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A new adhesion process of glass to metal using the redox reaction

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A new adhesion process of glass to metal was developed based on the redox reaction without oxidation of the metal surface. PbO-based glasses were strongly adhered to nickel metal at low temperature (400–500 °C) in a low-oxygen atmosphere (< 0.1 p.p.m.). The interfaces between glasses and metal were analysed by SEM–EDS. It was found that the reaction layer and lead metal were formed by the redox reaction at the interface. In the case of the adhesion of PbO-based glasses containing CuO to nickel, the main reduced product in the glass was Cu_2O, and lead was not detected. The redox reaction was simulated by a thermodynamic equilibrium theory; the results agreed with the analysis by SEM–EDS.

1. Introduction

The adhesion of glass to various materials is widely used for electronics. The main applications are metal packages (so-called hermetic can seal), ceramic packages for IC (so-called cerdip) and the Brown tube of a cathode ray tube, CRT (adhesion of glass panel to funnel). Other uses are magnetic heads; hybrid IC, displays (plasma and fluorescence), and so on. High reliability, high hermeticity and high adhering strength are the main important factors for these applications. The mechanism of glass adhesion has been studied to improve these electronics parts.

The mechanism of adhesion of SiO_2-based glasses to metals was studied by Pask and co-workers from 1953–1973 [1–9]. Their theory was based on the wettability of glass to base material, and applied to the adherence of glass to metal. Many electrical devices using glass–metal adherence, such as hermetic sealing packages, have been produced according to their theory. In those processes, the metal surface should be oxidized before adhering because the oxidized layer contributes to the maximum adhesion of glass to metal. However, the oxidized layer is not desired for subsequent processing, such as wire bonding, solder dipping, solder coating and welding. The oxidized layer must be removed for plating (copper, nickel, gold, etc.) to make wire bonding and/or solder coating.

Recently Matusita *et al.* [10, 11] reported the adhesion of glasses to magnetic metal (Sendust), in which the interface reaction was promoted by reduction–oxidation with the metal [10, 11].

In the present study, a new adhesion process was developed without oxidation of the metal surface. The redox reaction was applied to the adhesion of PbO-based glasses to metals such as in hermetic can packages in a low-oxygen atmosphere. The interface between glass and metal was analysed by SEM–EDS. The adhesion mechanism was discussed by the simulation of the reaction on the basis of the thermodynamic equilibrium theory.

2. Experimental procedure

To reduce the oxidation, low-temperature and low-oxygen atmosphere are desirable. PbO-based low-melting glasses were selected as adhering glass because they can flow and adhere at below 500 °C. Adhering materials, glasses and metals are shown in Tables I and II.

In Table I, 7590, T187M and T187MC are commercial PbO-based glasses or those modifiers for low-temperature sealing. 7590 is the devitrifiable sealing glass for CRT, the so-called CTV frit to adhere the glass panel to the glass fennel of CTVs Brown tube. T187M and T187MC are the mother glass or its modifier of IC frit, and that of the sealing glass for the alumina package for ICs. T187MC contains about 2 mol % CuO.

Glass 1 was prepared in our laboratory by melting a 50 g batch at 1000 °C for 30 min in an alumina crucible. The sample was cast on the steel and crushed to powder (100 mesh pass). The batch composition is shown in Table I.

ST is the commercial hermetic sealing glass, of SiO_2–BaO–Na_2O glass which adheres at about 960 °C.

Gloss metals (iron and Fe–Ni) and those plated with nickel, Ni–P and copper were used as adhered metals (see Table II).

For commercial glasses, the values of the glass transition temperatures, T_g, and the thermal expansion coefficients were taken from the catalogues

TABLE I Glasses and adhering conditions

Glass		System	Adhesion	
			Temp. (°C)	Time (min)
7590[a]	CTV frit (devitrify)	$PbO–B_2O_3–ZnO$	440	40
T187M[b]	Mother glass of IC frit	$PbO–B_2O_3$	430	10
T187MC[b]	T187M + 1 wt % CuO glass	$PbO–B_2O_3–CuO$	430	10
Glass-1[c]	Prepared in our laboratory	$PbO–B_2O_3–Bi_2O_3$	430	20
ST[d]	Hermetic sealing glass	$SiO_2–BaO–Na_2O$	960	10

[a] Corning Glass Works.
[b] Iwaki Glass Co. Ltd.
[c] Glass-1 62.5 PbO, $30B_2O_3$, $5SiO_2$, $2.5Bi_2O_3$ (mol %).
[d] Nippon Electric Glass Co. Ltd.

TABLE II Adhered metals

Ni	(electroplating on Fe or Fe–Ni)
Ni–P	(electroless plating on Fe or Fe–Ni)
Fe	
Fe–Ni	(50 wt % Ni–Fe alloy)
Cu	(electroplating on Fe or Fe–Ni)

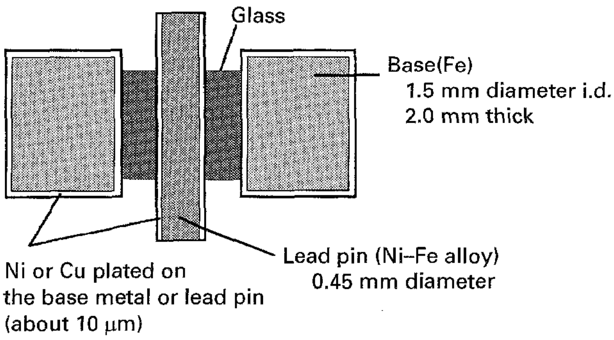

Figure 1 The schematic structure of an adhered body (Hermetic sealing structure.)

and/or technical data sheets. Those values of Glass-1 were measured using a Rigaku Denki TMA apparatus at a heating rate of 2.5 °C min^{-1}.

