$$

The curve shown yields an average  $d_{33}$  value of 0.47 pC/N for this film. The capacitance of the sample in the apparatus has been measured to be 0.382 nF. This technique gives an average  $d_{33}$  value of 0.87 pC/N for the 92 vol% film. Table II shows that the values of  $d_{33}$  obtained by our compression technique are slightly lower than those obtained by the Berlincourt quasi-static technique. This is due to the small time constant of the apparatus when measuring the PZT films. Normally, when the apparatus is used to measure the very high voltages produced by the compression of a disk sample of PZT, a 1- $\mu\text{F}$  capacitor is placed in parallel with the sample to reduce the voltage and increase the time constant. However, in the case of the thick films, the piezoelectric voltages are much smaller and the 1- $\mu\text{F}$

Table I. Dielectric Properties of Plasma-Sprayed Films and Sintered Disks\*

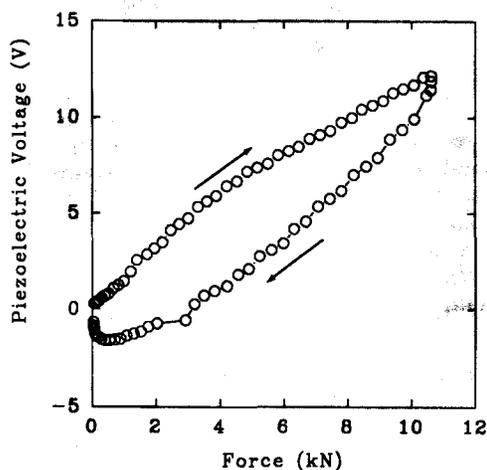
PZT (vol%)	Sintered disks		Plasma-sprayed films	
	$\epsilon_{33}^T/\epsilon_0$	$\tan \delta$	$\epsilon_{33}^T/\epsilon_0$	$\tan \delta$
100	3250	0.02		
92	1080–740	0.017	58–50	0.019
85	600–540	0.013	39	0.032
77	320–270	0.011	20	0.022

\*Measured at 1 kHz.

**Table II. Values of  $d_{33}$  for Sintered Disks and Plasma-Sprayed PZT-Glass Composites\***

PZT (vol%)	Sintered disks, (200-Hz ac force)	Plasma-sprayed films (200-Hz ac force)	Plasma-sprayed films (11-kN ramped stress)
	$d_{33}$ (pC/N)	$d_{33}$ (pC/N) ( $\pm <30\%$ )	$d_{33}$ (pC/N) ( $\pm <15\%$ )
100	580	N/A	N/A
92	88–68	1.1	0.87
85	34–28	N/A	N/A
77	10–6	0.97	0.47

\*Measured using a 200-Hz ac force and a 11-kN ramped stress. The 85 vol% films were too thin to pole and therefore are not reported. N/A is not available.



**Fig. 3.** Piezoelectric voltage generated by uniaxial compression of a plasma-sprayed PZT-glass film (77 vol% sample). Capacitance of the system including sample was 382 pF.

capacitor is removed to increase the sensitivity of the measurement. The resulting decrease in the time constant of the apparatus allows the charge generated by the film to leak across the electrode and so reduce the measured voltage. Hence, the value of  $d_{33}$  given by this experiment is lower than the real value, and hysteresis is observed.

Thus, our results show that the plasma-sprayed films are clearly piezoelectric, although the effect is very small. Film densities must be increased and surface roughness decreased to increase the piezoelectric effect in these samples. Adjusting the powder-size distribution may increase the densities. Note that plasma-sprayed PZT films produced previously<sup>2,3</sup> have had higher densities than the present samples. Another way to

increase the density of the films, and hence their piezoelectric effect, might be to use a starting powder of  $\text{PbZrO}_3$ -enriched PZT rather than a PZT-glass mixture. The excess amount of  $\text{PbZrO}_3$  would have to be adjusted to cancel the effect of its decomposition during the spraying process.

#### IV. Conclusions

Piezoelectric plasma-sprayed films have been produced with the proper crystal structure and a piezoelectric charge coefficient  $d_{33}$  ranging from 0.47 to 1.1 pC/N. The films have dielectric constants ranging from 58 to 20 and dielectric dissipations ranging from 0.032 to 0.019. This research has shown that the plasma-spray process can produce piezoelectric films. To improve the piezoelectric effect, it is suggested that processing methods be investigated that increase the film densities and improve the microstructure.

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