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Investigation of thin film end-termination on multilayer ceramic capacitors with base-metal-electrode

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Abstract

The thin film of copper, chromium and titanium as end-termination studies were performed on multilayer ceramic capacitors (MLCCs) based on $BaTiO_3$ ceramic with nickel internal electrodes. A green sheet was prepared by tape casting using the X7R/BME powders. Nickel paste was attached to the green sheet as an internal electrode. After lamination, the green chips were sintered at 1300 °C for 2 h, then the external electrodes were sputtered as thin films for end-termination. There is no extra curing process, so that thermal shock of the MLCCs is reduced. To improve the adhesion between thin film end-termination and dielectric body, chromium and titanium were applied as media in this study. The mechanical and electrical properties of the MLCCs were investigated subsequently. The results showed that end-termination with chromium/copper has good performances on electrical and mechanical properties of MLCC, compared to conventional end-termination.

Keywords: MLCC; Dissipation factor; X7R/BME; Thin film; End-termination; Tensile strength

1. Introduction

Multilayer ceramic capacitors (MLCCs) are composed of dielectric layers, interleaved inner electrodes, and outer termination electrodes. They constitute an important class of passive components, and are used invariably in almost all areas of electronics. The recent trends in MLCCs aim at getting higher capacitance values, miniaturization, high frequency application, high reliability and low cost [1–3]. Especially, the rapid progress in mobile and satellite communication system has increased the demand for the development of MLCCs for microwave frequencies. However, conventional termination is normally formed by a dipping process. This process has some disadvantages in the MLCCs. (1) Termination electrode may hamper the further downsize of chips in the future since the end-termination electrode is still thick in many MLCCs. (2) The current silver and copper terminations involve a number of problem, such as excessive thickness, surface irregularities, uneven thickness, looseness, pores, etc. (3) Tumbled bricks were first exposed to a heat treatment cycle normally used for the curing of standard Cu end-termination (maximum temperature >800 °C in air for 60 min). This curing treatment has a possible negative effect on the quality, electric properties and reliability of MLCCs.

For MLCCs application, strong end-termination/ceramic-body adhesion is necessary along with appropriate morphology for mounting on PC Board. A possibility to be replaced convention Cu end-terminations by thin film end-termination, because elemental Cu have low resistivities and better electromigration resistance [4]. However, the adhesive force of Cu film to MLCC substrate such as ceramic body is very weak, so that it restricts the use of the Cu film in MLCC field. In order to enhance the adhesion of Cu film to ceramic substrates, researchers have employed several methods. One of the more common of these is insert a metal glue layer or adhesion promoter prior to Cu film deposition. Inserting a layer inherently creates two new interfaces to replace the original one, and therefore one selects the proper interlayer such that each of the new interfaces is stronger than the one being replaced. The traditional material used for this purpose is Cr [5], but often it is another refractory metal such as Ti or Nb [6,7]. In this investigation, a Cr or Ti layer was formed between the Cu film and the MLCC substrate without

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a post-annealing treatment was carried out for the MLCC system. This subject describes experiments carried out on X7R/BME 0805 MLCCs with thin film end-terminations consisting of sputtering deposited Cu layer, Cr/Cu bilayer, and Ti/Cu bilayer, respectively, then plating Ni/Sn bilayer. They are discussed on electric and mechanical properties in this study. The flow chart of process is shown in Fig. 1. It is well known that the addition of a second element to a pure material can strongly affect its physical and mechanical properties and can be used to control the microstructure and grain size of a sputtered film [8]. Experiments show that the adhesion of thin film termination to ceramic body depends on the sputtered materials on MLCC substrates.

2. Experimental procedure

The MLCC consists of 10 active layers with an overall size of 2.0 mm × 1.25 mm × 0.6 mm, and a distance of 12 μm between the internal electrodes. The dielectric in the MLCC is a ceramic material based on a X7R/BME compound.