Fig. 1 shows the structure of an adhered body which was prepared by hermetic sealing. The base metal was iron plated with nickel, copper or Ni–P. The iron without plating was also used as the base metal. The expansion coefficient of iron is $140 \times 10^{-7} K^{-1}$, larger than those of glasses. The lead pin was 50 Ni–Fe alloy plated with nickel or copper. The 50 Ni–Fe alloy without plating was also used as a lead pin. The expansion coefficient of 50 Ni–Fe alloy is $97 \times 10^{-7} K^{-1}$, almost the same or smaller than those of glasses. Glass powders were pressed to tablet shape, 1.4 diameter o.d., 0.5 diameter i.d. and 2.5 mm height.

Glass tablets, base and lead pins were adhered to make the structure shown in Fig. 1 under the condition of Table I under a nitrogen atmosphere. The concentration of oxygen in the nitrogen atmosphere has been monitored by a zirconia oxygen–sensor during adhering.

The adhering strength was evaluated by the strength necessary to pull down the lead pin. The rate of pulling down was 5 mm min^{-1}.

The cross-sections of adhered bodies were cut and polished. The samples were analysed by SEM–EDS to examine the interface reaction between glasses and metals.

3. Results

3.1. Outlook of the adhered samples

All glasses have sufficient fluidity under the conditions in Table I. In order to examine the effect of oxygen, iron-based metal plated with nickel was fired at 450 °C in a nitrogen atmosphere. At 10 p.p.m. oxygen, the colour of the nickel surface was changed to blue, indicative of nickel oxide. However at 0.1 p.p.m. oxygen, the surface maintained the metallic lustre. It was found that the nickel surface was hardly oxidized at about 450 °C in a less than 0.1 p.p.m. oxygen atmosphere. According to this result, all samples were adhered in a less than 0.1 p.p.m. oxygen atmosphere.

3.2. Adhering strength

The adhering strength assessed by pulling down the lead pin, is shown in Table III together with the properties of the glass. The lead pin was always broken at about 120 N in the case of adhesion of PbO-based glass to the lead pin plated with nickel. The pin was broken at the position where glass was not adhered. After breaking, the adhered bodies were found to retain high hermeticity. It was observed that the interface between the lead pin plated with nickel and ST glass was peeled off when the pin was pulled down, as did the interface between the pin plated with copper and T187M glass.

The thermal expansion coefficients of 7590 glass and ST glass are almost the same, showing that the stress due to the mismatch of thermal expansion between glass and the lead pin is almost the same. However, the adhering strength between 7590 and the lead pin is much higher than that between ST glass and the lead pin. Therefore, it is clear that PbO-based glasses are strongly adhered to the lead pin.

TABLE III Glass properties and adhering strength. Base: iron ($\alpha = 140 \times 10^{-7}$ K^{-1}). Lead pin: 50Ni–Fe alloy (50 wt % Ni, 0.45 mm diameter, $\alpha = 97 \times 10^{-7}$ K^{-1})

Glass	α (10^{-7} K^{-1})	T_g (°C)	Plated on lead pin	Pulling strength(N)
7590	99	320	Ni	> 120
T187M	117	300	Ni	> 120
T187MC	114	303	Ni	> 120
Glass-1	112	340	Ni	
ST	95	450	Ni	40–50
T187M	117	300	Cu	60
T187MC	114	303	Cu	> 120

3.3. The analysis of the interface between glasses and metals

Fig. 2a shows the interface between 7590 glass (G) and Ni–Fe alloy (A) plated with Ni (N) by SEM. Fig. 2b is the result of the line analysis by EDS and the analysis line is shown in Fig. 2a as a real line. The starting point of the line analysis is shown as a cross mark in Fig. 2a. In Fig. 2b, (A), (N), (R) and (G) are the portions shown in Fig. 2a. For example (R) is the reaction layer in Fig. 2a. The thickness of the reaction layer was about 3–4 μm. The components of the layer were nickel, lead and oxygen as shown in Fig. 2b.

The diffusion of metal ions (Ni^{2+}) into the glass was hardly detected in this analysis. 7590 is the devitrifiable glass and many crystals were observed in it. High-lead and low-oxygen portions were also observed in the glass, although those portions are not seen in Fig. 2a. The lead-rich portions were guessed to be metallic lead which was formed by the redox reaction between 7590 glass and nickel. The increase of O K_α at the Ni–Fe alloy is the noise from Fe L_α lines, because our EDS could not perfectly separate both spectra, O K_α and Fe L_α.

Fig. 3a shows the interface between T187M glass (G) and Ni (N) layer on the Ni–Fe alloy (A). The reaction layer (R) is about 1 μm. The white spots (P) were observed near interface in the glass. In Fig. 3b, the reaction layer also contained lead, nickel and oxygen. In a white spot, the lead content is high and the oxygen content is low. The reaction layer and lead rich white spots were formed by the redox reaction between T187M glass and nickel. It was supposed that the white spots were metallic lead. Diffusion of Ni^{2+} into the glass was slightly observed, as shown in Fig. 3b.

Fig. 4a shows the interface between T187MC glass (G) and iron-base (F) plated with Ni (N). T187MC glass contained about 2 mol % CuO. The reaction layer (R) and dark spots (P) were observed as shown in Fig. 4a. In Fig. 4b it is seen that the reaction layer contains nickel, lead, copper, and oxygen. In a dark spot, the copper content is high and the lead and oxygen contents are low. A lead-rich area was not observed in T187MC glass.

