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THE EFFECT OF ATMOSPHERE AND GLASS COMPOSITION ON REACTIONS AT GLASS-METAL INTERFACES

John J. Brennan
(Ph. D. Thesis)

July 1969

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THE EFFECT OF ATMOSPHERE AND GLASS COMPOSITION ON REACTIONS AT GLASS-METAL INTERFACES

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ABSTRACT

Contact angles and adherence of sodium disilicate glasses with varying oxide additions on iron, cobalt, nickel, and their alloys, were studied at 1000°C in two vacuum furnaces, one with a graphite heating element. When the oxide containing glasses were melted on the substrate metals in the furnace with carbon present, the glasses generally wet the substrate, with a contact angle of approximately zero degrees, and adhered strongly. A crystalline phase of either silica (SiO_2) or an orthosilicate usually precipitated out of the glass. When the base metal had a higher oxidation potential than the metal oxide dissolved in the glass, i.e., CoO glass on Fe, a redox reaction took place. This resulted in the reduced metal forming a dendritic structure growing into the glass while the glass became enriched with the base metal oxide. The composition of the dendrite was determined by the relative activities of the metal oxides in the glass. In the furnace without carbon present, only the latter reaction took place.

It was determined that carbon present in the furnace produced CO in the furnace atmosphere which resulted in the substrate metals becoming unsaturated with respect to oxygen. A driving force was thus esatblished for a redox reaction involving the Na_2O in the glass and the metal

substrate which resulted in the wetting of the metal by the glass and the saturation of the glass at the interface with the base metal oxide. At this point, equilibrium compositions were established at the interface resulting in a continuous electronic structure existing across the glass-metal interface giving the observed good adherence. Good adherence was also obtained from the redox reaction involving the dissolved oxide in the glass and the base metal due to mechanical interlocking between the metal dendrites and the glass.

I. INTRODUCTION

A fundamental understanding of the mechanisms responsible for adherence between a glass and a metal is of prime importance to those interested in enameling and related glass-to-metal sealing techniques. The requirement of good adherence between the glass and the metal can be achieved either by means of surface roughening of the metal or by the establishment of a chemical bond across the interface, or both. A chemical bond usually produces the best adherence and has been the subject of many investigations.

Studies done by Pask and Fulrath[1] over a period of years indicate that for good adherence at the glass-metal interface a balance of bond energies must exist across the interface. This balance of bond energies can be achieved by the solution of the lowest valent oxide of the metal into the glass so that the glass at the interface is saturated with this oxide and a continuous electronic structure exists across the interface. The activity of the metal oxide in both phases would then be equal to one. The result is a smooth chemical transition from the base metal through an equilibrium transition zone into the glass. A necessary criteria for saturation at the interface is that the diffusion of the oxide away from the interface must be slower than the oxidation reaction at the interface.

Other researchers[2-6] have also investigated the glass-to-metal bonding field and have supported the general theory that chemical bonding occurs between a glass and a metal when thermodynamic equilibrium compositions relative to the lowest valent oxide of the metal exist at the interface.

Sessile drop or contact angle studies of oxide containing glasses on metals have not been done to any great extent. Adams, et al.[4] studied the contact angles and adherence of sodium disilicate ($Na_2O \cdot 2SiO_2$) glasses with varying iron oxide additions on platinum and iron at 1000°C in vacuum. As all the glasses were made under oxidizing conditions, it was expected that most of the iron in the glass would be in solution in the ferric state. The glass-iron systems showed a lowering of the contact angle from 34° with no oxide in the glass to 20° with 44 mole per cent ferric oxide added to the glass. The previously reported value for the contact angle of pure sodium disilicate (NS_2) glass on iron is 55°.[2] Adams explains this discrepancy by showing that the surface of the iron had become oxidized and that this oxide had been dissolved by the glass. The resulting higher iron content in the glass presumably caused the lower contact angle. Devitrification occurred in the glasses containing more than 9.1% ferric oxide with fayalite (Fe_2SiO_4) precipitating out at the interface. Adherence increased with increasing amounts of ferric oxide added to the glass. No explanation was given as to why devitrification occurred at such small percentages of iron oxide addition.

Gaidos, et al.[3] using seven different soda-silica compositions investigated the effect of the oxygen to silicon ratio in the glass on its wetting of iron. The effect of metal oxide additions was also studied by saturating sodium disilicate glass with ferric and ferrous oxides. It was found that ferric ions in the glass react with the iron substrate leading to an irregular interface; ferrous ions do not. It was also found that increasing the oxygen to silicon ratio either by increasing the amount of normal network-modifying cation oxides or substrate metal

oxides caused a decrease in the contact angle and the development of adherence with contact angles less than about 30°. Adherence was described as being due to chemical bond formation at the interface brought about by the lowering of the internal energy of the glass so that some thermodynamically stable state is reached. The lowering of the internal energy of the glass was due to the more effective screening of the Si^{+4} ions by an increase in non-bridging oxygens which occurred with the addition of network modifying oxides.

The purpose of the present investigation is to provide a comprehensive study of the interfacial reactions between metals and metal oxide containing glasses, degree of wetting and the resulting adherence. The systems under investigation are sodium disilicate glasses containing dissolved iron, cobalt, and nickel oxides in contact with iron, cobalt, and nickel metals as well as NiFe and NiCo alloys. The effect of furnace atmosphere on the interfacial reactions was also studied.

II. EXPERIMENTAL WORK

A. Preparation of Samples

The samples of iron, cobalt, and nickel were obtained from Materials Research Corporation, Orangeburg, New York, and were approximately 99.995% pure. The major impurities were carbon and oxygen at about 20 ppm each. The platinum and gold were obtained from the Lawrence Radiation Laboratory, Berkeley, California, and were of 99.999% purity. Armco iron (typical analysis: 0.015% C, 0.0285% Mn, 0.005% P, 0.025% S, 0.003% Si, and an unspecified amount of oxygen) was also obtained from the Lawrence Radiation Laboratory. The NiFe and NiCo alloys were of 50-50 composition and were made by the high-purity metals laboratory at the Lawrence Radiation Laboratory and had a purity of 99.99+%. All metal samples were approximately 15 mils thick and were cut into 1/2" by 1/2" squares. The metal plates were then polished through a set of dry polishing papers and given a final high metallurgical polish on a lap wheel with 1-μ diamond grit. All samples were cleaned in an ultrasonic cleaner and stored in a dessicator until ready to be used.

