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Lateral growth of coating on Co_2Z ferrite during electroplating of multilayer chip inductors

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Abstract

Lateral growth of nickel coating on a ferrite substrate during electroplating of multilayer chip inductors (MLCI) was investigated. It was found that the lateral growth occurred after a certain time of electroplating, but not at the initial stage. Resistivity of the ferrite and inductance of MLCI decreased continuously with electroplating time. Moreover, surface morphology of the ferrite changed significantly after electroplating, which indicated chemical reactions to take place during the plating process whereas corrosion effect of acid solution on the material can be neglected. Judging from the results obtained, it was inferred that the resistance degradation should be attributed to hydrogen reduction during electroplating, which consequently led to the lateral growth of on the ferrite.

Keywords: B. Surfaces; C. Electrical properties; D. Ferrite; Electroplating; Hydrogen

1. Introduction

Miniaturization of electronic components has become necessary with progress of electronic industry. Multilayer ceramic capacitors (MLCC) have been widely used for their high capacitance-volumetric efficiency and reliability while the usage of MLCI is restrained owing to the difficulty to control the fabrication techniques and the lack of proper ferrites, especially at high frequency. $Ba_3Co_2Fe_{24}O_{41}(Co_2Z)$-based ferrites have become one of the most promising candidate materials for their high cut-off frequency up to 1.5 GHz and have received much attention [1,2].

In general, MLCI are manufactured using a technology similar to MLCC. Three-layer-electrode technique is adopted in the fabrication of terminal electrodes. First, silver is fired on the MLCI as ground electrode. Then, a nickel coating of 2–4 μm in thickness is electroplated on silver. Finally, tin or tin-lead coating of 5–10 μm is electroplated to improve the solderability of the electrode. However, in many cases MLCI can not be properly electroplated because of serious lateral growth of nickel or Sn–Pb alloy coating on the ferrite substrate, which remained a worldwide problem. Manufacturers were obsessed with the poor compatibility between the ferrite materials and MLCI fabrication technology. Moreover, the unexpected lateral growth of metal coating denied the further miniaturization of MLCI or even led to short-circuit. It is now very necessary to find the cause and improve the reliability of electroplating process accordingly.

Some people believed that corrosion of the ferrite surface in the acid plating solution should be responsible for the improper coating growth. They managed to improve the situation by adjusting the electroplating solution [3], for example, increasing the pH value. Some other people suggested that it should be derived from the low resistivity of the ferrite materials. They increased the resistivity of the ceramics for example, by air annealing before electroplating. Nevertheless, the feasibility of these means was limited while the mechanism remained unclear till now.

The goal of the present work is to illustrate the cause of direct deposition of metal coating on the ferrite surface of MLCI. On the basis of our results, it was inferred that reduction reaction of the ceramics surface

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induced by hydrogen generated during electroplating had played an important role, which significantly increased the electronic conduction of the materials thereby, leading to the improper growth of metal coating.

2. Experimental procedures

The specimens studied were commercial $Ba_3Co_2Fe_{24}O_{41}$ (Co_2Z) hexaferrite. The powders were synthesized at 1250 °C using all reagent-grade chemicals $BaCO_3$, Co_3O_4 and Fe_2O_3. With the addition of Bi_2O_3 as lubricants, the powders were milled in alcohol using steel balls to obtain a fine size. Pellets with a diameter of 1 cm were pressed and then sintered at 890 °C for 6 h with a constant heat rate of 200 °C/h applied. MLCI were fabricated through several steps including tape casting, punching, screen-printing of Ag pastes, stacking and sintering. Finally, silver electrodes were fired onto both sides of the resulting specimens.

Before being electroplated, the specimens were cleaned with chemical solvent and then activated for 3 min. After being rinsed with distilled water, the specimens were electroplated in a nickel sulfamate-based solution using barrel plating method with steel balls of 1mm diameter acting as the conductor media. The composition of this solution and processing parameters are listed in Table 1.

Resistance was measured by applying 10V DC to the specimens for 1 min at room temperature using an HP4140B pA meter. Scanning electron microscope (SEM) was used to observe the microstructure of the specimens. Structural analysis of the ceramics was made through XRD by using Cu K_α radiation.

