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Matched glass-to-Kovar seals in N_2 and Ar atmospheres

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Abstract: The oxidation of Kovar alloy was investigated, the wetting and spreading behavior of hard and soft glasses on Kovar alloy were studed by using the sessile drop method, and the quality and the seal strength of glass-Kovar seals were tested. The experimental results indicated that the preoxidation of Kovar alloy for approximately 10 min at 700°C in air resulted in excellent adherence in glass-Kovar seals. The wetting and spreading behavior of glass on preoxidized Kovar alloy were superior to that on nonoxidized Kovar alloy. The wetting ability of ASF110 glass, at 950°C and 980°C in Ar and N_2 atmospheres, was significantly superior to that of ASF200R and ASF700 glasses. The seal quality of the glass-preoxidized Kovar seal was superior to that of the glass-nonoxidized Kovar seal. The shear strength of the ASF110 glass-preoxidized Kovar seal, which was prepared at 980°C for 20 min in an Ar atmosphere, was approximately 3.9 MPa.

Keywords: Kovar alloy; glass; sealing; argon; nitrogen; oxidation; wetting

1. Introduction

Glass-to-metal seals (GTMSs) are widely employed in electrical and electronics engineering and are used in incandescent lamps, electron tubes, and housing for semiconductors. In recent years, GTMSs have been implemented for new applications, for example, in complex miniature electrical and electronic components, solid oxide fuel cells, biomedical implants and monitoring components for biomedical applications, and solar receiver tubes in parabolic through solar power systems [1-2]. GTMSs can be classified in a number of ways: according to the type of glass or the geometry of the metal component. GTMSs can also be divided into two groups based on the coefficients of thermal expansion of the glass and of the metal: matched seals (the glass and the metal have similar coefficients of thermal expansion) and unmatched seals (the coefficients of thermal expansion are different). Matched seals are also subdivided according to the thermal expansion (α) of the glass: soft glass ($\alpha > 6 \times 10^{-6}$°C^{-1}; e.g., soda glass) and hard glass ($\alpha < 6 \times 10^{-6}$°C^{-1}; e.g., borosilicate-based glass and vitreous silica) [3]. A number of Fe-based alloys have been widely used for GTMSs in the electrical and electronics industries. In particular, Kovar alloy (ASTM F-15 alloy), which has similar thermal expansion characteristics to hard borosilicate-type glass, is used extensively for matched GTMSs in discrete transistors, integrated circuits, and microelectronic packages [4].

GTMS is traditionally a fusion technique, with the glass melted in contact with the metal components to which it is to be sealed. To form a high-quality seal, specific requirements must be met. The main requirement for the formation of a mechanically strong, adherent, and hermetic seal is that the thermal expansion characteristics of the glass must be closely matched to the metal to prevent residual thermal stress in the seal after cooling. Usually, the metal parts are preoxidized before sealing. The purpose of the preoxidation is to form an oxide film on the metal surface to be sealed to the glass. The oxide film on the metal surface acts as a thermal buffer, with a thermal expansion coefficient similar to that of the underlying metal. This addresses the poor adherence between the glass and the metal, which is the biggest cause of GTMS failure [5-6]. The preoxidation stage directly influences the quality of the final matched seal. If the oxide film is too thick or too thin or of the wrong type of oxides, the matched seal is weak or not hermetic. The duration and temperature of the sealing thermal treatment are two crucial factors in forming a nonporous oxide film [7]. The oxide film must adhere to the metal substrate and be wet by the glass. Other factors that affect the formation of the

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oxide film include the furnace dew point, hydrogen concentration, residence time, and the decarburization pretreatment [8-11].

The purpose of this study is to investigate the oxidation rate of Kovar alloy and the characteristic wetting and spreading behavior of ASF110, ASF200R, and ASF700 glasses on Kovar alloy in N_2 and Ar atmospheres by employing the sessile drop method. The glass flow shape of a glass-metal sandwich seal was used to observe the quality of the glass-Kovar seal. This study evaluated the effect of the sealing experimental parameters on the shear strength of the glass-to-Kovar alloy seal by using the shear stress test.

2. Experimental

2.1. Material preparation

The composition of Kovar alloy is Ni 29wt%, Co 17wt%, Fe 53.48wt%, Mn 0.3wt%, Si 0.2wt%, and C 0.003wt%, with the balance comprising Fe (JD, USA). This study used ASF110, ASF200R, and ASF700 glasses (AGC, Japan), as shown in Fig. 1, for fabrication of the seals. The properties and compositions of ASF110, ASF200R, and ASF700 glass are listed in Table 1. ASF110 is a hard glass ($\alpha < 60 \times 10^{-7}{}^\circ C^{-1}$), and ASF200R and ASF700 are soft glasses ($\alpha > 60 \times 10^{-7}{}^\circ C^{-1}$).

