SiO_2-CaO-Al_2O_3 Glass Solder for Joining of Al_2O_3 to Al_2O_3

B.-G. Ahn[1] and Y. Shiraishi[2*]

[1]*Faculty of Advanced Materials Engineering, Chonbuk National University, Chonju, 561-756, Korea*
[2]*AGNE Gijutsu Center Ltd., Minami-Aoyama 5-1-25, Minato-ku, Tokyo 107-0062, Japan*

(Received December 4, 1997)

ABSTRACT

To utilize glass as a solder for joining of ceramics, the joining of Al_2O_3 to Al_2O_3 by glass solders with the compositions (mass %) of $33SiO_2$-34CaO-$33Al_2O_3$ and $50SiO_2$-38CaO-$12Al_2O_3$ has been investigated. The thermal expansion of these glasses and the wettability between glasses and alumina have been measured to confirm the applicability of the glasses to joining of alumina. After joining at various temperatures, the bending strength of the joint was measured using a four-point-bending test at room temperature. The joint interface between alumina and glass solders was observed using a SEM-EDX microanalyser. A maximum bending strength of 210 MPa was obtained for a joint produced at 1773 K for 1.2 ks with 33 SiO_2-34CaO-$33Al_2O_3$ solder. This value corresponds to 70% of that for original alumina.

1. INTRODUCTION

Joining ceramics is one of the most fundamental and useful techniques in fabricating new functional materials. Thus, many attempts have been to join ceramics to ceramics or metals, using a number of methods such as high energy beam bonding, high temperature sintering, metal or ceramic filler, and glass solder /1/. Regarding the joining of alumina, high temperature sintering under pressure applied to Al_2O_3/Al_2O_3 joining /2,3/ and active metallic insert applied to Al_2O_3/metal joining /4,5/ have been reported. However, the work on the joining of Al_2O_3 by a glass solder is still limited /6/.

Since the composition of glass can be selected widely, an appropriate moderation-layer may be obtained at the interface of Al_2O_3/glass solder if the composition of the solder is properly chosen. This leads to the systematic research on the joining of alumina to alumina by SiO_2-CaO-Al_2O_3 glass solders with the measurements of thermal expansion coefficients of the solders and alumina, wetting of the solders with alumina, elements distribution and structure of the joined interface, and bending strength of the produced joint.

2. EXPERIMENTAL

2.1. Samples

A 99 mass% pure commercial alumina plate (Japan Ceratec #A-991) was used. At room temperature, the apparent density was measured to be 3.9 mg/m^3 by the Archimedean method using distilled water. The bending strength was determined to be 305 MPa as the mean of the results obtained on 5 samples by a four-point-bending test. The sample was polished using 1 μm diamond paste for the wetting and the bending test.

Compositions of glass solders listed in Table 1 were selected under the criterion that their thermal expansion coefficients were nearly equal to that of alumina /7/ and their melting points were in the temperature range 1623 to 1723 K. Glass solders were prepared from high grade chemicals of SiO_2, $CaCO_3$,

* To whom all correspondence should be addressed.

Table 1
Chemical composition of alumina and glasses in this work

Sample	Composition (mass%) SiO_2	CaO	Al_2O_3
Alumina	0.5	0.3	99
SCA-g glass*)	33	34	33
SCA-w glass*)	50	38	12

*) by batch

Table 2
Glass transition temperature Tg, crystallization temperature Tc and average thermal expansion coefficient α of the samples in this work

Sample	Tg,Tc/K crystalline form	$\alpha \times 10^{-6}(K^{-1})$,(obs.) over 323 ~ 1073 K	$\alpha \times 10^{-6}(K^{-1})$,(calc.)*) over 323 ~ 673 K
Al_2O_3		7.05	
SCA-g, glass	1108, 1314	7.14	6.25
SCA-g, cryst.	gehlenite	6.92	
SCA-w, glass	1080, 1246	8.32	7.97
SCA-w, cryst.	pseudo-wollastonite	9.95	

*) calculated by Takahashi's factor/7/

and Al_2O_3. Calculated amounts of the chemicals were weighed, thoroughly mixed, and melted in a Pt crucible in air. The melt was kept for 7.2 ks at 1773 to 1873 K, and then cast into a copper mould. The glass produced was cut or crushed into appropriate shapes for further experiments.

