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Influences of the Glass Composition and Firing Temperature on Oxidation of SiC Ceramics

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Abstract
Influences of glass composition and firing temperature on oxidation of SiC ceramics were investigated. It was found that glasses used for thick-film hybrid integrated circuit (IC) tended to enhance oxidation of SiC. The reason for such enhancement is assumed to be as follows: SiO_2 film generally formed on a surface of SiC ceramics, which functions to retard oxidation of SiC, is easily removed from the SiC surface by dissolution into the glasses. The phenomenon became more notable for glasses containing PbO or ZnO, both of which facilitated SiC oxidation. It is therefore concluded that glasses containing such compounds are generally unfit for the use as thick film electrode past on SiC substrates. On the other hand, SiO_2 and Al_2O_3 in glasses exhibited to retard SiC oxidation. And glasses comprised of SiO_2 30-35 mass%, Al_2O_3 20 mass%, B_2O_3 35-40 mass% prevent SiC substrates from oxidising.
Key-words: SiC Oxidation, Ceramics, Glass Composition

1. Introduction

Multichip packages have been used in supercomputers with a machine cycle of 6 ns since about 20 years ago,[1] at which time the era of multichip modules which are composed of multilayered ceramic substrates has begun in LSI mounting technology. Since the Joule energy of these multichip modules during computer operation exceeds 20 W/cm^2, SiC and AlN substrates, which have high-thermal conductivity, have attracted much attention. Examples include 208-pin PGA packages using SiC substrates[2] and serquad-type LSI packages for HDTV using AlN substrates,[3] as well as 600 pin PGA packages using AlN substrates.[4] Such higher exothermic Joule energy also cause problems in laser diode modules. Accordingly, laser diodes used for optical disk recording and laser printers are mounted on SiC and AlN substrates.[5] Because of the reason, studies on the thick-film metallization of nonoxide ceramics, such as SiC and AlN substrates which have 120-270 W/m・K and 70-270 W/m・K in thermal conductivity respectively, have been actively conducted.[6]

However, few studies have been conducted on the composition of thick glass films which can be used with nonoxide ceramics. In this study, influences of glass composition and firing temperature on oxidation of SiC ceramics were investigated. And the investigation was extended to decision of composition of glass pastes for thick electrode films in order to form a dense film on SiC substrate which is a representative nonoxide ceramic.

2. Experimental procedure

2.1 Materials

(1) SiC substrate

We used a fired SiC substrate with dimensions of 5.0 x 5.0 x 1.0 mm.

(2) SiC powder

In order to investigate a reaction of SiC with glasses, we used SiC powder (GC-500, 2 μm in grain diameter, Fujimi polishing).which is the same material as the SiC substrate.

(3) Glasses

We used both commercially available glasses and experimentally prepared glasses.

For standardisation of the experiments, glasses with particle size 40 μm or the greater were eliminated with #400 stainless steel sieve. We selected glasses on the basis of the composition, the thermal expansion coefficient and the softening temperature.

Table 1 shows a composition and characteristics of the glasses used in the present experiments.

(4) Preparation of SiC and glass mixture
Mixtures of 30 mass% SiC and 70 mass% glass powders were prepared in an alumina mortar with acetone as the dispersion medium. Mass change of the mixtures due to the SiC oxidation was measured.

Table 1. Composition of glass frits used in the present experiment.

Sample No	Glass composition (wt %)											Thermal expansion coefficient (×10⁻⁷/℃)	Softning temp. (℃)
	SiO_2	Al_2O_3	ZrO_2	B_2O_3	ZnO	PbO	CaO	BaO	MgO	V_2O_5	TiO_2	P_2O_5	
1										68	5	27	—	—
2	10	22		3	62	3							40	600~700
3	41	19	4	26			10						42	700
4	20			10	30	30	10						70	600~700
5	12	7		23	55	3							36	629
6	10	10		25	55								42.3	737
7	38	10				52							42.5	850
8	12			25		63							188.1	440
9	12	3		24		61							192.3	510
10	11	6		24		59							195.6	580
11	51	4		9			12	24					67	850
12	30	20	5	40			5						42	782
13	35	10	5	35			5		10				40	890
14	35	20	5	35			5						40	880

(5) Preparation of SiO_2-Added glasses
In order to prepare SiO_2 added glasses, We used crystallite AA (cristobalite structure, Tatsumori Chemicals) as SiO_2 source. 10, 30, 50, 70 and 90 mass% SiO_2 (crystallite AA) were added to commercially available glasses (glass #5, #6 and #11.Table 1). And the obtained samples were fused at 1500℃ in a kanthalsuper furnace (Burutenkanthal AB). A reaction between SiO_2 and SiC was investigated by using the SiO_2 added glasses.

2.2 Evaluation of effects of glasses on SiC oxidation
Effects of the glasses on SiC oxidation were evaluated by measuring a change in mass of the SiC/glass mixtures during thermal oxidation. The change in mass was measured by using thermogravimetric differential thermal analyzer (TGD1500, Shinku Riko). The mass change of the mixtures was divided by a mass of SiC powder in the mixtures to obtain the percentage of the mass change.

