Fundamental Study of Glass-Metal Bonding†

Nobuya IWAMOTO*, Yukio MAKINO**, Sei-ichi KARINO***, Toshio AWAJI*** and Hiroki WADA***

Abstract

A fundamental study of glass to metal bonding with the glasses of the systems Na_2O-SiO_2 and K_2O-SiO_2 and nickel was performed. From the result of bond strength, it was suggested that no difference between each bond strength was observed when the oxide film with proper thickness was preliminary formed at the surface of nickel metal. Further, it was suggested that it seems desirable to use soda-aluminosilicate glass as dental materials from the results of thermal expansivity, solution durability to distilled water and higher adherence strength. With X-ray diffraction analysis, the compound regarding as $Na_6Si_8O_{19}$ was found in the $3Na_2O \cdot 7SiO_2$ glass-nickel bonding at 700° C. Further investigation is necessitated because it remains unclear whether this compound is harmful or not.

1. Introduction

Recently, research of material has been more and more required to endure in severe conditions and it has become of difficult to satisfy those requirements by use of only a material. For example, the excellent materials which can be used in such a severe condition as over 1000°C is required in nuclear reactor and iron- and steel-making with atomic energy. Therefore, the development of the composite material combined with both the significant heat-resistance of ceramics and the superior ductility of metal has been desired. In ocean development, ceramic coating to metal must be investigated in order to prevent the corrosion of metal. On the other hand, metal-ceramics bonding such as nickel to alumina is also performed on the production of printed circuits in electronic industry. Then, glass to metal bonding has been applied to enamel and the protection of the active metals. Furthermore, ceramics to metal bonding has become of significant in medical science and dental surgery such as artificial organ, bonerepair and denture.

Although the bonding between different materials is very important, the mechanism of the bonding remains still unclear. The research in boundary fields such as glass to metal bonding is one of the most difficult fields to study because of the requirement of very wider knowledge. From histrical standpoits, the theory on ceramics or glass to metal bonding can be classified as follows: bonding can be classified as follows:

(1) Chemical bonding theory[1)−3)] ... the strength of bonding is attributed to energy balance through chemisorbed oxygen or oxide layer at interface.

(2) Mechanical bonding theory[4)−6)] ... the strength of bonding is attributed to highly irregular metal interface.

However, it is still questionable whether these theories are fully reasonable one because the exception is found in either theory and the state analysis of interface has been not enough investigated.

Comparing ceramics-metal bonding with glass-metal bonding, the epitaxial match must be taken into account as more important factor in order to interpret adhering behaviour between them. Generally, the glasses composed of soda- and potash-silicate are used in the case of enamel and dental materials respectively. As a metal, nickel metal is selected because its oxide is generally only NiO and it is one of metal used as a dental material. In this study, therefore, the bonding between soda- and potash-silicate and nickel was studied with considering thermal expansion coefficient of glass, solution durability to distilled water, the dependence of tensile strength of bonding upon oxide film thickness and the change of interface state.

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* Professor
** Research Associate
*** Wada Precision Dental Laboratries Ltd.

2. Experimental Procedures

Each material used for the preparation of glass was reagent grade Na_2CO_3, K_2CO_3 and the purity of nickel metal used was 99.9 per cent. Thermal expansion coefficient of each glass was measured with thermal mechanical analyser (Rigaku Denki Ltd., M8095 type). The disk with 9mmϕ x 3mm and the rod nickel metal with 8mmϕ x 50mm were fixed in a specimen holder as shown in Fig. 1, and then the assembly was heated for 1 hr in Ar-10%H_2 at 550°C in soda-silicate and at 600°C in potash-silicate glasses respectively. Pre-oxidation of nickel metal was performed at the temperature range from 600°C to 900°C by the interval of 100°C for 0.5 hr. When using pre-oxidized nickel metal, the assembly was heated for 0.5 hr in Ar atmosphere. Solution durability test were performed by immersion of rectangular glass in distilled water (100 cc) which surface area has between 350 and 400mm^2. Tensile strength test of bonding was performed with a autograph (Shimadzu Seisakusho Ltd., IS2000 type) at the 0.25 mm/min strain velocity. X-ray diffraction analysis of the nickel-glass interface was performed with polishing gradually from glass side to nickel metal. The experimental conditions of X-ray diffraction analysis were as follows:

Target: Cu Ka, Voltage and Current: 35KV x 10mA, Filter: Ni, Detector: S.C., Path: air, P. H..

