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Electrical properties and chemical compatibility of PZT thick film on Ni substrates

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The characteristics of Pb(Zr,Ti)O_3 (PZT) thick films that were printed and fired on Ni substrates were studied. The dielectric characteristics of samples sintered at 850°C on Ni substrates could not be measured due to the formation of a NiO layer at the Ni/PZT interface. The scanning electron microscope and energy dispersive X-ray analysis of cross-sections of the PZT thick films on Ni substrates, and of a mixture of PZT and NiO powders, fired at 850°C, did not indicate the formation of secondary phases. However, the transmission electron microscopy showed around 8% solid solubility of NiO in the PZT. A new structure with a prefired, Au thick-film layer was designed in order to prevent the diffusion of the NiO to the PZT layer during sintering. The dielectric properties of the PZT layers printed and fired on the Ni substrates with the prefired Au electrode were significantly better than those of the layers on the uncoated substrate, the dielectric losses decreased from 0.23 to 0.05. © *2003 Kluwer Academic Publishers*

1. Introduction

Ferroelectric ceramic materials based on solid solutions of Pb(Zr,Ti)O_3 (PZT) are used in the electronics industry for sensors and actuators and for electromechanical transducers, to name just a few examples. Thick-film technology, i.e., the deposition of thick-film pastes by screen printing, primarily on alumina substrates, is a relatively simple and convenient method to produce thicker layers with a thickness up to 100 μm. The characteristics of screen-printed thick-film ferroelectrics are similar to those of bulk materials and their main applications are in sensors [1, 2]. However, for some applications, silicon or metallic substrates are used [3–5]. Films on metal substrates offer some advantages, for example: mechanical flexibility of the substrate, low cost, and ease of handling. The disadvantage of base metal substrates, e.g., stainless steel or nickel, is mainly their low oxidation resistance. In this paper we reported on a structural and electrical characterization of PZT films fired on nickel substrates.

2. Experimental

PZT 53/47 powder ($PbZr_{0.53}Ti_{0.47}O_3$) with the addition of 6 mol% of PbO was prepared by mixed-oxide synthesis at 900°C for 1 h from high-purity PbO (litharge) 99.9% (Fluka), 99% ZrO_2 (Tosoh), and 99% TiO_2 (Fluka) and powders. We also added 2 wt% of lead germanate with the composition $Pb_5Ge_3O_{11}$ as a sintering aid. The details of the preparation are reported elsewhere [6].

Three kinds of structures shown schematically in Fig. 1, were tested. In structure A the PZT layer was printed and fired at 850°C for 8 h on a bare Ni substrate. Structure B was prepared by first printing gold film and then the PZT film; the gold and PZT layers were later cofired at 850°C for 8 h. For the structure C a gold layer on a Ni substrate was prefired at 950°C for 1 h in an argon atmosphere. Next, over the first gold layer a second gold layer and a PZT layer were printed and cofired at 850°C for 8 h. The thickness of each gold film and of PZT films after the thermal treatment were around 15 μm and 40 μm, respectively.

For the electrical measurements the gold top electrodes were sputtered onto the PZT films. The values of the remanent polarisation and the coercive field were determined from ferroelectric hysteresis curves measured with an Aixact TF Analyser 2000 at 50 Hz. The real and the imaginary parts of the complex dielectric constant were measured with an HP 4284 A Precision LCR Meter at 1 KHz.

For the study of possible interactions between the PZT and the NiO, a powder mixture of PZT and NiO was fired for 8 h at 850°C. The samples were characterised with X-ray powder-diffraction (XRD) analysis using a Philips PW 1710 X-ray diffractometer with Cu K_α radiation, and electron microscopy using a JEOL 5800 scanning electron microscope (SEM) and an EM 2010F analytical electron microscope (TEM), both equipped with a LINK ISIS 300 energy-dispersive X-ray spectrometer (EDS). The samples, i.e., the PZT and NiO mixture and the PZT thick films, were mounted in epoxy in a cross-sectional orientation and then polished using standard metallographic techniques. Prior to analysis in the SEM the samples were coated with carbon to provide electrical conductivity and avoid