2.3 Measurement of dissolved SiO_2 into glass
An amount of dissolved SiO_2 into glass was determined by X-ray diffraction, as follows.
(1)Preparation of standard mixtures and internal standard(Si powder)-contained samples10, 30, 50, 70 and 90 mass% SiO_2 (crystallite AA) were added to glasses (#5, #6 and #11) to prepare the standard mixtures. The internal standard (30 mass% Si powder) was added to each of the standard mixtures to prepare internal-standard-contained samples. Similarly, the internal standard (30 mass% Si powder) was added to the SiO_2 added glasses.
(2) Quantification of SiO_2 in glasses by X-ray diffraction(XRD)
A calibration curve was obtained by measuring the X-ray diffraction (XRD) intensity of the standard mixtures.
And mass percents of SiO_2 in glasses used for the experiments were obtained from the calibration curve. To improve the accuracy, an integrated intensity of XRD peak was used instead of a height of the XRD peak. An addition of the internal standard (Si powder) was necessary to reduce measurement errors. In actual procedures, a predetermined amount of Si powder was added to the mixture, and the relative intensity of SiO_2 was calculated from the integrated intensity of XRD peak of SiO_2 in the mixture as follws:
Relative intensity = (XRD intensity of SiO_2 in the mixture) / (XRD intensity of Si in the mixture).
We also determined the amount of SiO_2 dissolved into the glasses by calculating the difference between an amount of added SiO_2 crystal (crystallite AA) and that of SiO_2 crystal that remained in the mixture (not dissolved) after heat treatment at temperature 700,9001000℃.

2.4 Analysis of reaction products between SiC and glasses
Reaction products after a fusion of SiC /glass mixture were investigated by using an X-ray microanalyzer (X650, Hitachi Ltd.) and by using XRD apparatus (RAFIIIA, Rigaku Electric).

3. Results and Discussion

3.1 Foaming phenomenon in a reaction between SiC substrate and glasses
The foaming phenomenon was observed when Ag/Pd thick electrode film was formed on a SiC substrate by firing at 800~900℃ high temperature. We considered that the foaming phenomenon occurred for the following reasons. (1) Glass in Ag/Pd thick film paste reacts with SiC to generate CO_2 gas. (2) Organic compounds in the thick film paste are incinerated at 800~900℃ high firing temperatures and formed gases such as CO_2 and H_2O. (3) Volatile substances adsorbed on SiC and glass are disrobed and formed gases. (4) SiC was oxidized and formed CO_2 gas. In order to elucidate the foaming phenomenon, three samples, i.e. SiC powder (74 mg), glass (95 mg), and a mixture of SiC (74 mg) powder and glass (95 mg) were subjected to thermogravimetric analysis up to 900°C with 10°C/min in temperature ramp-up rate and held at 900°C for 10 min. When one mole of SiC (40 g) is oxidized, one mole of SiO_2 (60 g) and one mole of CO_2 (44 g)

are generated. Of these, CO_2 is dispersed out from the reaction system. Accordingly, mass increase after the oxidation should be 20 g (percentage of mass increase is 50%). However, as shown in Fig.1, approximately 3% (2.2 mg) of mass increase is observed for SiC powder after firing at 900°C.

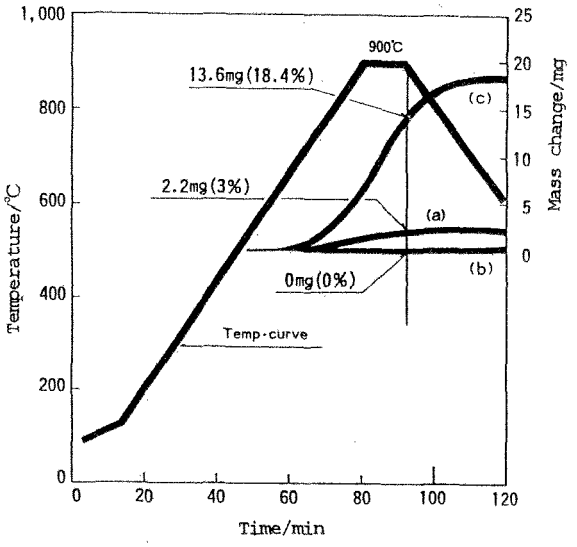

Fig.1. T.G. analysis curves of (a)SiC powder, (b)glass powder, and
(c) mixture of SiC(74mg)/Glass (95mg).

This result suggests that SiC is scarcely oxidized by firing at 900°C. In addition, no mass change was observed for the glass sample. In contrast, mass of the SiC /glass mixture increased to 13 6 mg after a firing at 900°C. The mixture contains 74 mg of SiC powder. Accordingly, the percentage of the mass increase of the mixture is 18 4%, which is six times larger than that of the SiC powder alone (3%). It is doubtful that the coexistence of SiC with glass promotes the oxidation of the glass. Furthermore, if the foaming in glass occurred from the reasons ((2) or (3)) as described above, mass decrease should be observed. We assumed that oxidation of SiC was promoted when SiC coexisted with glass rather than the sample without glass; ie., an oxidation of SiC was enhanced under the coexistence of glass and SiC.

As is well known that SiO_2 film is formed on the surface of SiC by direct oxidation of SiC. Since the SiO_2 film acts as a barrier layer against oxidation of SiC, further progress of oxidation into SiC may be suppressed. As shown in Fig. 1, an oxidation of SiC, however, is promoted by an addition of glass. We speculated that this phenomenon resulted from an effect of the glass addition; because SiO_2 film was dissolved into glass, the film could not act as a barrier layer against an oxidation of SiC. An oxidation process of SiC was considered as follows, 1) SiO_2 film is formed on the surface of SiC by heat treatment, 2) the SiO_2 film is dissolved into the glass, 3) a fresh surface of SiC is formed due to the dissolution of the SiO_2 film into glass, 4) the fresh SiC surface is oxidized again to form SiO_2 film, and 5) new SiO_2 film is dissolved into glass again. These steps are repeated and fresh SiC surfaces are formed one after another. Because of these repetitions, a rapid oxidation occurs on SiC.