2.1. Fabrication of multilayered X7R/BME capacitors

The starting materials were mixed with resin (polyvinyl butyral), plasticizer (butyl benzyl phthalate) and solvent (toluene and ethanol). The resultant slurry was tape-casted to a green sheet with a 25-μm thickness using the Doctor-blade method.

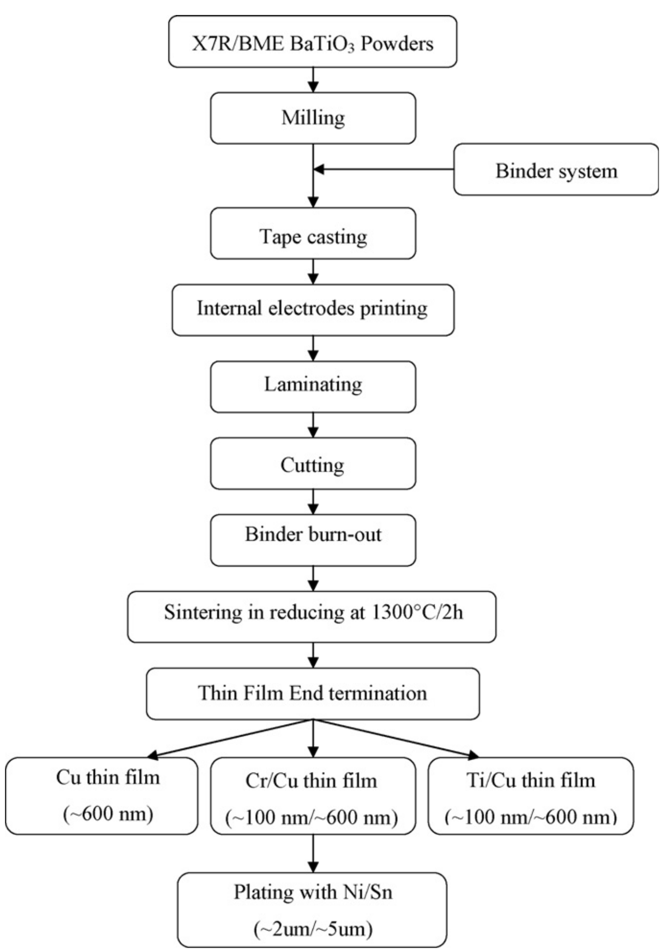

Fig. 1. Flow chart of experimental procedure.

Nickel paste was screened as an internal electrode onto the green sheet. These printed sheets were stacked, pressed at 70 °C under a pressure of 5.2×10^7 Pa and cut into chips. The laminated green sheet was sintered at 1300 °C for 2 h after binder burn out (300 °C), and the sintered chip is called brick. After sintering, bricks were tumbled to eliminate the sharp corners.

2.2. Sputtering silver, chromium, and titanium films

Copper, chromium, and titanium films were deposited on MLCC as the end-termination at room temperature by magnetron sputtering. The used sputtering targets were Cu (99.9%), Cr (99.9%), and Ti (99.9%) with 2-in. diameter. There are three kinds of films deposited on samples (refer Fig. 1). The vacuum system consists of a diffusion pump backed by a mechanical pump. The base pressure of the chamber was 5×10^{-6} Torr. The flow rate of Ar (99.99%), which was used as the sputtering gas, was controlled with a mass flow controller and was fixed at 10 sccm.

2.3. Plating conditions

The plating process was the final procedure for manufacturing multilayer ceramic capacitor. For the purpose of applying in the surface mounting technology, tin should be covered outside the end-termination. First layer plated is nickel (∼2 μm) at 12 A for 120 min, and plating solution is nickel sulfonate. Second layer plated is tin (∼5 μm) at 13 A for 120 min, and plating solution is stannous methane-sulfonate.

2.4. Characterization analysis

2.4.1. Electrical properties measurement

The capacitance and dissipation factor were measured at 1 MHz and 23 °C (HP4278A).

