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# Ni-BaTiO$_3$ interface phenomenon of Co-fired PTCR by aqueous tape casting

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**Abstract:** The green sheets with Ni paste as inner electrodes were sintered at 1 320 ℃ for 1 h under a $N_2$/$H_2$ mixing gas at an oxygen partial pressure $p(O_2)=10^{-8}-10^{-12}$ MPa, and then reoxided at 900−1 000 ℃ to form multilayer positive temperature coefficient of resistance(PTCR). During the experiments, electronic characteristic effects of PTC with different thicknesses were contrasted. A certain extending of Ni diffusion is beneficial to the ohmic contact of multilayer PTCR but excessive diffusion is harmful to PTCR. The diffusion was studied by scanning electron microscopy(SEM) and energy-dispersive X-ray spectrometry(EDS). Inter-diffusion of element takes place along the Ni-BaTiO$_3$ interface, especially Ni diffusion to BaTiO$_3$ dominated the process. Furthermore, the degree of Ni diffusion is very severe as ceramic layers are very thin.

**Key words:** Ni; positive temperature coefficient of resistance; BaTiO$_3$; diffusion

## 1 Introduction

With the rapid development of electronics and telecommunication technologies and the requirements for miniaturization, light mass, high-speeding cutting technology, multifunction and high reliability of electronic components, more and more electronic manufacturer adopt SMT (surface mount technology)[1]. Also, the achievement of applications in the market has made new chip components developed by electronic elements manufacturers, in the long term, the main trend of research and development of SMC/SMD will be miniaturization, multi-layer, high precision, modulization and greenalization. As to the progress of the SMT, the traditional leaded components are focused on less and less, while the chip surface mounting components attract much attention[2].

Thus, the BaTiO$_3$ semiconductor ceramic thermal-sensitive material based thermal resistor follows the way to become miniature and chip[3]. Because of the natural characteristics of BaTiO$_3$ based PTCR, the reduction of room temperature resistance is difficult to meet the demand of low resistance of chip PTC current limiting component, then, there initiates the research of multi-layer PTCR, adopting the structure similar to MLCC and fabricating multilayered devices, which increase the area of the devices and decrease the room temperature resistor[4]. This type of chip elements were initiated by German Siemens Co.[5] and then surpassed by Japanese enterprise. At present, Japan accounts for the most patents in this field, having apparent technology advantages.

The green sheets after aqueous tape casting are printed by Ni paste alternately, forming multi-layer structure, and are sintered at 1 320 ℃ for 2 h in a $N_2$/$H_2$ reducing atmosphere under oxygen partial pressure $p(O_2)=10^{-8}-10^{-12}$ MPa, then annealed at 800−1 000 ℃

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in weak oxidizing atmosphere[6], finally external Ag-Zn electrode is sintered to form multi-layer PTCR. In this work, under the same condition, the PTCR of 0.3 mm/0.5 mm was respectively analysed by SEM and EDS, and the interface morphology was observed as well as the diffusion of metal-ceramic. The micro-nano PTCR was prepared according to the physic-chemical process among the grain boundaries of ceramics. The interfacial effect of metal-ceramic is not only related with the depth of ceramic but also affected by the grain size, in the process of co-fired PTCR, the study of interfacial effect appears to be rather important.

## 2 Experimental

### 2.1 Preparation of PTC by aqueous tape-casting

Firstly added powder, solvent and dispersing agent, and dispersed them by ball milling, then added adhesive, plasticizer and other functional additives, and ball milled them again; finally the stable and uniform tape-casting slurry was prepared[7]. The powder was $BaTiO_3$ with average grain size of 1 um, which was $BaTiO_3$ based PTC powder prepared by solid state synthesis presintering, and its average size was 1.0 μm, the adhesive was PVA solution with concentration of 12% and B−1070 emulsion; the dispersing agent was D−3019 (Rohm-Hass); the plasticizer were chemically pure glycerol, DBP and polyethylene glycol PEG400 respectively; the autifoaming agent was chemically pure caprylic acid; and the solvent was water.