To confirm above mechanism, we prepared glass #1 with a composition of 68 mass% V_2O_5, 27 mass% P_2O_5 and 5 mass% TiO_2, which does not contain SiO_2. Figure 2 showed the cross-sectional images of screen printed glass #1 film on a SiC substrate, which was fired at 500°C for 10 min in air.

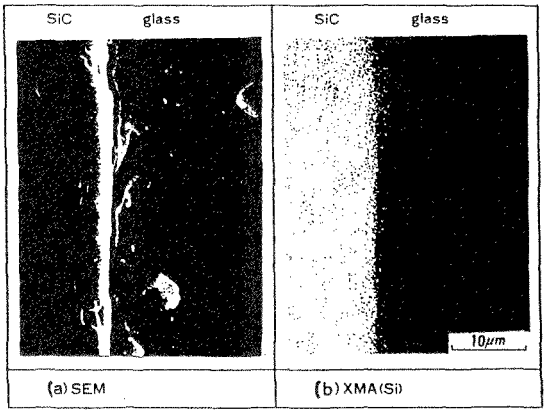

Fig.2. SEM and XMA cross section pictures of glass #1(SiO_2 free glass) film prepared on SiC substrate at 500°C for 10 min.

Figure 2(a) showed SEM image. Fig. 2(b) showed the XMA map of Si element in the glass film. As shown in the figures, Si element, which was not originally existed in the glass film, was detected in the experimentally fabricated glass film. In addition, when glass #1 was mixed with SiC powder and fused at 600°C, an increase in mass of the mixture was observed to be 6.1 mass%. These results indicated that diffusion of Si element into glass and glass promotes SiC oxidation. Rapid oxidation of SiC caused a generation of large amount of CO_2 which we consider to responsible for the foaming in glass. Therefore, a glass film in which the foaming phenomenon is not observed may not dissolved SiO_2 formed on the SiC surface,

or does not contain compounds which promotes SiC oxidation upon releasing free oxygen.

3.2 Effects of composition of glass on SiC oxidation

The results presented in the previous section indicated that glass showed great effects on SiC oxidation. Therefore, we investigated effects of glass composition on SiC oxidation to measure a change in mass of SiC/glass mixture after fusion. SiC /glass mixtures were subjected to a thermogravimetric analysis with temperature ramp-up rate 10°C/min and kept at a maximum temperature of 800°C for 10 min.

(1) Effects of ZnO and PbO in glass

Figure 3 shows effects of ZnO and PbO in glass on SiC oxidation. As shown in the figure, the degree of mass change greatly varied depending on a glass composition.

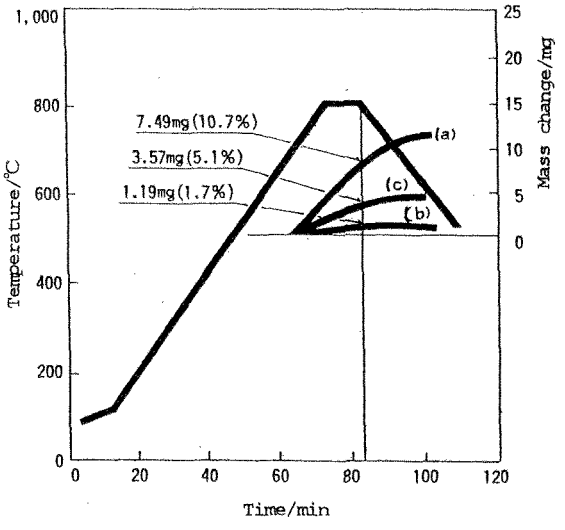

Fig.3. T.G. analysis curves of SiC/glass mixtures composed of three kind of glasses (a)glass #2, (b)glass #3 and (c)glass #4.

For example, glasses #2 and #4, which contained a large amount of ZnO 62mass% or PbO 30mass%, showed much larger mass gain than that of glass #3 which contained neither ZnO nor PbO. However, even if a large amount of ZnO or PbO existed in glass, an increase in SiO_2 resulted in a decrease in mass gain, as was observed for glass #4. The reason may be considered as follows: mass gain of glass/SiC mixture is affected by a degree of oxidation progress in SiC and by a glass composition. In other words, PbO promotes SiC oxidation and SiO_2 suppresses the one.

Therefore, effects of glass composition on a change in mass of SiC due to thermal oxidation was investigated for glasses containing PbO or ZnO which are considered to promote SiC oxidation. Three kinds of glasses were prepared, ie., glass #5 which is a borosilicate alumina zinc lead glass with 55 mass% ZnO and 3 mass% PbO, Glass #6 which is a borosilicate alumina zinc glass with 55 mass% ZnO, and Glass #7 which is a silicate lead glass composed mainly of PbO and SiO_2 and no ZnO.

Mixtures of SiC powder and these glasses #5,#6 and #7 exhibit large mass gain of 10, 10.5, and 14 mass%, respectively, as shown in Fig. 4.

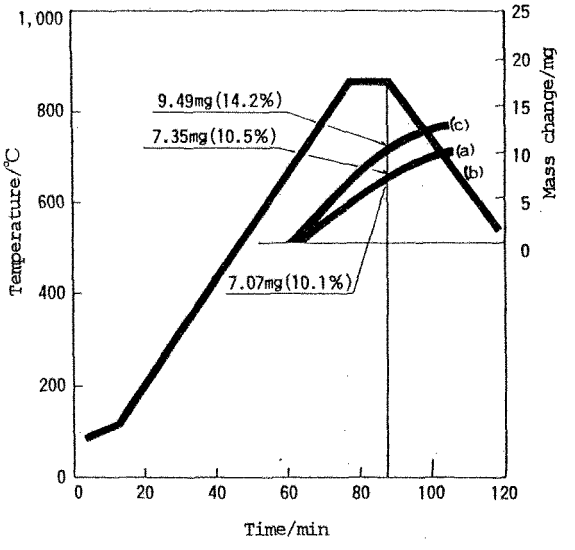

Fig.4. T.G. analysis curves of SiC/glass mixtures composed of three kind of glasses (a)glass #5, (b)glass #6 and (c)glass #7.