The crystallization temperature, Tc, of the prepared glass solder was measured using a differential scanning calorimeter (Seiko Densi Kogyo; DSC-300) at a heating rate of 0.167 ks in the temperature range between room temperature and 1473 K with Al_2O_3 powder as a reference. Results are summarized in Table 2. The crystalline phases were also identified by an X-ray diffraction technique. They were precipitated from the glassy state by a two-step heat treatment with 1113 K for 3.6 ks and Tc for 7.2 ks. The crystalline phases were identified to be gehlenite ($2CaO.Al_2O_3.SiO_2$) for $33SiO_2$-$34CaO$-$33Al_2O_3$ (referred to as SCA-g) and pseudo-wollastonite ($CaO\ SiO_2$) for $50SiO_2$-$38CaO$-$12Al_2O_3$ (referred to as SCA-w).

Thermal expansion of materials is one of the most important factors affecting residual stress after joining. For this reason, the thermal expansion coefficients of both glassy and crystallized samples were measured using a dilatometer (Rigaku Denki; TMA 8140) in the temperature range 323 to 1273 K. The results are shown in Table 2 together with the calculated values using Takahashi's factor /7/, which is assigned to each cation based on the strength of the electrostatic attraction between cation and oxygen anion.

2.2. Wetting between glass solder and alumina

Since wetting is known to be a good indicator of the adhesion behavior between liquid and solid phases, the contact angle between glass solder and alumina was

measured by the sessile drop method. A polished glass sample having a cylindrical shape of 3 mm in diameter and 2 mm in height was placed on the polished surface of the alumina sample, and heated up to a desired temperature at a rate of 1.67 ks by infrared radiation heating. Just after reaching the desired temperature, the shape of the sample was photographed successively in a course of increasing temperature.

2.3. Joining process

The alumina sample of a rectangular shape with an area of 11.5 x 7 mm^2 and a height of 20 mm was used for the joining experiment. A desired amount of glass solder sieved into 100 to 200 mesh was spread on the polished surface of an alumina sample with ethanol and another alumina sample was placed on it. Then a pair of the samples was set in a graphite cassette as shown schematically in Fig. 1. The pair of samples was heated in a radio frequency type furnace up to a desired temperature in an Ar atmosphere and kept for 1.2 ks, and then cooled in the furnace. The time required for cooling to room temperature was about 7.2 ks.

2.4. Characterization for the joints

Structure observation and element distribution analysis for the area close to the joined interface were carried out using a SEM-EDX analyser (Hitachi; X-650). Bending strength was measured by a four-point-bending test (after JIS-R1601) using an Instron type tensile testing machine (Shimazu; AG 5050-c). A test piece of 4 x 3 x 40 mm^3 was sliced from the joint and its surface was polished. Tests were carried out under the following conditions; upper span - 12 mm, lower span - 28 mm, and cross head speed - 0.2 mm/s. The results were expressed as an average value obtained from 3 to 5 samples.

3. RESULTS AND DISCUSSION

3.1. Thermal expansion of the glass solder

The thermal expansion of glassy and crystallized samples is illustrated in Fig. 2 together with that of Al_2O_3. For glassy samples, the measurements were re-