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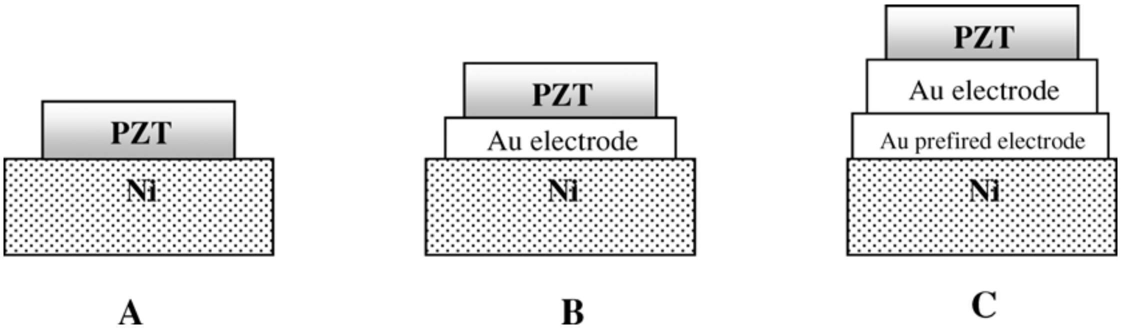

Figure 1 The three structures used in this investigation: PZT layer on uncoated Ni substrate (A), cofired Au/PZT structure (B) and cofired Au/PZT layers on prefired gold-coated structure (C).

charging effects. SEM micrographs were obtained using back-scattered electrons for the imaging. The TEM samples were prepared by mechanical thinning, dimpling and ion milling using 3.8 keV argon ions. The Cliff Lorimer method and appropriate absorption corrections were employed for the quantitative analysis. The $NiTiO_3$ compound synthesized from 99.9% NiO (Alfa) and TiO_2 at 1200°C and sintered PZT 50/50 ceramics were used as standards. EDS spectra were collected from areas where the foil thickness was estimated to be around 100 nm.

3. Results and discussion

The electrical characteristics of the PZT on the bare Ni substrate (structure A) could not be measured due to the formation of an insulating NiO layer between the PZT film and the Ni substrate. In Table I the electrical parameters, i.e., remanent polarisation Pr, coercive field Ec, dielectric constant ε' and dielectric loss tan δ, of the cofired Ni/Au/PZT (structure B) are presented. The electrical characteristics of this structure compared with the characteristics of a similar structure printed on alumina substrates [7], also shown in Table I, were poor (e.g., high dielectric losses, low remanent polarisation).

An SEM micrograph of the cross-section of structure B is shown in Fig. 2. Between the nickel substrate and the PZT layer, a layer of NiO can be seen. During sintering NiO was formed from metallic nickel. The microstructural analysis detected around 2.5 wt% of NiO in PZT close to the PZT/Au boundary, decreasing with increasing distance from the interface. Presumably, this solid solution is the reason for the degradation of the electrical properties. Bright areas in the nickel substrate are gold impurities.

The X-ray spectrum of the fired mixture of NiO and PZT, after firing at 850°C for 8 h, is shown in Fig. 3. The X-ray spectra of NiO and PZT are also presented for comparison. The bold line shows the X-ray peaks of the fired mixture. After firing, all the peaks associated with the starting materials are present in the fired mixtures and no new peaks were observed. Hence, it follows that no other phase formed during firing, at least under the described experimental conditions and within the experimental uncertainty of the method.

TABLE I Electrical parameters of the cofired Ni/Au/PZT (structure B)

Structure	Ni/Au/PZT	Al_2O_3/PZT [7]
Pr ($\mu C/cm^2$)	7.3	29
Ec (kV/cm)	63	25
ε'	150	780
tan δ	0.23	0.033

The microstructure of the mixture of NiO and PZT powders, fired at 850°C, is shown in Fig. 4. Dark grains are NiO and the lighter grains are PZT. The microstructural analysis did not detect any secondary phase; however, the results of the SEM-EDS analysis indicated the solid solubility of NiO in the PZT. The solid solubility was estimated to be around 10 at.% of NiO in PZT, but because of the relatively small size of the phases present, around 1 μm, the influence of the matrix grains on the EDS measurements could not be neglected (see Fig. 4). Using the Kanaya-Okayama approach [8] the interaction volume in the PZT grains at an accelerating voltage of 20 kV is estimated to be close to 1 μm^3. To determine the solid solubility of the NiO in the PZT more accurately, TEM equiped with EDS was used. Fig. 5 is a TEM micrograph of a PZT grain from the NiO-PZT mixture that was fired at 850°C for 8 h. Inside the grain is a complicated ferroelectric domain structure. Using bright-field and dark-field experiments no precipitates of NiO were found in the PZT grains.