We investigated on a reaction occurred in glass/SiC mixtures (mass ratio: 70/30) which were heated at 900°C for 10 min and fused. Glass #5 showed some XRD peaks attributed to Zn_2SiO_4, $Zn_3(BO_3)_2$ and Pb crystal, as shown in Fig. 5. A refraction intensity of XRD peak of Zn_2SiO_4 was particularly marked for the mixture SiC/glass #5(compare (a) to (b) in Fig.5).

This tendency is remarkably observed for glass #6, as shown in Fig. 6(a) and 6(b). Fig. 6(a) showed that glass #6 has a noncrystalline structure even after fusion. When SiC was added to glass #6, XRD peaks attributed to Zn_2SiO_4 were

observed for the fired sample as shown in Fig.6(b).
It is considered that Zn_2SiO_4 is formed by the following reaction.

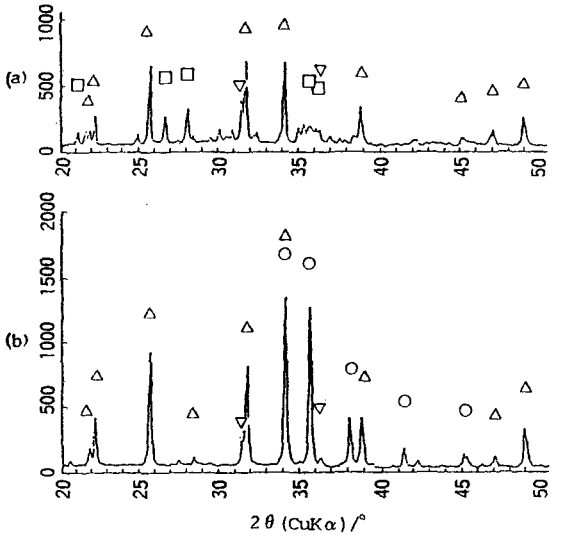

Fig.5. XRD patterns of (a)glass #5 and (b)SiC/glass #5 mixture fired at 900℃ for 10min. ○:SiC, △:Zn_2SiO_4, □:$Zn_3(BO_3)_2$ and ▽:Pb.

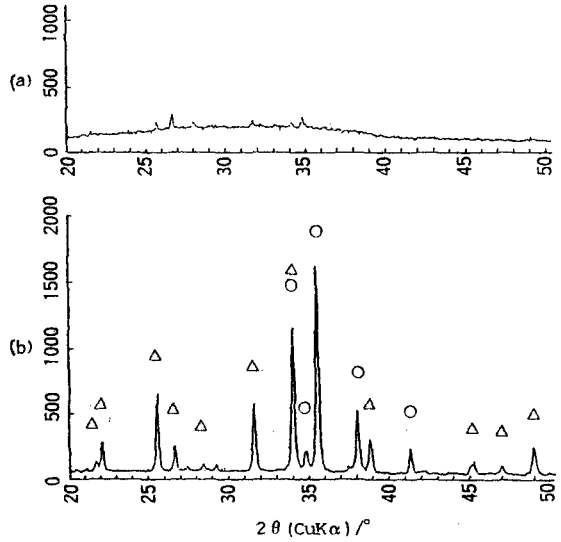

Fig.6. XRD patterns of (a)glass #6 and (b) SiC/glass #6 mixture fired at 900℃ for 10min. ○:SiC, △:Zn_2SiO_4.

First, the surface of SiC powder is oxidized to generate SiO_2. Then SiO_2 was dissolved into borosilicate alumina zinc glass as Si^{4+} and O^{2-} ions. Finally, Si^{4+} and O^{2-} ions are reacted with ZnO in the glass to form Zn_2SiO_4. Since SiO_2 is consumed by formation of Zn_2SiO_4, oxidation of the SiC powder is extremely promoted with coexistence of borosilicate alumina zinc glass. In any case, SiO_2 seems to be dissolved into the borosilicate alumina zinc glass easily.
XRD measurements showed that glass #7 fired at 900℃ had noncristalline structure, as shown in Fig. 7(a). Fig.7(b) showed that Pb metal was generated after firing at 900 ℃ for glass #7 fused with SiC powder. As is well known that crystalline PbO decomposes to release O_2 and is easily reduced to Pb metal. This tendency is also observed for PbO in glass. O_2 was formed under a certain condition due to a decomposition of PbO in glass contained with PbO. And O_2 oxidized SiC to generate SiO_2 and CO_2. Thus generated SiO_2 is easily dissolved into glass. Accordingly, an addition of PbO to silicate alumina glass promotes SiC oxidation. The results above mentioned demonstrate that glasses containing ZnO which has strong reducing ability and easily form silicate or aluminate compounds upon reaction with SiO_2, are not suitable for the use with SiC substrates. And glasses containing PbO which has strong reducing ability and easily releases O_2, are not suitable for the use with SiC substrates.

