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Influences of the electroless nickel electrode on the electrical characteristics of $BaTiO_3$-based PTCR ceramics

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Abstract

This paper investigated the influences of the microstructure of electroless nickel electrode on the a.c. shock characteristics of $BaTiO_3$-based PTCR ceramics and the degradation and failure of PTC thermistors with electroless nickel electrode. In the experiments, we coated metal nickel electrode on the surface of PTCR ceramics samples by employing the different electroless plating baths and analyzed the microstructure of electroless nickel electrodes by SEM. The experimental results indicated that the various baths made the microstructure of nickel electrodes different. The nickel electrodes from acid bath possessed the densified stacked structure, which resulted in being cracked when being shocked by 220 V, 3 A a.c. power; owing to having sparse branch-and-tendril structure, those from alkaline bath had no effects on the ceramics samples being shocked. The work came to the conclusion that the microstructure of electroless nickel electrodes varied the thermal stress in the body of PTCR ceramics. In addition, the a.c. shock characteristics of $BaTiO_3$-based PTCR ceramics were related to the content of phosphorus in the electroless nickel-phosphorus alloy and thickness of the nickel electrodes. According to the experiments, the thickness of the electroless nickel alloy should be less than 1 μm and the phosphorus content, 4 wt.% in the alloy. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$; Electrical properties; Electrodes; Ni; PTCR

1. Introduction

Since doped $BaTiO_3$ ceramics was found to have the position temperature coefficient of resistance (PTCR) effect, PTCR has been widely used for household appliances, computer, automobiles and other communication products. $BaTiO_3$-based ceramics are n-type semiconductors. It must be coated with metal electrodes for being used as electrical elements.

When $BaTiO_3$-based semiconducting ceramics are coated with electrodes of metals, such as Au, Ag, Pt, Pd, the asymmetrical nature of electrical conduction will emerge between metal contacts and ceramics, resulting in non-ohmic behaviour and rectification characteristics, which brings about the difficulties in the applications of semiconductive ceramics.[1] Seiter[2] concluded that contact resistances Rc between metals and ceramics were related to the oxidation reactions of electrode metals. He thought that using base metals with strong reducing property, such as Fe, Zn, Ni, Sn, Cu, could form excellent ohmic contact. Sauer[3] believed that the prerequisite of forming good ohmic contact was to remove the oxygen absorbed on the surface of ceramics. According to above views, researchers have made many kinds of electrode materials for PTCR semiconductive ceramics.

During fabrication of those PTCR components designed for motor starter of refrigerators, current-limiting elements of telephones and automobile low-voltage motors, electroless nickel and copper plating is usually employed to form a nickel or copper electrode. The electroless plating process often has a negative influence on the properties of $BaTiO_3$-based semiconducting ceramics.[4,5] Sometimes some PTCR elements fail completely after electroless plating, which is generally believed to be caused by the permeation of plating bath into the $BaTiO_3$ ceramic bodies[6] and the electrochemical reactions during electroless plating.[7,8] We carried out some comparison experiments for this purpose and got some results, reported in this paper. The results

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are helpful for a detailed understanding of the chemical and physical processes that lead to the failure and degradation in PTCR. Their implications for the stability and reliability of PTCR are also discussed.

2. Experimental procedure

Some current-limiting PTCR samples with the basic composition of $BaTiO_3$, Y_2O_3, SiO_2, $CaCO_3$, $SrCO_3$ and $MnNO_3$ were chosen for the experiment. The samples were divided into two groups, and respectively dipped into electroless nickel plating baths (bath A and bath B). The solution composition of bath A, $NiSO_4 \cdot 7H_2O$ 0.15 mol/l; reducing agent $NaH_2PO_2 \cdot H_2O$ 0.50 mol/l; complexing agent butane diacid (or butanedioic acid, i.e. $HOOCCH_2CH_2–COOH$) 0.50 mol/l; the pH, 6.0 (adjusted by 20% NaOH), and the temperature 85–90°C. The solution composition of bath B, $NiSO_4 \cdot 7H_2O$, 0.15 mol/l; reducing agent $NaH_2PO_2 \cdot H_2O$, 0.50 mol/l; complexing agent triammonium citrate, 0.50 mol/l; the pH, 9.0 (adjusted by 25% $NH_3 \cdot H_2O$) and the temperature 65–70°C. Before electroless nickel plating, the samples were washed thoroughly with deionized water, sensitized by the solution of 5% $SnCl_2$ and activated by the solution of 0.35% $PdCl_2$. The baths were kept agitated with a magnetic stirrer, dispersing the hydrogen bubbles produced in the course of the nickel plating. The samples in two baths were removed from the solution after 15–30 min, washed thoroughly with deionized water, and then dried. After grinding the nickel on the cylinder by a cylindrical grinder and being treated for 90 min at 300°C.