The sodium disilicate glass (NS_2) was obtained in powder form from the Philadelphis Quartz Company, Berkeley, California. Reagent grade CoO and NiO were added to the glass powder, mixed, and melted in a platinum crucible in air at 1400°C in varying percentages from zero to saturation. The saturation point of CoO in NS_2 glass at 950°C is reported to be approximately 25 wt. %.[6] The saturation point of NiO in NS_2 glass at 1000°C is reported to be 7.55 wt. %.[7] The glasses containing dissolved CoO very likely contained some cobaltic ions since the reaction:

$$3CoO_{(gl)} + 1/2\ O_{2(g)} \rightarrow Co_3O_{4(gl)} \qquad \Delta F^{\circ}_{827} = -5 \text{ kcal} \qquad (1)$$

has a negative free energy below 1000°C. On cooling from the melting temperature some cobaltic ions most likely formed in the glass. The glasses containing dissolved NiO, however, did not form Ni^{+3} ions on cooling since no evidence exists in the literature that Ni^{+3} ions are stable under these conditions. The glasses containing dissolved CoO were deep blue in color while those containing dissolved NiO were brown.

The glasses containing dissolved FeO* were made by mixing appropriate amounts of reagent grade Fe and Fe_2O_3 powder together with NS_2 powder and melting the mixture in an iron crucible in a flowing CO/CO_2 mixture at 1000°C. The CO/CO_2 ratio was such that the resulting oxygen pressure was 5×10^{-15} atm. This oxygen pressure insures that most of the iron in the glass is in the ferrous state. However, some ferric ions are also likely to be present. Ferrous glasses are blue in color while ferric glasses are yellow-brown. It has been reported[8] that Fe^{+3} in combination with Fe^{+2}, both in six-fold coordination in the glass, gives rise to a green coloration. Since most glasses containing dissolved iron oxide made in this investigation were greenish-blue in color, it is assumed that some ferric ions are present in the glass. Glass was made with dissolved iron oxide content varying from zero to saturation, which has been reported to be 44.4 wt. percent at 1000°C.[9]

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* The formula FeO is used throughout the text for convenience; in actuality the compound is non-stoichiometric with the formula Fe_xO where x is 0.875-0.946 at 1000°C.

All glass samples were broken up into approximately 3/16" chunks and stored in a dessicator until used.

B. Contact Angle Test Procedure

Two contact angle furnaces were used during this research. The first, which shall be referred to as furnace I, consisted of a graphite tube resistance heating element inside of which was placed an alumina "dee" tube on which the sample rests. This furnace is shown in Fig. 1. The zirconium getter indicated in the figure was not used during these experiments. Temperature measurement and control were by means of a platinum-platinum/rhodium thermocouple which rested on the alumina "dee" with the thermocouple tip just touching the sessile drop substrate. Contact angle measurements were made by sighting along the alumina "dee" through fused silica windows incorporated in the vacuum chamber with a telescope fitted with a protractor with movable cross hairs. With the cross hairs fixed on the glass-metal-vacuum triple point, the contact angle could be read with an accuracy of plus or minus one degree.

Furnace II consisted of a tantalum wound alumina tube inside of which was also an alumina "dee." Temperature control and contact angle measurements were carried out in a manner similar to furnace I. The total pressure inside the vacuum chamber of furnace II was approximately 7×10^{-5} mm Hg. while the total pressure inside furnace I was 3×10^{-5} mm Hg., both measured when the furnace temperature was 1000°C.

All glass-metal sessile drop experiments were run for a period of two hours at 1000°C. This time was found to be sufficient for steady state conditions to be attained in furnace II. Steady state conditions in furnace I were never reached. The contact angle was measured every