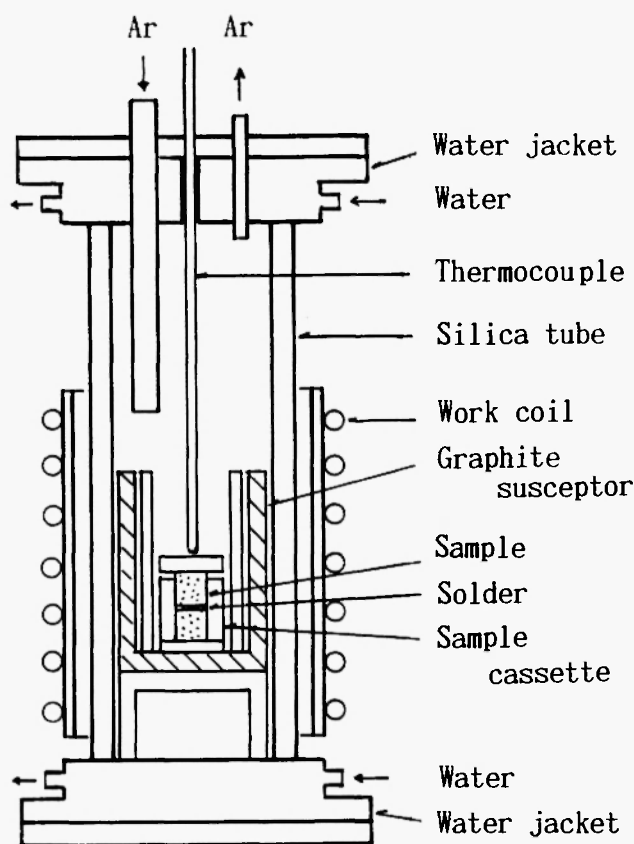

Fig. 1: Schematic illustration of joining apparatus.

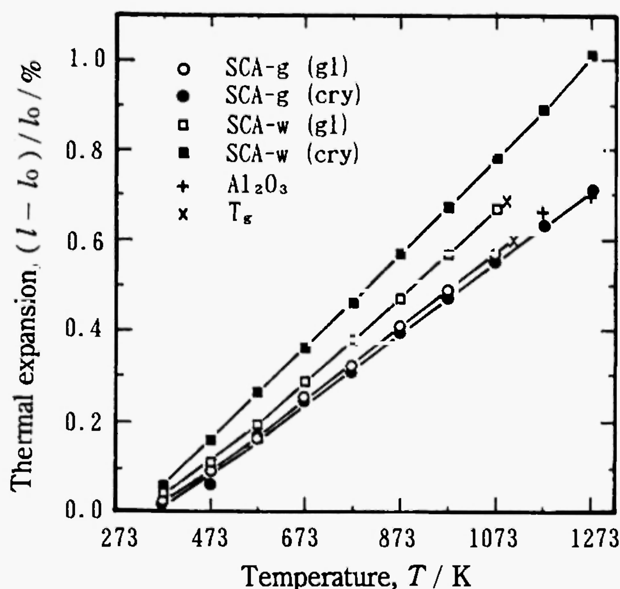

Fig. 2: Thermal expansion of the glassy and crystallized solders.

stricted up to 1073 K due to the softening behavior of glasses. Expansion of both glasses indicated a marked increase near and above this temperature which corresponds to the glass transition temperature Tg (see Table 2). The thermal expansion coefficient of gehlenite was similar to that of the mother glass (SCA-g). On the other hand, the thermal expansion coefficient of wollastonite (9.4×10^{-6}/K for 373 to 473 K) /6/ differs from that of SAC-w glass (6.3×10^{-6}/K for 323 to 473 K). Since the thermal expansion of alumina is almost identical to that of crystalline gehlenite, the residual stress may be minimized in the joint with this SCA-g glass.

3.2. Wetting of the glass solders on alumina

The apparent contact angle measured by the sessile drop method is shown in Fig. 3 as a function of temperature. Since the contact angle was measured within a minute of the temperature reaching the desired value, the results of Fig. 3 may differ from the true equilibrium value.