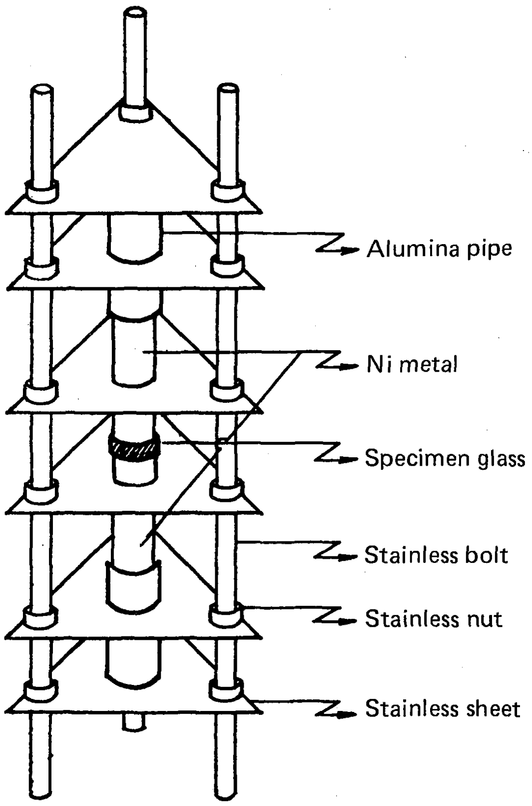

Fig. 1 The assembly of specimen and specimen holder

3. Experimental Results and Discussion

3-1 Choice of specimen composition

As is evident from the results of other investigators, the consideration on the matching of the thermal expansion coefficient of glass with that of metal is a significant factor[7]. Generally, the difference of thermal expansion coefficients should be within 10 per cent of each other, with that of the metal being higher. Fig. 2 shows the thermal expansion coefficient of each glass in the systems Na_2O-SiO_2 and K_2O-SiO_2 and both coefficients show the linear dependence on composition.

q The glasses of $3Na_2O{\cdot}7SiO_2$ ans $K_2O{\cdot}3SiO_2$ were selected as the specimens used for tensile strength test, considering that the thermal expansion coefficient of pure nickel metal is 154 x 10^{-7} cm/°C in our measurement. From the solution durability to distilled water, as described later, it becomes difficult to experiment practically with the glasses containing Na_2O or K_2O more than 30 or 25 mole per cent respectively. On the contrary, in the glasses containing silica more than 70 or 75 mole per cent in each system, enough strength could not be obtained in pre-experiment because of the large difference in thermal expansion coefficient between glass and metal.

3-2 Solution durability of glass to distilled water

The solution durability of alkaline silicate glass to water can generally be improved with the addition of

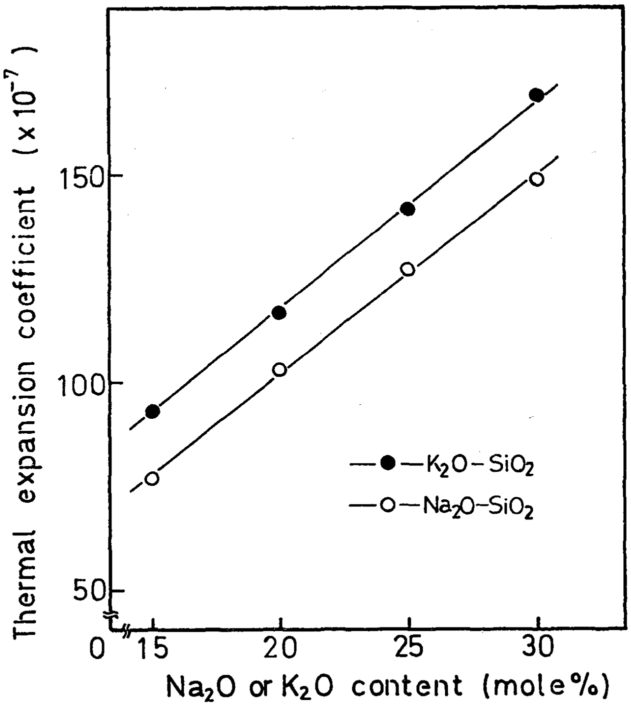

Fig. 2 Thermal expansion coefficient of each glass in the systems Na_2O-SiO_2 and K_2O-SiO_2.

other oxide but other problems such as the rise of melting point occur. Therefore, the lesser addition of other oxide, for example Al_2O_3, is desired without drop of solution durability to water. In this study, the solubility of sodium or potassium ion to distilled water was measured. Fig. 3 shows the comparison of the solubility between these cations in weight loss per unit area. The data concerning 24 hr duration test in the soda silicate glasses was compared with those concerning 2 hr test in the potash silicate glasses because the each glass of the system K_2O-SiO_2 was very rapidly dissolved. As shown in Fig. 3, the solubility of soda silicate glass becomes about 100 times larger than that of potash silicate glass and the solubility of the glass in the system Na_2O-SiO_2 seems to be saturated at 80 mole per cent SiO_2. Hence, although leucite has been generally used as dental materials without definite reason, it is expected that the use of soda aluminosilicate glass as a dental material has a greater advantage than potash aluminosilicate glass from the standpoint of solution durability. It is desirable to investigate the solubility of these glasses to artificial saliva because the more reliable result is required for the purpose of biological use.