2.2. Preformation using glass powder

The starting glass is a dense, solid preform of suitable shape that is positioned on the metal component. Fig. 2 is a schematic diagram of the preformation step, using glass powder. First, the glass powder was added to 3.0wt% polyvinyl butyral (PVB) and granulated by ball milling for 24 h. The resultant slurry was then baked in a precision oven at 90°C to remove the solvent. After grinding and meshing, the glass powder with PVB was pressed into the desired form.

2.3. Oxidation of Kovar alloy

The Kovar samples were cut into squares of 10 mm × 10 mm × 0.3 mm and ultrasonically cleaned with acetone. The Kovar samples were oxidized in air at 650, 700, 750, and 800°C with oxidation time of 0, 5, 10, 15, and 30 min, respectively. After cooling to room temperature, the samples were weighed using a precision balance. The precision balance was accurate to ±0.1 mg. The surface area of each Kovar alloy sample was measured using a digimatic caliper. Dividing the difference in mass of each sample (before and after oxidation treatment) by its surface area would yield the rate of oxidation. The quartz tube furnace used proportional-integral-derivative (PID) control with a thermoregulation precision of ±1%, and the temperature distribution in the center of the quartz tube was measured with a K-type thermocouple, as shown in Fig. 3. No decarburizing treatment was performed because of the low carbon content.

2.4. Wetting procedures

The sessile drop technique was used in the wetting process. The ASF110, ASF200R, and ASF700 glasses were weighed at (10 ± 0.01) mg. A glass ingot was placed on the center of the Kovar alloy plate, as shown in Fig. 4. Preoxidized and nonoxidized Kovar alloy plates were used. The samples were heated under a vacuum to 850, 900, 950, or 980°C at 11°C/min. The temperature was kept constant for 20 min in flowing atmospheres of either N_2 or Ar. After

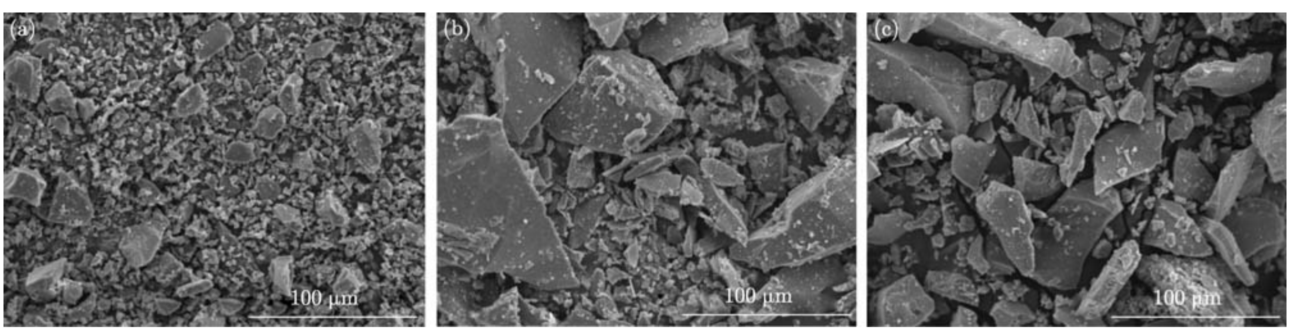

Fig. 1. SEM micrographs of ASF110 (a), ASF200R (b), and ASF700 (c) glass powders.

Table 1. Properties and composition of ASF110, ASF200R, and ASF700 glasses

Code	Glass type	Firing condition		Thermal expansion coefficient (25-300°C) / ($10^{-7}{}^\circ C^{-1}$)	Average particle size / μm
		Temperature / °C	Time / min		
ASF110	$SiO_2{\cdot}B_2O_3{\cdot}R_2O$	980	5	48	5.5
ASF200R	$SiO_2{\cdot}RO$	980	5	92	10.0
ASF700	$SiO_2{\cdot}RO$	980	5	99	10.0