Once the reaction starts between a glass solder and alumina, a glass solder will spread over the alumina substrate so as to reduce markedly the contact angle. This implies that the contact angle of the SCA-w glass

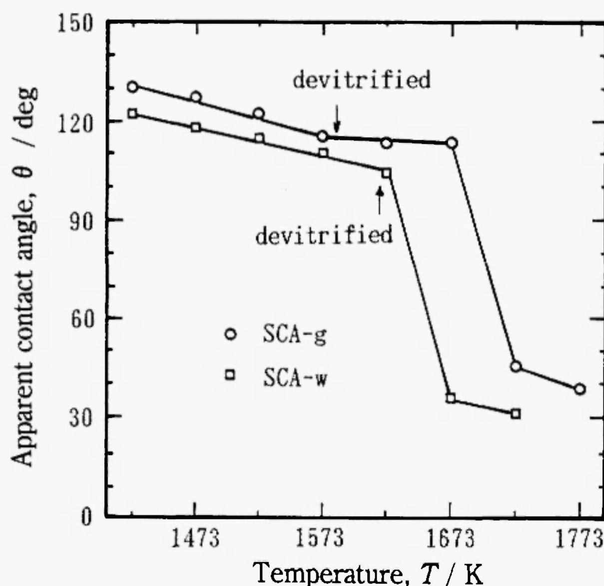

Fig. 3: Apparent contact angle between glass solders and alumina substrate as a function of temperature.

solder is quite likely to decrease at temperatures close to the melting point (~ 1623 K). This assumption is accepted in the case of the SCA-g glass solder whose melting point (~ 1723 K) is higher than that of the SCA-w glass solder. The results of Fig. 3 are consistent with such an argument. In general, good adhesion needs a lower contact angle than 90°. From this point of view, the temperatures required for joining must be higher than 1673 K and 1723 K for the SCA-w and SCA-g glass solders, respectively.

The glass solders were also devitrified during the course of heating. The arrows in Fig. 3 indicate a possible temperature where the glass solders start to be devitrified. Disagreement between these observed temperatures and crystallization temperatures for these glass solders (given in Table 2) may be attributed to the difference of the heating rate used in the measurements. From the results of Fig. 3, the SCA-g glass easily devitrified compared to the SCA-w glass. Such a finding may be explained by the difference of their melting points.

Figure 4 shows the SEM micrographs of the interface of the Al_2O_3/SCA-g joint. It is clear in Fig. 4 that the interface of the Al_2O_3/SCA-g joint remains smooth at temperatures up to 1673 K and becomes rough at 1773 K. This change of the interface corresponds to the change of the contact angle from 115° to 45°. This variation in the interface is considered to play an important role in joining Al_2O_3. In the SCA-w glass, on the other hand, devitrified crystals at 1623 K are melted at 1673 K and spread over a rough interface.

3.3. Dissolution of alumina into the solder layer

In order to investigate the dissolution of Al_2O_3 into a glass solder, the chemical composition of the soldered layer (5 μm away from the joint interface) was analysed using a EDX. Figures 5(A) and 5(B) show the composition change as a function of temperature for two glass solders of SCA-g and SCA-w, respectively. The black mark in this figure indicates the composition of crystals precipitated from the glass matrix and the white mark shows the matrix composition. In Fig. 5(A), the crystals which were produced at 1573 K are considered to be gehlenite, $2CaO \cdot SiO_2 \cdot Al_2O_3$ whose composition remains unchanged at temperatures above 1823 K. On

