Effect of Cu conductor properties on crack generation around through holes of Cu/glass ceramic co-fired substrate

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We investigated crack generation and methods for preventing it in glass ceramics when Cu-glass paste and glass ceramics were co-fired. Cu-glass paste was used to fill the through holes of a glass-ceramic green sheet consisting of borosilicate glass/ Al_2O_3 /cordierite by screen-printing. Cracks are generated in the glass-ceramic portion that surrounds the through holes parallel to the circumference. These cracks occur when the tensile stress generated at the interface between the conductor in the through hole and the glass ceramic as a result of a mismatch in the coefficients of thermal expansion (CTEs) between Cu and glass ceramic exceeds the mechanical strength of the glass ceramic. The magnitude of the tensile stress was calculated by performing stress analysis using a model based on a thick multilayer cylinder. These cracks can be prevented by either greatly reducing the CTE of Cu conductor by adding a large amount glass or by reducing the Young's modulus of the Cu conductor and without adding additives to the Cu paste for promoting sintering (e.g., glass), which increase the density of the Cu conductor.

Key-words : Copper conductor, Glass-ceramics, Co-fire, Crack, Young's modulus, Coefficient of thermal expansion, Hardness

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1. Introduction

Ceramic multilayer circuit substrates are necessary for producing large-scale integrated (LSI) circuit chips (Si) for 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 to realize high computational speeds, to be applied. Glass ceramics best fulfill these requirements.^{1)–8)} It is necessary to ensure that the coefficient of thermal expansion (CTE) of the glass ceramic, which accounts for the majority of the volume of a multilayer circuit substrate, to be similar to that of Si (i.e., $3.0 \times 10^{-6}/\text{K}$) in order to enable high joint reliability with the Si chip. However, since Cu has a high CTE ($16.5 \times 10^{-6}/\text{K}$), this creates the problem of crack generation near the through holes in the glass ceramics as a result of a mismatch between the CTEs of Cu and the glass ceramic when cooling the substrate after sintering.^{9)–11)} Cracks are generated most easily near through holes that have large concentrations of Cu in the Cu/glass ceramics multilayer circuit substrate.¹¹⁾ Crack generation has been widely assumed to be caused by a mismatch between the shrinkages of the ceramic and of the conductor that occurred during sintering,^{9)–11)} but cracks may be generated even when there is a good match between their shrinkages. In the present study, we investigated the relationship between the properties of various Cu-glass type conductors and crack generation around through holes in the glass ceramic of Cu/glass ceramic multilayer circuit substrates by using these Cu-glass type conductors as conductors for the through holes. By doing this, we were able to clarify the properties that conductors for through holes are required to have to prevent crack generation in the vicinity of through holes of

ceramic multilayer circuit substrates.

2. Experimental procedure

The glass ceramic used in this experiment consisted of 65 vol% of borosilicate glass (GA-50/F013, Nippon Electric Glass Co., Ltd., Japan; mean particle diameter of $3.4 \mu\text{m}$), 15 vol% of $\alpha\text{-Al}_2\text{O}_3$ (AL-45-2, Showa Denko K. K., Japan; mean particle diameter of $2.1 \mu\text{m}$) and 25 vol% of cordierite (ASF-1999, Asahi Glass Co., Ltd., mean particle diameter of $1.8 \mu\text{m}$). The composition of GA50/F013 was SiO_2 : 79 mass%, B_2O_3 : 19 mass%, K_2O : 2 mass%. This composite glass ceramic had 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 inorganic powder. An approximately 0.23-mm-thick glass-ceramic green sheet was made from the slurry by the doctor-blade method. The Cu paste consisted of Cu powder (FMP-CU-E, Fukuda Metal Foil and Powder Co., Ltd., Japan; mean particle diameter of $1.0 \mu\text{m}$) and glass powder (CRG-F, Asahi Glass Co., Ltd., mean particle diameter of $1.9 \mu\text{m}$; a CTE of $1.8 \times 10^{-6}/\text{K}$; same composition as cordierite). A vehicle consisting of a binder of ethyl cellulose (5 mass%) and a solvent of texanol was added to the prescribed amount of Cu powder and glass powder and Cu paste with a viscosity in the range $77\text{--}130 \text{ Pa}\cdot\text{s}$ at a shear speed of 4 s^{-1} was produced by mixing with a mixer and a three roll mill.