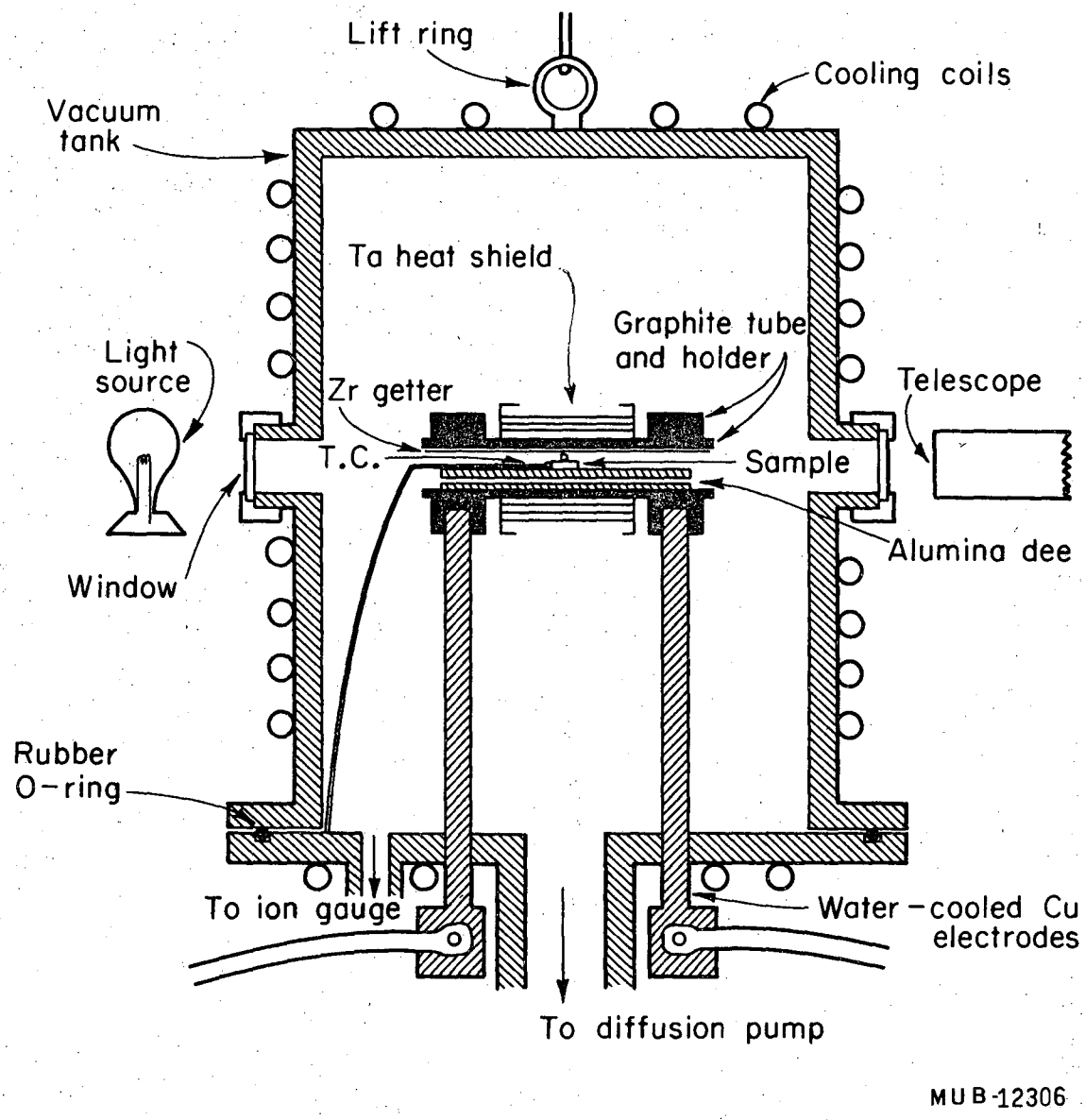

Fig. 1 Schematic of contact angle furnace I.

ten minutes to determine if any change with time took place. All samples were furnace cooled, reaching room temperature in 40 to 60 minutes.

C. Measurement of Oxygen Pressures

The oxygen pressures in the hot zone of the two furnaces were measured with the use of an oxygen gage. The closed end of a small zirconia tube was filled with a mixture of nickel oxide containing excess nickel. A platinum wire was imbedded in the NiO and extended out the open end of the tube which was then sealed shut. A second platinum wire was extended along the outside of the tube and wrapped around the tip. When the end of this tube was inserted into the hot zone of the furnace an emf was established between the two platinum wires and was measured with a potentiometer. The emf established was due to the transfer of electrons in one direction through the end of the tube coincidental with the opposite movement of oxygen ions, the oxygen ions moving from the high oxygen pressure region to the low oxygen pressure region according to the half-cell reactions:

$$Ni_{(s)} + O^{=} = NiO_{(s)} + 2e^{-} \qquad (2)$$

$$1/2\ O_2 + 2e^{-} = O^{=} \qquad (3)$$

The difference in oxygen pressures between the inside and the outside of the tube can be calculated from the equation:

$$E = \frac{RT}{nf} \ln K \qquad (4)$$

E = measured emf

R = 1.987 cal/°K

T = temperature °K

n = number of electrons transferred

f = Faraday's constant

where K is the equilibrium constant for the full equation:

$$Ni_{(s)} + 1/2\ O_2 = NiO_{(s)} \qquad (5)$$

K is equal to $p(O_2)^{1/2}$ since the activities of Ni and NiO are both equal to one. Since the equilibrium oxygen pressure over NiO is known (3×10^{-11} atm at 1000°C), one can easily determine the oxygen pressure inside the hot zone of the furnace. The oxygen pressure inside furnace II was found to be approximately 10^{-16} atm. The oxygen pressure in furnace I was measured to be 10^{-11} atm but it is believed that this is an erroneous value.

Furnace I, with the graphite heating element present, should exhibit an oxygen pressure of approximately 10^{-19} atm which is the equilibrium oxygen pressure for the reaction:

$$C + 1/2\ O_2 \rightarrow CO \qquad (6)$$

at 1000°C. It is believed that 10^{-19} atm is the true oxygen pressure in furnace I and that the erroneous reading of 10^{-11} atm was due to induction currents set up in the oxygen probe due to the large current flowing through the graphite tube. Furnace II used very small current, thus no erroneous readings due to induction were expected.

D. Analysis of Sessile Drop Specimens

Selected samples of sessile drop specimens were subjected to electron microprobe analysis. All interfacial zones were probed in order to determine the presence of any reaction products and their composition and also to determine the species and amount of metal oxide in the glass. X-ray fluorescence pictures and photomicrographs of the interfacial zones were also taken.

Representative sessile drop specimens were subjected to bending which either separated the glass from the metal substrate or fractured the glass. Qualitative data concerning the strength of interfacial bonding was obtained from this test.

III. RESULTS AND DISCUSSION

A. Iron Oxide Containing Glasses

The change in contact angle for sodium disilicate glass with increasing amounts of dissolved FeO on various metal substrates is shown in Table I. Also shown are the relative adherences and the colors of the resulting glasses. The contact angles of ferrous glasses on the various substrates tend to be between approximately zero and five degrees in furnace I and tend to remain high in furnace II.

Fe-FeO Glass

The oxidation of elemental iron by sodium disilicate glass has been shown empirically by Hagan and Ravitz[10] to occur by the reduction of sodium ions in the glass to sodium vapor. The overall reaction can be represented by:

$$Fe_{(s)} + Na_2Si_2O_5{}_{(gl)} = FeO_{(gl)} + 2SiO_{2(gl)} + 2\,Na_{(g)}\uparrow \qquad (7)$$

From the thermodynamic data listed in Table IV in the Appendix, the standard free energy of the above reaction was calculated to be 85,850 cal at 1000°C. By using the expression $\Delta F^{\circ}_{1000} = -RT\ \ln(P_{Na})^2$ the equilibrium partial pressure of sodium for the reaction at 1000°C was calculated to be approximately 5×10^{-8} atm. Therefore, if the partial pressure of sodium in the system is 5×10^{-8} atm or less, reaction (7) is thermodynamically feasible.

