Control of shrinkage on the behavior of co-firing of ferrite and varistor multi-layers composite with organic content

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Abstract When make multi-layer ceramics device such as EMI filter, there are a lot of process problems. Specially, crack, camber and delamination should be controlled surely by different sinter shrinkage rate of interface of two materials. The purpose of this work was to co-fire defect-free ferrite/varistor ceramic multi-layers fabricated via a calcination temperature and organic vehicle contents of ferrite. Sintering shrinkage of both calcined ferrite and varistor materials were measured using dilatometer. X-ray diffraction analysis indicated that no significant phase change occurred in the materials under investigation as a result of the sintering process. Crack and delamination of each interface were observed by scanning electron microscopy and optical microscope. We obtained the defect-free and co-fired ferrite/varistor ceramic multi-layer by controlling calcinations temperature.

Keywords Ferrite · Varistor · Co-firing · Multi-layer · Shrinkage

1 Introduction

Recently, multi-layer chip EMI filters have been developed as a type of promising surface mounting device. They are made by stacking ferrite layers and varistor layers with internal electrode pastes, and then co-firing. The sintering temperature of ferrite and varistor must be below 900 °C so as to co-fire with Ag internal electrode. The properties of devices depend on the electromagnetic properties of the sintered ferrites, varistors and the quality of the interface. On the on hand, interfacial diffusion is inevitable, which will affect electromagnetic properties near the interface. On the other hand, the mismatch in sintering kinetics between different ceramics may cause residual stresses or cracks. Therefore, the matching and compatibility during co-firing process is the key to achieve multi-layer chip composites.

ZnO varistors are semiconducting ceramics having non-ohmic current–voltage characteristics which are fabricated by sintering of ZnO powders with small amounts of additives such as Bi_2O_3, CoO, MnO and Sb_2O_3 [1]. The non-ohmic property comes from grain boundaries between the semiconducting ZnO grains. Due to their superior electrical properties, these materials have become important as varistor materials for voltage surge protectors in electrical circuits [2]. Varistors provide bidirectional transient protection and are very effective in suppressing high amplitude and low-frequency transients.

Ni-Zn-Cu ferrite are soft ferrimagnetic ceramic materials and are commonly the ferrites of choice for EMI applications, having very high resistivity, high permeability values and little eddy current loss in high frequency operations [3]. Ferrite components are known to be efficient and cost-effective for the prevention of spurious signals transmitted by conductance and by radiation. Yue et al [4]. investigated the properties of ferrite-cordierite composites for use in multi-layer chip inductors and point out that substrates with high permeability may decrease EMI between components in integrated circuits.

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Layers cosintered at high temperature possess residual stresses at room temperature if the thermal expansion coefficients of the various layers differ. This can cause cracking. The two primary modes of cracking in multi-layers are delamination (in the case of weakly bonded layers) and transverse cracking (either channel cracks or tunnel cracks) of layers subjected to in-plane tensile stresses [5]. Differences in thermal coefficients, shrinkage and elastic modulus can lead to stress (tensile or compressive) and ultimately lead to delamination, micro-cracking or pore formation in the ceramic materials.

Among the many variables governing the shrinkage of the ceramic substrate, packing density is the most important. The packing density of the green sheets depends on the slurry composition: paste properties [6], composition and particle size distribution of ceramic powders and the ratio of organics to inorganics [7]. Many works have been carried out to investigate the effect of particle size distribution of ceramic powders on the sintering shrinkage behavior of the green sheets. In addition, the lamination conditions (i.e., laminating pressure, time and temperature) also play an important role in the determination of the final sintering shrinkage of the substrate [8].

In this study, the effect of calcinations temperature and binder content on the shrinkage behavior of a multilayered ceramic substrate is investigated.

2 Experimental procedure

2.1 Powder preparation

Ni-Zn-Cu ferrite powder (NZCF) mixed 24 hours with ethanol uniformly through wet ball milling adding NiO, ZnO, CuO, α-Fe$_2$O$_3$ (High Purity Chemical Co.) and small amount sintering additives. Mixed powder was dried in 80 °C dry oven. The powder was granulated by 100mesh test sieve and powder calcined to 700 °C to 900 °C 50 °C interval.

Used commercialized ZnO varistor powder that is added ZnO and Bi$_2$O$_3$, CoO, MnO, Sb$_2$O$_3$ etc. (Latron Co. Korea).