Fig. 5a shows the interface between Glass-1 (G), which contains 2.5 mol % Bi_2O_3, and iron-base plated with Ni (N). The reaction layer (R) and white spots (P) were also observed. Nickel, lead, bismuth

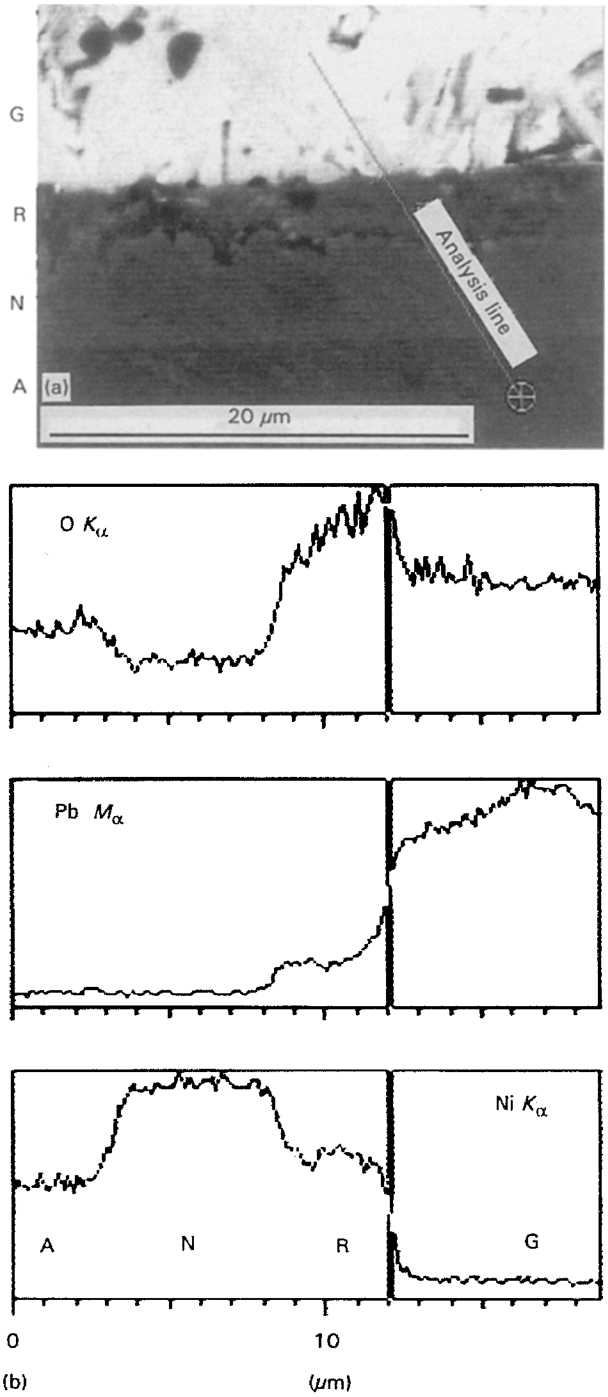

Figure 2 The interface between 7590 glass and nickel heated at 440 °C for 40 min. (a) Scanning electron micrograph, (b) line analysis by EDS. G, glass; R, reaction layer; N, nickel plating; A, Ni–Fe alloy.

and oxygen were contained in the reaction layer. In white spots, it is seen that the main component was bismuth (Fig. 5b). The diffusion of Ni^{2+} into the glass was slightly observed.

Fig. 6a shows the interface between ST (G), which is SiO_2–BaO–Na_2O glass (960 °C adhering, see Table I) and Ni–Fe alloy plated with Ni (N). No reaction layer was observed and nor any deposits. It is seen that the diffusion of nickel into the glass was slight, over a distance of a few micrometers (see Fig. 6b). Iron diffuses into the nickel layer because of the high-temperature adherence. In Fig. 6b, sodium seems to diffuse into the nickel layer. In the EDS analysis, it was difficult to distinguish the X-ray spectra of Ni L_α and Na K_α.