From experiment, it was found that when a 9.1% FeO glass, for example, was placed on a pure iron substrate and heated to 1000°C for 2 hours in furnace I, the contact angle fell to zero and over half of

TABLE I

Contact Angles of Sodium Disilicate Glass
with Varying Amounts of FeO

Substrate \ Wt. % FeO →	0	2.94	5.98	9.1	16.1	28.0	44.5	Color of Oxide Containing Glass
Fe Furn I	55°	52°	47°	0°	0°	0°	0°	green
Adherence	poor	poor	fair	good	very good	very good	very good	
Fe Furn II	60°		47°	45°		36°	27°	green-blue
Adherence	poor		poor	fair		fair	good	
Ni Furn I	56°	0°	0°	0°			0°	brown
Adherence	poor	poor	good	very good			very good	
Ni Furn II	60°			55°			45°	green-brown
Adherence	poor			poor			poor	
CO Furn I	56°	5°	0°	0°		0°	0°	blue
Adherence	poor	poor	poor	poor		good	very good	
CO Furn II	60°			56°			49°	green-blue
Adherence	poor			poor			poor	
NiCo Furn I	57°	52°	0°	0°	0°		0°	blue
Adherence	poor	poor	fair	good	very good		very good	
NiCo Furn II	60°			55°			47°	green-blue
Adherence	poor			poor			poor	
NiFe Furn I	55°	51°	5°		0°		0°	green
Adherence	poor	poor	good		very good		very good	
NiFe Furn II	60°			47°			31°	green-blue
Adherence	poor			fair			good	

the original sodium in the glass was removed, depositing on the cold parts of the vacuum chamber. The dissolved FeO content of the glass increased to 25% at the edge of the drop and to 17% in the middle with SiO_2 precipitating out of the glass around the edge, as determined from electron probe measurements. When a longer heating time was used, the SiO_2 precipitated throughout the glass drop. Figures 2 and 3 are oscilloscope traces of this interface using Fe and Si radiation which show plainly the SiO_2 precipitates. Figure 4 is a photomicrograph showing the cross-section in greater detail. The glass-metal interface is at the bottom of the photograph.

From the Na_2O-SiO_2-FeO phase diagram (Fig. 5) it can be seen that when an NS_2 glass containing dissolved FeO loses sodium, SiO_2 would precipitate out of the glass when the original FeO content of the glass was approximately 15% or less. When the original FeO content of the glass was 15-40%, Fe_2SiO_4 (fayalite) would be the precipitating phase on sufficient loss of sodium. From 40-45% FeO content, FeO itself would precipitate on loss of sodium from the glass. When the precipitate forms at or near the interface, which is experimentally observed, then the glass remaining at the interface is saturated with FeO with respect to a second phase, either SiO_2, Fe_2SiO_4, or FeO. Adherence develops at this point. Good adherence was found to exist around the edge of the glass where the SiO_2 precipitated out and where the FeO content of the glass was 25% while rather poor adherence existed in the middle of the drop where the FeO content was 17% and where no precipitate was present. More sodium was lost from the edge of the glass drop than in the middle. This is due to reaction (7) proceeding faster at the edge of the drop since

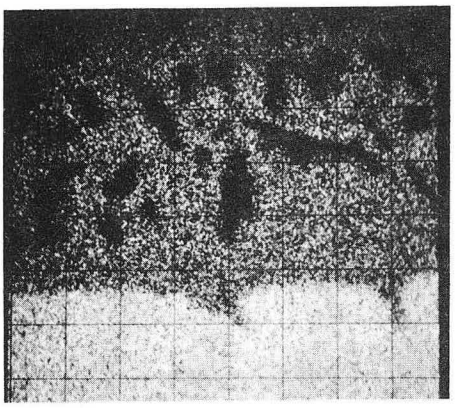

Fig. 2 Oscilloscope trace of 9.1% FeO glass-Fe interface, Fe radiation (640×).

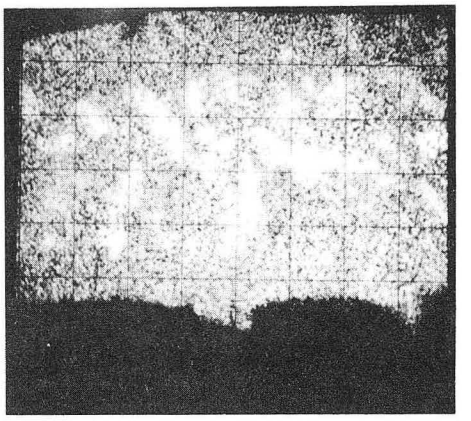

Fig. 3 Oscilloscope trace of 9.1% FeO glass-Fe interface, Si radiation (640×) 140μ square.



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Fig. 4 9.1% FeO glass-Fe interface showing SiO_2 reaction product; Fe substrate at bottom of photograph. (250×)