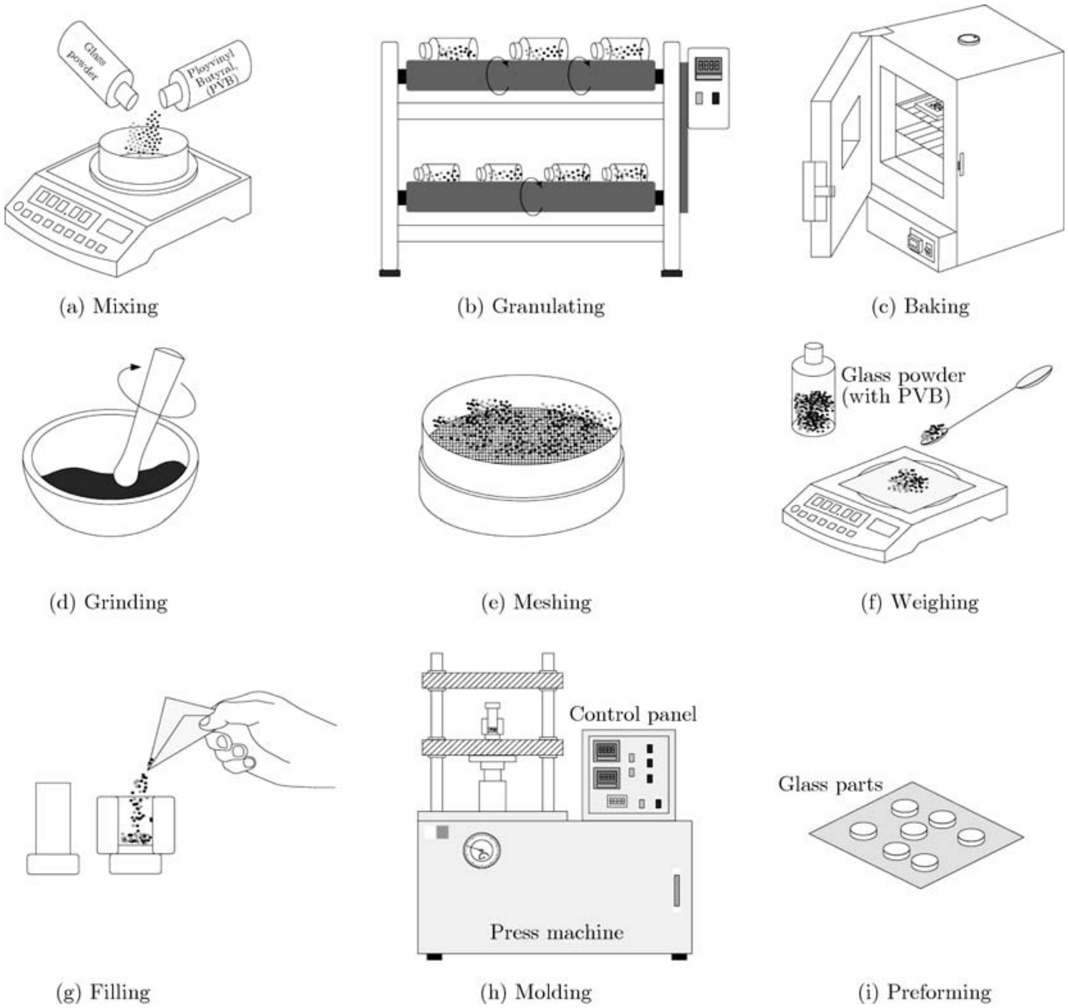

Fig. 2. Preformation using glass powder.

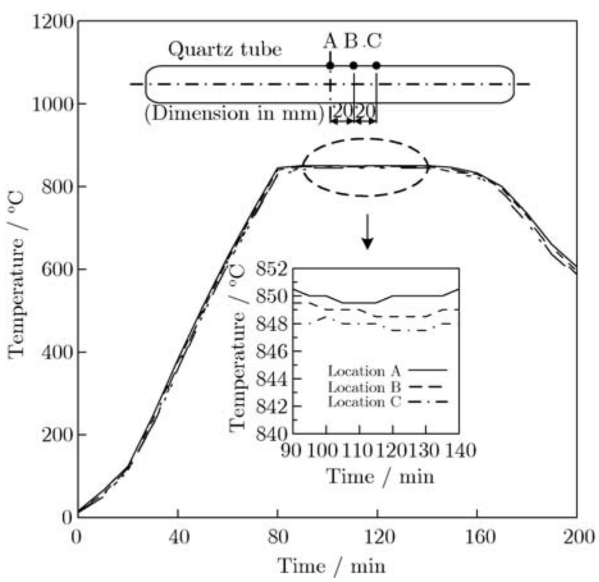

Fig. 3. Temperature distribution in the center of the quartz tube furnace.

the samples had cooled to room temperature, the wetting angle and the wetting area were measured using an optical microscope by employing measuring software. Fig. 5 is a schematic diagram of glass-to-Kovar seals in a vacuum tube furnace with an image-capturing system.

2.5. Sealing procedures

The glass-Kovar sandwich seal was used to test the quality of the seals. Fig. 6 shows a schematic diagram of a glass-Kovar sandwich seal. In the sealing procedures, the glass that had shown the highest degree of wetting ability was used. The mass of the glass was set at (40 ± 0.01) mg. A glass ingot was placed in the center of the preoxidized and the nonoxidized Kovar alloy plates. Another Kovar plate (preoxidized and nonoxidized) was then placed on top of the glass ingot. All samples were heated under a vacuum to the optimal wetting temperature. The temperature was kept constant for a holding time of 20 min under flowing atmospheres of N_2 and Ar.

Fig. 4. Schematic diagram of wetting test.

2.6. Sealing strength test

The shear strength test was used to examine the metallurgical properties of glass-to-Kovar seals. The configuration and size of the shear samples were in accordance with international organization for standardization (ISO) 4587, as shown in Fig. 7. The shear strength of the sealing samples was measured using a materials testing system (MTS) testing machine.