Substrates with through holes were produced by the following procedure. Through holes of $130 \mu\text{m}\phi$ were produced in the glass ceramic green sheet at intervals of $531 \mu\text{m}$ by a numerical control punching machine. A screen-printing machine was used to fill these through holes with Cu paste. Pads of $130 \mu\text{m}\phi$ were printed at the through hole positions using the same Cu paste. After matching the positions of these four sheets, they were accumulated and thermo-laminated at 120°C in 19.6 MPa for 5 min. The green sheet

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laminate produced was cut to a size of 30×30 mm. A substrate with through holes was obtained by burning out the binder of the laminate at 850°C for 10 h in $\text{N}_2 + 0.4$ atm H_2O and sintering the laminate at 925°C for 1 h in N_2 . The heating rate was $100^\circ\text{C}/\text{h}$, and the cooling rate was $200^\circ\text{C}/\text{h}$. A Cu-glass sintered compact was obtained using the following procedure. The prescribed amount of Cu powder and glass powder with ethyl acetate and Al_2O_3 balls were mixed by ball milling. The resulting mixture was dried and the dry cake was granulated to a -32 mesh powder and uniaxially pressed into a $10 \times 10 \times 60$ mm green compact having a relative density of about 45% that was equal to the volume fraction of the inorganic ingredient in the Cu paste. A Cu-paste-based sintered compact was obtained by burning out the binder of the compact at 850°C for 10 h in $\text{N}_2 + 0.4$ atm H_2O and sintering the compact at 925°C for 1 h in N_2 . The heating rate was $100^\circ\text{C}/\text{h}$, and the cooling rate was $200^\circ\text{C}/\text{h}$.

The microstructures of the samples were characterized using a scanning electron microscope (SEM S-570, Hitachi). Since the samples were insulating, they were coated with Au and Pd prior to SEM characterization. The CTEs were measured using a double-pass Michelson-interferometry dilatometer (LIX-1, ULVAC-RIKO, Inc.) at a heating rate of $3^\circ\text{C}/\text{min}$ (from RT to 200°C) in 0.26 atm of helium. The test samples for the CTE measurements were prepared by cutting capsule-shaped samples that were about 6 mm in diameter and about 12 mm in length. The hardness was measured using a micro Vickers Sclerometer (Fisherscope HCU, Fisher Scientific Inc, USA) at a load of 0.245 N and a creep time of 25 s. Seven points were measured; the maximum and minimum values were discarded and the remaining five measurements were averaged. The Young's modulus and Poisson's ratio were measured by the rectangular parallelepiped resonance method.^{12),13)} The test pieces were prepared by cutting into cubes of about 4 mm in length. The Young's modulus and Poisson's ratio of selected samples were also measured at a high temperature by the same method.

3. Results and discussion

3.1 Crack generation around through holes in Cu/glass ceramic co-fired substrates

Table 1 shows the compositions of the Cu pastes used for the through hole conductors and the occurrence of crack generation around the through holes of Cu/glass ceramics co-fired substrates when these pastes were used. The measured CTEs of the Cu paste sintered compacts are also shown in Table 1. The inorganic components of the Cu paste were only Cu powder and cordierite glass powder. We varied the fraction of glass in the range 0–50.9 vol%. Figure 1 shows the relationship between the fraction of glass and the CTE of the Cu paste sintered compacts. Additional data besides that given in Table 1 is plotted in Fig. 1. The solid line is what approximated by the minimum mean square method as for the plotted data. The CTE decreases as the proportion of cordierite glass increases. The actual measured values lie between the simple mixture rule (Eq. (1)) and Turner and Kerner's equation (Eq. (2)).^{14),15)}

$$\alpha = \frac{\alpha_1 V_1 + \alpha_2 V_2}{V_1 + V_2} \quad (1)$$

$$\alpha = \frac{\alpha_1 E_1 V_1 + \alpha_2 E_2 V_2}{E_1 V_1 + E_2 V_2} \quad (2)$$

Table 1. Cu-glass Conductor Compositions for Through Holes and Occurrence of Crack Generation around Through Holes of Cu/glass Ceramic Co-fired Substrates

Paste No.	Cu conductor composition / vol%		α^{*2} / 10^{-6}K^{-1}	Crack generation
	Cu	Glass ^{*1}		
T1	100	0	16.5	none
T2	83.5	16.5	14.7	crack
T3	81.7	18.3	14.6	crack
T4	67.6	32.4	11.1	crack
T5	64.8	35.2	10.0	none
T6	52.2	47.8	8.2	none
T7	49.1	50.9	7.1	none
Glass ^{*1}	0	100	2.3	

^{*1} $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ (cordierite composition)

^{*2} RT - 200°C

Fig. 1. Relationship between glass content and the CTE of Cu-glass sintered compact. (glass composition: $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ (cordierite), glass fraction = glass / (Cu + glass)).