Using the optimised analytical parameters and procedures described in [9], the chemical composition and compositional variations within a single grain and for the different grains of the PZT phase were determined. EDS spectra were collected from different points in one grain (up to 10 points per grain) and from points in different grains (one point per grain). It was found that the chemical composition fluctuations inside one grain are smaller than the compositional fluctuation between different grains.

In most grains the relative standard deviation of the concentration measurements of all elements, i.e., Ti, Ni, Zr and Pb, was around 5%; however, in around one third of the grains relative standard deviations of up to 20% were found. The relative standard deviation of the average concentration within all the investigated grains was around 10%. Fig. 6 shows the relative standard deviation of the concentration measurements measured in one grain, where just the grains with the higher homogeneity were taken into account, and the relative

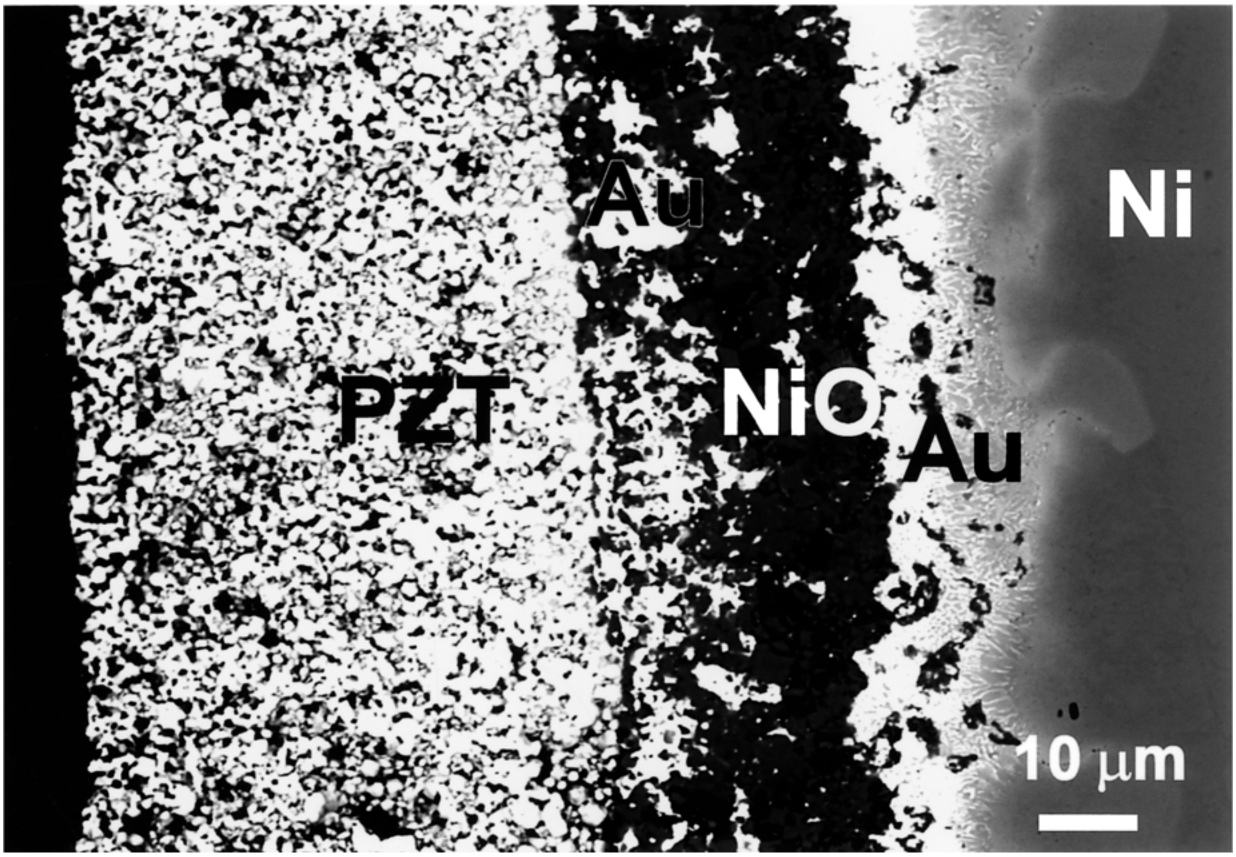

Figure 2 SEM micrograph of the cross-section of the structure B. During firing NiO was formed from Ni and diffused through the Au layer to the PZT layer. Bright areas in the Ni substrate and NiO layer contain gold.

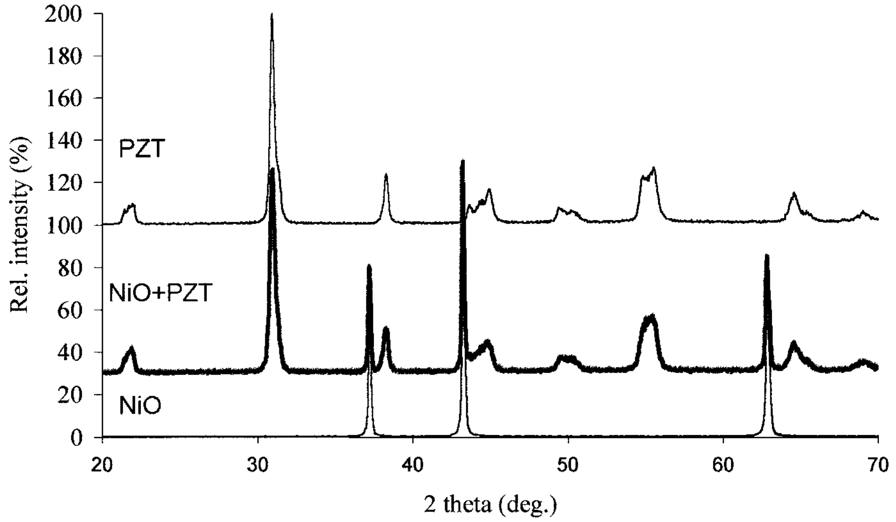

Figure 3 X-ray spectrum of the NiO and PZT mixture, fired at 850°C (bold line). The X-ray spectra of NiO and PZT are shown for comparison.

standard deviation of measurements for several grains. The results show that around two thirds of the grains are relatively chemically homogeneous. The 10% relative standard deviation of the measurements within different grains indicates that there is a certain amount of inhomogeneity among the PZT grains. Based on the results for the PZT grains, the average atomic concentration of NiO was found to be 7.7 ± 0.6%.

The results obtained with XRD, SEM and TEM of the powder mixture confirms the solid solution of NiO in PZT. The poor electrical properties of the cofired structure B can therefore, as previously mentioned, be tentatively attributed to the interaction between the PZT and the NiO that formed on the surface of the Ni during firing, and diffused through the Au layer to the PZT. In order to prevent the diffusion of Ni to the PZT layer a new structure with a prefired, Au thick-film layer (structure C) was designed. In Fig. 7 is a SEM micrograph of structure C. From the left to right is Ni substrate, thin layer of Au/Ni alloy which formed during first firing, NiO layer with inclusions of gold, second Au layer, and PZT layer. The thickness of the NiO layer,