3. Results and discussion

3.1. Oxidation rate of Kovar alloy

Fig. 8 shows the mass gain of the oxide film for the various temperatures. The mass gain of the oxide film increased slowly with an increase in holding time at each temperature. The oxidation rate of Kovar alloy at 800°C was much higher than that at 650 or 700°C. Therefore, the preoxidation rate is primarily determined by the temper-

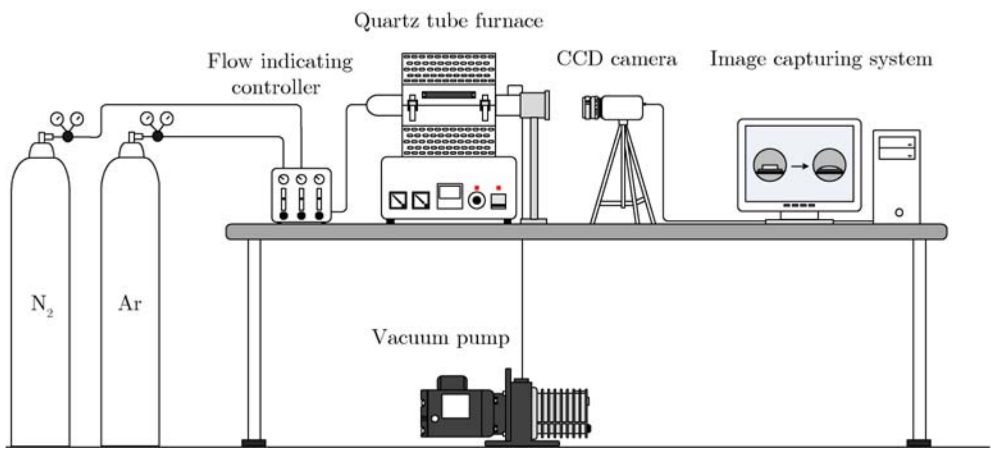

Fig. 5. Glass-to-Kovar seals in a vacuum tube furnace with an image capturing system.

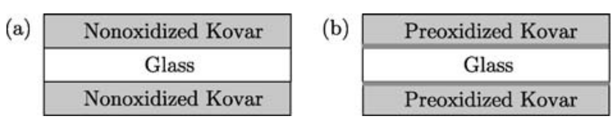

Fig. 6. Schematic diagram of a glass-Kovar sandwich seal (ASTM F144-80(2005)).

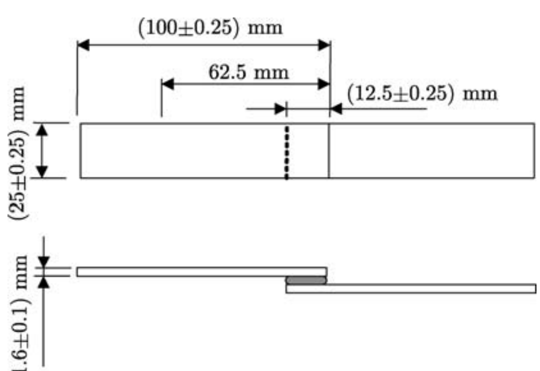

Fig. 7. Schematic diagram of shear strength test (ISO 4587(2005)).

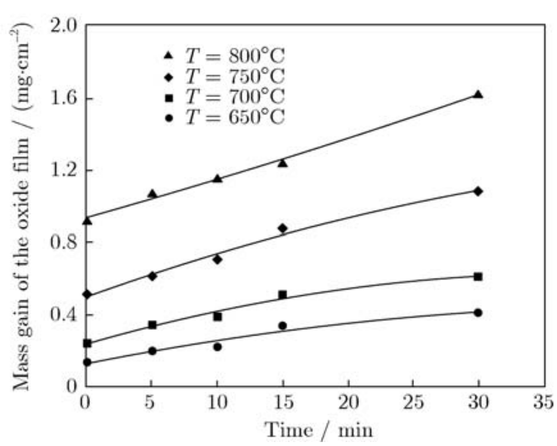

Fig. 8. Mass gain of the oxide film for the various temperatures.

ature and the holding time. Pask [12] recommended an oxidation mass gain of Kovar alloy of 0.3 to 0.7 mg/cm^2 for optimal adherence of glass to Kovar alloy, whereas Lei *et al.* [13] suggested a Kovar oxidation mass gain of approximately 0.3 to 0.8 mg/cm^2. Chern and Tsai [7] showed that preoxidation of Kovar alloy for approximately 10 min at 700°C in N_2 would produce good wettability, and Yext *et al.* [8] suggested that a Kovar oxide layer between 2 and 10 μm in thickness promoted strong bonding in the production of matched GTMSs. The overoxidation of Kovar alloy improved the strength of the seal but caused the seal to leak and bubbles to form in the glass. In this study, when Kovar alloy was preoxidized at 800°C, flaking of the oxide layer occurred when cooling to room temperature. The findings show that preoxidation of Kovar alloy for approximately 10 min at 700°C in air produced optimum glass-to-Kovar adherence.