The size of $BaTiO_3$ thermistor disk components was 6.8 mm in diameter and 1.8 mm thick. The $BaTiO_3$ ceramics were a standard commercial formulation with a grain size in the range of 3–5 μm. The room-temperature resistance (R_0) was 20±2 Ω; Curie temperature, 105±5°C; and a steep increase in resistance occurs at temperatures >110°C (Fig. 1). A part of samples were coated Ag paste on the nickel electrode and fired for 30 min at 450°C. A.c. shock property was measured by withstanding current-shock meter model CJ-III (developed and made by Huazhong University of Science and Technology, PR China) by 220 V, 3 A a.c. power, and for the rest of the disks, gold sputtering was applied on the surface for microstructural observation by scanning electron microscope (SEM: JSM-35C made in Japan).

3. Results and discussion

3.1. Effect of bath composition and microstructure of Ni electrodes

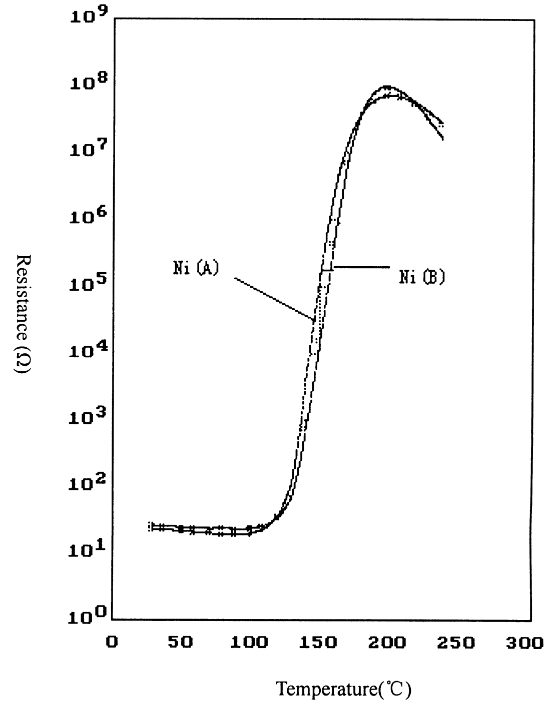
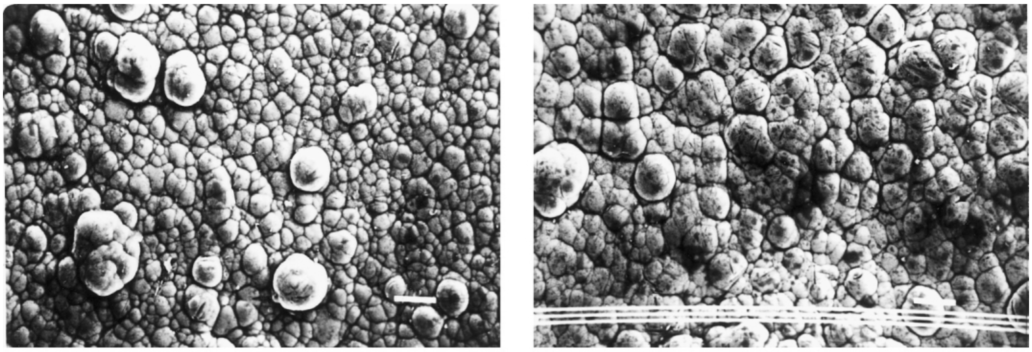