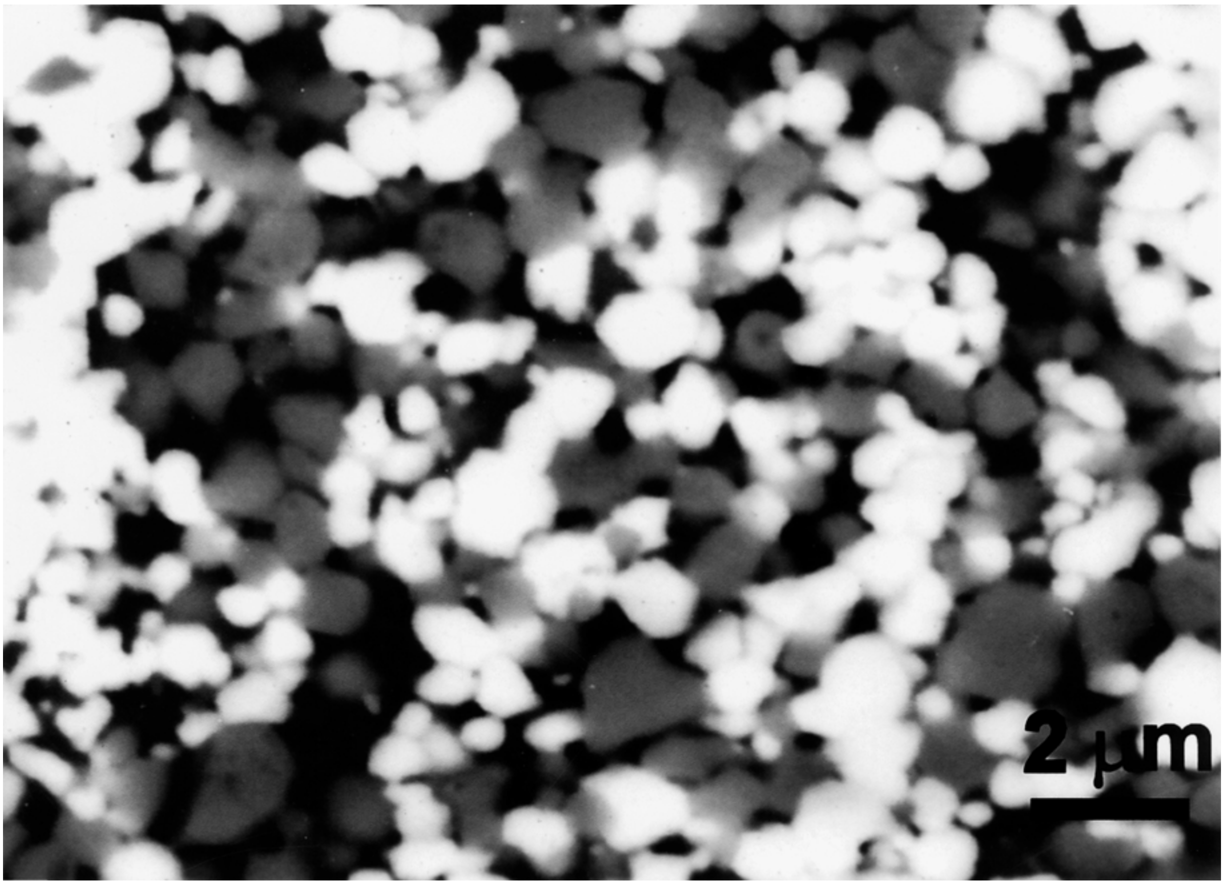

Figure 4 SEM microstructure of the mixture of the PZT and NiO powders, fired at 850°C. Dark grains are NiO, lighter grains are PZT.