2.4.2. Film thickness measurement

Measurement of the Cu, Cr, and Ti film thickness was achieved with α-step 500 profiler (TENCOR Instruments).

2.4.3. Mechanical strength test

For applications of MLCCs, mechanical strength is an important property. Mounted products are subject to mechanical forces caused by separation of boards. Tensile test can well quantitate the adhesion is enough in the correct between ceramic body and end-terminations. A scheme of tensile test is shown in Fig. 2.

2.4.4. Morphology analysis

Microstructure of MLCC with thin film end-termination was studied by a scanning electron microscope (SEM, JEOL JEL 6400 Japan) equipped with energy-dispersive spectroscopy (EDS).

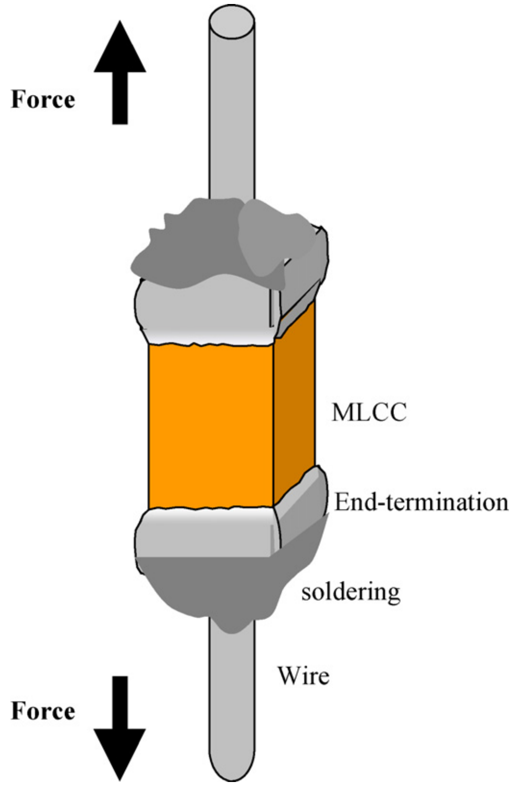

Fig. 2. A schematic showing the tensile test geometry.

3. Results and discussion

3.1. Microstructural and mechanical analysis with different thin film coated on MLCC substrates

To investigate the effect of thin film materials as end-terminations on the mechanical and electric properties, e.g. Cu film, Cr/Cu films, and Ti/Cu films were prepared as end-terminations of the MLCCs by magnetron sputtering.

Table 1 shows the variation of film thickness of the Cu, Ti and Cr films with deposition time. It can be seen that the film thickness increases with the deposition time, especially, Cu film enhanced more than Ti and Cr films. The film thickness of Cu, Ti and Cr after a deposition time of 40 min amounts to 600, 95 and 125 nm, respectively.

A very important property of end-termination is the adhesion on MLCC body. Its function is connected with inner electrodes and apply in a given surface mounting device (SMD) application. A poor adhesion of end-termination which is made by thin film strongly limits industrial utilization. Therefore, it is required to produce films that have good adhesive and other mechanical properties, which can apply in a given SMD application. As shown in the previous study [9], the adhesion of the Ag termination with ceramics addition was investigated. It was concluded that the electric properties are significantly influenced if adhesion between MLCC body and termination is not good.

Table 1
The variation of film thickness of the Cu, Ti and Cr films with deposition time

Film thickness (nm)	Deposition time (min)					
	10	20	30	40	50	60
Cu	40	180	410	600	825	1250
Ti	5	20	55	95	130	160
Cr	5	32	90	125	170	230