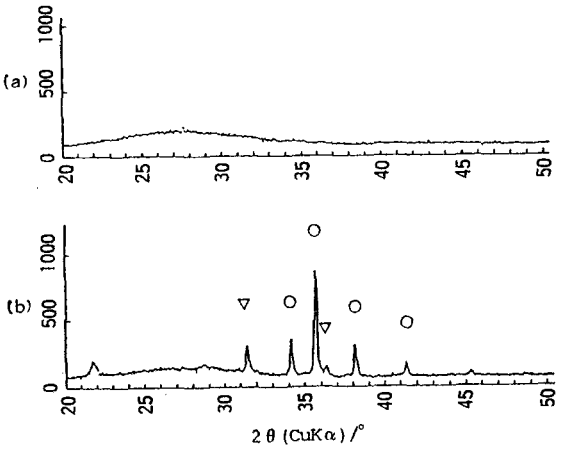

Fig.7. XRD patterns of (a)glass #7 and (b)SiC/glass #7 mixture fired at 900℃ for 10min. ○:SiC and ▽:Pb.

(2) Effects of Al_2O_3 in glass

We investigated on effects of Al_2O_3 on SiC oxidation. Glass #8 comprised of 63 mass% PbO , 12 mass% SiO_2, and 25 mass% B_2O_3 (lead borosilicate glass) was used as a base material. 3 mass% and 6 mass% Al_2O_3 were added to glass #8 to prepare glass #9 and glass #10, respectively. The mixtures were refused to prepare glass samples with various Al_2O_3 contents. The experiments were performed in similar way to that described in the previous section; mass changes of SiC/glass mixture after fusing at 800°C were measured by T.G. analysis. As shown in Fig.8, mass gain of the glass #8/SiC mixture was measured to be 7.7 mass% after a heat treatment at 800°C.

In contrast, those of the glass #9/SiC mixture and the glass #10/SiC mixture were measured to be 1.3 mass% and 0.8 mass%, respectively. Mass gain of the glass #10/SiC mixture is approximately 1/10 of that for the glass #8/SiC mixture.

We investigated on the causes of the decrease in mass gain for the glass #10/SiC mixture. The glass softening temperature of glass #8(the temperature at which glass viscosity becomes $10^{7.6}$ poise) became higher with increase in Al_2O_3 addition.

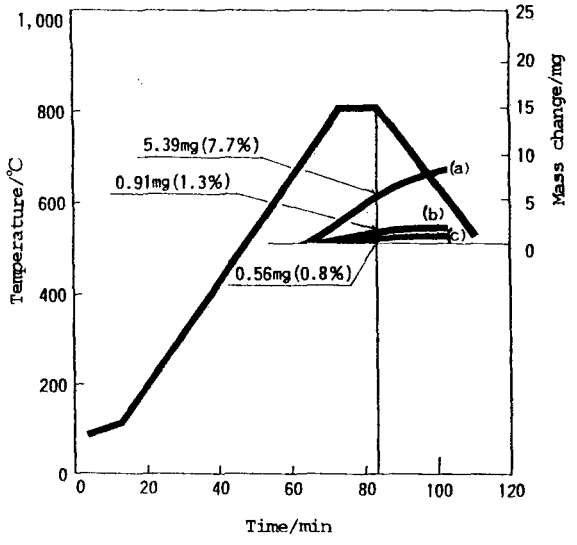

Fig.8. T.G. analysis curves of SiC/glass mixtures composed of lead boro silicate glass with various amount of Al_2O_3
(a)glass #8(Al_2O_3 free), (b)glass #9(3 mass% Al_2O_3) and (c)glass #10(6 mass% Al_2O_3).

Then, we measured a viscosity of glasses #8 , #9 and #10 in the temperature range from 600℃ to 870℃. Figure 9 showed that the viscosity of glasses containing Al_2O_3 rapidly increased below 750°C.

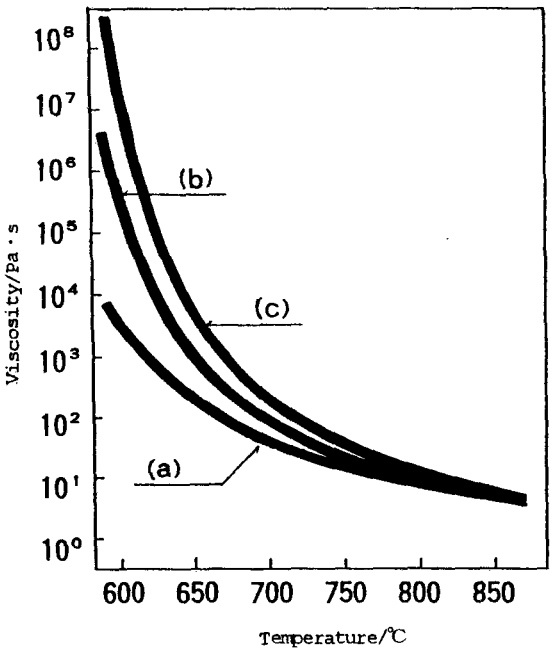

Fig.9. Viscosity of lead boro silicate glasses with various amount of Al_2O_3 (a)glass #8(Al_2O_3 free), (b)glass #9(3 mass% Al_2O_3) and (c)glass #10(6 mass% Al_2O_3) at temperature range from 600℃ to 870℃.

However, an effect of Al_2O_3 addition on the viscosity of glasses was negligible above 750°C. And the viscosity of glasses #8, #9 and #10 showed almost the same value at 800°C (10 poise or less). Therefore, the viscosity of glasses do not induce the rapid decrease in the mass change (SiC oxidation) after heat treatment of the glass #10/SiC mixture.