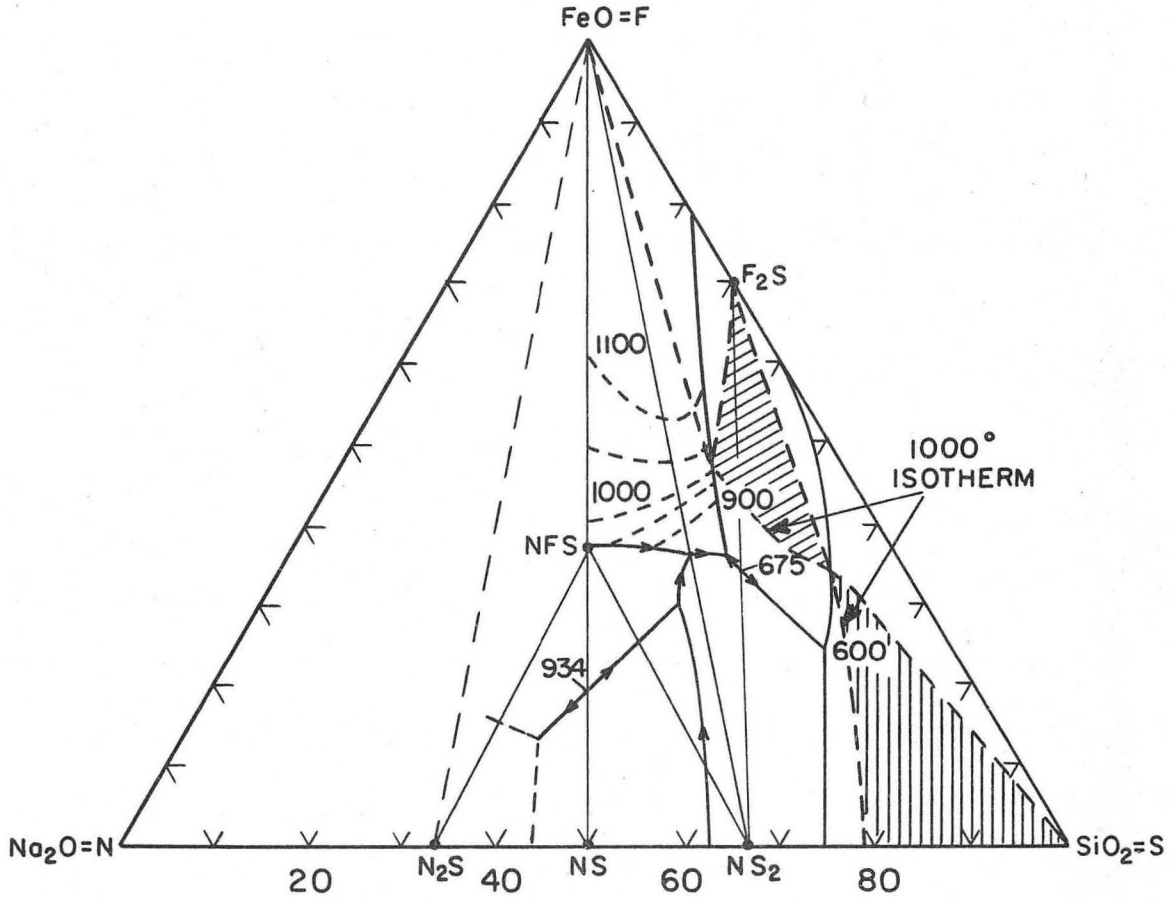

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Fig. 5 $Na_2O \cdot SiO_2 \cdot FeO$ phase diagram.

the diffusion path for escape of the sodium from the glass is shorter there than in the middle of the drop.

Iron oxide glasses on Armco iron in furnace I did not wet or react as readily as glasses on pure iron. For example, a 9.1% FeO glass melted on Armco iron for 2 hours at 1000°C exhibited a contact angle of 32° with no noticeable reaction. Only after 4 hours at 1000°C did the contact angle drop towards zero with a noticeable reaction taking place precipitating SiO_2 at the interface. Reaction (7) was retarted with the use of Armco iron whereas it proceeded readily with pure iron. Armco iron is reported to contain small particle of iron oxide in its structure.[11]

In furnace II, no noticeable reactions took place between glasses containing dissolved FeO and iron substrates. The contact angles remained quite high with a drop in angle from 60° at 0% FeO to 27° at 44.5% FeO (saturation). A corresponding increase in adherence was observed due to the approach to equilibrium compositions at the interface which resulted in a lowering of the interfacial energy with addition of FeO. At saturation, equilibrium compositions exist across the interface with the adherence being due to chemical bonding, i.e., a continuous electronic structure existing at the interface. In the absence of reactions the contact angle is determined by a balance of the horizontal components of the three surface energy forces acting at the three phase junction between gas, metal, and liquid; this is represented by Eq. (8) (Young's equation) where ${}_s\gamma_g$, ${}_s\gamma_\ell$, and ${}_\ell\gamma_g$ are the solid-gas, solid-liquid, and liquid-gas surface tensions, respectively.

$$ {}_s\gamma_g - {}_s\gamma_\ell = {}_\ell\gamma_g \cos\theta \qquad (8) $$

θ is the interior angle the drop makes with the substrate.

Using the values of 1990 dynes/cm and 300 dynes/cm for the surface tensions of iron and sodium disilicate glass respectively at 1000°C,[12] one can calculate the interfacial energy of the glass-metal drops knowing the contact angle.* For $\theta = 60°$, ${}_s\gamma_\ell = 1840$ dynes/cm and for $\theta = 27°$, ${}_s\gamma_\ell = 1723$ dynes/cm. Thus, by adding 44.5% FeO to an NS_2 glass melted on iron the amount of reduction of the surface energy of the metal by the glass is equal to about 89% of the surface tension of the glass. This balance indicates that the bonding forces between the atoms at the interface are closely equivalent to the bonding energies of the atoms in the glass, which is the requirement for a continuous electronic structure or chemical bonding at the interface. The increase in adherence as the reduction in interfacial energy approaches the surface energy of the glass is supported by this analysis.

When sodium disilicate glass with dissolved Fe_2O_3 is melted on iron, a reaction between the ferric ions and the iron takes place:

$$2Fe^{+3}_{(gl)} + Fe_{(s)} = 3Fe^{+2}_{(gl)} \qquad \Delta F^{\circ}_{1000} = -12 \text{ kcal} \qquad (9)$$

The contribution of the free energy of this reaction lowers the interfacial energy, thus lowering the contact angle.