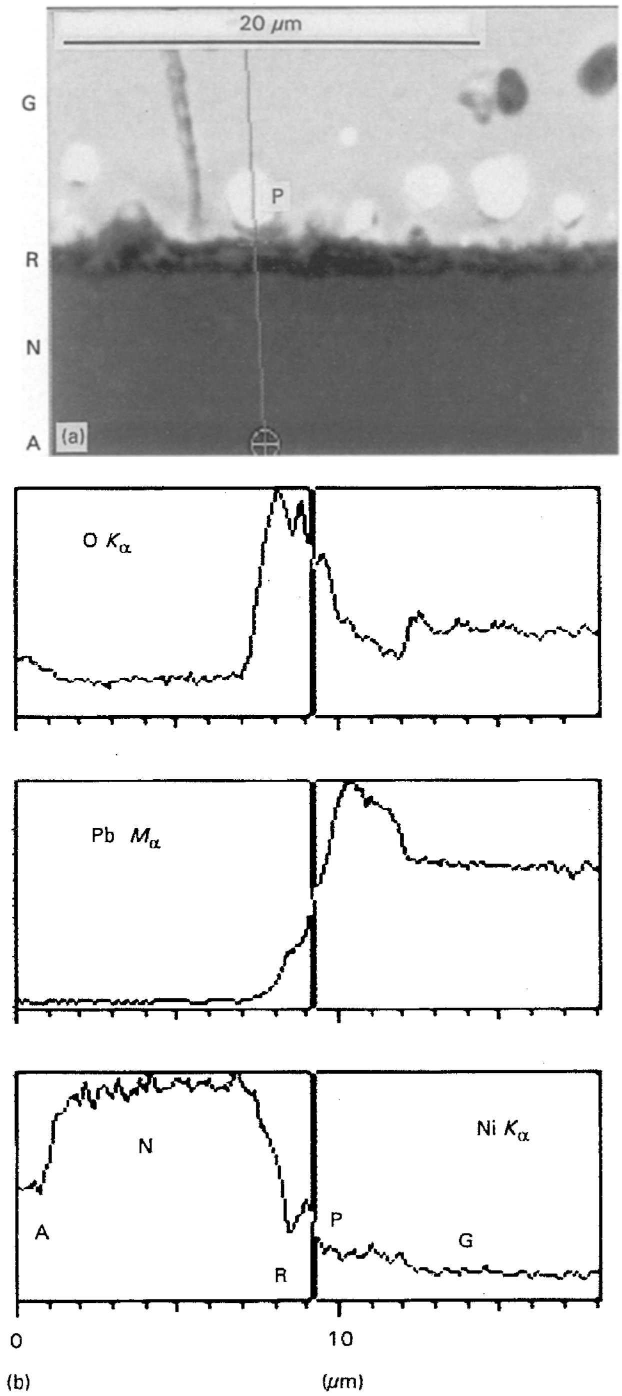

Figure 3 The interface between T187M glass and nickel heated at 430 °C for 10 min. (a) Scanning electron micrograph, (b) line analysis by EDS. G, glass; P, white deposit; R, reaction layer; N, nickel plating; A, Ni–Fe alloy.

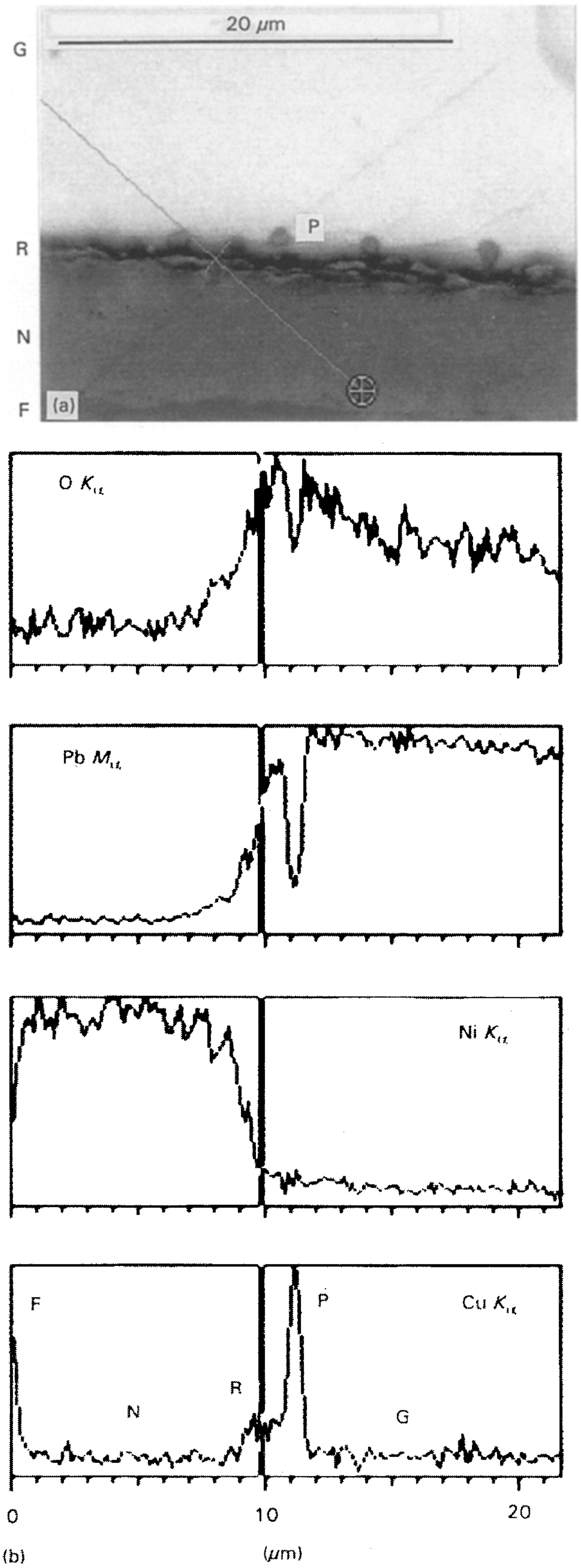

Figure 4 The interface between T187MC glass and nickel heated at 430 °C for 10 min. (a) Scanning electron micrograph, (b) line analysis by EDS. G, glass; P, dark deposit; R, reaction layer; N, nickel plating; F, iron-base.

Consequently, Na K_α seems to be increased by noise from Ni L_α in the high-nickel region. O K_α in the nickel layer also seems to be increased from the noise of Fe L_α for the same reason.

4. Discussion

4.1. Adhering strength and interface reaction between glasses and metals

The results of the interface analysis and strength measurements are summarized in Tables IV and III respectively. At the interface between ST glass and nickel, no reactions were detected and the pulling strength was low. At the interfaces between PbO-based glasses and the nickel layer, interface reactions were detected and the pulling strength were high.

At interfaces between PbO-based glasses and the copper layer, no interface reactions were detected, but the interface between T187MC glass and the copper layer had a high pulling strength.