2.2 Dilatometer analysis

A differential thermal dilatometer was used to measure the sintering shrinkage properties of the ceramics.

The dilatometer used was an Orton 1600D horizontal pushrod type dilatometer with a temperature range of 25 °C~1200 °C. Pellets measuring 5mm in diameter were pressed using a pressure of 1t for 20s. These were then sintered using a constant heating rate of 10 °C/min and cooled in air to room temperature.

2.3 Slurry preparation and tape casting

Casting slurries were prepared by mixing powders in a commercial non-aqueous organic vehicle (B73225 binder, Ferro) containing binder, plasticizer, and solvents.

The 900 °C calcined Ni-Zn-Cu ferrite powders were mixed with a commercial vehicle system in a weight ratio of 60/40(NZCF1), 55/45(NZCF2) and 50:50(NZCF3). (Table 1)

On the other hand, organic vehicle of varistor slurry was fixed by 45wt %. Mixed slurry was aged for 24 hours by 15 rpm. The slurry was cast using a comma-type tape caster. Tape casting speed is 2 m/min and dry temperature is 80 °C The green tapes were uniform and had a thickness of about 90 μm..

2.4 Lamination method

NZCF1, NZCF2, NZCF3, varistor green sheets were made multi-layer structure using laminator. Laminating temperature was 60 °C, laminating pressure was 80 kg/cm^2, and laminating time kept by 30 s per 1 sheet.

Multi-layer structure makes as ferrite sheet thickness becomes 10 mm in middle and thickness of each varistor sheet made to become 5 mm on ferrite upper part and bottom. Finally, ferrite/varistor multi-layer was pressured by cold isostatic pressure. (CIP: 100MPa during 1 min) Multi-layer green-body cut to 10×10 mm size by cutting machine.

2.5 Sintering profile

Samples were ramped from room temperature to 650 °C in 10 h 50 min, held at 650 °C for 8 h and then ramped to 950 °C in 1 h. They were held at 950 °C for 3 h then ramped down to room temperature.
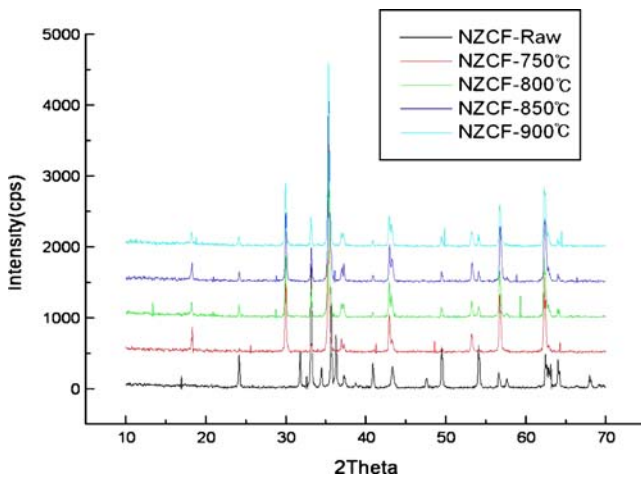
2.6 Scanning electron microscopy (SEM)

Sintered samples were cut perpendicular to the interface, mounted in bakelite and then polished to a 1μm finish to allow for the observation of the microstructure at the interface.

All samples were ground for 20 min using 2000grit SiC paper, polished for 10 min with 4000grit SiC paper by auto

Table 1 Ni-Zn-Cu ferrite organic vehicle content.

Sample no.	Powder: binder (wt%)	Powder: binder (g)
NZCF 1	60:40	100:66.7
NZCF 2	55:45	100:81.8
NZCF 3	50:50	100:100

Fig. 1 XRD pattern of ferrite calcined at 750 °C~900 °C for 3 h

polisher (M-PREP, ALLIED Co. USA). Finally for a further 5 min using 1 μm diamond polish.

Crack, delamination, and micro structure were observed using scanning electron microscopy (SM-300, Topcon).

2.7 X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) analysis was carried out on both varistor and calcined ferrite samples. X-ray diffraction (Mac Science KFX-987228-SE) used Cu Kα X-ray.

3 Result and discussion

Figure 1 shows the XRD of Ni-Zn-Cu ferrite by each calcination temperature. XRD analysis confirmed that no significant phase change occurred during calcining of the materials under investigation here.

