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The influence of shaping process on microstructure and properties of $BaTiO_3$-based chip thermistors

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Abstract

$BaTiO_3$-based chip ceramics with a thickness of 0.3 mm were prepared by three different forming techniques: gelcasting, slipcasting and roll-forming. The resistance–temperature and voltage–current characteristics of the obtained chip ceramics were studied. The influence of forming process on microstructures of green sheets and ceramic bodies was also analyzed in detail. The results indicate that gelcast and slipcast ceramics possessing more uniform microstructure exhibit stronger PTC (positive temperature coefficient) effect and higher withstand voltage than roll-formed ones.

Keywords: C. Electrical properties; Shaping process; Microstructure; Chip thermistors

1. Introduction

With the development of surface-mounted technology, the trend is for $BaTiO_3$-based positive temperature coefficient thermistors with much smaller size, lower room resistivity [1,2]. A possible approach to reduce the resistivity is to fabricate multiplayer devices so as to reduce the thickness and increase the area of the devices. Since ultra-thin and flat green sheets are required for preparation of $BaTiO_3$-based multilayer PTCR (positive temperature coefficient of resistance), shaping processes are quite important. However, very little information is available in the literatures on the methods of processing such ceramics as $BaTiO_3$-based chip PTCR.

Nowadays, several shaping methods for thick films, such as gelcasting [3], slipcasting [4] and roll-forming [5] are available. Among them, gelcasting and slipcasting are colloidal processes that offer the potential to reliably produce ceramic films and components through control of the initial suspension and its evolution during shaping. In addition, gelcasting and slipcasting allow the binder to be used in small quantities, and thereby, avoiding long and complicated binder burnout schedules and minimizing deformation. As one of the major forming techniques for large-scale fabrication of both monolithic and composite ceramic components, roll-forming has some advantages, such as facility and high efficiency.

In this work, experiments were carried out to find the influence of forming process on the properties and microstructures of green sheets and ceramic bodies, and to confirm the characterization of the PTC chips by three different forming processes through comparing.

2. Experimental

$BaTiO_3$-based PTCR ceramic powder (the named composition is followed: $(Ba_{0.8}Sr_{0.2})Ti_{1.01}O_3$ + 0.25 mol% Y_2O_3 + 2.50 mol% SiO_2 + 0.5 mol% Al_2O_3 + 0.08 mol%

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$Mn(NO_3)_2$) was synthesized at 1155 °C for 2 h. The average particle size was 1.0 μm. The obtained powder was screened through a 200-mesh sieve.

Green sheets were obtained by following three kinds of processes, and then sectioned into the size of 15 mm × 10 mm and placed on refractory plates covered with stabilized zirconia powder to sinter under the same sintering schedule that is shown in Fig. 1. The differences between the typical sintering schedule for PTCR $BaTiO_3$ in reference [6] and the presented schedule in this paper lie in the fact that the latter schedule has a lower increasing rate from room temperature to 500 °C, a long stage of soaking temperature at 500 °C, and a relatively short soaking time (30 min) at the sintering temperature of 1310 °C. Using this schedule, deformations such as crack, curl or warp which often appear in thin chips during sintering are minimized. Aluminum paste that gives good ohmic contact was screen printed onto the major surface of the sintered chip ceramics as external electrodes.

Scanning electron microscopy (JSM-35C, JEOL, Japan) was used to observe the microstructure of the green sheets and chip ceramics. The resistance–temperature and voltage–current characteristics of chip thermistors were, respectively, measured using *R–T* and *V–I* automatic testing system (ZWX-B, Huazhong University of Science and Technology, China). The minimum current value of the voltage–current characteristics is defined as the residual current, at steady-state power, and the voltage corresponding to the minimum current is taken as the withstand voltage. The density of the ceramics was measured by the Archimedes principle.