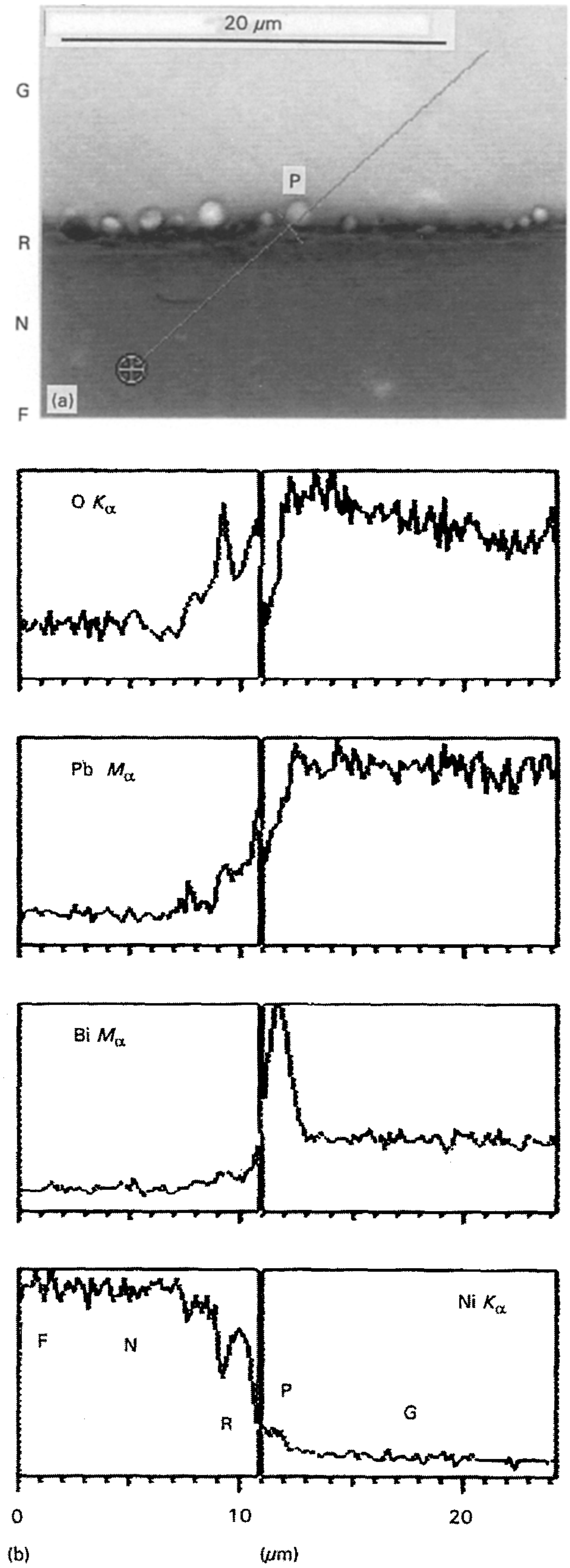

Figure 5 The interface between Glass-1 and nickel heated at 430 °C for 20 min. (a) Scanning electron micrograph, (b) line analysis by EDS. G, glass; P, white deposit; R, reaction layer; N, nickel plating; Fe, iron-base.

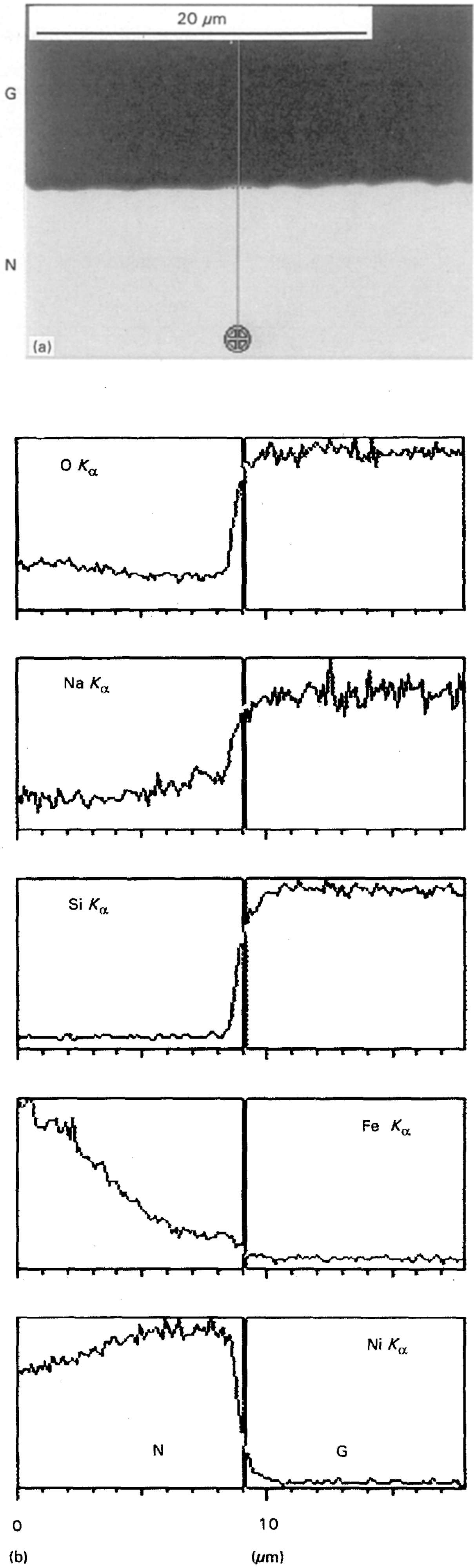

Figure 6 The interface between ST glass and nickel heated at 960 °C for 10 min. (a) Scanning electron micrograph, (b) line analysis by EDS. G, glass; N, nickel plating.

