Mechanism for generation of voids bounded on Cu conductors in Cu/glass ceramic co-fired multilayer wiring substrates

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Voids of 50–100 μm in size may be generated adjacent to the Cu conductor when a Cu/glass ceramic multilayer wiring substrate is co-fired. Carbon residue derived from the binder (ethyl-cellulose) in the Cu paste is related to the generation of such voids. The main components of the gas that generates a void are H_2O and CO . In addition, Cr-Fe-O particles from Cr and Fe impurities in the Cu powder of the Cu paste are present in the void. The mechanism for generation of a void is presumed to be that carbon residue derived from the binder in Cu paste is oxidized by H_2O introduced at the binder burnout stage, and as a result, H_2 and CO are generated (water gas shift reaction). Cr_2O_3 and Fe_2O_3 function as catalysts for a reaction that becomes a trigger for the water gas shift reaction. CuOH can be formed on the surface of the Cu conductor by reaction with the OH generated from this trigger reaction. H_2O is generated by the dehydration of CuOH on the surface of the Cu conductor during the sintering stage. When the Cr and Fe content in the Cu powder of the Cu paste, the carbon residue derived from binder in the Cu paste, and the amount of H_2O introduced when the binder is burnt out, were decreased according to the derived void generation mechanism, the number of the voids bounded on the Cu conductor was decreased.

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1. Introduction

Ceramic multilayer circuit substrates are necessary for the production of large-scale integrated (LSI) circuit chips (Si) for the mounted boards of mainframe computers. These substrates are required to have high reliability and high heat dissipation characteristics. Ceramic materials used for this application require low-temperature sinterability to enable Cu, which is used as a conductor to realize high computational speeds, to be applied. Glass ceramics best fulfill the low-temperature sinterability requirement.^{1)–9)} In a ceramic multilayer wiring substrate, sintering is not generally uniform, and cracks and voids can be generated by the difference between the coefficients of thermal expansion of the ceramic and the metal conductor, or the difference between the sintering shrinkage rate of the ceramic and the metal conductor.^{10)–12)} In case of a Cu/glass ceramic co-fired multilayer wiring substrate, spheroidal voids can be generated near the Cu conductor wiring. The size of these voids is approximately 50–100 μm . When the Cu conductor wiring is thin, the wiring can be disconnected by this void, and in the case of a multilayer wiring substrate, it is very difficult to repair the disconnected part, because the wiring is present within the substrate. In the present study, the cause of void generation and the mechanism for generation of voids bounded on Cu conductors in Cu/glass ceramic co-fired multilayer wiring substrates were investigated, and a deterrent plan for void generation is proposed.

2. Experimental procedure

The glass ceramic used in this investigation consisted of 65 vol% of borosilicate glass (GA-50/F013, Nippon Electric Glass Co., Ltd., Japan; mean particle diameter of 3.4 μm), 15 vol% of $\alpha\text{-Al}_2\text{O}_3$ (AL-45-2, Showa Denko K. K., Japan; mean particle diameter of 2.1 μm) and 25 vol% of cordierite (ASF-1999, Asahi Glass Co., Ltd., Japan; mean particle diameter of 1.8 μm). The composition of GA50/F013 is SiO_2 : 79 mass%, B_2O_3 : 19 mass%, K_2O : 2 mass%. This composite glass ceramic has a bending strength of 200 MPa after sintering at 925°C for 2 h.⁸⁾ A slurry was produced by adding a water-soluble organic binder (a modified acrylic resin), a dispersing agent, and water to this glass ceramic powder. The amount of the binder addition to slurry was set to be about 12 mass%. The doctor-blade method was used to prepare an approximately 0.23 mm thick glass-ceramic green sheet from this slurry. Cu paste (TR890K, Tanaka Precious Metals Group) was used to prepare the wiring. Ethyl-cellulose is used as a binder in the Cu paste, which has a viscosity of 50–100 Pa·s at a shear speed of 4 s^{-1} . This paste contains ethyl-cellulose by 1 mass%.