3.2. Wetting and spreading

Sessile drop experiments have been widely used to study solid-liquid interfaces. The experiments provide information on the formation of interfaces and the presence of reactions at the interfaces. Fig. 9(a) shows the wetting test of the glass-Kovar seals. The shape of a sessile drop is described by the wetting angle θ. Fig. 9(a) shows that the wetting angle of the glass-preoxidized Kovar seal was smaller than that of the glass-nonoxidized Kovar seal. A smaller wetting angle indicates a greater degree of wetting; thus, the preoxidized seal showed superior wetting.

The Young-Dupre equation expresses the wetting phenomenon as follows:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv}\cos\theta \quad (1)$$

where γ_{sv}, γ_{sl}, and γ_{lv} denote the interfacial energies of the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively. Fig. 9(b) shows the spreading behavior with the sessile drop method. The driving force ($\gamma_{sv} - \gamma_{sl}$) acts on the interface between the glass and the Kovar alloy. When γ_{sl} is greater than γ_{sv} (i.e., $\gamma_{sl} > \gamma_{sv}$), the liquid tends to form a ball with a small interface area. If γ_{sv} is greater than γ_{sl} ($\gamma_{sv} > \gamma_{sl}$), the drop tends to spread. The spreading of the melted glass stops when the reaction is complete [14].

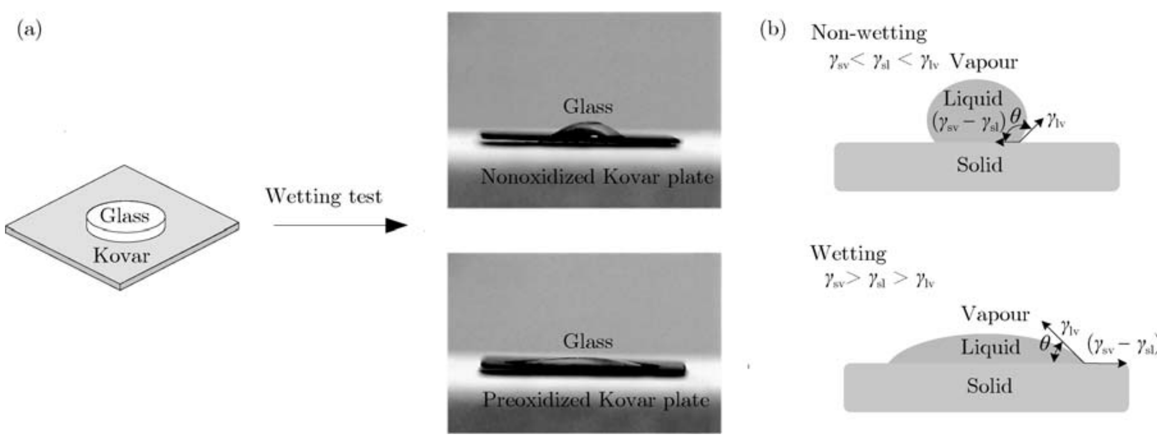

Fig. 9. (a) Schematic diagram of wetting test of glass-Kovar seals and (b) sessile drop configurations.

Fig. 10 shows the wetting angle and the wetting area as a function of temperature for the wetting of Kovar alloy (nonoxidized and preoxidized) with ASF110 glass in Ar and N_2 atmospheres. The wetting ability of ASF110 glass on preoxidized Kovar alloy at 900, 950, and 980°C in Ar and N_2 atmospheres was more extensive than on nonoxidized Kovar alloy. Fig. 11 shows the wetting angle and the wetting area as a function of temperature for the wetting of Kovar alloy (nonoxidized and preoxidized) with ASF200R glass in Ar and N_2 atmospheres. ASF200R glass shows good wetting ability on preoxidized Kovar alloy. However, the study found that the wetting ability of preoxidized Kovar alloy to be different in Ar and N_2 atmospheres. Preoxidized samples that had been heated in a furnace containing Ar at 980°C showed poorer wettability than those that had been heated at 850°C. Fig. 12 shows the wetting angle and the wetting area as a function of temperature for the wetting of Kovar alloy (nonoxidized and preoxidized) with ASF700 glass in Ar and N_2 atmospheres. The study found that the wetting ability of ASF700 glass on preoxidized Kovar alloy at 900, 950, and 980°C in Ar and N_2atmospheres was more extensive than that on nonoxidized Kovar alloy. The wetting ability of ASF110, ASF200R, and ASF700 glasses on preoxidized Kovar alloy was thus more extensive than on nonoxidized Kovar alloy. In particular, the wetting ability of the ASF110 glass (hard glass) at 950°C and 980°C in Ar and N_2 atmospheres was superior to that of the ASF200R and ASF700 glass (soft glass) (Fig. 13).