In Eqs. (1) and (2), α is the CTE, E is Young's modulus and V is the volume fraction. When the amount of the glass addition is a little, the CTE of Cu paste sintered compact nearly equals to the CTE of the frame of Cu. The CTE of compact lowers when the amount of the glass addition becomes more than a value. Cracks were observed in the substrates made using the Cu paste whose glass fraction was in the range 16.5–32.4 vol%. No cracks were observed in the substrates made using the Cu paste whose glass fraction was in the range 35.2–50.9 vol%. When the fraction of glass in the Cu conductor increases, the CTE of the Cu conductor decreases (Table 1, Fig. 1) and the difference between the CTEs of the Cu conductor and the glass ceramic becomes small (Table 1). This is the reason why cracks were not observed in the glass ceramic portion around Cu conductors having a high fraction of glass. On the other hand, no crack generation was observed in the substrate made using pure Cu paste without glass. Figure 2 shows an example of a crack that was generated in the glass ceramic portion around a through hole parallel to the circumference. The tensile stress and the compression stress were generated in right-angled to the tangent direction and in the tangent direction, respective-

Fig. 2. Example of crack generation in glass ceramic near through hole Cu-glass conductor. (Cu-glass paste No.: T2, sintering conditions: 925°C, 2 h).

Table 2. Various Properties of Cu-glass Sintered Compacts having the Same Compositions as the Cu-glass Pastes Used for the Through Hole Conductor

Paste No.	α ^{*1} / 10 ⁻⁶ K ⁻¹	Cu conductor sintered compact				Through hole conductor	
		H_v ^{*2}	E ^{*3} / GPa	ν ^{*4}	RD ^{*5} / %	H_v ^{*2}	E ^{*3} / GPa
T1	16.5	62	8.7	0.282	-	48	6.4
T2	14.7	-	-	-	-	112	16.5
T3	14.6	146	33.9	0.315	64.1	143	28.7
T4	11.1	138	26.6	0.335	59.7	168	40.3
T5	10.0	110	17.0	0.317	53.8	104	16.7
T6	8.2	157	25.4	0.334	58.7	183	52.0
T7	7.1	128	-	-	-	136	26.0
GC ^{*6}	3.0	687	118.2	0.248	-	-	-

^{*1} RT - 200°C ^{*2} Micro Vickers hardness ^{*3} Young's modulus

^{*4} Poisson's ratio ^{*5} Relative density ^{*6} Glass ceramic

ly at the glass ceramic portion near the interface between Cu and the glass ceramic of the substrate. The former caused the crack as the temperature decreased from the softening point of glass to room temperature during the post-sintering cooling process due to the mismatch in the CTEs of Cu (high CTE) and that of glass ceramic (low CTE). It is thought that this tensile stress⁽⁶⁾ produced the crack shown in Fig. 2. The details of tensile stress are described in section 3.3.

3.2 Properties of Cu paste sintered compact

Table 2 shows various properties of the Cu paste sintered compacts that have the same compositions as the Cu pastes mentioned in section 3.1. **Figure 3** shows the relationship between the relative densities and Young's modulus of the Cu paste sintered compacts. The theoretical densities were calculated from the Cu/glass fraction by assuming that the Cu powder did not react with the glass powder. The data of Table 2 together with additional data and the Young's modulus of Cu bulk are plotted in Fig. 3. There is a high correlation between the Young's modulus and the relative density of the Cu paste sintered compacts. The Young's modulus reaches about 130 GPa, which is almost the same as that of Cu bulk, when the relative density is 100%. The Young's modulus increased monotonously with the relative

Fig. 3. Relationship between relative density and Young's modulus of Cu-glass sintered compact.

Fig. 4. Relationship between micro Vickers hardness and Young's modulus of Cu-glass sintered compact.

density. The Young's modulus becomes near 0 when becoming 50% or less in a relative density. This relative density almost equals to that of molding body. The Young's modulus of molding body is almost 0, because only necking occurs in it. **Figure 4** shows the relationship between the micro Vickers hardness and the Young's modulus of the Cu paste sintered compacts. Additional data besides that shown in Table 2 is also included in Fig. 4. The lines are quadratic curve what approximated by the minimum mean square method as for the plotted data. There is a high correlation between the micro Vickers hardness and the Young's modulus of the compacts. The Young's modulus increased monotonously with the micro Vickers hardness. Though the Young's modulus has only the correlation with the inclination of the load displacement curve in measurement of hardness, there is no theoretical direct correlation between them. However, it is reported that the hardness is four or five times of the Young's modulus in the same material series.¹⁷⁾ The hatching area shows this range in Fig. 4. The plotted data is almost corresponding to the range reported.¹⁷⁾ **Figure 5.**