3. Results

As shown in Fig. 1, the specimens were mainly of Z-type hexagonal structure according to JCPDS file 19–97 and no other phase was observed. The specimens were all blue-black and bright. By using SEM, we examined the microstructure of the Co_2Z ferrite. As shown in Fig. 2(a) and (b), the ceramics surface was a little chip-shaped and densified while some isolated pores were observed in the ceramics. Seeing this, we do not believe that the plating solution could penetrate into the ferrite for a long distance through these cavities and further damage the properties of MLCI.

Table 1
Components and process parameters of the nickel electroplating

Nickel sulfamate (g/l)	60
$NiCl_2$ (g/l)	15
Boric acid (g/l)	40
pH	4.0
Temperature (°C)	55
Cathodic current density (A/dm^2)	1.0

To study the cause of the lateral growth of nickel coating, electroplating experiments were carried out on pellets specimens and MLCI. It was found that all the

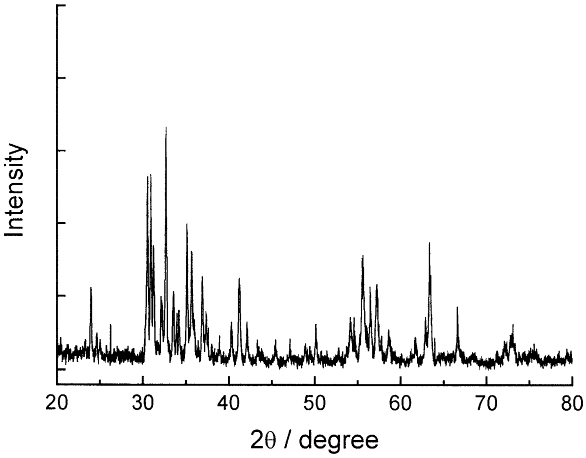
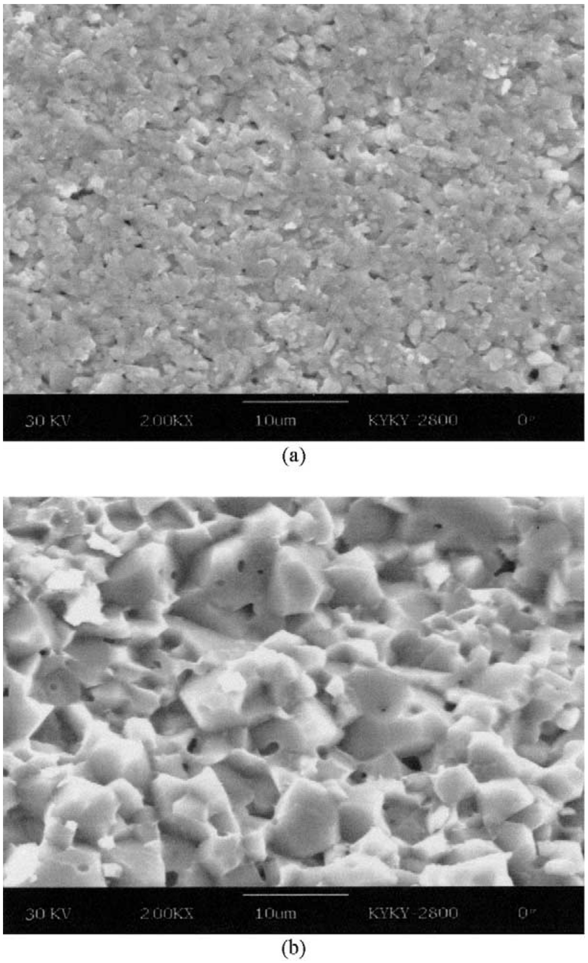


Fig. 1. XRD pattern of the resulting Co_2Z ferrite.



(a)

(b)

Fig. 2. (a) SEM surface micrograph of the as-sintered specimens; (b) fracture morphology of the Co_2Z ferrite.

ferrite surfaces turned dim soon after the electroplating process began. As the plating continued, the surfaces near the electrodes even became black and these black areas expanded slowly towards the central part of the ceramics. Then after the specimens were plated for about 20 min, lateral growth the nickel coating occurred. Finally, the specimens became all metal-covered. It was worthwhile to point out that once the improper growth began, the whole ceramics surfaces were coated rapidly by nickel within only few minutes. We called the beginning time of rapid lateral growth of metal coating as critical time, T_c.