Figure 2 shows the sintering shrinkage behavior of calcined ferrites (750 °C~900 °C) and varistor. 750 °C calcined ferrite begins to densify at a low temperature, sinters gradually and finishes up with a linear shrinkage of approximately 12%. The varistor begins to shrink after the ferrite and then the gradient is very sharp with a final linear shrinkage of approximately 15%. There is thus quite a large degree of mismatch between the materials in terms of
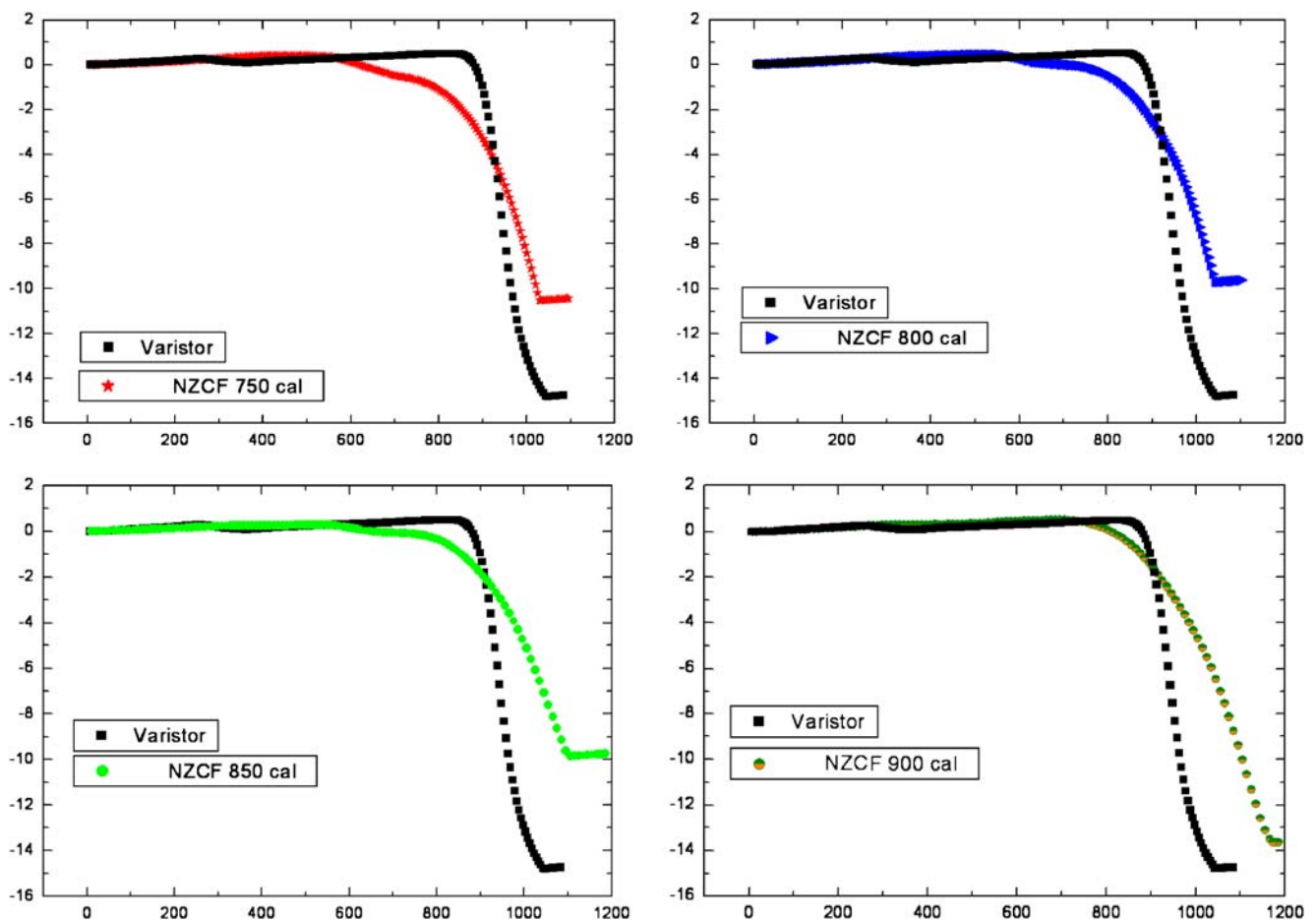
Fig. 2 Shrinkage curve of calcined ferrite and varistor
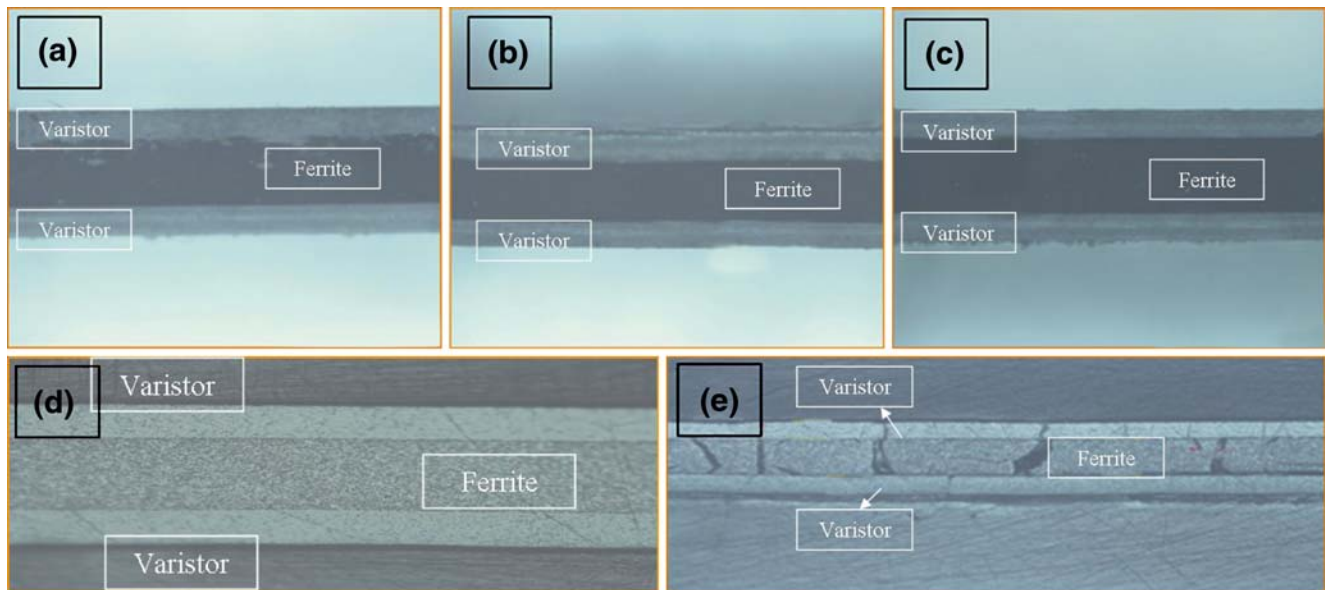
Fig. 3 (a), (b), (c) before sintering multi-layers. (d) sintered multi-layer organic contents 40wt%, (e) sintered multi-layer organic contents 45wt%