This was observed in furnace II. The color of the glass changed from yellow-brown to green-blue as reaction (9) proceeded. For example, a 10% Fe_2O_3 glass on Fe heated for 2 hours at 1000°C resulted in a 31°

* Although surface energy and surface tension are not numerically equal for solids, they will be used interchangeably throughout this text.

contact angle and fair adherence. Figure 6 shows the interfacial zone for this specimen (bottom of photo). Notice that the iron at the interface is roughened due to reaction (9) but that no trace of a second phase in the glass exists. No sodium was lost from the glass which indicated that reaction (7) did not proceed.

Also, the presence of the ferric ions in the glass weakens the Si-O-Na or non-bridging oxygen bodning due to the greater screening demands of the ferric ions than the ferrous ions and the addition to the glass of more oxygen per iron atom. The sodium is therefore more available for reaction. For example, a 10% Fe_2O_3 glass on iron in furnace I at 1000°C exhibited a zero contact angle after only two minutes. The color of the glass changed from yellow-brown to green-blue indicating the presence of ferrous ions. Sodium was lost from the glass and SiO_2 precipitated out. Reaction (7) is thus enhanced by the presence of ferric ions in the glass. Reaction (9) also took place.

Ni-FeO Glass

Sodium disilicate glasses containing dissolved FeO when melted on nickel substrates quickly attained a zero contact angle in furnace I. For example, when a 9.1% FeO glass was melted on Ni at 1000°C the FeO content decreased to 8%, the NiO content increased from zero to 7%, the contact angle dropped to zero, and Ni_2SiO_4 with some Fe^{2+} (i.e. $Ni_{1.8}Fe_{0.2}SiO_4$) precipitated out at the interface. Sodium was also lost from the glass. It appears that a reaction similar to reaction (7) is taking place.

$$Na_2Si_2O_{5(gl)} + Ni_{(s)} = NiO_{(gl)} + 2SiO_{2(gl)} + 2Na_{(g)} \uparrow \qquad (10)$$

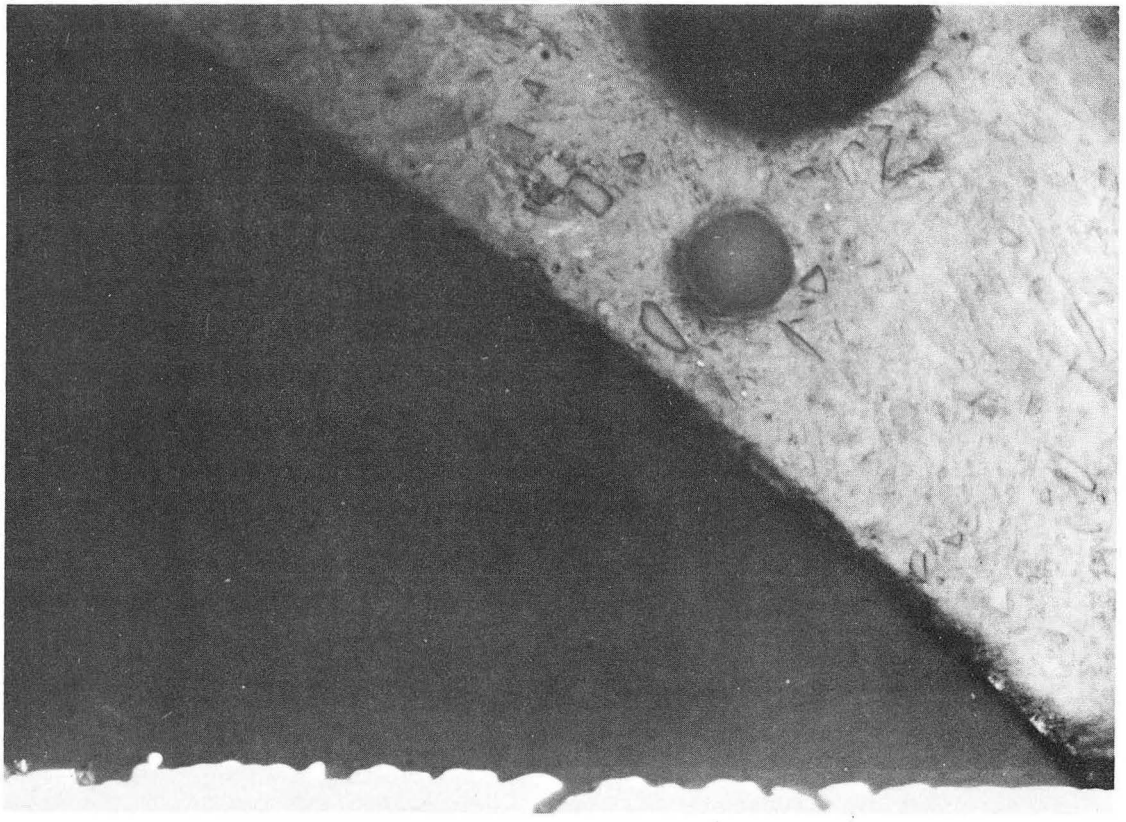

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Fig. 6 10% Fe_2O_3 glass-Fe interface showing attack of Fe, no rxn product. Fe substrate at bottom of photograph, glass on left, plastic holder on right. (32×).

The Na_2O-SiO_2-NiO phase diagram is not known; however, it is apparently similar to the Na_2O-SiO_2-FeO diagram except that the Ni_2SiO_4 and SiO_2 phase regions are smaller and shifted down toward the SiO_2 corner of the diagram due to the lower solubility of NiO in NS_2 as compared to FeO. As sodium is lost by reaction (10) the glass becomes saturated with NiO and Ni_2SiO_4 precipitates out. When ferrous ions are also present in the glass, they enter into the precipitating phase to the extent that equilibrium compositions at the glass-silicate interface, or equal activities of iron and nickel oxides in the two phases, are maintained.

Figures 7, 8, and 9 are oscilloscope traces of the interface showing the formation of the iron nickel silicate phase at the interface and within the glass. Figure 10 is a photomicrograph of the same interfacial area with the interface at the bottom of the photograph.