In order to elucidate the causes of the rapid decrease in the mass gain of the glass #10/SiC mixture, XRD analysis was carried out on these glasses and glass/SiC mixtures. Figures 10, 11 and 12 showed X-ray diffraction patterns of glasses #8, #9 and #10 and their glass/SiC mixtures after heat-treated at 800°C for 10 min. As shown in the figures, for glass #8 and glass #9, small XRD peaks of Pb metal were observed. For the samples in which SiC was added, no XRD peaks of crystals other than SiC and Pb metal were observed. However, an intensity of refraction peaks of Pb metal gradually decreased with an increase in the Al_2O_3 addition. Based on this result, we assumed that Al_2O_3 tends to prevent a decomposition of PbO and suppress the diffusion of O^{2-}, Pb^{2+} and Si^{4-}. Aside from this assumption, it is likely that an addition of Al_2O_3 in glass prevent SiC from oxidation.

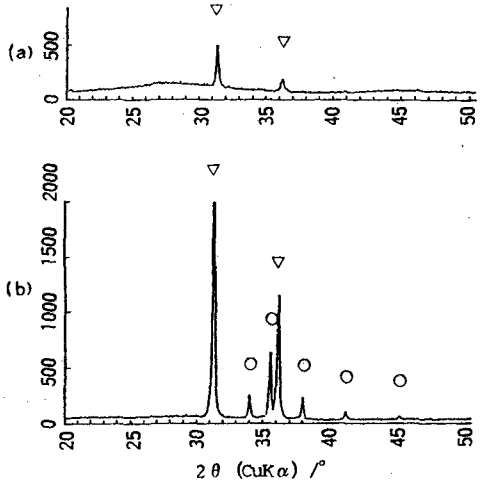

Fig.10. XRD patterns of (a)glass #8 and (b)SiC/glass #8 mixture fired at 800℃ for 10min. ○:SiC and ▽:Pb.

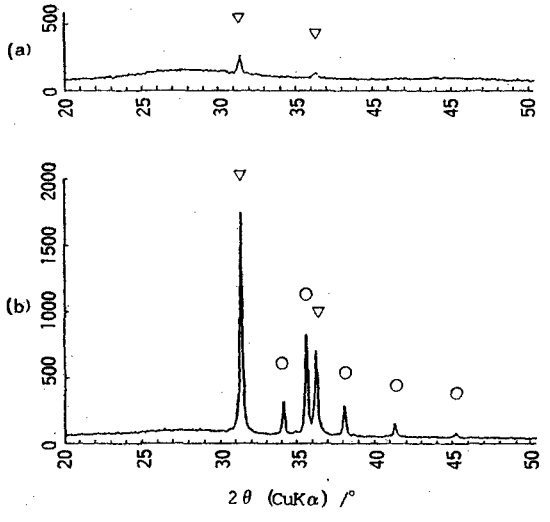

Fig.11. XRD patterns of (a)glass #9 and (b)SiC/glass #9 mixture fired at 800℃ for 10min. ○:SiC and ▽:Pb.

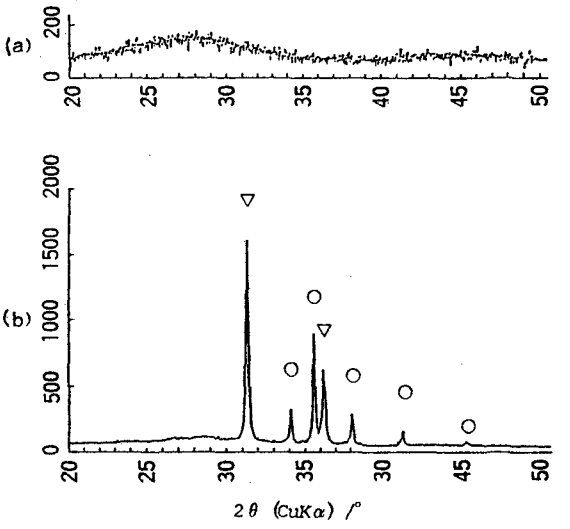

Fig.12. XRD patterns of (a)glass #10 and (b)SiC/glass #10 mixture fired at 800℃ for 10min. ○:SiC and ▽:Pb.

(3) Effects of SiO_2

We investigated on the effects of SiO_2 on SiC oxidation. 10, 30, 50, 70 or 90 mass% SiO_2 (crystallite AA)was added to glass #5 (SiO_2: 12 mass%, ZnO: 55 mass%, B_2O_3: 23 mass%, PbO: 3 mass%, Al_2O_3: 7mass%), and each sample was refused at 700°C, 900°C or 1000°C for 30 min and then pulverized. XRD peaks of SiO_2 (crystallite AA) in these samples were analyzed. Figure 13 showed the relationship between an amount of SiO_2 added to the glass sample and ratio of an integral intensity of XRD peak (I_{SiO_2}/I_{Si}) of SiO_2 to Si. Dotted line in Fig.13 represents the previously obtained calibration curve of SiO_2 content in the glass.

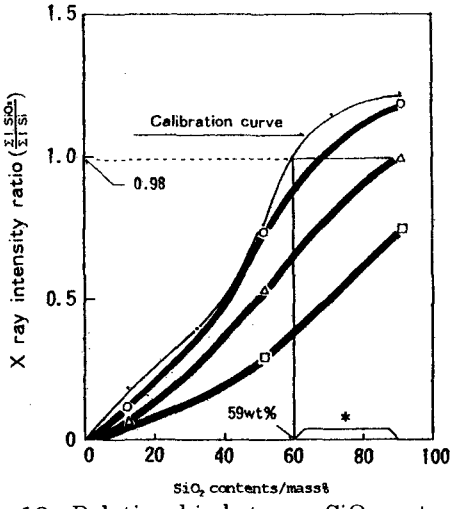

Fig.13. Relationship between SiO_2 content in glass #5 and XRD intensity ratio (I_{SiO_2}/I_{Si}) as a function of fusion temperatures. ○:fused at 700℃ for 30 min, △:fused at 900℃ for 30 min and □:fused at 1100℃.