It is the purpose of this research to find ways of improving the adherence of the ceramic body and end-termination. According to the literature [10–12], there are two kinds of materials commonly applied to achieve the goal, i.e. Cr and Ti. The two materials are introduced as an interlayer between ceramic body and Cu thin film to improve the adhesion. To investigate the effect of thin film materials on the adhesion, Cu layer, Cr/Cu bilayer, and Ti/Cu bilayer were coated on MLCC substrate by magnetron sputtering, the adhesion test were done on these samples. The thickness of Cu film was about 600 nm (and the thickness of Cr and Ti films was approximately 100 nm). The reliability of thin film coatings in engineering applications depends critically on the adhesion of the coating to its substrate. If the adhesion is poor, the coating may fail even if the coating itself satisfies the design criteria. Despite this fact, relatively few measurement techniques are available to quantify the energy or forces required to separate a coating from the substrate, particularly for brittle substrates [11]. Here we adopt the tensile strength test for evaluating the adhesion of MLCCs. Fig. 3 shows the interfacial microstructure between end-termination and dielectric body, it can be seen that Cu, Ti and Cr film thickness are the same as above mention (Table 1). Fig. 3a shows the morphology of conventional end-termination.

Mechanical strength is an important issue in the applications of MLCCs. Evaluation of the mechanical properties of the MLCCs was carried out by a set-up, in which the mounted components were subject to uniaxial tensile forces. Fig. 4 shows the tensile strength results which are the adhesion between ceramic body and end-termination. Ti/Cu and Cr/Cu-sputtered materials as end-terminations exhibit much better performance than only Cu-sputtered material. In a word, the samples of sputtered Ti/Cu and Cr/Cu films have the larger mechanical strength (similar standard MLCC). This conclusion is further confirmed by the fracture morphology shown in Fig. 5. Unlike the Cu-coated specimens that fractured along the ceramic body and end-termination, the Ti/Cu and Cr/Cu-coated specimens fracture within the ceramic body upon tensile testing. Another benefit coming along with the thin film end-termination is to avoid the thermal process associated with conventional dipping and curing. Nevertheless, all the specimens pass the requirement specified by EIA, >13.4 MPa except Cu-sputtered material.

3.2. Electrical properties analysis with different thin film coated on MLCC substrates

In order to evaluate the effect of sputtered materials as end-termination on the dielectric properties of the MLCCs, the capacitor and dielectric loss (at 1 MHz) were measured. Dielectric losses are usually the most important losses in a