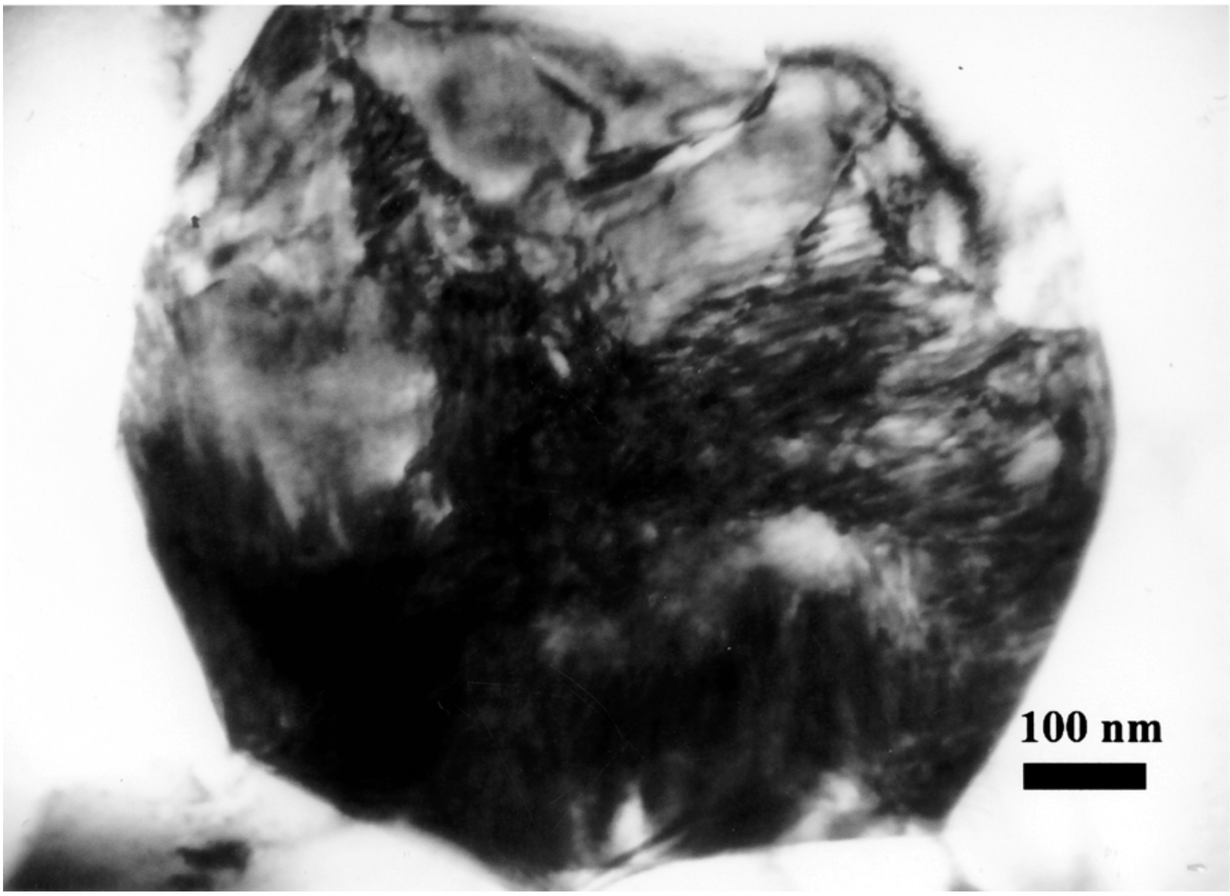

Figure 5 TEM micrographs of the PZT grain from the NiO-PZT mixture, fired at 850°C for 8 h.

TABLE II Electrical parameters of PZT films in Ni/Au prefired/Au/PZT (structure C)

Structure	Ni/prefired Au/Au/PZT
Pr (μC/cm^2)	13
Ec (kV/cm)	12
ε'	450
tan δ	0.05

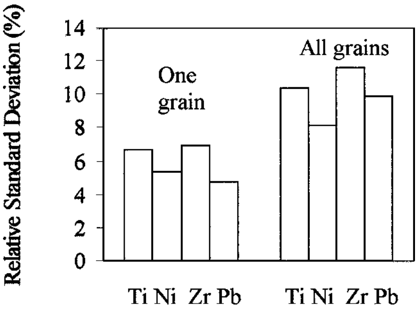

Figure 6 Relative standard deviation measurements measured in one grain and in various grains of PZT.

which is formed from metallic Ni or Au/Ni alloy during the second firing in air, is around 15 μm. The "second" Au layer under PZT, with a thickness of around 5 μm, prevented the diffusion of NiO to the PZT while NiO prevents direct contact between Au and Ni and therefore the formation of alloy between Au and Ni is avoided. Dielectric properties of PZT layers in structure C, shown in Table II, were significantly better than characteristics of layers in structure B (see Table I).