Good adherence resulted as soon as the precipitate formed since at that point the glass became saturated with the base metal oxide thus establishing equilibrium compositions at the interface with a continuous electronic structure existing across it. The color of the glass changed from green-blue to brown as the reaction proceeded, indicating the presence of NiO in the glass.

In furnace II the contact angle remained quite high with addition of FeO to the glass, falling to 45° at 44.5% FeO content. The glass retained its green-blue color indicating that FeO is the only dissolved oxide. The adherence remained very poor on addition of FeO to the glass. No sodium was lost from the glass indicating that reaction (10) did not proceed. From these observations it is apparent that no nickel oxide enters the glass, therefore no chemical bonding exists at the interface,

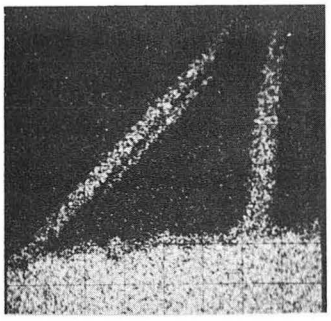


Fig. 7

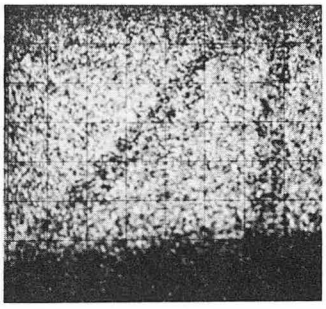


Fig. 8

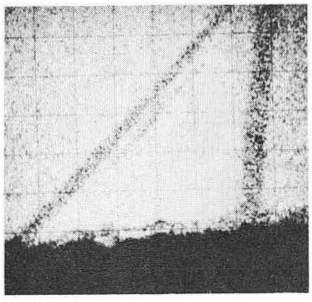


Fig. 9

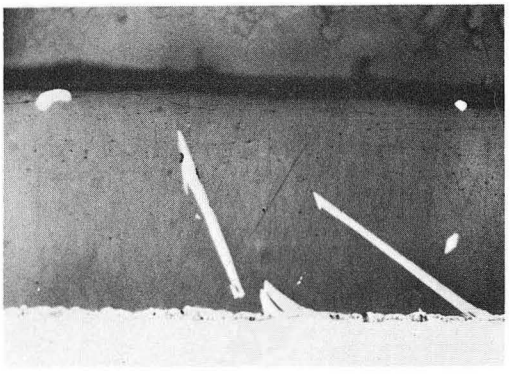


Fig. 10 XBB 697-4570

Fig. 7 Oscilloscope trace of 9.1% FeO glass-Ni interface Ni radiation. (640×).

Fig. 8 Oscilloscope trace of 9.1% FeO glass-Ni interface, Fe radiation. (640×).

Fig. 9 Oscilloscope trace of 9.1% FeO glass-Ni interface, Si radiation. (640×).

Fig. 10 9.1% FeO glass-Ni interface showing reaction product; Ni substrate at bottom of photograph, glass in center, plastic at top. (250×).

resulting in the observed poor adherence of the FeO glasses to nickel.

Co-FeO Glass

This system is similar to the previous one in that when an FeO glass was melted on cobalt in furnace I the contact angle fell to zero, the glass changed color from green-blue to a cobalt blue, and the adherence increased with increasing FeO content, as shown in Table I. Very good adherence was observed at high percentages of FeO. For example, when a 9.1% FeO glass was melted on Co for 2 hours at 1000°C in furnace I, the resulting glass composition, as determined by the electron probe, was 9% FeO and 15% CoO. The contact angle was essentially zero and sodium was lost from the glass. However, no second phase was precipitated and very poor adherence was observed. This is a good example of the fact that wetting of the metal by the glass does not necessarily result in good adherence. The wetting, in this case, resulted from the contribution of the free energy of the reaction:

$$Na_2Si_2O_{5(gl)} + Co_{(s)} = CoO_{(gl)} + SiO_{2(gl)} + 2Na_{(g)} \uparrow \qquad (11)$$

to the reduction of the interfacial energy. Good adherence resulted only when the reaction proceeded to the point where the glass became saturated with CoO and a second phase of composition $(Fe_{1-x}Co_x)_2\ SiO_4$ was precipitated. When the 9.1% FeO glass was held for a longer period of time at 1000°C or when a higher percentage of FeO was dissolved in the glass, good adherence to Co resulted.

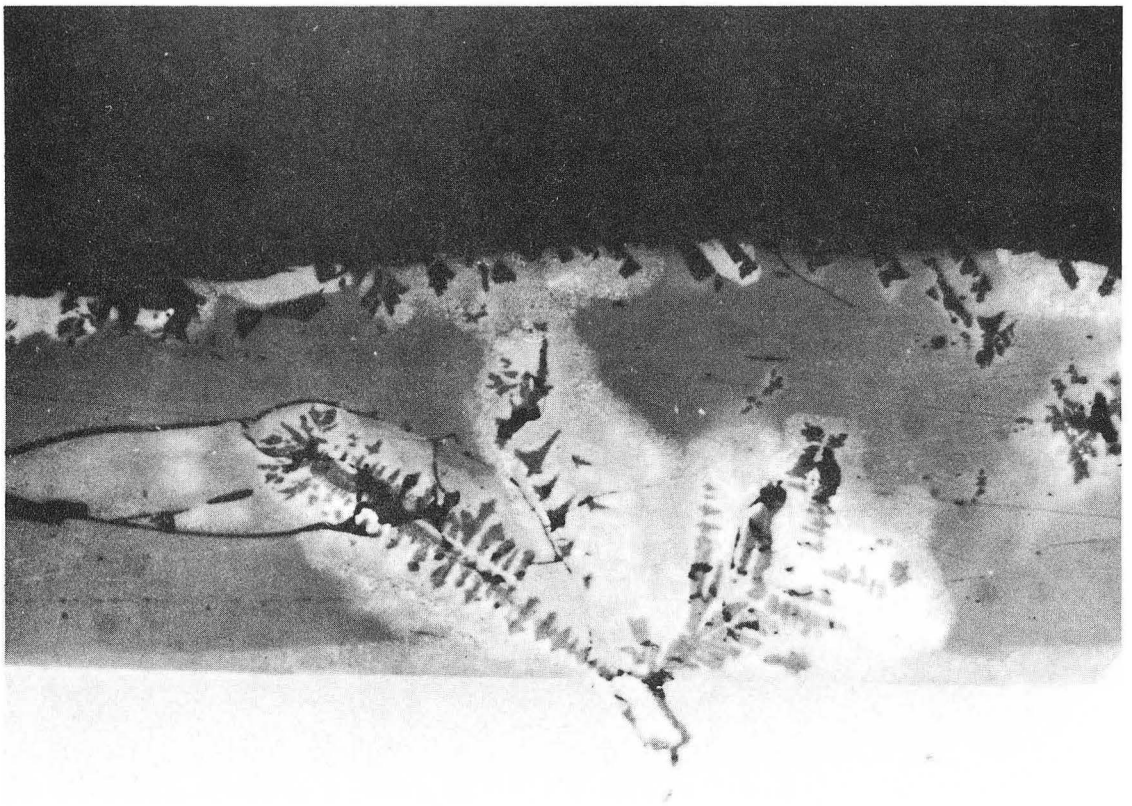
In furnace II the adherence remained poor and the contact angle remained high with addition of FeO to the glass, as in the case of FeO