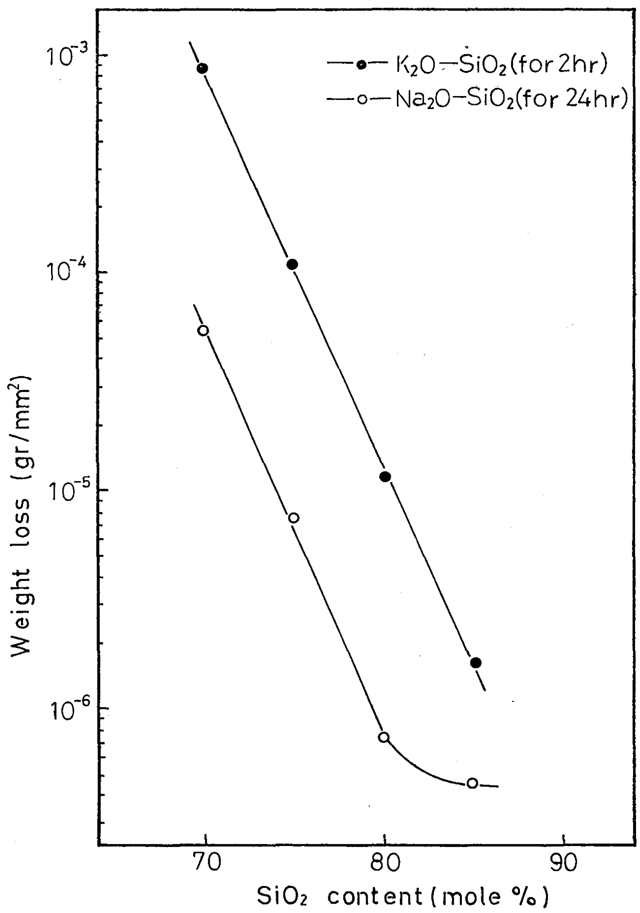

Fig. 3 Solution durability of glass to distilled water

3-3 Tensile strength of bonding and the effect of oxide film thickness

As descrived above, many investigators have emphasized that adherence strength strongly depends on surface roughness, matching of thermal expansion coefficient and oxide film thickness at the interface.[7] In this study, surface roughness was kept definite with the polish by number 800 emergy papers because this factor was regarded as less important than oxide film thickness at the interface. The dependence of tensile strength of bonding upon oxide film thickness in shown in Fig. 4. The abscissa in this figure is represented in unit of gram per unit area.

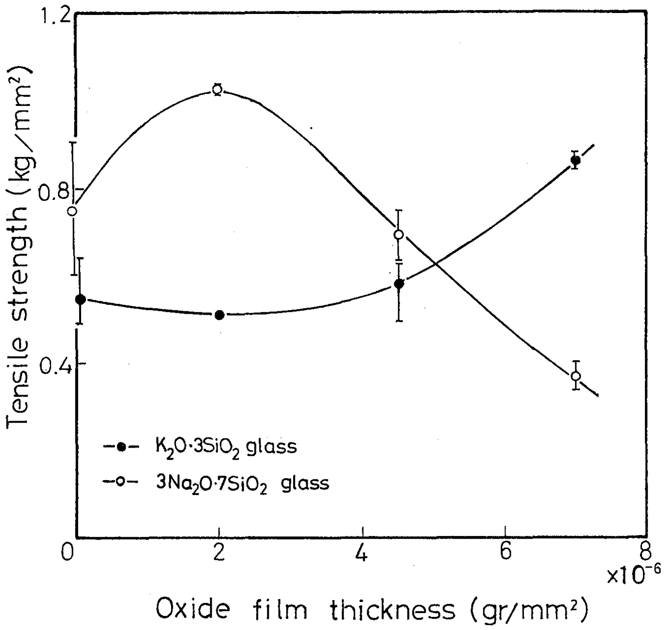

Fig. 4 The dependence of each bond strength upon the thickness of preliminaly oxide film on the nickel surface

Oxide film thickness of each specimen was determined with the measurement of weight increase. As is evident from Fig. 4, the tensile strength of $3Na_2O\cdot 7SiO_2$ glass to nickel bonding shows maximum at about 2 x 10^{-6} gr/cm^2.

On the contrary, the strength of $K_2O\cdot 3SiO_2$ glass to nickel bonding seems to show maximum at about 10 x 10^{-6} gr/cm^2. Hence, it seems that no difference between each bonding strength is not found when the oxide film with proper thickness was preliminary formed at the surface of nickel metal. It is expected that the appearance of the maximum at the different oxide thickness is attributed to following effects:

(1) the difference of the solubility of NiO between $3Na_2O\cdot 7SiO_2$ and $K_2O\cdot 3SiO_2$ glass
(2) the difference of diffusion velocity of Ni ion in $3Na_2O\cdot 7SiO_2$ and in $K_2O\cdot 3SiO_2$ glass

(3) the easiness of the crystallization of any compound in glass

Therefore, microanalysis at and near interface is required in order to clarify the above described proposals.