Experimental Cu/glass ceramic co-fired multilayer wiring substrates were produced by the following procedure. Cu wiring of 60 μm in width was printed on the glass ceramic green sheet using Cu paste for wiring and a screen-printing machine. 35 sheets were accumulated and thermolaminated at 1.76 kgf/mm² for 55 min at 130°C. The green sheet laminate produced was cut to a size of 100 × 100 mm. A substrate was obtained by burning out the binder of the laminate at 850°C for 10 h in N_2 + 0.4 atm H_2O , and sintering the laminate at 1000°C for 2 h in N_2 . H_2O was

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introduced as an oxidant of the binder. The oxygen concentration in $N_2 + 0.4 \text{ atm H}_2\text{O}$ atmosphere is less than 100 ppm. The heating rate and cooling rates used were 100°C/h and 200°C/h , respectively.

A combined thermogravimetric-mass spectroscopy (TG-MS) system (TG-40x, GCMS-QP1000, Shimadzu Corporation) was used for TG-MS analysis. Measurements were obtained in a high purity helium flow. The heating rate was 100°C/h , and the sample was maintained at 1000°C for 2 h. The weight of the analyzed sample was 130–240 mg.

The microstructures of the samples were characterized using a scanning electron microscope (SEM; S-900, Hitachi, Japan). The insulating samples were coated with Au and Pd prior to SEM characterization. An energy dispersive X-ray analyzer (EDAX; Kevex X-Ray Inc.) was used for elemental analysis of the sample.

The amount of carbon residue from ethyl-cellulose was measured according to the following procedure. Ethyl-cellulose was dissolved in ethyl acetate and then dried. Thus, an ethyl-cellulose film was obtained. The film was placed in an alumina boat and burned out under the same conditions as that used for the substrate. The carbon residue of this sample was quantified by oxidation in air using a C, S simultaneous analysis device (Horiba, Ltd.). The amount of CO and CO_2 generated was quantified using infrared (IR) absorption spectrometry.

3. Results and discussion

3.1 Voids bounded on Cu conductors in Cu/glass ceramic co-fired multilayer wiring substrates and their cause

An example of a void generated around the Cu conductor wiring in a Cu/glass ceramic co-fired multilayer wiring substrate is shown in **Fig. 1**. The void on the Cu conductor wiring was observed after grinding the substrate from the surface. The void was round with a size of approximately $50 \mu\text{m}$. The pattern of the Cu conductor wiring is transparent in the figure.

The void in the ceramic sintered body could be caused by the gas generated from oxidation of the carbon residue derived from the binder.¹³⁾ The causal relationship between the binder used in the manufacturing process of the Cu/glass ceramic co-fired multilayer wiring substrate and the void was examined. Experimental samples with varied combinations of binder in the glass ceramic and Cu paste, and the status of void generation are shown in **Table 1**. We counted the number of void whose size was $30 \mu\text{m}$

or more by observing each Cu paste printed area of 0.1 cm^2 . A glass ceramic body after binder burn out and sintering was used as the binder-free glass ceramic. A paste made by mixing only the TR890K solvent and Cu powder without ethyl-cellulose was used as a binder-free Cu paste. From the results of samples 1, 2 and 3, it was observed that no voids were generated, regardless of the presence of binder in the glass ceramics, as seen in the case of a binder free Cu paste, and voids were generated, regardless of the presence of binder in the glass ceramics, as seen in the case of Cu paste with binder. It was determined that there was no causal relationship between the binder in a glass ceramic green sheet and void generation, and that the void originates from the binder in the Cu paste. Trace minerals remain after sintering, because the raw ethyl-cellulose binder material is prepared from a wood pulp. Trace minerals such as CaO , Na_2O , ZrO_2 , SiO_2 and P_2O_5 were detected. The paste for sample 4 was prepared using ethyl-cellulose that contains only a small amount of minerals. The paste for sample 5 was made by mixing minerals, extracted by sintering ethyl-cellulose in air, with binder-free Cu paste. From the results of samples 4 and 5, it was seen that voids were generated in the case of Cu paste with binder and low levels of minerals, whereas no voids were generated for binder free Cu paste with high levels of minerals. It was determined that there is a possibility that voids originate not from the mineral in ethyl-cellulose, but from the carbon residue derived from ethyl-cellulose. An example of decomposition curve of ethyl-cellulose in $N_2 + 0.4 \text{ atm H}_2\text{O}$ is shown in **Fig. 2**. The amount of residue /initial weight becomes less than 0.2 mass% at 875°C .