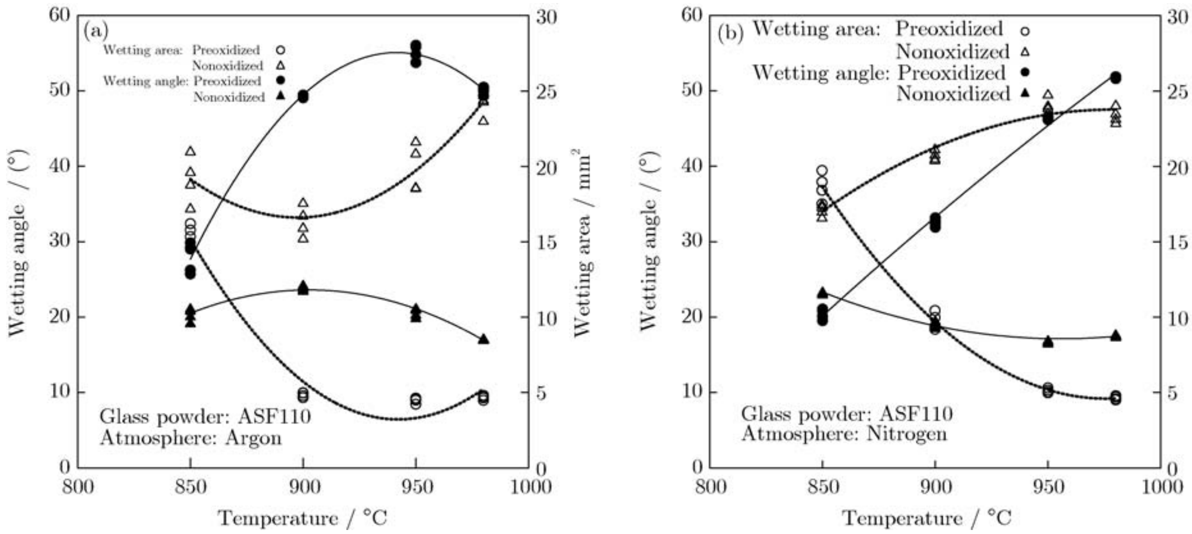

Fig. 10. Wetting area and wetting angle as a function of temperature for wetting of Kovar alloy (nonoxidized and preoxidized) with ASF110 glass in Ar (a) and N_2 (b) atmospheres.

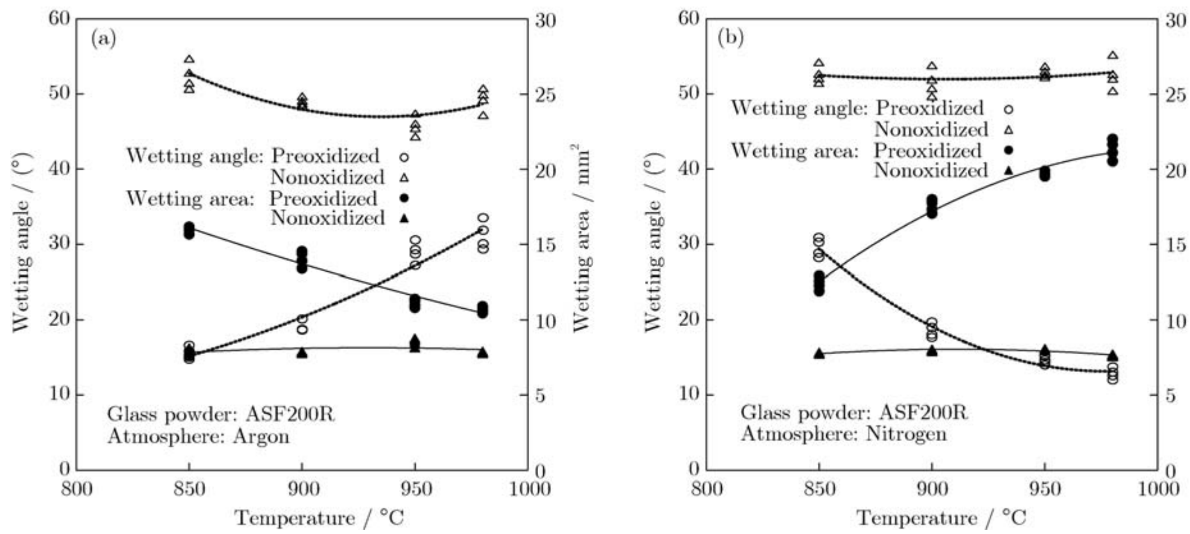

Fig. 11. Wetting area and wetting angle as a function of temperature for wetting of Kovar alloy (nonoxidized and preoxidized) with ASF200R glass in Ar (a) and N_2 (b) atmospheres.

3.3. Quality of glass-to-Kovar seals

Based on the results of the wetting test, the ASF110 glass in the glass-metal sandwich seal (ASTM F144-80) was used. This study set the sealing temperature at 950°C and 980°C in Ar and N_2, respectively. Fig. 14 shows the ASF110 glass-Kovar (nonoxidized and preoxidized) sandwich seals at 950°C and 980°C in Ar and N_2, respectively. Based on the ASTM test standard (ASTM F144-80), as shown in Fig. 15, the findings showed the ASF110 glass flow shapes of the nonoxidized Kovar alloy to be acceptable, as displayed in Figs. 14(a), (c), (e), and (g). The ASF110 glass flow shapes of the preoxidized Kovar alloy were good, as shown in Figs. 14(b), (d), (f), and (h). Preoxidized Kovar alloy thus provides a high-quality glass-Kovar seal, which is consistent with previous studies.