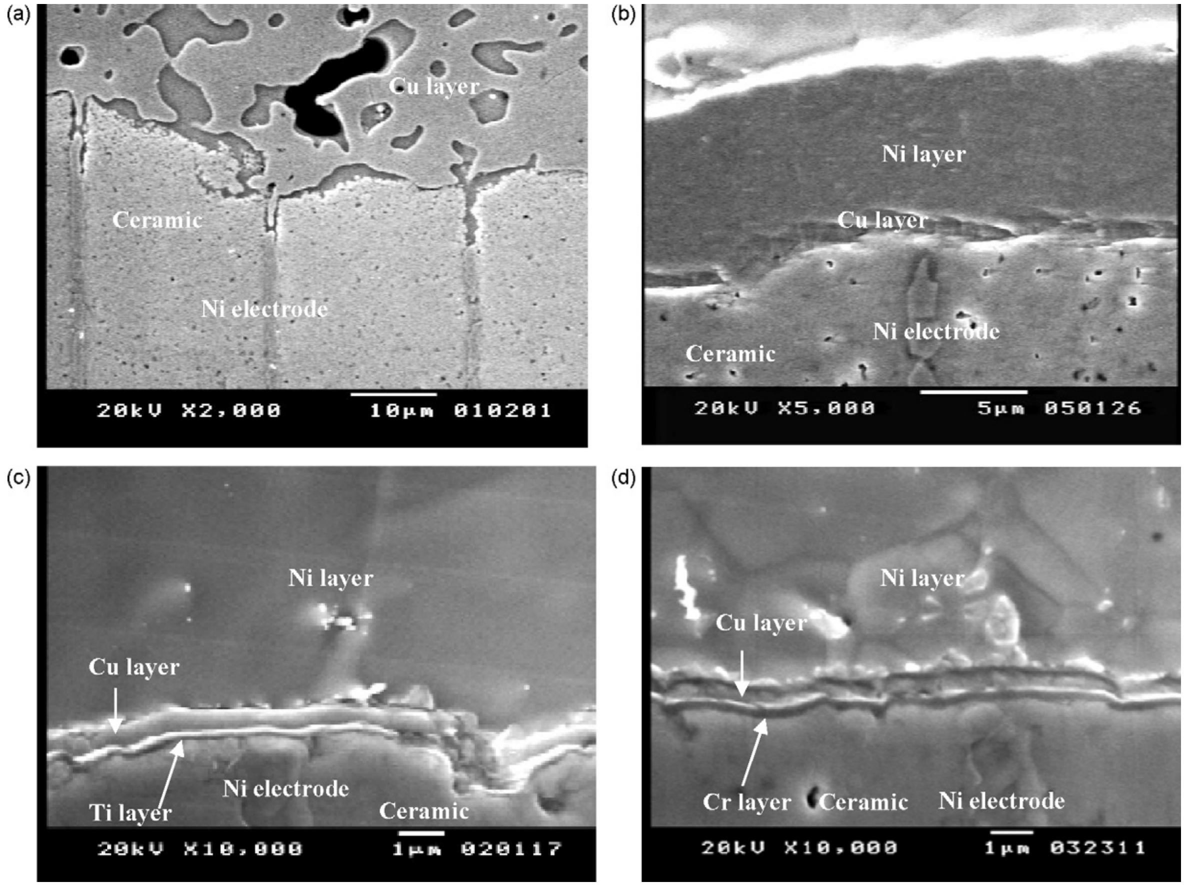

Fig. 3. SEM micrographs of the interfacial microstructure between dielectric body and end-termination with different materials: (a) conventional glass/Cu, (b) Cu thin film, (c) Ti/Cu thin film and (d) Cr/Cu thin film.

capacitor. These losses are associated with the polarization and relaxation of the dielectric material in response to the application and removal of voltage from the capacitor. The dielectric losses of a given material can be described by its dissipation factor (DF). However, the capacitor and DF do depend on the electrodes and their configuration. Ohmic resistance losses occur within the metallic electrodes, the internal wiring, and the terminals of the capacitor. The resistance losses in the metal are quite constant as a function of temperature and frequency. Losses in the internal wiring and the terminals can be important in high current applications, and should not be ignored [13].

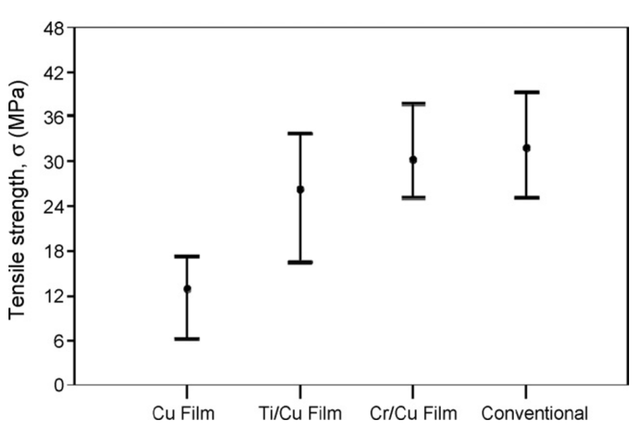

Fig. 4. The pull strength of the MLCCs with different thin film end-terminations.