Next, the stage of the sintering process at which the void was generated was examined. **Figure 3** shows the binder burn out and sintering profiles of three substrates. The void generation status of two samples that were rapidly cooled from 950°C and 1000°C , and one that was cooled after a 2 h dwell time at 1000°C , were examined and the results are given in the table of **Fig. 3**. Many voids were observed in the third sample, while no voids were generated in the first and second samples. This indicates that voids are generated when the temperature is maintained at 1000°C for 2 h during the sintering stage.

Experimental substrates were then printed using the void-free Cu paste and the Cu paste that caused many voids, and these were pre-sintered at 975°C without a dwell time. The Cu conductor films were peeled off from the pre-sintered substrates. These Cu conductor films were sintered at 1000°C for 2 h and the type and amount of gas generated were analyzed using TG–

Fig. 1. Example of a void bounded on a Cu conductor in a Cu/glass ceramic co-fired multilayer wiring substrate.

Table 1. Occurrence of Voids Bounded on Cu Conductors in Various Cu/glass Ceramic Fired Substrates

Sample No.	Glass ceramics	Cu paste	Number of void*
1	binder free	binder free	0
2	with binder	binder free	0
3	binder free	with binder	> 30
4	binder free	with binder, low minerals	> 30
5	binder free	binder free, high minerals	0

Sintering condition: 1000°C for 2 h, according to the profile given in Fig. 2.

*Void size: $\geq 30 \mu\text{m}$, Observed Cu paste printed area: 0.1 cm^2 .

Fig. 2. An example of decomposition curve of ethyl-cellulose in N_2 + 0.4 atm H_2O . Average polymerization molecular weight of ethyl-cellulose: 40,000. Heating rate: $100^\circ\text{C}/\text{h}$.

Fig. 3. Specifications for the void generation temperature region. Sample: Cu/glass ceramic multilayer wiring substrate. Heating rate: $100^\circ\text{C}/\text{h}$. Cooling rate: $200^\circ\text{C}/\text{h}$. Atmosphere: N_2 + 0.4 atm H_2O (binder burn out plateau), N_2 (another temperature region).

MS. The results are given in **Table 2**. H_2O , CO and CO_2 were generated from both the void-free sample and from the sample with many voids. There was some generation of SO_2 observed. The difference between the amount of gas generation from the sample with many voids and that from the void-free sample was ca. $70 \mu\text{g/g}$ H_2O , ca. $70 \mu\text{g/g}$ CO, and almost $0 \mu\text{g/g}$ CO_2 and SO_2 . Therefore, it was determined that the main gases that generate voids are H_2O and CO. There is a possibility that gases with mass number < 10 are contained as void generation gases besides H_2O and CO, because the mass number detection limit of the TG-MS used for the analysis was 10–500.

The causes of void generation on the boundary of the Cu con-

Table 2. TG-MS Results of the Gases that form Voids

Gas	Amount of gas generation at 1000°C for 2 h		
	(1) Sample with voids	(2) Void free sample	(1)–(2)
H_2O	$137 \mu\text{g/g}$	64	73
CO	94	24	70
CO_2	23	29	–6
SO_2	3	4	–1
Total	257	121	136

Sample: Cu conductor foil peeled off from Cu/glass ceramic pre-co-fired substrate at 975°C for 0 h according to the profile given in Fig. 2. Heating rate: $100^\circ\text{C}/\text{h}$. Atmosphere: He. Range of mass number that can be detected by TG-MS: 10–500 (H_2 cannot be detected).

ductor in Cu/glass ceramic co-fired multilayer wiring substrates are summarized as follows.

- 1) Carbon residue from the binder (ethyl-cellulose) in the Cu paste is related to void generation.
- 2) The main gases that generate voids are H_2O and CO.

3.2 Proposed void generation mechanism

It is thought that voids bounded on the Cu conductor are mainly caused due to the burn out of carbon residue derived from the binder (ethyl-cellulose) in the Cu paste and the generation of CO. Although, there is almost no oxygen present in the furnace during binder burn out and sintering, H_2O was introduced as an oxidant for binder burn out. It is thought that this H_2O remains in the sintering furnace or substrate, and therefore, the carbon residue is oxidized by H_2O . Generation of CO by the oxidation of carbon residue derived from the binder (ethyl-cellulose) in the Cu paste is thought to be caused by the water gas shift reaction.¹⁴⁾ A reactive type of water gas shift reaction is shown in the upper part of **Fig. 4**. The water gas shift reaction consists of three elementary reactions. It is not possible to detect H_2 , even if H_2 is generated, due to the detection limit of the TG-MS equipment used for the analysis, although H_2 is surely generated by the water gas shift reaction. The other main component of the gas that generates voids is H_2O , which is seemed to be generated by the dehydration of CuOH on the surface of the Cu conductor (the lower part of Fig. 4.).