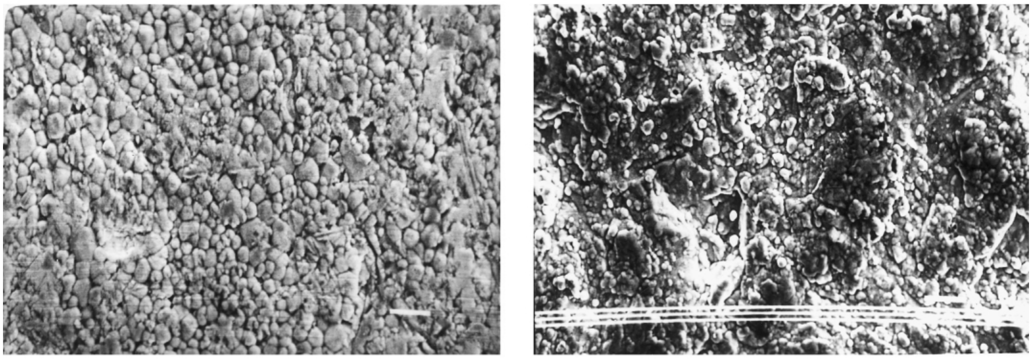
Fig. 1. Resistance versus temperature for $BaTiO_3$-based PTCR ceramic thermistor (electrodes Ni electrode).

In order to study the differences between the electroless nickel electrode from bath A and that from bath B, the microstructures of Ni electrodes were observed by SEM as shown in Fig. 2. The most noticeable difference was the structure of the electroless Ni electrode from bath A, which was obtained in an acidic plating solution, had a dense stacked structure. On the other hand, Ni electrode from bath B, with an alkaline plating solution, had a sparse branch-and-tendril structure. Observing dozens of SEM photomicrographs, it was confirmed that the difference of the microstructure was remarkably dependent on the bath composition. When the above two kinds of specimens were shocked by 220 V, 3 A a.c. power, the specimens from bath A would be cracked easily (as Table 1). This was the reason that sealing effect of dense Ni film produced during electroless plating made the moisture, permeating into ceramic bodies, unable to disperse, resulting in uneven thermal stress in the specimens. In contrast, the specimens from bath B, even shocked for 50 times, would be stable because sparse branch-and-tendril structure of Ni film help to disperse the moisture and give off the transient heat produced during a.c. shock. Generally considering, there exist micro-cracks in PTCR ceramics after a.c. shock.[9] We studied the tested specimens, and observed that there were many micro-cracks in the specimens from bath A, which was consistent with the view of Heywang.[9] The volume and stress of $BaTiO_3$-based PTCR semiconductive ceramics would change with the changes of rapid temperature and microstructure under the action of a.c. electrical field. The change of volume



(a)Ni Electrode (A) without Being Heat-treated

(b) Heat-treated Ni Electrode (A)



(c) Ni Electrode (B) without Being Heat-treated

(d) Heat-treated Ni Electrode (B)

Fig. 2. SEM morphology of various electroless Ni electrodes (×600).

Table 1
Resistance (Ω) changes of PTCR samples of various electrodes after 220 V a.c. current shocking

Electrode	R_0 (Ω)	Resistance after being shocked for different times						
		1	2	4	4	10	50	100
Ni (A)	17.5	15.7	17.6	(most damaged)			(all cracked)	
Ni (B)	18.8	16.9	16.9	16.7	17.0	17.0	17.2 (partly delamination)	

needed to be buffered by grain boundaries or pores. If not so, there would produce microcracks in the ceramics body to release the stress, resulting to the resistance rise of disks. When ceramics were shocked for several times, the cracks would expand and lengthen. But not all cracks resulted in the damage and failure of PTCR ceramic components. The short microcracks would change from steady state to unsteady state only when some temperature difference could supply energy, namely by the repeated action of a.c. current shock. Expanded longer cracks would lead to the damage of ceramics only under the action of less energy. Fig. 3 showed the relationship of micro-crack length versus transient temperature differences before and after a.c. shock. According to Smith and his co-workers,[10] variations in electrode quality or symmetry, such as non-perfect centering, can easily lead to the formation of asymmetric transient thermal gradients. Fig. 4 is plot of temperature versus radial (r) and axial (z) positions for a symmetric disk.