2.1. Chip ceramics prepared by gelcasting

$BaTiO_3$ aqueous slurry for gelcasting was composed of $BaTiO_3$-based ceramic powder, dispersant, organic monomers, plasticizer, pH adjustor and deionized water. An ammonium salt of poly(methacrylic acid) ($PMAA\text{-}NH_4$)

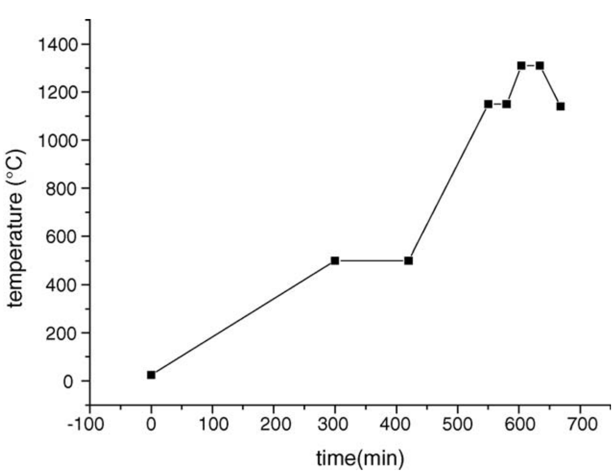

Fig. 1. The firing schedule for chip ceramics.

with an average molecular weight of 10,000–160,000 g/mol was used as the dispersant. After addition of the $PMAA\text{-}NH_4$, pH of the slurry was controlled at the range 8–10 using 10% $NH_3{\cdot}H_2O$ solution because pH value of the range 8–10 has a good effect on the viscosity of the slurry. The reactive organic monomers: acrylamide (AM) and *N*,*N*′-methylenebisacrylamide (MBAM) were the essential components of the gelcasting. Ammonium persulfate (APS) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were used as an initiator and a catalyst, respectively, for the free-radical polymerization reaction of monomers. Glycerol was chosen as plasticizer to modify the flexibility and strength of green sheets. Based on a suitable choice, a well-dispersed suspension with high $BaTiO_3$-based ceramic powder loading (80 wt.%) and low viscosity (170 mPa s), stabilized with $PMAA\text{-}NH_4$ (0.45 wt.% of ceramic powder) at pH 9.2 was obtained for gelcasting. Then APS and TEMED were added and the suspension was cast onto a glass surface at room temperature in N_2 to form 0.3 mm thickness sheets after gelation [7]. Then the gelated, wet green sheets were dried carefully under room ambient.

2.2. Chip ceramics prepared by slipcasting

$BaTiO_3$ aqueous slurry for slipcasting was composed of $BaTiO_3$-based PTCR ceramic powder, dispersant, plasticizer, binder and deionized water. $PMAA\text{-}NH_4$ and glycerol were used as dispersant and plasticizer, respectively. Polyvinyl alcohol (PVA, MW = 2400, 5 wt.%) was utilized for binder (for green strength). pH of the slurry was controlled at the range of 8–10 using 10% $NH_3{\cdot}H_2O$ solution. A well-dispersed suspension with 75 wt.% $BaTiO_3$-based ceramic powder loading and low viscosity (310 mPa s), stabilized with $PMAA\text{-}NH_4$ (0.45 wt.% of ceramic powder) at pH 9 was obtained for slipcasting. The green chips were obtained after pouring the slips into white plaster molds.

2.3. Chip ceramics prepared by roll-forming

$BaTiO_3$-based PTCR ceramic powder was mixed with the binder (a 18 wt.% aqueous solution of PVA) and glycerol to obtain a mixture having suitable plasticity for roll-forming process. The content of those organic additives is about 32–37% of the weight of ceramic powders. The roll-forming was conducted at room temperature using a laboratory roll-forming machine. The mixture was passed between two cylinders that are rotating in opposite direction. The plastic mix could be compacted, as well as being pressed to a thickness equivalent to the spacing of the rolls. Multiple passes with 90° reverse of the sheet at diminishing roll separation were needed to yield a constant-thickness sheet of high uniformity. The mixture was finally formed into green tapes with thickness of 0.3 mm.