shrinkage. This is believed to be due to the lack of liquid phase for the ferrite materials, as opposed to the varistor material, which contains additives such as Bi_2O_3 and Sb_2O_3.

Lu et al [9]. report rapid shrinkage of zinc oxide-based varistors containing additions of Bi_2O_3 and Sb_2O_3 at around 1000 °C. They attribute this rapid shrinkage to the reaction between the pyrochlore phase and ZnO which accelerates the sintering rate of ZnO through a liquid-phase sintering mechanism.

Therefore, increase calcination temperature of Ni-Zn-Cu ferrite to control initial shrinkage rate of Ni-Zn-Cu ferrite and attempted shrinkage rate control with varistor.

As a result, shrinkage temperature also increased according as calcination temperature of Ni-Zn-Cu ferrite increases. Sintering shrinkage rate mismatch of calcined Ni-Zn-Cu ferrite and varistor in 900 °C was shown about 1%.

Therefore, control delamination controlling initial shrinkage rate between two materials by calcination temperature control of Ni-Zn-Cu ferrite.

So that is conjectured that crack and camber may be controlled because is dissolved residual stress in each interface.

Figure 3 shows optical microscope image of multi-layer composite cross section. a), b), c) are cross section before sintering and d), e) are cross section of NZCF1/varistor and NZCF2/varistor after sintering at 950 °C for 3 h. All multi-

Fig. 4 SEM image: (a), (b): NZCF1/varistor multi-layer, (c), (d): NZCF2/varistor multi-layer
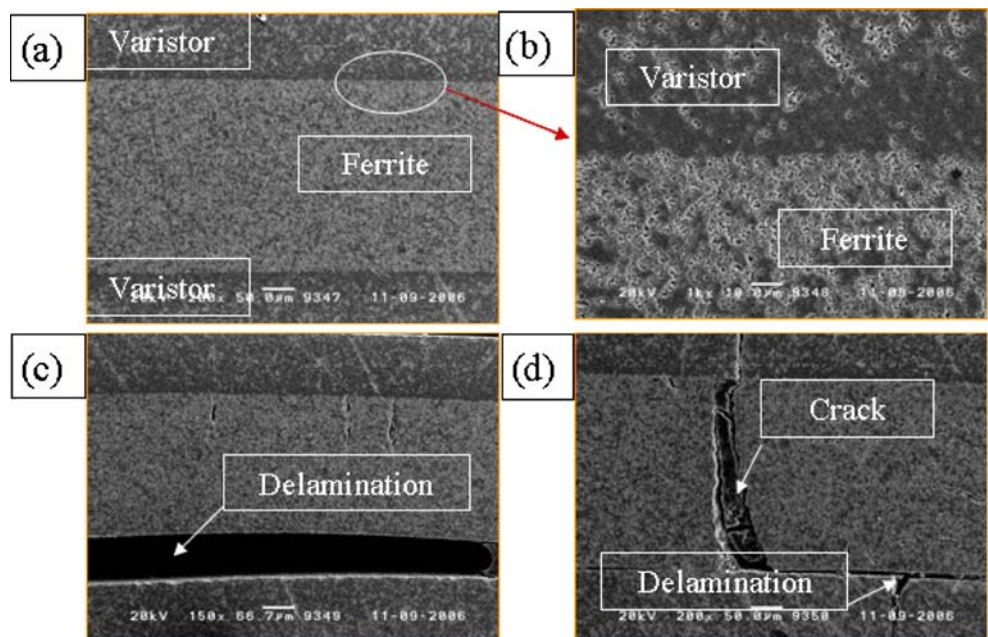
layer composites were laminated to equal thickness. Multi-layer composite of NZCF1/varistor including organic vehicle 40wt % showed less than any defect in sintered multi-layer composite.

M. Hagymási et al [10]. reported that the dielectric tape should densify at low temperature, where it is constrained by non-sintering green ferrite tape and the ferrite tape should densify at higher temperature, but the shrinkage is inhibited by the already dense dielectric tape. Therefore, NZCF1 layer that display higher shrinkage at low temperature was sintered by constrained sintering of varistor layer.

And shrinkage behavior of varistor layer by NZCF1 layer that is already sintered at high temperature was constrained.

As content of organic vehicle increases in experiment by organic vehicle content, crack happened to vertical direction on interface. This result is due to packing density that is less relatively by increase of organic vehicle content of ferrite. So, internal stress is enlarged because difference of shrinkage speed by large density difference of two materials increases and crack may be produced.

Figure 4 shows SEM image of NZCF1/Varistor and NZCF2/Varistor. NZCF1/Varistor could confirm defect-free sintered multi-layered composite that some delamination and crack between two materials do not happen.

On the other hand, delamination and from ferrite to varistor gone crack in interface by different shrinkage between two materials happened as content of organic vehicle increases in NZCF2/Varistor. Was broken by increase of internal stress in NZCF3/Varistor composite that have the most organic vehicle contents.

4 Conclusion

This study shows that it is possible to co-fire defect-free ferrite/varistor multi-layers made using calcination temperature of Ni-Zn-Cu ferrite.

Dilatometer analysis confirmed that initial shrinkage mismatch rate of 900 °C calcined Ni-Zn-Cu and varistor are almost equal. (Less than shrinkage rate difference 1%).

Controlled initial sintering shrinkage rate of varistor that start shrinkage in 900 °C by controlling shrinkage temperature of NZCF at calcination temperature as is equal. So, is considered that delamination by the initial shrinkage rate is controlled.

Ni-Zn-Cu ferrite that is calcined in 900 °C changing organic vehicle content by 60/40 (NZCF1), 55/45 (NZCF2), 50/40 (NZCF3) in 950 °C 3 hours sinter. As a result, could make multi-layer composite that defect does not exist entirely in NZCF1. However, crack and delamination happened to NZCF2, NZCF3 that organic vehicle content is more than NZCF1, in interface by relatively less packing.

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