Fig. 6 shows the capacitance of the MLCCs with different sputtered materials, it can be seen that the large capacitance variation exists for the samples of pure Cu thin film. This reason may be due to poor contact between MLCC body and end-termination. Stable capacitance distributions were observed for other samples (Ti/Cu and Cr/Cu films), this result is similar to conventional MLCC. Variation of the dielectric loss for different sputtered materials as end-termination is illustrated in Fig. 7. The tan δ for the Cr/Cu, and Ti/Ag films are lower than Cu film. The result is similar to that mentioned in the previous study [9], the dielectric loss was higher when the adhesion between ceramic body and end-termination was poor, it also was proved in previous mention as shown in Fig. 5. For the specimen with Cu thin film that has higher dielectric loss, its value is larger distribution from 1.75 to 2.75%. The average of dielectric loss of Ti/Ag and Cr/Cu thin films are around 1.6%. The results are similar to standard MLCCs which have the dielectric loss about 1.5%. On the other hand, an interesting thing was observed which the tan δ of Cr/Cu films was lower than Ti/Cu. This result may be explained by the electric resistance of metals, which has the sequence: Cu (1.6 $\mu\Omega$ cm) $<$Cr (12.9 $\mu\Omega$ cm) $<$Ti (54 $\mu\Omega$ cm). In a real MLCC, the dielectric loss is caused by the time dependence of the polarization mechanisms and by the finite conductivity of the

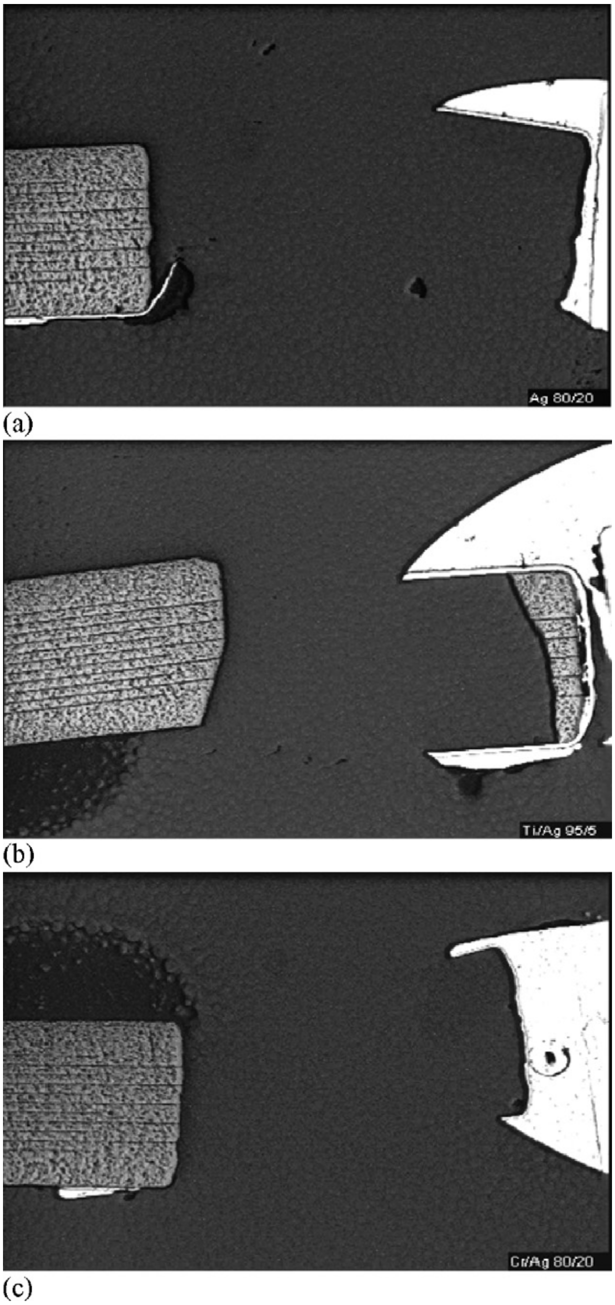

Fig. 5. The fracture morphology of the MLCCs with: (a) Cu thin film, (b) Ti/Cu and (c) Cr/Cu end-terminations after pull strength testing.

dielectric material as well as the ohmic resistance of the metal parts, i.e. electrodes and terminations. Temperature coefficient of capacitance (TCC) of the MLCCs with different end-termination were measured at various ambient temperatures ranging from −55 to +125 °C by using HP4284A impedance analyzer (Fig. 8). TCC of samples with Cr/Cu and Ti/Cu-sputtered materials are similar to conventional MLCCs, which are within X7R specification. However, the sample with Cu end-termination is a little out of specification at high temperature side. The reason for this is attributed to delamination which happened between Cu layer and ceramic body at higher temperature as shown SEM diagram in Fig. 8.