3.4. Sealing strength

This study used the shear stress test to evaluate the effect of experimental parameters on the shear strength of the glass-Kovar alloy seal. Table 2 presents the experimental results. The seals made with preoxidized Kovar alloy (Group 2) exhibits superior shear strength compared with seals made with nonoxidized Kovar alloy (Group 1). The shear strength of the ASF110 glass-preoxidized Kovar alloy seal, which was sealed at 980°C for 20 min in an Ar atmosphere, was approximately 3.9 MPa. If the Kovar al-

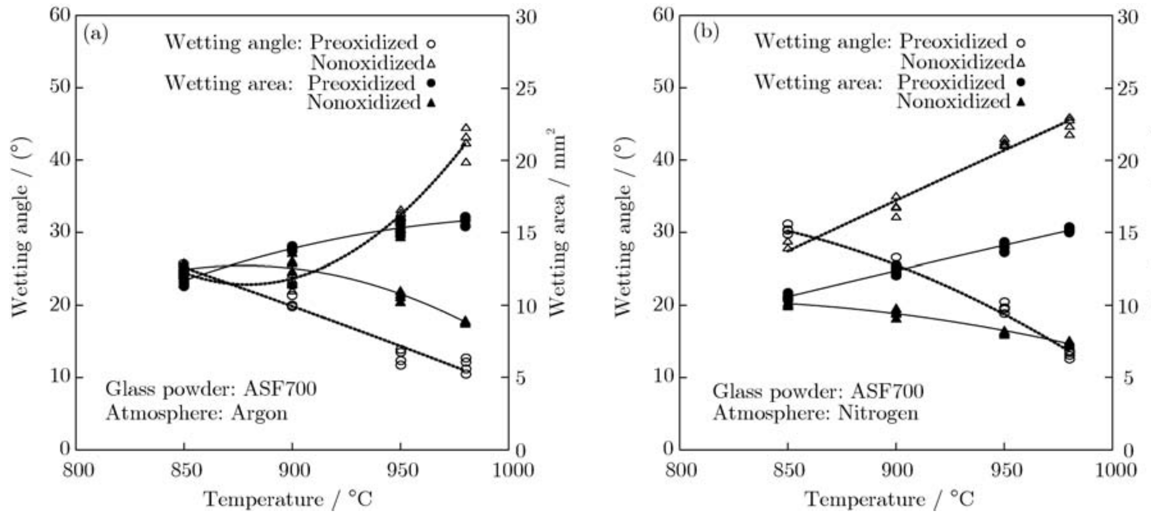

Fig. 12. Wetting area and wetting angle as a function of temperature for wetting of Kovar alloy (nonoxidized and preoxidized) with ASF700 glass in Ar (a) and N_2 (b) atmospheres.

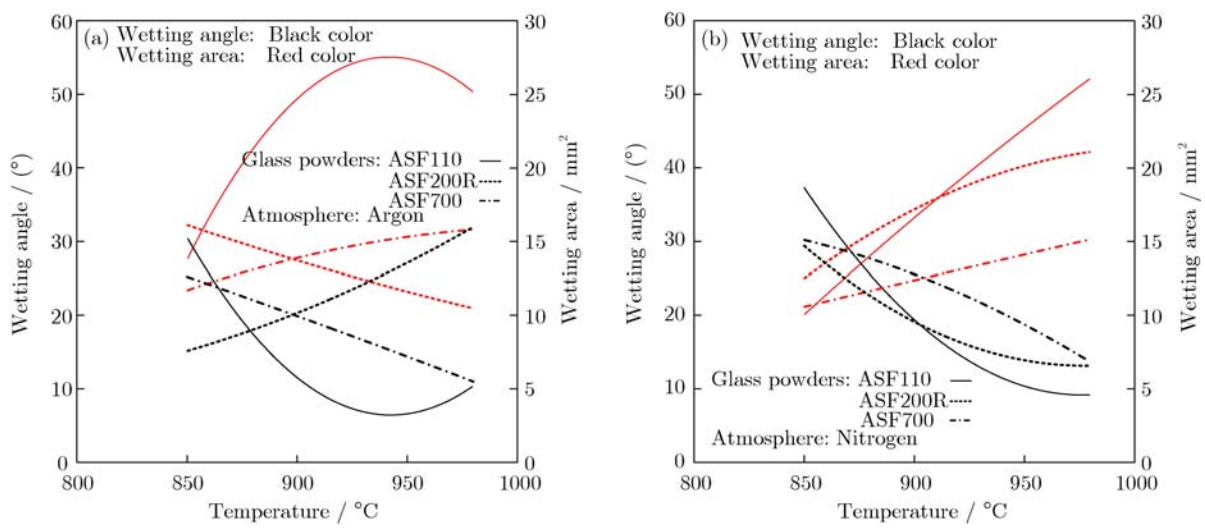

Fig. 13. Wetting ability of ASF100, ASF200R, and ASF700 glasses in Ar (a) and N_2 (b) atmospheres.