The tape-casting slurry finally processed tape casting on the flat glass foundation slab, which was a self-made tape-casting device (as shown in Fig.1), the rate of the blade was 1.2 m/min, and after drying the tape-casting slurry tape was cast out of PTC of 100−600 μm respectively. To simplify the device, we adopted the simple single-blade system, while in industry double-blade system was usually used and its advantage was that the first blade was used to brake the slurry to decrease the viscosity of the slurry, and the second blade was used to tape cast the slurry to some thickness[8].

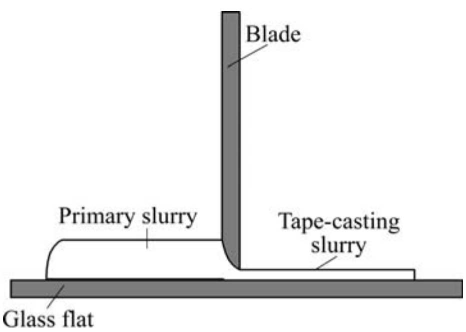


**Fig.1** Sketch of aqueous tape-casting by blading process

### 2.2 Preparation of Ni paste

Ni-Cr alloy has excellent anti-oxidant capacity, for a long time it is used as thermoelectric material, and its highest service temperature is as high as 1 350 ℃, having the potential of co-firing with the PTC ceramics. Therefore in this experiment we mainly studied the basic-metal co-fired electrodes conditioned with Ni-Cr. When Ni-Cr was used as co-fired electrode, the principle acquirement was that it could endure the high sintering temperature around 1 320 ℃, and could escape oxidation when it was processing heat treatment in the oxidant atmosphere at around 800 ℃, as well as maintaining some ohmic contact property. In this experiment, we used 2 g Ni powder with the size ranging from 1 μm to 2 μm, and mixed it with Cr powder with the content of 10% that screened through sieves as well as $BaTiO_3$ powder with its particle size of 1 μm and the content of which was also 10%, then added Terpineol organic carrier and ethylene cellulose functioned as adhesive, inputting drops of DBP to use as thixotropy, and then grinded them in the agate to prepare the Ni-Cr electrode slurry[9].

### 2.3 Preparation of multi-layer sheets

We prepared crude ceramics film with the thickness of 100 μm and 400 μm by aqueous tape-casting, using $BaTiO_3$ powder prepared by solid-state reaction and emulsion acted as adhesive, after drying the internal electrode map was printed using screen printing technique that is shown in Fig.2, the components of the electrode slurry used were Ni90/Cr10, after drying, put the 5 films staggeredly according to the alignment baseline, then pressed the films with a stress of about 10 MPa in the normal direction on the film surface, in the pressing process. Finally 3-layer samples in the size of 6 mm×8 mm×0.65 mm[10] were prepared.

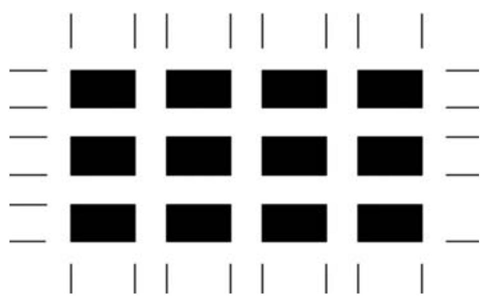

**Fig.2** Internal electrode map by screen printing technique

### 2.4 Co-firing and oxidation of multi-layer sheets

The degumming and excluding fat of the sample were processed in air, and their velocity of heating was less than 60 ℃/h. If the velocity was higher, bubbles would appear on the surface of the ceramics, maintaining the temperature at 450 ℃, and lasted for 30 min, making sure that the electrodes was not oxidant. After degumming, the sample could process high temperature sintering in reducing atmosphere[11], the component was 2.5% $H_2$+$N_2$ and the sintering curve is shown in Fig.3.