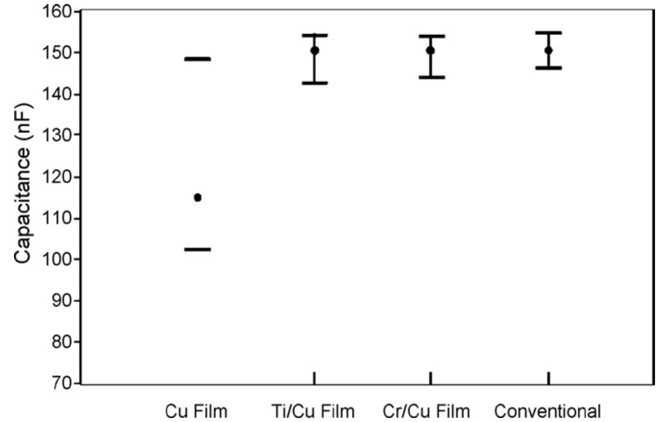

Fig. 6. The capacitance of MLCCs with different materials of thin film end-termination at 1 MHz.

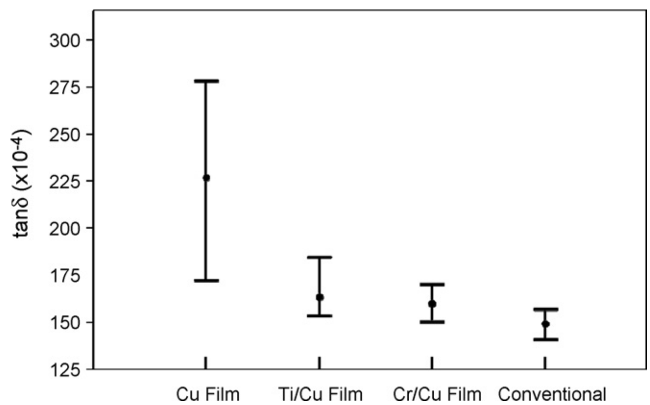

Fig. 7. The dielectric loss of MLCCs with different materials of thin film end-termination at 1 MHz.

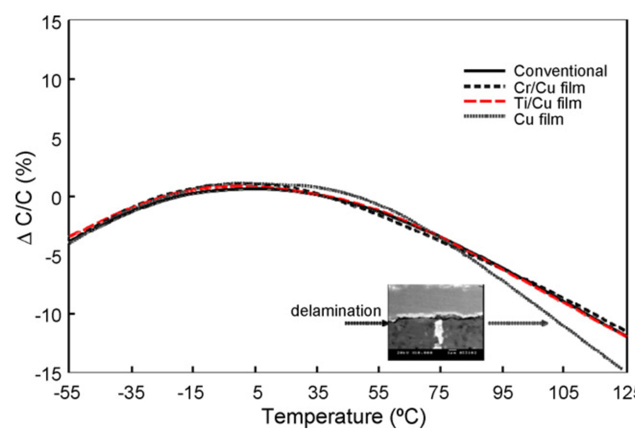

Fig. 8. Temperature coefficient of capacitance for samples with different end-terminations.

4. Conclusions

In the thin film end-termination, poor adhesion was found for the specimens with only Cu thin films sputtered on the MLCCs as the end-termination. The Ti/Cu and Cr/Cu thin film end-terminations have quite high adhesion force on the ceramic body, the pull out strength is similar to the conventionally prepared specimens. The dielectric properties of Ti/Cu and Cr/Cu end-terminations can be comparable with conventional MLCCs.

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