3-4 State analysis of glass- nickel interface

First of all, X-ray diffraction measurement was performed in order to investigate whether any compound is formed at glass-nickel interface. From X-ray difraction measurement, any pattern as crystalline material was not found from the interface when bonding was done below 600°C. However, from the interface in the $3Na_2O{\cdot}7SiO_2$ glass to nickel bonding formed at 700°C the diffraction pattern with some crystalline materials found as shown in Fig. 5. This pattern seems to be originated from the compound $Na_6Si_8O_{19}$ although several diffraction peaks were not exactly fit to the result after Williamson and Glasser.[8] According to their result, the compound is metastable phase and is decomposed into β-$Na_2Si_2O_5$ and quartz below 700°C. The result in this study showed good agreement with the consideration from phase diagram. However, it can also be considered that $Na_6Si_8O_{19}$

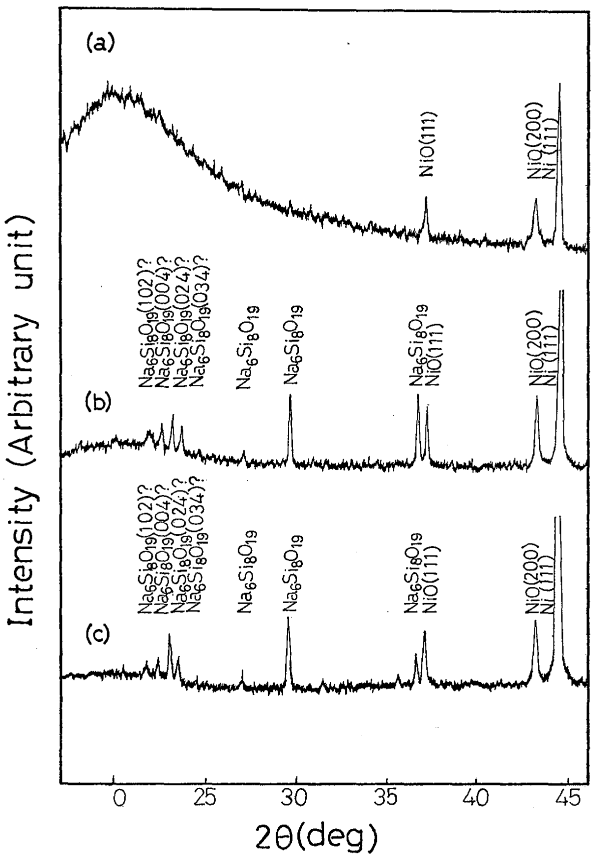

Fig. 5 X-ray diffraction patterns at the $3Na_2O{\cdot}7SiO_2$ glass-nickel interface bonded at 700°C (Polish stage, (a) → (b) → (c))

precipitates together with β-$Na_2Si_2O_5$. In the system K_2O-SiO_2, on the contrary, the compound $K_2Si_4O_9$ corresponds to $Na_6Si_8O_{19}$ but it is still stable at room temperature. In spite of the stability of $K_2Si_4O_7$, the compound did not seem to crystallize with any reason. It may be attributed to lower diffusivity of potassium ion. From this result, it is anticipated that sodium silicate glass to nickel bonding must be performed below 700°C. Other approaches such as X-ray diffraction with micro-Laue method and IMA were also performed, but the insufficient results with these methods were obtained. Therefore, it is desired to obtain new information with other methods.

4. Summary

A fundamental study of glass to metal bonding with the glasses of the systems Na_2O-SiO_2 and K_2O-SiO_2 and nickel was performed. Any difference of the adherence strength between each bonding was scarcely observed, but the remarkable difference was obtained in the effect of the thickness of preliminary oxide film. The $3Na_2O{\cdot}7SiO_2$ glass-nickel bonding showed the maximum strength at very thinner oxide film in comparison with the $K_2O{\cdot}3SiO_2$ glass-nickel bonding.

The pattern of the compound regarding as $Na_6Si_8O_{19}$ was found at the interface of $3Na_2O{\cdot}7SiO_2$ glass to nickel bonding with X-ray diffraction measurement when this bonding was performed over 700°C. Hence, it is necessitated to pay attention to the crystallization of this compound when soda-silicate glass is used for glass-metal bonding. Although the above mentioned attention is necessitated, it is suggested that it seems possible to use soda-aluminosilicate glass as dental materials. However, further investigation is desired with various methods because the sufficient data were not obtained with other methods except X-ray diffraction.

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