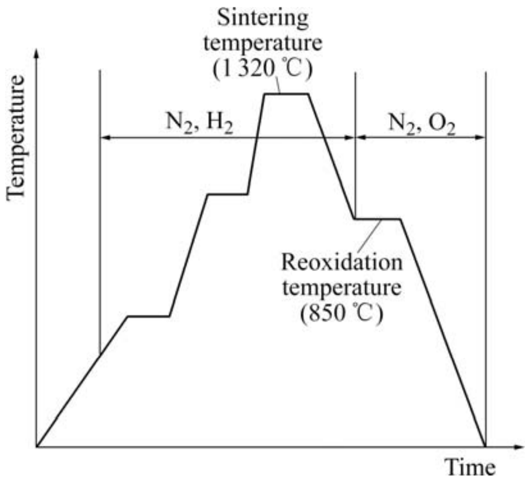


**Fig.3** Sintering curve of co-firing multi-layer PTCR

During the period of firing, the $N_2$+$H_2$ could protect the internal electrode from oxidizing, when the temperature reduced to 850 ℃, annealed the chips with weak oxidizing atmosphere. Finally printed Ag paste and sintered it at 800 ℃ to form external electrode[12].

## 3 Results and discussion

### 3.1 Aqueous tape casting chips, SEM of Ni paste before and after firing

Fig.4 shows the morphology of green sheets prepared according to Fig.1 before and after firing. Fig.5 shows the morphology of Ni paste before and after firing, which consists of 10% $BaTiO_3$, 10% Cr and 80% Ni.

Comparing Fig.4(a) with Fig.4(b), it is indicated that before firing the $BaTiO_3$ particle size is small but disperses well, after firing the particles are more compact, with the size of 1−2 μm, realizing the fine grain strengthening and densification.

Fig.5(a) shows that Ni particles highly disperse before firing, and it contacts with each other after firing at 1 320 ℃, forming good electrode film.

### 3.2 Depth of PTC

During the experiment, the PTC chips of 100 μm and 400 μm were respectively printed by Ni paste consisting of 10%$BaTiO_3$, 10%Cr and 80%Ni, then cut them into 3-layer sample, with the size of 6 mm×8 mm×0.65 mm, the samples were sintered in a $N_2$+$H_2$ reducing atmosphere, and annealed at 850 ℃ in weak oxidizing atmosphere, through SEM analysis. The morphology of sample is shown in Fig.6.