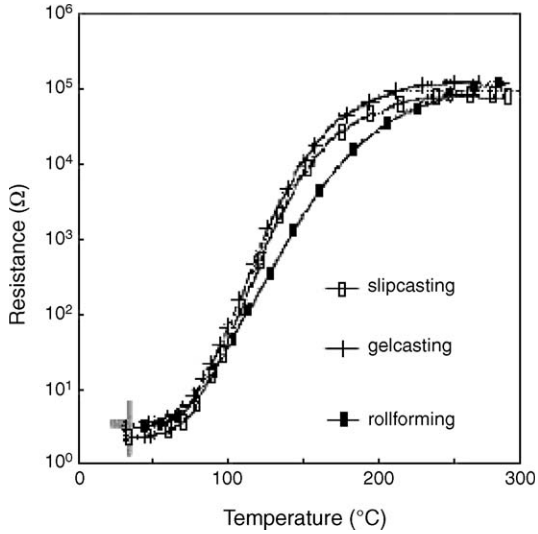

Fig. 2. Resistance vs. temperature characteristics of chip thermistors.

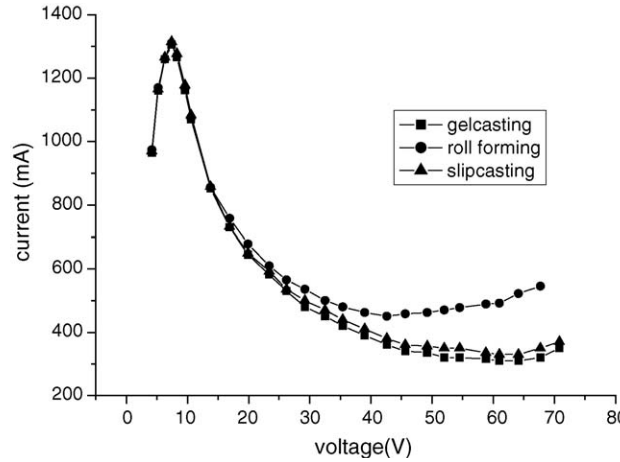

Fig. 3. Voltage vs. current characteristics of chip thermistors.

3. Results and discussion

3.1. Electrical characteristics of chip thermistors

Fig. 2 shows the resistance–temperature characteristics of chip thermistors sintered at 1310 °C for 30 min. In terms of the test results of slipcasting, gelcasting and roll-forming samples, the ratio of the maximum resistance to the minimum (R_{max}/R_{min}) is, respectively, 7.3×10^4, 7.2×10^4, 7.0×10^4 and the temperature coefficient of resistance (α) is 9.7, 9.7 and 8.2%/°C. It is obvious that, at the same sintering condition, samples from three processes nearly have the same minimum resistance (R_{min}). Both gelcast and slipcast samples have a higher ratio of the maximum resistance to the minimum and a higher temperature coefficient of resistance in comparison with the roll-formed one. Apparently, the gelcast and slipcast chip ceramics exhibit stronger PTC effect than the roll-formed one at the same sintering condition.

The voltage–current characteristics of chip thermistors are shown in Fig. 3. It shows that the resistant voltage of chip thermistors has a direct relationship with the shaping process. The withstand voltages of both gelcast and slipcast samples are nearly 65 V with the residual current are at about 320 mA as illustrated in Fig. 3, whereas the withstand voltage of roll-formed samples is 45 V with a residual current about 450 mA. It is obvious that the electrical properties of PTCR ceramics by gelcasting and slipcasting are remarkably improved.

3.2. Microstructure homogeneity of green sheets and ceramics

In order to explain the above phenomenon, we investigated the microstructures of green sheets and chip ceramics via the three forming routes.

The SEM micrographs of sintered samples are shown in Fig. 4. It is clearly seen that gelcast and slipcast samples have more homogeneous microstructures than the roll-formed one. The microstructure homogeneity of gelcast ceramic bodies may be attributed to the good dispersion and the in situ gelation of the suspension in green sheets (Fig. 5). It is well known that ceramic PTC effect is the synthetic behavior of all grain boundaries [8,9], that is to say, the PTC effect of thermistors depends directly on the grain size, grain boundary and homogeneity of ceramics, so the homogeneous microstructure of gelcast samples may result in strong PTC effect. Compared with gelcast samples, slipcast ceramics have less homogeneous microstructure, because of the lamination of ceramic powders when the liquid was slowly absorbed by plaster mold during the final stages of forming process, although slipcast ceramic also exhibit strong PTC effect because of the more or less well-developed binder networks in the slipcast green sheets and some homogeneous microstructure of slipcast ceramics. The roll-formed sample contains grains with different sizes as