Voids can be generated anywhere near the Cu conductor wiring in a Cu/glass ceramic co-fired multilayer wiring substrate, and the occurrence of voids is sure to be more frequent if the proposed mechanism sufficiently describes void generation. However, very few voids are actually generated near the Cu conductor wiring, which suggests that, when examined in more detail,

Fig. 4. Water gas reaction and the dehydration reaction of CuOH.

Fig. 5. Trigger reaction for the water gas reaction, and presumed causes and mechanism of void generation.

another reaction becomes the trigger¹⁴⁾ that is indispensable for the water gas shift reaction, as shown in the left side of Fig. 5. Methane is generated from carbon reacting with activated H atoms in the first elementary reaction of the water gas shift reaction, shown in Fig. 4.¹⁵⁾ In this case, activated H atoms react with carbon by surface diffusion and/or spilling over.¹⁶⁾ “Spilling over” is the phenomenon where a reactant adsorbs the surface of the catalyst support and then migrates to the surface of the catalyst. Activated H atoms are generated from H₂O (H₂ activation reaction) and this becomes the trigger for the water gas shift reaction. It is also known that Cr₂O₃ and Fe₂O₃ exhibit high revitalization as catalysts for this reaction.^{17)–19)} Therefore, it is proposed that Cr₂O₃ and Fe₂O₃ are indispensable for the water gas shift reaction. Besides activated H atoms, OH is generated in the H₂ activation reaction. CuOH is seemed to be generated at the surface of Cu by OH reacting with Cu. It is thought that this becomes the source of H₂O at high temperature, as shown in the lower part of Fig. 4.).

If the proposed causes and mechanism for generation of voids bounded on the Cu conductor are as such, then this can be schematically shown by the right side of Fig. 5. That is to say, it is thought that voids bounded on the Cu conductor are generated by the water gas shift reaction when all three factors (carbon residue from the binder (ethyl-cellulose) of the Cu paste, H₂O, and Cr₂O₃ and/or Fe₂O₃) are present.

3.3 Plan for control of void generation

The average failure number by voids was compared for two kinds of Cu/glass ceramic substrates, based on the proposed generation mechanism given in section 3.2. There were differences in the contents of Fe and Cr impurities in the Cu powder of Cu paste in these two substrates, as shown in the results of Fig. 6. The average failure number by voids in the substrate prepared using Cu paste consisting of Cu powder B was approximately half of that in the substrate prepared using Cu paste consisting of Cu powder A; the Fe and Cr content of Cu powder B is half of that of Cu powder A. Therefore, it was found that there is a high correlation between the content of Fe and Cr impurities in the Cu powder and the number of voids generated. The voids generated in the substrate prepared using Cu paste consisting of Cu powder A were observed by SEM, and analyzed in detail using EDAX, as shown in Figs. 7(a) and (b). One particle was observed in a void (Fig. 7(a)), and from the EDAX analysis it was determined that this particle is composed of Cr and Fe oxides. Although Cr and Fe are present as metals in the Cu powder, it is thought that they are oxidized during the binder burnout process. In another void, where no particle was observed, the merging of Fe into the glass ceramic portion in this void was detected (Fig. 7(b)). Cr and Fe oxide particles or the merging of

Fig. 6. Dependency of the Fe and Cr content in Cu powder on the average failure number by voids in a substrate.

Fig. 7. Detailed observation and analysis of a void bounded on a Cu conductor. (a) Cr-Fe-O particle in a void bounded on a Cu conductor. (b) Inner surface of the glass ceramic portion of a void bounded on a Cu conductor.

Fe into the glass ceramic portion was observed in all of the void portions in the substrates analyzed. Generally, small amounts of impurities such as Fe and Cr are contained in the Cu powder that is used as the raw material for the Cu paste. Therefore, it is thought that the voids bounded on Cu conductors can be controlled by using a Cu powder that does not contain these impurities.