As well known, only when the metal ions in the aqueous solution get electrons from the cathode could they be reduced and deposit from the solution onto the cathode surface, forming metal coating. As mentioned above, no lateral growth occurred before T_c. It meant that the ceramics could not provide electrons to the metal ions during this period. In contrast, the metal ions could get electrons directly from the ferrite surface after T_c and deposit in the form of atom, which suggested that conductivity of the ceramics had increased during electroplating. To testify this inference, we measured the resistance of specimens as a function of electroplating time, as shown in Fig. 3(a). The resistivity decreased by about two orders of magnitude within 20 min of electroplating. Fig. 3(b) presents the inductance change of MLCI during the electroplating. Similar with the resistivity change in Fig. 3(a), the inductance declined just from the beginning of electroplating. Then we examined the surface morphology of specimens after 20 min of electroplating. Quite different from that of the blank one, the surface microstructure became amorphous and unorderly, as shown in Fig. 4. These results indicated that the ceramics surfaces had suffered some chemical reactions, which decreased the resistivity and changed the surface structure.

To evaluate the corrosion effect of plating solution on the ceramics, we dipped the specimens into the solution for 1 h before electroplating. Fig. 5 gives the SEM surface micrograph of the resulting specimen. No difference between it and Fig. 2(a) was observed and the resistivity of specimens did not change after the dipping. T_c of the resulting specimens was also the same as that of the blank ones. All these results suggested that the corrosion had no influence on the lateral growth of nickel and electrical properties of the ceramics.

4. Discussions and interpretations

In the present paper, electrical measurements and SEM observations were carried out to study the lateral growth of nickel coating on Co_2Z ferrite. It was noted that conductivity of the specimens increased with the electroplating and the surface morphology changed significantly. It was found that the lateral growth of coating occurred only after a certain time of electroplating. Moreover, no corrosion effect of plating solution on the ceramics was observed.

If the lateral growth of nickel on the ferrite was caused by the low initial resistivity of the specimens, it

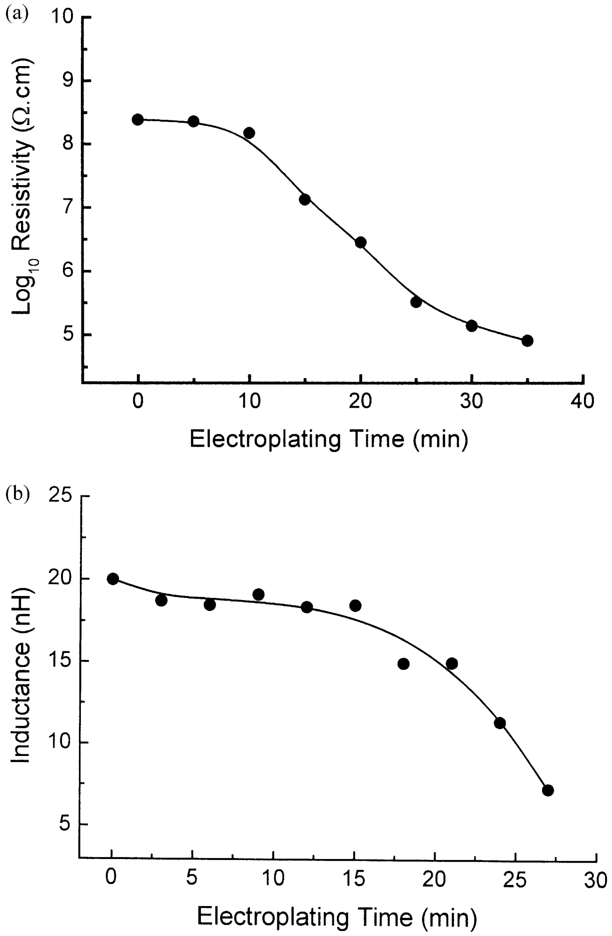


Fig. 3. (a) Resistivity of the ceramics as a function of electroplating time; (b) inductance of the inductor as a function of electroplating time.

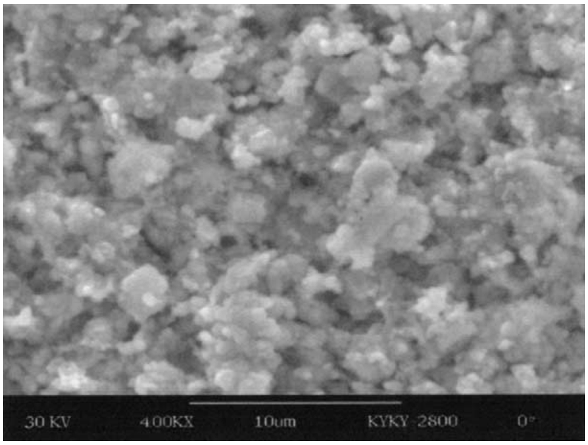


Fig. 4. Surface morphology of the $Co_{23}Z$ ferrite after 20 min of electroplating.