In addition, thickness of nickel film had some effects on the current-withstanding property of PTCR disks. In the view of our experimental results (as Table 2), thickness of nickel film had better be controlled below 0.5–0.7 μm.

3.2. Chemical degradation

The chemical degradation will emerge in the case the PTC thermistor in bath A was contacted with electroless nickel and fired Ag paste. The silver firing was conducted at 450°C for 30 min. Two kinds of samples experienced reduction in R_o and loss of R_{max} (as Table 3). But the samples from bath A was more significant and more severe than those from bath B. The reduction in R_{max} may be due to the absorption of hydrogen produced in the course of electroless plating (as a reducing agent) leading to decrease in resistivity of PTC samples[11] and reduction in R_o to the absorption of CO_2 and/or CO[12–16] produced during the firing of Ag paste. H_2 and CO tend to act as electron donors. The acidity in bath A was stronger than that in bath B, so bath A would produce more hydrogen than bath B according to the mechanism of electroless nickel plating[7] accepted by researchers.

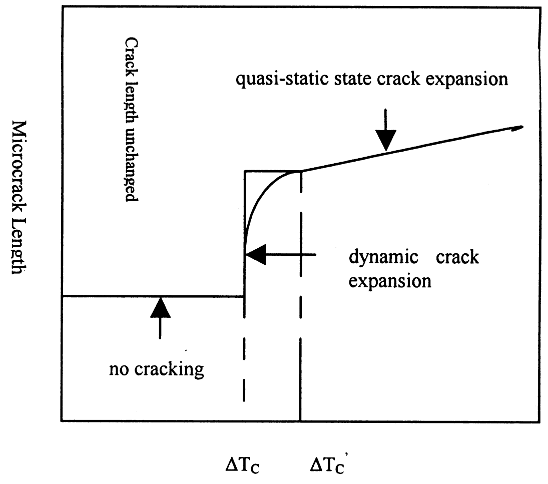


Fig. 3. Relationship between crack length and temperature.

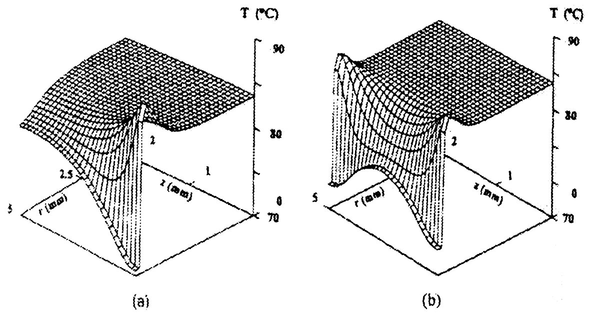


Fig. 4. Plot of temperature versus radial (r) and axial (z) positions for a symmetric disk: (a) coated with 95% electroless nickel electrode (B) at $z = 0$ and 100%, at $z = 1.8$ mm; (b) coated with 95% electroless nickel electrode (B) at $z = 0$ and $z = 1.8$ mm.

Table 2
Resistance (Ω) changes of PTCR samples of various thickness (μm) of electrodes after 220 V a.c. shocking

Electrode	R_0 (Ω)	Resistance (Ω) after being shocked for 20 times									
		0.1	0.2	0.4	0.4	0.5	0.6	0.8	1.0	2.0	5.0
Ni (A)	17.5	15.7	17.6	17.5	(most damaged)			(all cracked)			
Ni (B)	18.8	16.9	16.8	16.7	17.0	16.9	17.1	17.2	(partly delamination)		

Table 3
Reduction in R_o (Ω) and loss of R_{max} (Ω) for PTCR samples of various of electrodes

Electrode	$R_{In\text{-}Ga}$	Firing Ag–Zn	Firing Al	Ni(A)	Ni(B)
R_o (Ω)	19.5	19.9	20.2	17.5	18.8
R_{max} (Ω)	6.9×10^6	6.7×10^6	6.5×10^6	8.7×10^6	4.1×10^6

The problem of chemical degradation must be addressed in the product design stage. For some cases where reason for serious concern exists, lengthy, elaboration testing may be required for developing a detailed theory from which predictive models can be applied.