TABLE IV Reaction products and possible reactions in the adhesion of glass to metal. Base: iron plated by Ni or Cu. Lead pin: 0.45 mm diameter of Ni–Fe alloy (50 wt % Ni) plated by Ni or Cu

Glass	Metal	Reaction products		Possible reaction
		Interface layer	Droplet in glass	
7590	Ni	Ni–Pb–O	Pb	$Ni + PbO = NiO + Pb$
T187M	Ni	Ni–Pb–O	Pb	$Ni + PbO = NiO + Pb$
T187MC	Ni	Ni–Pb–Cu–O	Cu	$Ni + CuO = NiO + Cu$ $Ni + 2CuO = NiO + Cu_2O$
Glass-1	Ni	Ni–Pb–Bi–O	Bi	$3Ni + Bi_2O_3 = 3NiO + 2Bi$
ST	Ni	Not detected		No reaction
T187M	Cu	Not detected		No reaction
T187MC	Cu	Not detected		$Cu + CuO = Cu_2O$

According to the analysis of the interface, the possible reactions anticipated are listed in Table IV. All reactions are redox reactions of glass oxides with metals and have negative standard free energies, $\Delta G°$. The standard free energy diagram for the formation of oxides is shown in Fig. 7. It is presumed that the component of the upper side in Fig. 7, i.e. higher $\Delta G°$, is more easily reduced. The order is as follows:

$$\Delta G^{\circ}_{CuO} > \Delta G^{\circ}_{Cu_2O} > \Delta G^{\circ}_{Bi_2O_3} > \Delta G^{\circ}_{PbO} > \Delta G^{\circ}_{NiO}.$$

If PbO-based glass contains CuO or Bi_2O_3, CuO or Bi_2O_3 will be reduced more easily than PbO. In fact, in the reactions of glass containing CuO or Bi_2O_3 with a nickel layer, reduced copper or bismuth was detected, but lead was not. In the case of the adhesion between T187MC glass and copper metal, although no reactions were detected, a high adhesion strength was observed. In this case, it is supposed that the following reaction may occur at the interface, but the reaction layer is too thin to be detected by SEM–EDS, being less than 0.1 μm.

$$Cu + CuO = Cu_2O \qquad (1)$$

The result is similar to the adhesion mechanism of SiO_2–PbO–Na_2O glass to dumet (42 Ni alloy coated with copper) studied by Takashio [12].

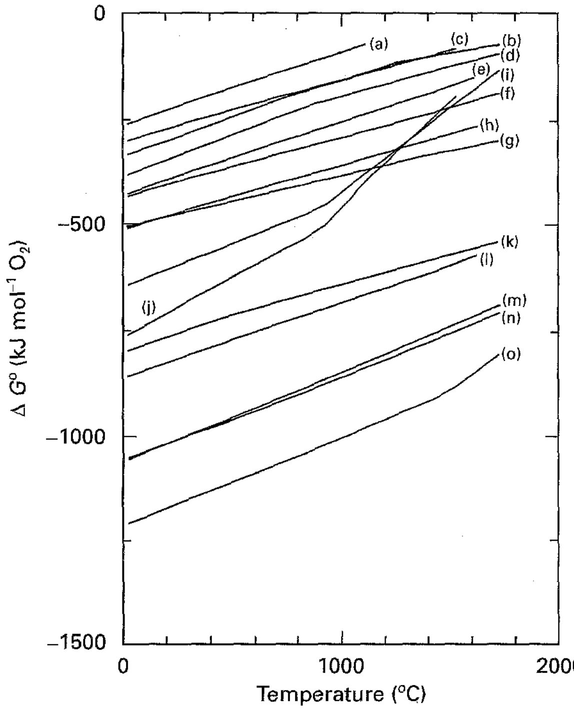

Figure 7 Standard free energy diagrams for the formation of oxide. (a) $2Cu + O_2 = 2CuO$, (b) $4Cu + O_2 = 2Cu_2O$, (c) $4/3Bi + O_2 = 2/3Bi_2O_3$, (d) $2Pb + O_2 = 2PbO$, (e) $2Ni + O_2 = 2NiO$, (f) $2Co + O_2 = 2CoO$, (g) $2Fe + O_2 = 2FeO$, (h) $3/2Fe + O_2 = 1/2Fe_3O_4$, (i) $2Zn + O_2 = 2ZnO$, (j) $4Na + O_2 = 2Na_2O$, (k) $4/3B + O_2 = 2/3B_2O_3$, (l) $Si + O_2 = SiO_2$, (m) $4/3Al + O_2 = 2/3Al_2O_3$, (n) $2Ba + O_2 = 2BaO$, (o) $2Ca + O_2 = 2CaO$.

4.2. The simulation of the redox reaction by thermodynamic equilibrium theory

The order of $\Delta G°$ of oxide formation is valid for oxidation of a single metal only. For a multicomponent system, thermodynamic calculation is useful for a quantitative discussion, such as the interface reaction between adhering glasses and metals. In PbO-based glasses such as 7590 and T187M, only Pb^{2+} ions are reduced by the reaction with nickel. However, in the adhesion between CuO-containing glasses (probably T187MC glass) and nickel, the reaction products from the glass were Cu_2O, copper and lead. The mutual ratio of those components will be changed with adhering conditions, such as temperature, oxygen partial pressure, CuO content in the adhering glass and so on. On the basis of the following assumptions, the ratios of those products can be calculated by the thermodynamic equilibrium theory.

Assumption I: the system of the reaction is in the equilibrium state.

Assumption II: reduced product layer which consists of Cu_2O, copper and lead is forming a single phase.

Assumption III: glass and the reduced product phase are ideal solutions. (Activities are equal to mole fractions.)

Assumption IV: the PbO/CuO ratio in the glass does not change through the reaction. (The change is so small that it can be negligible.)