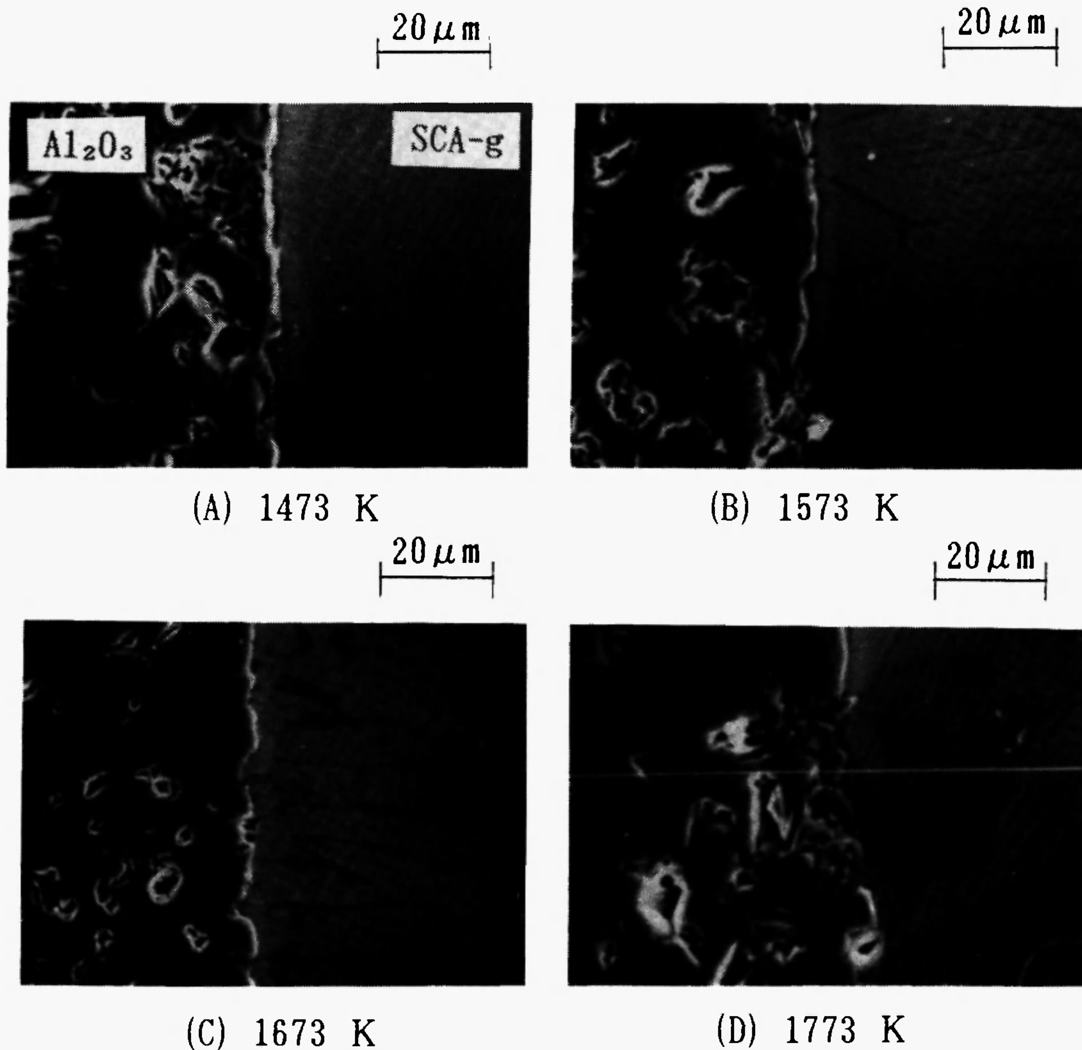

Fig. 4: SEM micrographs of the interface of the Al_2O_3/SCA-g joint.

the other hand, the composition of the glass matrix changes at 1573 K by the crystallization of gehlenite and remains constant until the melting of the glass solder. The contents of Al and Ca show their variation near the interface at temperatures above 1723 K. Figure 5(B) shows that the crystals precipitated at 1573 K from SCA-w glass are considered to be wollastonite, CaO SiO_2 which is melted again at 1673 K, and the dissolution of alumina into the solder layer also occurs from 1723 K.