3.3. The content of phosphorus in Ni–P Alloy

$BaTiO_3$ thermistors that are subjected to progressively higher inrush power levels eventually fail by cracking or delamination.[15] Generally considering, irregular cracking was caused by the homogeneous in the ceramics. Resistance gradients within the material can produce high local temperature gradients during self-heating and correspondingly high thermal expansion stresses and microcracking can occur at grain interfaces.[15] Delaminating is predicted due to the occurrence of maximum tensile stress at the center of the disk. The experiments revealed that the disks from bath B were delaminated by a.c. power shock for sufficient times. Generally speaking, the content of phosphorus in electroless nickel is related to the pH value of bath solution. The smaller pH value is, the more the content so phosphorus, and the type and amount of stress strongly depend on the content of phosphorus in the Ni-P alloy. According to Duncan[17] and Riedel,[18,19] the type of internal stress between Ni–P alloy and substrate was related to the phosphorus content. The phosphorus content of less than 7 wt.% would produce tensile stress; and the phosphorus content above 7 wt.% would produce pressure stress. Analyzing the composition of Ni electrodes from both baths, we found that phosphorus content in the alloy from bath A was 8.5–9.0 wt.%, and that from bath B was 3.0–5.0 wt.%. At the same time, we observed that phosphorus content less 4 wt.% in the alloy would delaminate the tested PTC disks. The reason for delamination of PTCR ceramic thermistors was that under the action of a.c. current, the temperature rose rapidly and the electrical field was not well-distributed in the ceramics, aggravating the uneven distribution of heat. $BaTiO_3$-based semiconductive ceramics are not good at conducting heat. Thus, heat would gather in ceramics and not release timely, so the temperature of in the center of ceramics would be higher than other position (about 30–50°C according to our measurement). Consequently, thermal stress and internal stress would cause the damage. As mentioned in Tables 1 and 2, damage modes varied with the electrodes. For Ni(B) electrode, ceramic thermistors would be delaminated by a.c. electrical current because of their tensile stress; but those coated with Ni(A) electrode would crack owing to their pressure stress. Therefore, in order to assure the reliability of the product, the conditions of electroless nickel electrode must be controlled.

4. Conclusion

$BaTiO_3$ thermistors are susceptible to similar types of instability as other ferroelectric ceramics. The failure and degradation of PTC resistors with electroless nickel have been studied.

1. The samples from the acid bath failed completely after 220 V, 3 A a.c. power shock, but those from the alkaline bath did not fail. This was the reason that the dense stacked electrodes (obtained in acid plating solution) sealed the ceramic body. This made the moisture and large amount of transient heat (produced at a.c. shock) unable to disperse, and led to uneven of the thermal stress distribution in PTCR samples and thus PTCR ceramics samples were cracked by 220 V, 3 A a.c. power shock. On the other hand, the sparse branch-and-tendril structure (obtained in alkaline plating bath) helped the moisture and transient heat to let out, and had no effects on the ceramics samples being shocked by a.c. power.
2. Chemical degradation, namely decrease in R_o and loss of R_{max}, emerged after firing Ag paste. And the disks from bath A were more severe than those from bath B, which results from hydrogen produced during electroless plating and CO_2 and/or CO produced during firing silver paste. H_2, and CO_2/CO tend to act as electron donors.
3. The failure modes depended on the phosphorus content in electroless Ni–P alloy. The less phosphorus content in the alloy (namely bath B) might cause the delamination of the tested disks. In contrast, cracking would occur in the case of more amount of phosphorus (bath A).
4. The thickness of electroless nickel film had some effects on the current-withstanding property of PTCR disks, which had better be controlled under 0.5–0.7 μm.

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