Fig. 5. Temperature dependence of Young's modulus and Poisson's ratio of Cu-glass sintered compact (Cu-glass paste No.: T5).

shows an example of measuring the temperature dependence of Young's modulus and Poisson's ratio of the Cu paste sintered compact. The lines are what approximated by the minimum mean square method as for the plotted data. It shows that Young's modulus and Poisson's ratio vary little with temperature between room temperature and 700°C. It is important to note that the properties of the Cu paste sintered compact investigated in this study are not the properties of the through hole conductor, but only the properties that are simulated for the through hole conductor. In particular, the Young's modulus of the through hole conductor does not necessarily correspond to that of the sintered compact; this is because the degree that the paste fills the through hole and the sintering shrinkage of the glass ceramic greatly influence the relative density, consequently the Young's modulus of the through hole conductor. The relative density of the through hole conductor can't be measured directly. However, there is a high correlation between the Young's modulus and the micro Vickers hardness, and it is possible to measure the micro Vickers hardness of a portion of the through hole conductor. Consequently, we measured the micro Vickers hardness of the through hole conductor. The Young's modulus of the through hole conductor was determined using the measured micro Vickers hardness of the through hole conductor and the correlation in Fig. 4. The Young's modulus of the through hole conductor thus obtained is shown in the right column of Table 2 together with the measured micro Vickers hardness. **Figure 6** shows the relationship between the volume fraction of glass in the through hole conductor (glass/(Cu + glass + void)) and the estimated Young's modulus of the through hole conductor. The solid line is what approximated by the minimum mean square method as for the plotted data. It shows that the Young's modulus increases as the volume fraction of glass increases. For this reason, it is considered that the presence of glass promotes sintering.

3.3 Stress generated at the interface between through hole conductor and glass ceramic

The stress generated at the interface of the through holes was calculated by performing a two-dimensional stress anal-

Fig. 6. Relationship between glass content and Young's modulus of Cu-glass sintered compact (glass content: glass/(Cu + glass + voids)).

ysis of the through hole section, since the glass ceramic almost deforms elastically until fracture and cracks are generated on the glass ceramic side. In the stress analysis, we assumed that the substrate deforms elastically until crack generation. Expressions for the plane stress given by a thick cylindrical multilayer model were used for the two-dimensional stress analysis. The stress radially generated at the interface between the through hole conductor and the glass ceramic was approximated using a thick cylindrical multilayer model for the case when a cylindrical through hole conductor is heated by a columnar glass ceramic (see **Fig. 7**) and is expressed by Eq. (3).¹⁶⁾ The stress is generated at the interface between the through hole conductor and the glass ceramic during the cooling stage after co-firing of the Cu/glass ceramic substrate by the mismatch in the CTEs of the Cu conductor and the glass ceramic.

$$P_m = \frac{\frac{\delta}{c} + 2 \left\{ \frac{P_a}{E_1} \frac{a^2}{c^2 - a^2} + \frac{P_b}{E_2} \frac{b^2}{b^2 - c^2} \right\}}{\left\{ \frac{1 - \nu_1}{E_1} + \frac{1 + \nu_2}{E_2} \right\} + 2 \left\{ \frac{1}{E_1} \frac{a^2}{c^2 - a^2} + \frac{1}{E_2} \frac{c^2}{b^2 - c^2} \right\}} \quad (3)$$

The stress generated at the interface of the through hole P_m is given by Eq. (4), which is derived by substituting $a=0$, internal pressure $P_a=0$, external pressure $P_b=0$, and tightened width $2\delta=2c\Delta T(\alpha_1 - \alpha_2)$ into Eq. (3).

$$P_m = \frac{\Delta T(\alpha_1 - \alpha_2)}{\frac{1 - \nu_1}{E_1} + \frac{1 + \nu_2}{E_2} + \frac{2}{E_2} \frac{c^2}{b^2 - c^2}} \quad (4)$$

In Eq. (4), ΔT is temperature interval over which the stress is generated, α_1 is the CTE of the Cu conductor, α_2 is the CTE of the glass ceramic, E_1 is Young's modulus of the Cu conductor, E_2 is Young's modulus of the glass ceramic, ν_1 is Poisson's ratio of the Cu conductor, ν_2 is Poisson's ratio of the glass ceramic, b is half the pitch of the through hole, c is the radius of the through hole. In this study, ΔT (799°C)

P_m : Stress at interface, 2δ : Shrink length on tightening,
 P_a : Internal pressure, P_b : External pressure,
 α : Coefficient of thermal expansion,
 E : Young's modulus, ν : Poisson's ratio

Fig. 7. Thick cylindrical multilayer model.