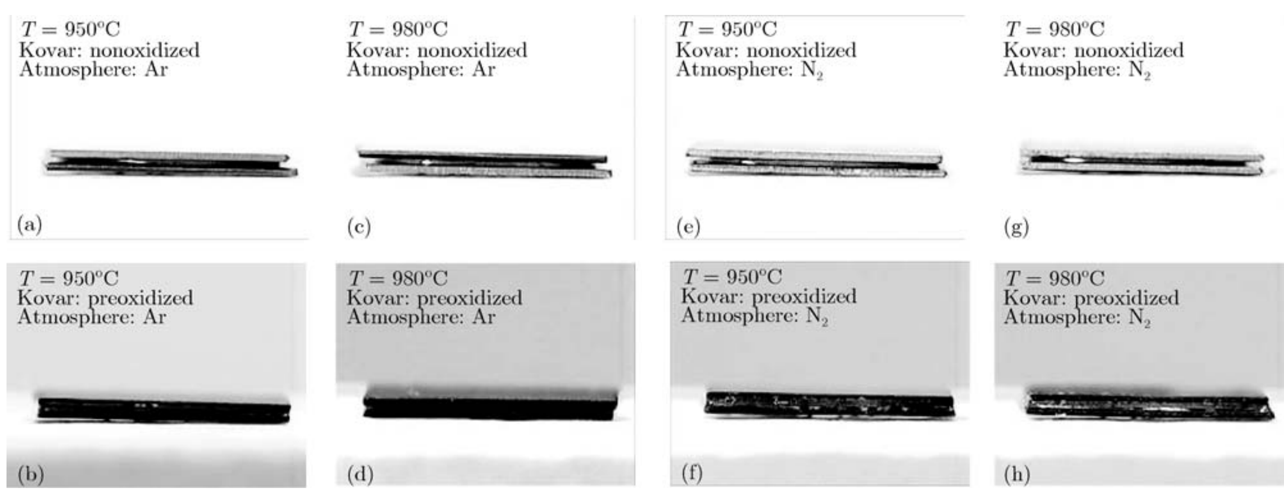

Fig. 14. ASF110 glass-Kovar (nonoxidized and preoxidized) sandwich seals.

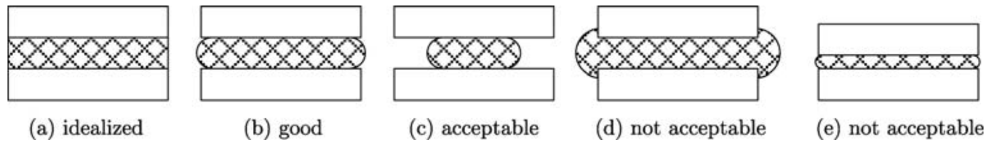

Fig. 15. Glass flow shapes of glass-metal sandwich seals (ASTM F144-80).

Table 2. Results of sealing strength

Group	Sealing temperature / °C	Holdingtime/ min	Preoxidized	Atmosphere	Quality of the seal	Shearstrength/ MPa
1	950	20	No	Ar	Acceptable	0
	980	20	No	Ar	Acceptable	0
	950	20	No	N_2	Acceptable	0
	980	20	No	N_2	Acceptable	0
2	950	20	Yes	Ar	Good	3.8
	980	20	Yes	Ar	Good	3.9
	950	20	Yes	N_2	Good	3.4
	980	20	Yes	N_2	Good	3.6

loy is not preoxidized, the glass cannot effectively wet the metal. The seal strength decreases, which results in seal failure, as shown by the shear strength results of Group 1.

4. Conclusions

This article describes the sealing of Kovar alloy (nonoxidized and preoxidized) with two types of glasses: hard glass (ASF110) and soft glass (ASF200R and ASF700). The oxidization rate of Kovar alloy was measured at a number of controlled temperatures for various time. The sealing process was optimized using a series of tests to measure the wetting ability of the glass, the glass flow shape, and the shear strength. This study reached the following conclusions.

(1) The oxidation of Kovar alloy for approximately 10 min at 700°C in air resulted in optimal adherence of glass to Kovar alloy.

(2) The wetting and spreading behavior of glass on preoxidized Kovar alloy was superior to that on nonoxidized Kovar alloy.

(3) The wetting ability of ASF110 glass (hard glass) on preoxidized Kovar alloy was superior to that of ASF200R glass and ASF700 glass.

(4) The quality of the ASF110 glass-preoxidized Kovar seals was much higher than that of the ASF110 glass-nonoxidized Kovar seals.

(5) The shear strength of the ASF110 glass-preoxidized Kovar alloy that was sealed at 980°C for 20 min in an Ar atmosphere was approximately 3.9 MPa.

Acknowledgements

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