Figures 6(A), 6(B) and 6(C) are the SEM and X-ray images near the joint interface between Al_2O_3 and the SCA-g glass solder at 1723, 1773, and 1823 K, respectively. Figure 6(A) shows a rather smooth interface without dissolution of alumina into the glass solder. However, a rough interface can be observed in Figs. 6(B) and 6(c) when there *is* dissolution of alumina, producing a new phase, probably classified as $CaO{\cdot}Al_2O_3$ or $CaO{\cdot}2Al_2O_3$

3.4 Strength of joint

A four-point-bending test at room temperature was made in order to evaluate the strength of the joints. Since the same amount of glass solder was used throughout all the experiments, the thickness of the joint layer showed an almost constant value ranging from 30 to 50 μm. Good joining was obtained for most

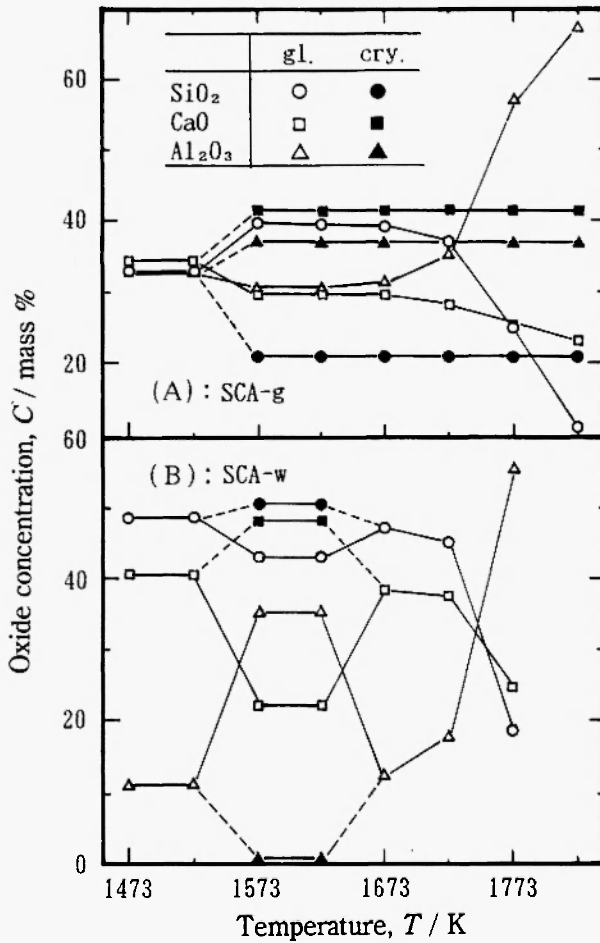

Fig. 5: Change of the chemical compositions of the glass matrix and the crystalline phase near the joint interface as a function of temperature. (A) SCA-g and (B) SCA-w.

of the samples, except some samples joined at 1873 K.

Since temperature is one of the most important factors for governing the toughness of the joint, the joining experiments were carried out at 50 K intervals between 1623 and 1873 K. At the lowest temperature, 1623 K, complete wetting of the glass solders was not clearly observed. While the time for joining was fixed at 1.2 ks by referring the results reported previously, it is also an important factor with respect to the toughness of the joint.

Figure 7 gives the bending strength of joints by two glass solders of SCA-g and SCA-w as a function of joining temperature. Although the results are somewhat scattered, a maximum value of bending strength is found at 1773 K for the SCA-g glass solder and at 1723 K for the SCA-w case. These maximum values correspond to 70% (for SCA-g) and 65% (for SCA-w) of the bending strength for alumina. The fracture surface of the joints with the maximum strength ran through the