In other words, amounts of SiO_2 crystal in the glass after heat-treatments are shown in Fig.13. In order to quantify an amount of SiO_2 dissolved into the glass, it is necessary to subtract an amount of crystal SiO_2 remained after heat-treatments from one added to the glass prior to heat treatments. Actually, for 90 mass% SiO_2-added sample which was heat-treated at 900°C for 30 min, the ratio of XRD intensity obtained from the calibration curve was 0.98 as shown in Fig.13. The SiO_2 content obtained from the calibration curve is 59 mass% for the ratio of XRD intensity of 0.98; namely, 59 mass% SiO_2 was remained in the glass as crystals. Accordingly, subtraction of 59 mass% from 90 mass% (originally added value) gives 31 mass% SiO_2 which is dissolved into the glass. Table 2 showed amounts of SiO_2 which was dissolved into the glass after the heat treatments under various conditions.

Table 2. Relationship between the heated condition and amount of the dissolved SiO_2 in the glass #8 (Lead boro silicate glass) as function of the addition of the crystal SiO_2.

Heated condition	700℃, 30min		900℃, 30min		1100℃, 30min	
Added Crystal SiO_2	Crystal SiO_2	Disolved SiO_2	Crystal SiO_2	Disolved SiO_2	Crystal SiO_2	Disolved SiO_2
10	5	5	2	8	—	—
50	50	0	40	10	22	28
90	90	0	59	31	50	40

SiO_2 crystal was scarcely dissolved into the glass upon heat treatment at 700°C. The dissolution of SiO_2 into the glass was promoted by heat-treatments above 900°C. The more the SiO_2 addition, the more the SiO_2 dissolved into the glass. In the present experiment, measurements could not carried out for 10 mass% SiO_2-added sample heat treated at 1100°C because the shoud mention the condition ("stainless crucible was used") corroded severely. And then effects of SiO_2 addition on SiC oxidation were investigated to measure a mass gain of glass/SiC mixtures. We prepared glass to which sufficient amount of SiO_2 (crystallite AA) was added, because the further dissolution of SiO_2 into glass is not likely to occur. Because we think that if SiO_2 film formed on a surface of SiC is not dissolved into the glass, the SiO_2 film layer would prevent SiC from oxidation. We initially added SiO_2 to the glass and heated it at 900°C for 30 min. Then, the effects of SiO_2 addition on the SiC oxidation were investigated by using glass #6 (SiO_2: 10mass%, ZnO: 55mass%, B_2O_3: 25mass%, Al_2O_3: 10mass%) and glass #11 (SiO_2: 51mass%, B_2O_3: 9mass%, Al_2O_3: 4mass%, CaO: 12mass%, BaO:24mass%) which has higher SiO_2 content. The magnitude of the effects on SiC oxidation was evaluated by measuring a percentage of mass change before and after heat treatment. When SiO_2 (crystallite AA) was added to glass and was fused at high temperature, SiO_2 was scarcely dissolved into glass; it is almost impossible to remove SiO_2 (crystallite AA) which was not dissolved in glass and remained as crystal. Because of above reason, we only attempted to clarify the effects of SiO_2 addition on SiC oxidation.

Figure 14 shows the dependence of mass gain of glass/SiC mixture on the SiO_2 content in the glass after heat treatment at 900°C for 30 min. When SiO_2 content was 10 mass%, the largest percentage of mass gain was observed for glass #5 (i.e., approximately 35 mass%).
In contrast, the percentage of mass gain for glass #11, which has more SiO_2 content, was very small (i.e., approximately 11 mass%). The mass gain of glass/SiC mixture decreases with increase in the SiO_2 content; namely, it was demonstrated that SiO_2 addition suppresses SiC oxidation.

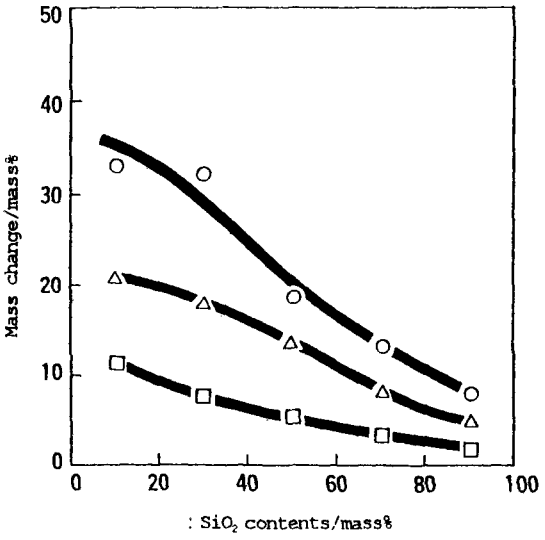

Fig.14. Percentage mass gain of SiC/glass mixtures composed of various amount of SiO_2 after firing at 900℃ for 30min. ○:glass #5, △:glass #6 and □:glass #11.