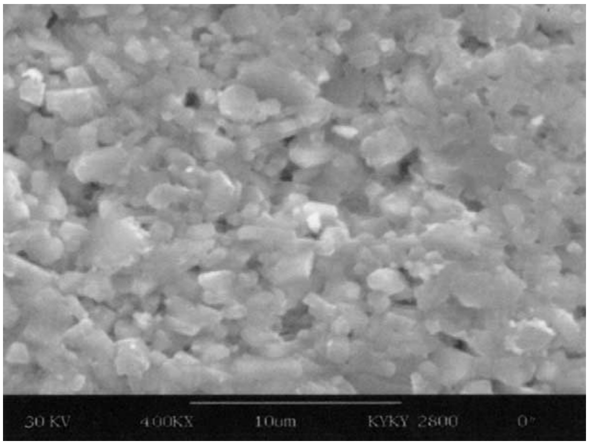


Fig. 5. Surface microstructure of the ferrite specimen after 1 h of immersion in the plating solution.

should process once the electroplating began. However, this inference was obviously inconsistent with the experiment results. In view of electrodeposition, only after nickel ions in the aqueous solution get electrons from the cathode could they deposit onto the cathode. If the cathode is poorly electronic conductive or even insulative, the polarization potential would not reach the deposition potential of nickel and the metal ions could not deposit on the cathode accordingly. In the present study, only after the electroplating reached T_c could the nickel ions deposit on the ferrites when the resistivity decreased by two orders of magnitude. That is to say, without the resistance degradation of the material, there would not be lateral growth of nickel. All these results strongly suggested that the main cause of the lateral growth of nickel coating was not the initial low resistivity, but the increasing conductivity of the ceramics during electroplating, even though the low initial resistivity was only 2.3×10^8 Ω cm.

Concerning the resistance degradation, there must be some chemical reactions happened to the ceramics surface during electroplating. As well known, hydrogen generation was unavoidable in nickel electroplating and the efficiency of cathodic current can not get to 100% [4]. Many hydrogen atoms were absorbed on the cathode during electroplating and most of them diffused into the solution body in the form of atom or molecule after de-absorption. However, still a little part of hydrogen atoms could permeate into or react with the cathode [5–7]. The negative effects of atomic hydrogen on metals and alloys have been studied extensively, for example, hydrogen embrittlement of high strength steel. Nevertheless, the influence of hydrogen atoms on ceramics has long been neglected because it was generally thought that the ceramic materials were chemically inert at lower temperatures. In fact, it proves feasible for many oxides to be reduced by atomic hydrogen near room temperature according to the thermodynamics. In the present case, hydrogen generated during electroplating can be considered to supply a reducing atmosphere. Metal ions in the Co_2Z ferrite may be reduced to lower valence by atomic hydrogen, as shown in Eqs. (1) and (2):

$$H \rightarrow H^+ + e \tag{1}$$

$$M^{n+} + xe \rightarrow M^{n-x} \tag{2}$$

where M^{n+} represents the metal ions in the Co_2Z ferrite. Because of the reduction, M^{n+} and M^{n-x} co-existed in the ceramics, which facilitated electron transition between the forbidden band and conduction band. The resistivity of specimens decreased as the reaction processed. Finally, the resistivity became lower enough [as shown in Fig. 3(a)] and the deposition potential of nickel was reached, thereby nickel deposited onto the ferrite surface. In addition, reduction of the ferrite changed the surface structure to be amorphous, as given in Fig. 4. As to the inductance decrease of MLCI during electroplating, it could be attributed to the leakage current through the device surface due to resistance degradation of the ferrite.

Based on these results obtained, the lateral growth of nickel coating should be ascribed to the resistance degradation of the ferrite induced by hydrogen reduction during electroplating. More detailed work about the reduction mechanism of the Co_2Z ferrite are needed and will be published in another paper.

5. Conclusions

1. It was found that the lateral growth occurred only after a certain time of electroplating, T_c.
2. Resistivity of the specimens declined continuously with the electroplating, which resulted in the lateral growth of nickel coating.
3. Reduction of metal ions to lower valences in the ceramics by hydrogen produced during nickel electroplating should be responsible for the resistance degradation.

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