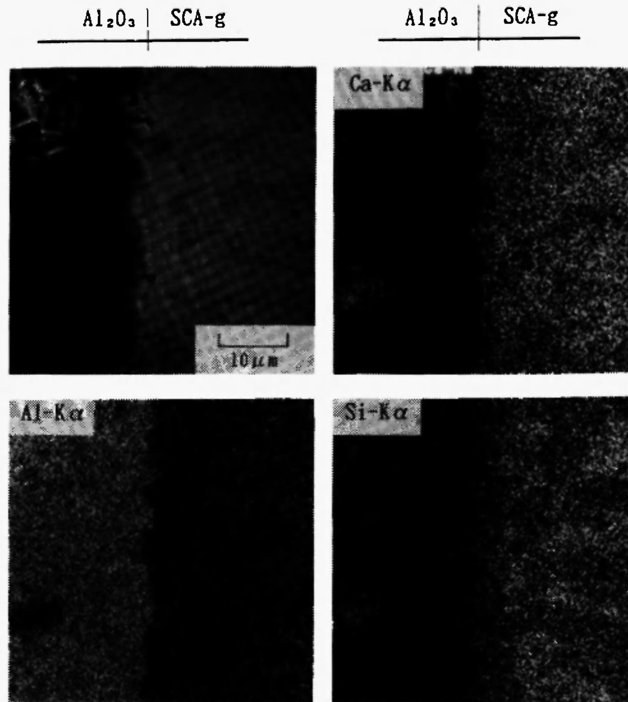

Fig. 6(A): SEM and X-ray images of the joint interface between alumina and glass solder (SCA-g) produced at 1723 K.

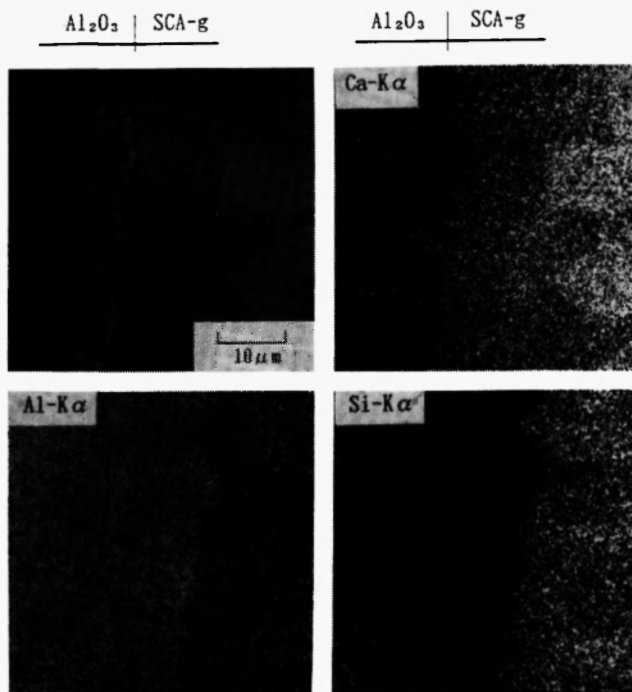

Fig. 6(B): SEM and X-ray images of the joint interface between alumina and glass solder (SCA-g) produced at 1773 K.

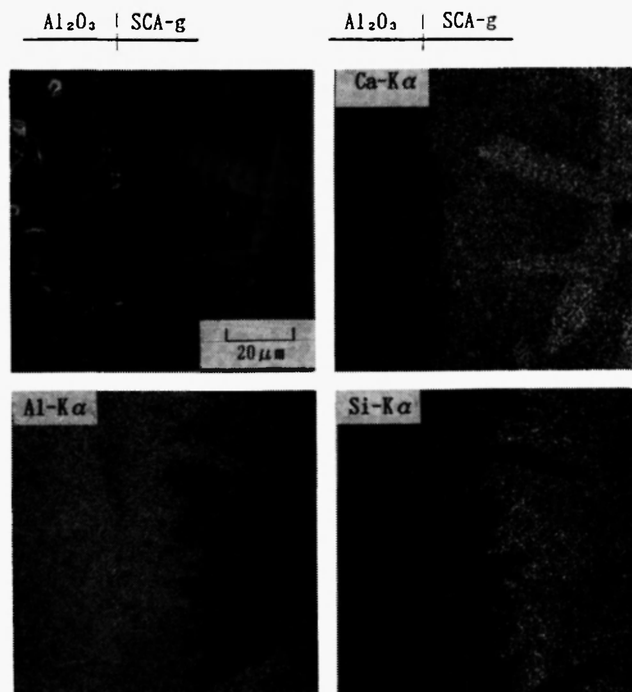

Fig. 6(C): SEM and X-ray images of the joint interface between alumina and glass solder (SCA-g) produced at 1823 K.