Figure 8(a) shows the relationship between the amounts of carbon residue in three kinds of ethyl-cellulose, and the number of voids bounded on Cu conductors in Cu/glass ceramic substrates prepared using Cu pastes containing these three kinds of ethyl-cellulose. Two different conditions were used for the ethyl-cellulose binder burnout. Under both conditions, fewer voids were bounded on the Cu conductor in the substrate prepared using Cu paste that contained ethyl-cellulose with less carbon residue. Figure 8(b) shows the relationship between the binder burnout temperature and the carbon residue in the Cu con-

Fig. 8. Effect of decreasing carbon residue from ethyl-cellulose on the void number in a substrate. (a) The relationship between carbon residue from ethyl-cellulose and void number. Condition 1: 860°C, 10 h + 1000°C, 2 h. Condition 2: 800°C, 10 h + 875°C, 5 h + 1000°C, 2 h. (b) The relationship between binder burn out temperature and carbon residue from the Cu conductor, and the void number.

ductor, and the number of voids bounded on Cu conductors in Cu/glass ceramic substrates. Carbon residue is minimized for a binder burnout temperature around 840°C. As for the number of the voids bounded on Cu conductors, a similar tendency to that for carbon residue was observed, and the number of voids was minimized for a binder burnout temperature around 830°C. It is thought that the reason for the minimization of carbon residue at a binder burnout temperature around 840°C is that the decarbonization reaction rate is low below this temperature, and as the Cu sintering advances, the carbon is confined in the Cu film over this temperature. Therefore, it was confirmed that application of Cu paste containing ethyl-cellulose with less carbon residue, and burning out the binder under the condition where less carbon residue is produced, are effective for the prevention of voids bounded on Cu conductors.

Figure 9 shows the average failure number by voids in each of the two kinds of substrates, A and B, in two different atmospheres at the binder burnout stage; in $N_2 + 0.4$ atm H_2O for 9.5 h followed by 0.5 h in N_2 for a total 10 h hold time, and in

Fig. 9. Effect of decreasing the time of H_2O supplied at binder burn out temperatures on the average failure number by voids in a substrate.

$N_2 + 0.4$ atm H_2O for 7.5 h followed by 2.5 h in N_2 for a total 10 h hold time. The failure numbers for both substrates decreased by decreasing the time for H_2O introduction. Therefore, it was confirmed that decreasing the time in a H_2O containing atmosphere at the binder burnout stage is effective for control of void generation.

The presumed causes and mechanism of void generation (right side of Fig. 5.) seem to be almost certain from the experimental data.

A plan for control of void generation was determined, and is shown below.

1) Cu powder that does not contain Cr and Fe impurities is used as the raw material for the Cu paste.

2) Ethyl-cellulose with low levels of carbon residue is applied as the binder for the Cu paste, and binder burnout is performed under conditions that reduce the amount of carbon residue.

3) The amount of H_2O introduced to the atmosphere as an oxidant for removal of carbon in the Cu paste binder and the green glass ceramic sheet binder burnout stage is decreased.

4. Conclusions

Voids of 50–100 μm in size adjacent to the Cu conductors in Cu/glass ceramic multilayer wiring substrates are generated during co-firing. The cause and mechanism of void generation were examined, and the following conclusions were obtained.

(1) Carbon residue from the Cu paste binder (ethyl-cellulose) is related to void generation. The main gases that generate voids are H_2O and CO . In addition, Cr and Fe oxide particles or the merging of Fe into the glass ceramic portion was observed in all of the voids.

(2) The mechanism of void generation is presumed to be as follows. Carbon residue derived from the binder in the Cu paste is oxidized by H_2O that remains from binder burn out, and as a result, H_2 and CO are generated (water gas shift reaction). Cr_2O_3 and Fe_2O_3 function as catalysts for the reaction that becomes a trigger of the water gas shift reaction. $CuOH$ can be formed on the surface of the Cu conductor from the OH generated from this trigger reaction. H_2O is generated by the dehydration of $CuOH$ on the surface of the Cu conductor.

(3) The Cr and Fe content in the Cu powder of the Cu paste, the carbon residue derived from the binder in the Cu paste, and the amount of H_2O introduced during binder burn out were all

decreased, based on the derived void generation mechanism, and as a result, the number of the voids bounded on the Cu conductor could be decreased.

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