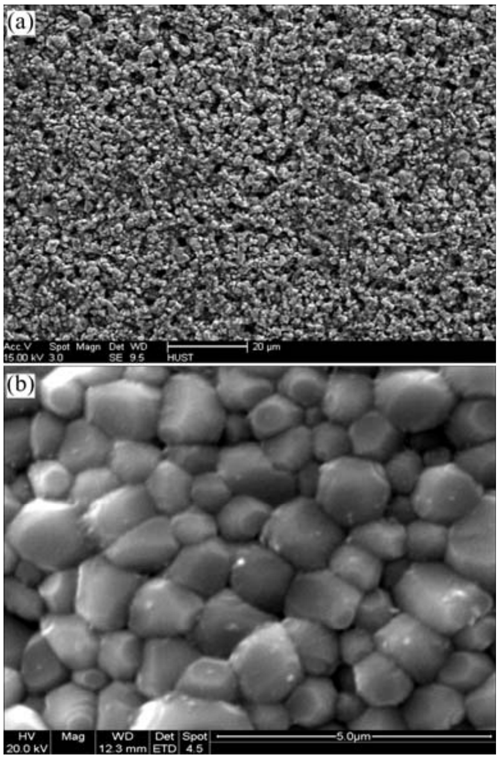


**Fig.4** SEM images of aqueous tape casting chips before (a) and after (b) firing

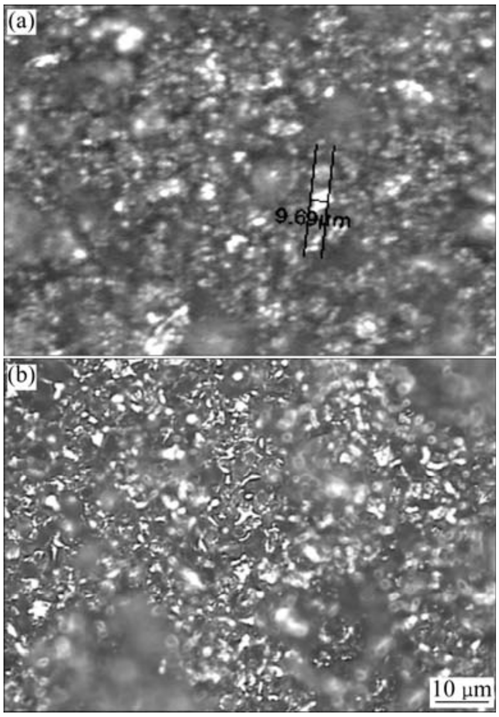


**Fig.5** SEM images of Ni electrode before (a) and after (b) firing

From Fig.6(a), it can be seen that the diffusion of Ni to ceramic is modest, but from Fig.6(b) the diffusion is more severe, without obvious metal/ceramic layer. This

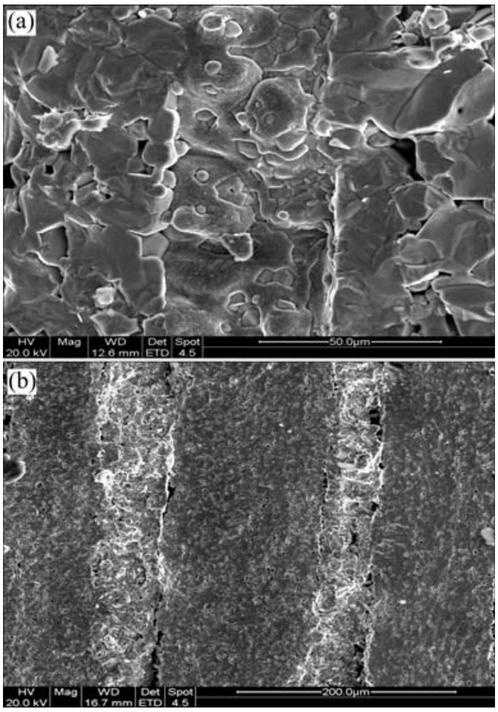


**Fig.6** SEM images of PTC chips of 100 μm (a) and 400 μm (b)

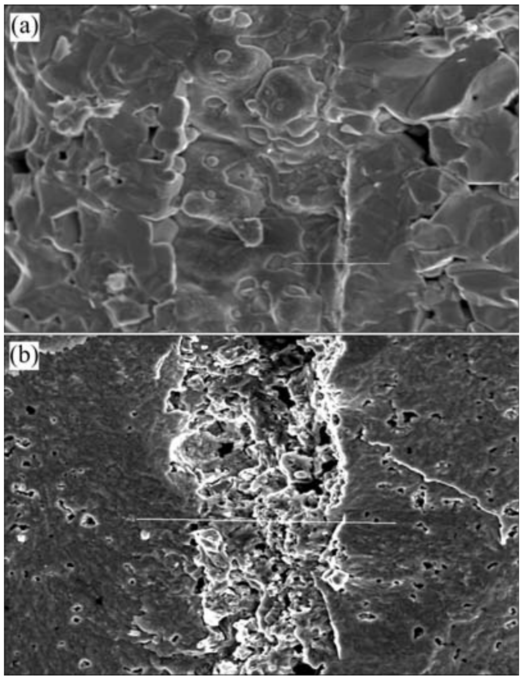


**Fig.7** SEM images of PTC with different sizes after sintering: (a) 100 μm; (b) 400 μm

proves that modest diffusion is beneficial to multiplayer PTCR property, for example, it can improve the ohmic contact, R-T characteristic and current voltage property, but excessive incorporation of Ni elements is harmful to PTCR property. In order to compare the diffusion of different depths of interface, the authors carried out EDS analysis in the SEM.