Fig. 8. Stress generated at through hole interface and occurrence of crack generation.

was taken to be the difference between the softening point of glass (824°C) and room temperature (25°C), b and c were determined from the size of the through hole after sintering and were taken to be 225 μm and 55 μm respectively, and the value of the CTE in the range 0–200°C was used for α . The values of Young's modulus and Poisson's ratio at room temperature were substituted for E and ν respectively, since they vary little with temperature from room temperature to 700°C (see Fig. 5). Consequently, the stress P_m at the interfaces of through holes that were filled with pastes T1–T7 and then sintered were calculated and are shown in Fig. 8 together with whether cracks were generated or not. The assumed value from micro Vickers hardness given in Section 3.2 was used for the Young's modulus of the through hole conductor. The Poisson's ratios of some Cu conductors were not measured, but were assumed to be 0.3, since the Pois-

Fig. 9. Relationship between Young's modulus and coefficient of thermal expansion of Cu-glass conductor in through hole.

son's ratios of all the Cu paste sintered compacts were close to 0.3. Stress analysis was performed by keeping the CTE constant, even though the CTE is temperature dependent. As a result, the relationship between the properties of the through hole conductor and the stress generated at the interface of the through hole have been clarified. Figure 8 shows that only substrates whose stresses P_m exceed 170 MPa exhibit crack generation. This value is approximately equal to the bending strength of the glass ceramic (200 MPa). The relationship between Young's modulus and the CTE of the through hole conductor is expressed by Eq. (5) by substituting 170 MPa for P_m , the properties of the glass ceramic, and 0.3 for ν_1 in Eq. (4).

$$\alpha_1 [\times 10^{-6}/^\circ\text{C}] = \frac{148.9}{E_1 [\text{GPa}]} + 5.475 \quad (5)$$

This expression is plotted as the curve shown in Fig. 9. The region above this curve is for $P_m > 170$ MPa and the region

beneath the curve is for $P_m < 170$ MPa. This figure shows that cracks are not generated even for the case when a low-CTE component (e.g., glass) is not added to the Cu paste and the through hole conductor has a high CTE, provided the relative density and Young's modulus are sufficiently low. In contrast, when glass is added to the through hole conductor, the CTE decreases, but Young's modulus increases because of densification. The results show that to prevent the generation of cracks it is necessary to greatly reduce the CTE by adding a large amount of glass. In other words, we found that lowering either Young's modulus or the CTE is effective for preventing the formation of cracks. Adding a large amount of glass causes a dramatic increase in the electric resistance of conductor. Moreover, when the temperature increases the CTE increases while the Young's modulus of the Cu conductor hardly changes (see Fig. 5). It is thought that the former technique, namely, that of reducing Young's modulus is more effective, in light of the high temperatures generated during manufacture and in applications.

4. Conclusions

The effect of the properties of Cu-glass conductor on crack generation at the glass portion near the through holes in Cu-glass conductor paste/glass ceramic green sheet co-fired substrates was investigated. The following findings were made.

1) There is a high correlation between Young's modulus and micro Vickers hardness of a Cu paste sintered compact. Thus, the Young's modulus of a through hole conductor can be estimated by measuring its micro Vickers hardness.

2) Cracks are generated in a glass ceramic near through holes parallel to the circumference due to the tensile stress generated at the interface of a through hole during post-sintering cooling stage due to a mismatch between the CTEs of Cu and glass ceramics. This stress was calculated by performing a two-dimensional stress analysis of the through hole section. Cracks are generated when this stress exceeds the strength of the glass ceramic. An expression for the plane stress based on the thick cylindrical multilayer model was used for the two-dimensional stress analysis.

3) Cracks are not generated even for the case when a low-CTE component (e.g., glass) is not added to the Cu

paste and the through hole conductor has a high CTE, provided the relative density and Young's modulus are sufficiently low. In contrast, when glass is added to the through hole conductor, the CTE decreases, but Young's modulus increases because of densification. It was found that to prevent the generation of cracks it is necessary to greatly lower CTE by adding a large amount of glass.

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