3.3 Investigation of SiO_2-Al_2O_3-B_2O_3 glasses

The above results indicated that PbO and ZnO in glass promote SiC oxidation but Al_2O_3 and SiO_2 suppress it. Glasses containing a large amount of PbO or ZnO tend to foam on SiC substrate when they are fused. Therefore, we investigated on glasses composed mainly of Al_2O_3 and SiO_2, which contained no PbO or ZnO, for the use on SiC substrates. When large amounts of Al_2O_3 and SiO_2 are added to glass, the temperature at which glass formation occurs is increased and the production of glasses becomes difficult. Therefore, we added B_2O_3 to the glass, which is known to decrease the glass formation temperature; we prepared Al_2O_3-SiO_2-B_2O_3 glasses. Using these glasses, we investigated on effects of SiO_2 and Al_2O_3 addition on the SiC oxidation. Figure 15 shows the results.

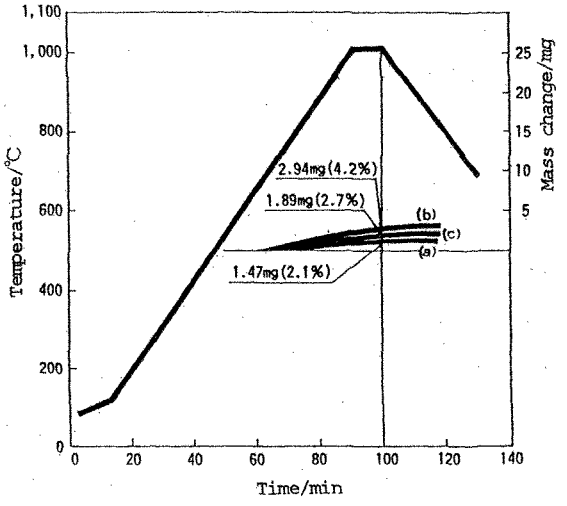

Fig.15. T.G. analysis curves of SiC/glass mixtures composed of zinc and lead free glass (a)glass #12, (b)glass #13 and (c)glass #14.

We prepared mixtures of Al_2O_3-SiO_2-B_2O_3 glasses and 30 mass% SiC powder. The mixtures were heated up to 1000°C. Their mass gain were measured after heat treatment. Glass #13 has a composition that a part of the Al_2O_3 in Al_2O_3-SiO_2-B_2O_3 glass was replaced with MgO. The percentage of mass gain after heat treatment at 1000°C was 4.2mass% for glass (#13) /SiC mixture, which was larger than those of mixtures glasses #12 (2.1mass%) and #14 (2.7mass%). However, in terms of SiC oxidation at 1000°C, this percentage of mass gain is fairly small compared with that of the glasses investigated so far. Therefore, SiO_2-Al_2O_3-B_2O_3 glasses paste were prepared and screen-printed on a SiC substrate in order to investigate a reaction between the glass and SiC. The glass paste printed on SiC substrate was and heat-treated at 850°C, 900°C or 950°C for 10 min. Figure 16 shows SEM images of the glass films.

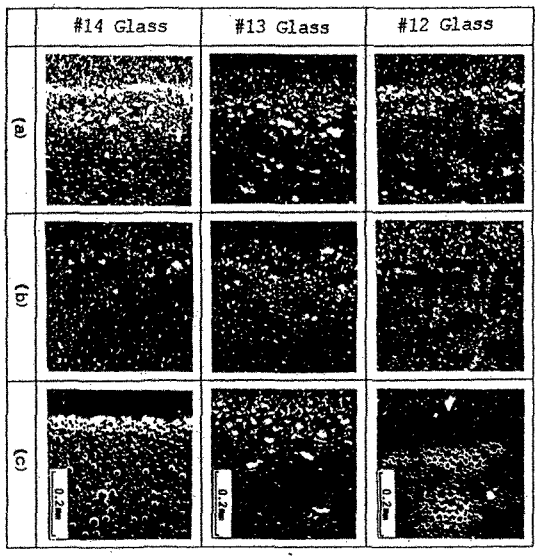

Fig.16. SEM pictures of glass films formed on SiC substrate at various temperatures (a)850℃, (b)900℃ and (c)950℃.

As for the glass #12, no glass flow was observed below 850°C. At 900°C, a mesh pattern was still observed on the film surface, but the film became fairly dense. Fine bubbles were generated and expansion occurred in the film at 950°C. Therefore, it was confirmed that the temperature range for firing glass #12 was narrow around 900°C. In the case of the glass #13, no glass flow was observed below 850°C. Foaming in the glass film was observed above 900°C. Accordingly, the glass #13 was not suit for the past for SiC substrates. As for the glass #14, glass flow was observed at 850°C and a sufficiently dense film was formed at 900°C. Foaming occurred at 950°C.

Therefore, the glass #14 was suitable past for forming film on SiC substrates over a temperature range of 850°C to 900°C.

4. Conclusions

We investigated on effects of glass composition on SiC oxidation and determined an effective glass composition to form a dense electrode film on a SiC substrate. The following conclusions were obtained.

1) Since SiO_2 film formed on the SiC surface was easily dissolved into the glass, SiC oxidation was promoted when it coexisted with glass.
2) PbO in glass was reduced to Pb metal upon reaction with SiC.
   SiC was simultaneously oxidized to SiO_2 and CO_2.
3) ZnO in glass oxidized SiC to generate SiO_2 and CO_2. ZnO thoroughly reacted with SiO_2 to generate silicate compounds such as Zn_2SiO_4, that promoted the dissolution of SiO_2 into the glass.
4) SiO_2 and Al_2O_3 in glass suppress the reaction of glass with SiC.
5) Glass composed of SiO_2 30-35 mass%, Al_2O_3 20 mass%, B_2O_3 35-40 mass%, CaO 5 mass% and ZrO_2 5 mass% can form a sufficiently dense glass film on a SiC substrate after heat treatment at 850-950°C.

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