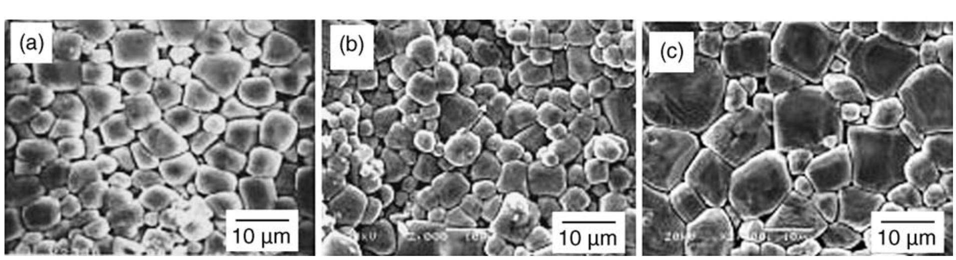

Fig. 4. Scanning electron micrographs of nature surfaces of chip thermistors: (a) gelcasting; (b) slipcasting; (c) roll-forming.

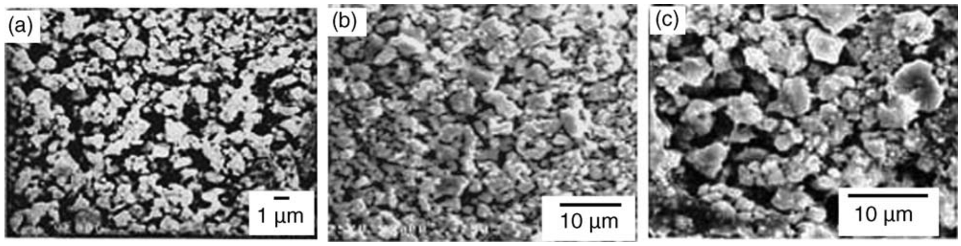

Fig. 5. Scanning electron micrographs of green tapes prepared by different shaping process: (a) gelcasting; (b) slipcasting; (c) roll-forming.

shown in Fig. 4, and this result can be explained from two aspects: first, the roll-formed green sheets, with high content of organic additives which volatilized in the period of sintering and leaving pore in the body, have uneven microstructure; secondly, because the roll-forming was conducted by pressing green sheets in direction of thickness and length, there exists the anisotropy of strength and density in green sheets, which will result in uneven grain growth in sintering process.

It is proposed that the intergranular contacts of doped $BaTiO_3$ ceramics function as *n–i–n* junction by Heywang [8], Jonker [9] and Daniels et al. [10]. For applications it is necessary to have not only fine-grain-size ceramic material but uniform grain size, otherwise the junctions around large grains probably have the opportunity to overheat, giving rise to localized cracking. The withstand voltage is useful for judging the voltage blocking capability of a device. From the ceramic microstructure shaped by three processes, it is easy to expect the difference in the voltage blocking capability of device.

It is worth mentioning that the densities of ceramic samples via different shaping processes are distinct. The relative densities of gelcasting, slipcasting and roll-forming ceramics were 97.29, 97.67 and 92.57%, respectively. That is to say, slipcast chips have slightly higher densities than gelcast ones, and the roll-formed ones hold the lowest density. According to Kuwabara [11], we know that, for PTC ceramics, when density is high (above about 80% theoretical density), the magnitude of PTC effect decreases as density increases because of the incomplete grain boundary of ceramics with higher density. Therefore, the higher densities of slipcast and gelcast samples may reduce the PTC effect. Of both the homogeneous microstructure and slightly incomplete grain boundary for gelcast and slipcast samples in comparison with roll-formed ones, maybe the homogeneous microstructure plays a dominant role in the PTC effect; therefore, gelcast and slipcast samples show stronger PTC effect than roll-formed ones.

4. Conclusions

Chip thermistors were prepared via gelcasting, slipcasting and roll-forming. Due to well-dispersed slurry, well-developed binder networks and high packing density in green sheets, and homogeneous microstructure of green sheets and chip ceramics, gelcast and slipcast chip thermistors exhibit stronger PTC effect and higher withstand voltage than roll-formed ones at the same sintering condition.

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