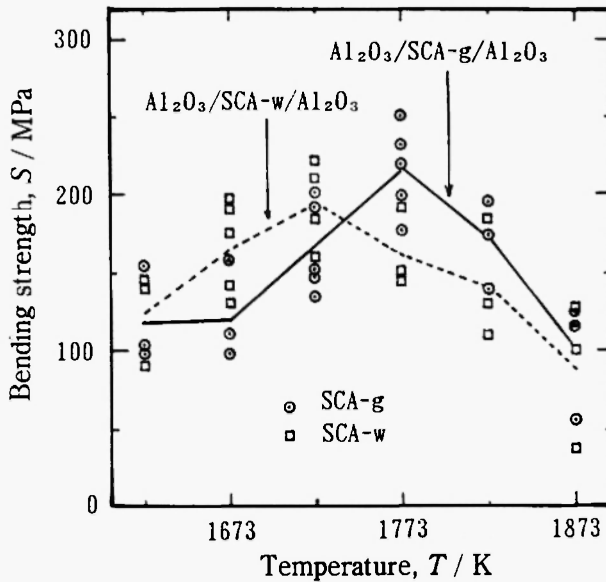

Fig. 7: Bending strength of the samples joined at various temperatures.

bulk of the solder layer. Difference of the maximum strength between the joints with SCA-g and SCA-w may be attributed to the difference of the residual stress.

4. CONCLUSION

Joining of alumina to alumina using two kinds of glass solders ($33SiO_2$-$34CaO$-$33Al_2O_3$ and $50SiO_2$-$38CaO$-$12Al_2O_3$ in mass %) has been carried out without applied pressure. The results are summarized as follows:

1) The thermal expansion coefficients of $33SiO_2$-$34CaO$-$33Al_2O_3$ both in the glassy and crystallized (gehlenite) states were found to be almost identical to that of alumina used in this work.
2) The apparent contact angle between the glass solder and alumina substrate varies from 110 to 120° to less than 50° as a function of temperature up to the melting point of the glass solder.
3) From the results of SEM-EDX observation, the dissolution of Al_2O_3 into the glass solder occurred at a temperature slightly higher than the melting point of the glass solders. Adequate dissolution of alumina into the joining layer contributes to the strengthening of the joining.
4) A maximum bending strength of 210 MPa was obtained for a joint produced at 1773 K for 1.2 ks with the glass solder of $33SiO_2$-$34CaO$-$33Al_2O_3$. This maximum value corresponds to 70% of the original bending strength for alumina presently used.

ACKNOWLEDGMENT

One of the authors (B.-G. Ahn) is greatly indebted to the Department of Education, the Government of Japan for financial support through a Monbushoh scholarship.

REFERENCES

1. B.-G. Ahn and Y. Shiraishi, *Tohoku Daigaku Senken Iho*, 45, 77 (1989).
2. C.E. Scott and J.A. Brewer, *J. Am. Ceram. Soc.*, 69, c178 (1986).
3. G. Elssner, W. Diem and J.S. Wallace, in: *Surfaces and Interfaces in Ceramics and Ceramic-Metal Systems*, J.A. Pask and A.G. Evans (eds.), Plenum Press, 1981.
4. H. Takashiro, *Yogyokyokai-shi*, 84, 548 (1976).
5. K. Sakata, K. Honma, K. Ogawa, O. Watanabe and Kn. Nii, *Nippon Kinzoku Gakkai-shi*, 49, 540 (1985).
6. B.-G. Ahn, Y. Okamoto, S. Watanabe and Y. Shiraishi, *Tohoku Daigaku Senken Iho*, 47, 86 (1991).
7. K. Takahashi, *Yogyokyokai-shi*, 63, 142 (1955).