Fig. 8 shows the conceptional scheme of the redox reaction. The components, except PbO and CuO in the glass, such as SiO_2, B_2O_3, Al_2O_3 and so on, are regarded as inert compounds for the redox reaction. It is assumed that the oxygen which is generated from reduction of PbO and CuO reacts with nickel metal. The reaction formulae are as follows

$$Cu + 1/2O_2 = CuO \quad K_1$$

(equilibrium constant of the reaction) (2)

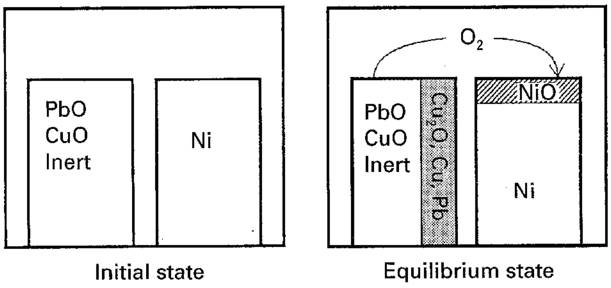

Figure 8 The conceptional scheme of the redox reaction.

$$2Cu + 1/2O_2 = Cu_2O \quad K_2 \tag{3}$$

$$Pb + 1/2O_2 = PbO \quad K_3 \tag{4}$$

$$Ni + 1/2O_2 = NiO \quad K_4 \tag{5}$$

The sum of the mole fractions of the glass composition is 1, so

$$I_{PbO} + I_{CuO} + I_{inert} = 1 \tag{6}$$

where I_{PbO} is the mole fraction of PbO in the glass, I_{CuO} is that of CuO and I_{inert} is that of the sum of inert components such as SiO_2, B_2O_3, Al_2O_3 and so on. The sum of the mole fraction of reduced products is also 1, and

$$X_{Cu_2O} + X_{Cu} + X_{Pb} = 1 \tag{7}$$

where X_{Cu_2O} is the mole fraction of Cu_2O in a reduced substance, X_{Cu} is that of copper and X_{Pb} is that of lead. Equilibrium constants, K_1, K_2 and K_3 can be written as

$$K_1 = a_{CuO}/(a_{Cu} \cdot P_{O_2}^{1/2}) = I_{CuO}/(X_{Cu} \cdot P_{O_2}^{1/2}) \tag{8}$$

$$K_2 = a_{Cu_2O}/(a_{Cu}^2 \cdot P_{O_2}^{1/2}) = X_{Cu_2O}/(X_{Cu}^2 \cdot P_{O_2}^{1/2}) \tag{9}$$

$$K_3 = a_{PbO}/(a_{Pb} \cdot P_{O_2}^{1/2}) = I_{PbO}/(X_{Pb} \cdot P_{O_2}^{1/2}) \tag{10}$$

where a_{xx} is the activity of component xx and P_{O_2} is the partial pressure of oxygen in the equilibrium state. From the above equations, the ratios of reduced products can be calculated.

$$X_{Cu}/X_{Pb} = (K_3/K_1)(I_{CuO}/I_{PbO}) \tag{11}$$

$$X_{Cu_2O}/X_{Pb} = (K_2K_3/K_1^2)(I_{CuO}^2/I_{PbO}) \tag{12}$$

Fig. 9 shows the result of the calculation for the condition of $I_{PbO} = 0.6$ and $I_{CuO} = 0.02$ when the temperature is changed. T187MC glass contains about 2 mol % CuO and its adhering temperature was about 430 °C. Under this condition, it is seen that $X_{Cu_2O} = 0.6$, $X_{Cu} = 0.4$ and X_{Pb} is so small that the value can be negligible. It is also seen that lead and copper increase and Cu_2O decreases with increasing temperature.

Fig. 10 shows the ratios of reduced product at 427 °C when I_{CuO} is changed. It is seen that Cu_2O increases with increasing CuO content.

Reduced substances are seen as small dark spots (about 1 μm diameter) near the interface in the T187MC glass, as shown in Fig. 4a. The spots were too small to be analysed quantitatively. However, in the PbO-based glasses containing high CuO (6–10 mol %), larger dark spots were observed (about 2–3 μm diameter). Quantitative analysis of the larger

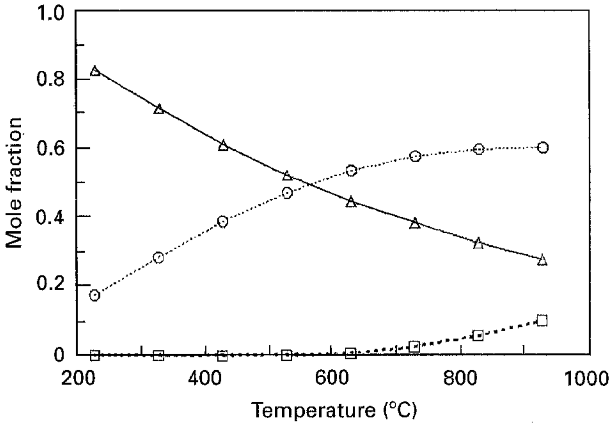

Figure 9 The relationship between the mole fraction of reduced products and temperatures. (□) Pb, (○) Cu, (△) Cu_2O. PbO = 0.6, CuO = 0.02.