4. Conclusions

The electrical properties and the chemical compatibility of thick PZT films, printed and fired on Ni substrates were studied. The reaction between the PZT and the NiO, which formed during firing, significantly degrades the dielectric characteristics, chiefly the dielectric losses. These interactions were investigated using XRD, SEM and TEM on a NiO-PZT powder mixture that was fired for 8 h at 850°C. No secondary phases were detected. However, a solid solution of around 8% NiO in the PZT was observed. Presumably, this is the reason for the degradation of the electrical properties of the PZT material on Ni substrates. To avoid this degradation a new structure with a prefired, Au thick-film layer on a metallic substrate was used, which resulted in significantly improved electrical properties of the PZT thick films.

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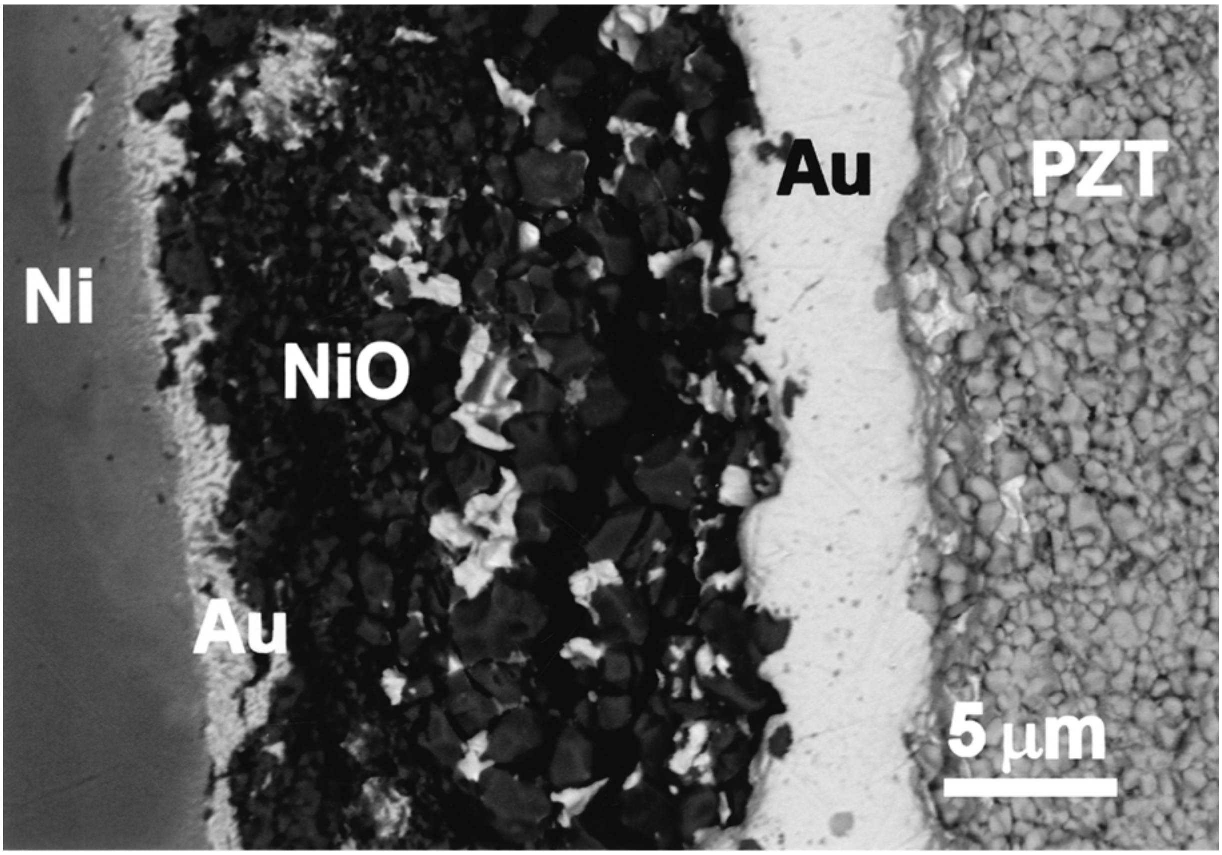

Figure 7 SEM micrograph of the cross-section of structure C. The "second" Au layer, with a thickness of around 5 μm , prevented the difusion of NiO to the PZT. Bright areas in the NiO layer contain gold.

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