### 3.3 EDS analysis

In order to get more about the diffusion activity of the metal-ceramics, we chose the area as shown in Fig.7 to carry out EDS analysis. We intercepted chips of −400−400 nm to depict element variation curves, just as shown in Fig.8, at the same depth interface, the diffusion rate of Ni is relatively more serious in 100 μm chips than that of 400 μm, the analysis of the resistance—temperature curve shows that the resistance of the 400 μm chips is much less. When it becomes thin, the diffusion is serious and its function becomes exacerbate, while too thick, it is meaningless. Series of physical-chemical phenomena may happen at inner interface, therefore making the inner interface a particular interfacial layer area[13−14]. Certain commutative diffusion is of great help to form good implemental function, as the tile becomes fine grain and more thinner, these phenomena would be more obvious, finding out commutative matching passive devices is of great importance. The research by the authors showed that these commutative diffusion phenomena came into forming in the oxygen vacancy

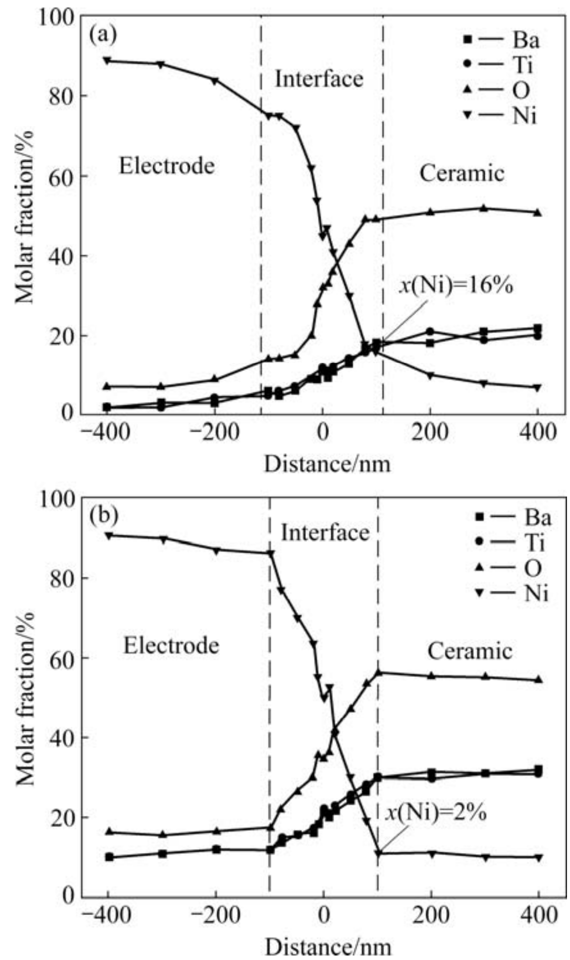


**Fig.8** EDS curves of PTC with different sizes after sintering: (a) 100 μm; (b) 400 μm

drifting environment when the temperature decreased. Finding out commutative matching crude flake and electrode was critics to form good ohmic contact, lower resistivity, and higher enduring voltage[15].

## 4 Conclusions

1) Using the aqueous tape-casting method, PTC chips are prepared, which are suitable to superposition and co-firing, and their thicknesses are 100 and 600 μm, respectively.

2) When the thickness of the slice is 400 μm, the contact of the metal-ceramics is good, the diffusion is moderate and the contact quality of the metal-ceramic is high. While the thickness of the chip is 100 μm, the diffusion of the metal-ceramic is more severe, and structure defect appears accordingly, which will be harmful to the resistance and high enduring voltage of the multilayer PTCR.

3) The Ni diffusion in the multiplayer PTCR with different PTC layer thicknesses is different. The diffusion strengthens as the ceramic chip gets thin. But this is harmful to the miniaturization of PTCR.

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