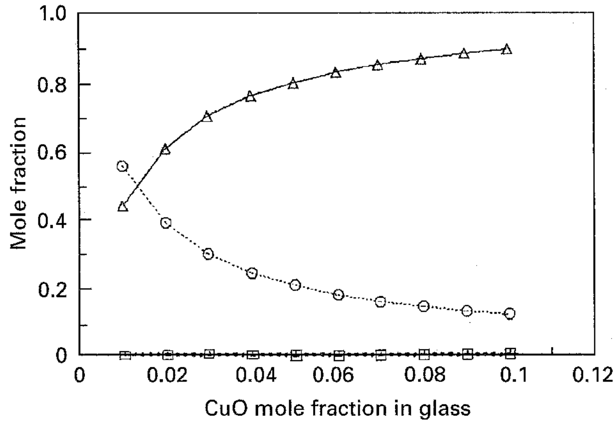

Figure 10 The relationship between the mole fraction of reduced products and CuO mole fraction in the glass. (□) Pb, (○) Cu, (△) Cu_2O. $T = 700$ K, PbO = 0.6.

dark spots was carried out by EDS, and it was found that those spots contained 55–60 at % copper and 35–45 at % oxygen, but contained less than 1 at % other components such as silicon, lead, aluminium and nickel. Even though those spots were not so large that the signals from the glass body may be added into the quantitative data, it can be concluded that Cu_2O was mainly formed from reduction of a glass containing 6–10 mol % CuO at 430 °C. This result is similar to that obtained from thermodynamic calculation. From both treatments of the analysis by SEM–EDS and thermodynamic calculation, it was found that the interfacial reaction between PbO-based glasses and metals could be controlled by the selection of the components of glasses and/or metals and adhering conditions. For example, in the adhesion of PbO-based glass to nickel, the reduction of PbO to lead metal could be inhibited by the addition of a small amount of CuO (1–2 wt %) into the glass at low temperature in a low-oxygen atmosphere.

4.3. Comparison of adhesion mechanisms

Fig. 11 shows the adhering mechanisms of the present work and conventional processes. In the conventional process, the initial step is the oxidation of the metal surface (A). After contact of surfaces of the oxidized

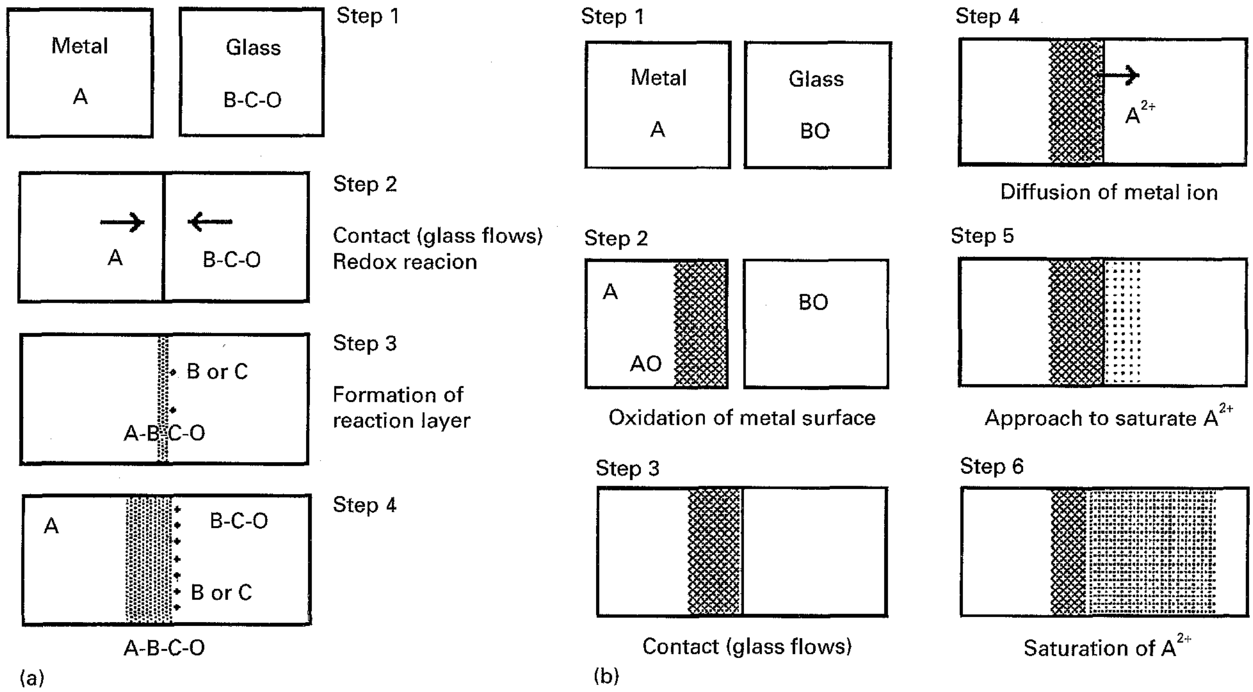

Figure 11 The adhering mechanisms of (a) the new process in the present study and (b) the conventional process.

metal (AO) and glass (BO), metal ions ($A''\bullet$) diffuse into the glass. In maximum adhesion, the metal ion content in the glass approaches saturation [9]. The diffusion progressed only into the glass side. In the conventional process, the interface can be stabilized by the diffusion of metal ions.

In the present study, the metal surface was not oxidized. The initial step was the contact of glass and metal surface, and the redox reaction occurred at the interface. It is possible to determine which elements, glass network former (B) or modifier (C), react with metal on the basis of the thermodynamic theory. The reaction progresses into the metal side rather than the glass side. In the present study, it is possible to stabilize the interface by the reaction layer of both elements of glass and metal.

5. Conclusions

A new adhesion process of glass to metal was developed based on the redox reaction without oxidation of the metal surface. PbO-based glasses were strongly adhered to nickel metal at low temperature (400–500 °C) in a low-oxygen atmosphere (< 0.1 p.p.m.). The interfaces between glasses and metal were analysed by SEM–EDS. It was found that the reaction layer and lead metal were formed by a redox reaction at the interface between glass and metal. In the case of the adhesion of PbO-based glasses containing CuO to nickel, the main reduced product in the glass was Cu_2O, and lead was not detected. The redox reaction was simulated by thermodynamic equilibrium theory. The simulation results agreed with the analysis by SEM–EDS.

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