glass on nickel. The color of the glass remained green-blue indicating no dissolution of CoO into the glass, and no sodium was removed from the glass. These results indicate that reaction (11), like reactions (7) and (10), does not proceed in furnace II.

NiFe-FeO Glass

From Table I, it can be seen that the results for an FeO glass melted on NiFe alloy substrate are very similar to an FeO glass on an iron substrate. For example, a 9.1% FeO glass melted on an NiFe substrate at 1000°C in furnace I resulted in a contact angle approaching zero, good adherence, loss of sodium from the glass, and the precipitation of SiO_2 at the interface. Figure 11 shows the precipitate phase at the interface (bottom of photograph). Notice that the precipitate appears to have nucleated at a crack in the metal substrate and then to have grown out into the glass.

An interesting observation in this system is that the SiO_2 particles were surrounded by Fe_2SiO_4. This phenomenon is associated with increase of FeO in the glass as the reaction proceeds, the final glass containing 36% FeO near the precipitate phase. As sodium was lost from the glass through reaction (7), SiO_2 first precipitated out. As the reaction continued the FeO content of the glass increased and the SiO_2 content of the glass decreased. When the FeO content reached about 35%, Fe_2SiO_4 started to precipitate out, as can be seen from the $FeO-SiO_2-Na_4O$ phase diagram, Figure 5. As reaction (7) continues, the composition of the glass follows the 1000°C liquidus line which forms the left side of the cross-hatched phase fields. If the reaction were allowed to proceed long enough, FeO would begin to precipitate out of the glass. Finally,



XBB 697-4561

Fig. 11 6% FeO glass-NiFe interface showing reaction product; NiFe substrate at bottom of photograph, glass in center, plastic at top. (250×).

when all the sodium had left the glass, the resultant product would be a SiO_2, Fe_2SiO_4, FeO composite. The nickel in the substrate did not enter into the reactions due to the much higher oxidation potential of the iron. The absence of any brown coloration of the glass supports the absence of NiO.

The contact angle data and adherence values for FeO glass on NiFe in furnace II are very similar to the values in the FeO glass-Fe system, as expected. The drop in contact angle and increase in adherence as the FeO content of the glass increases is due to the attainment of equilibrium compositions at the interface which result in a lowering of the interfacial energy. At saturation, equilibrium compositions exist across the interface with the adherence being due to chemical bonding, i.e., a continuous electronic structure across the interface.

NiCo-FeO Glass

The behavior of this system is a combination of both the Ni-FeO glass and Co-FeO glass systems in that both reactions (10) and (11) took place when the glasses were melted in furnace I. The oxidation potentials of Ni (+0.250) and Co (+0.277) are very close so that both substrate metals enter into the reaction, unlike the FeO glass-NiFe system. The oxidation potential for Fe is +0.44. For example, a 6% FeO glass on NiCo when heated at 1000°C for 2 hours resulted in a zero contact angle, good adherence, a glass composition of 4% FeO, 10% CoO, and 2% NiO, and a precipitate phase of approximate composition $(Fe_{0.4}Ni_{0.4}Co_{1.2})SiO_4$. Again sodium is lost from the glass. When the glass became saturated with the oxide of the substrate metal with the highest oxidation potential, a precipitate formed. The composition of the precipitate was

determined by the relative activities of the oxides in the glass. Figures 12, 13, 14 and 15 are oscilloscope traces of a cross-section of this interface showing the precipitate phase and the location of each of the four principal elements, Ni, Fe, Si, and Co.

In furnace II, no reactions between the FeO glass and the NiCo substrate took place with resulting high contact angles and poor adherence. Again, with no base metal oxide in the glass, the glass still being green-blue in color, chemical bonding was lacking at the glass-metal interface resulting in poor adherence.

B. Cobalt Oxide Containing Glasses

From Table II, it can be seen that glasses containing dissolved CoO generally exhibit low contact angles in furnace I on all substrates except iron. In furnace II the contact angles remain fairly high on all substrates.

Co-CoO Glass

This system parallels almost exactly the FeO glass-Fe system in that in furnace I a CoO glass melted on Co attained a contact angle of zero and sodium was lost from the glass through reaction (11). For example, a 19.35% CoO glass on Co melted at 1000°C for 2 hours showed a zero contact angle, good adherence, a final glass composition containing 22% CoO, and a Co_2SiO_4 precipitate. Figure 16 shows the precipitated phase at the glass-metal interface. Almost 60% of the original soda content of the glass was reduced to sodium which vaporized and condensed onto the cold parts of the furnace. The good adherence was due to the saturation of the glass with the substrate metal oxide so that chemical bonding and a continuous electronic structure existed across the interface.

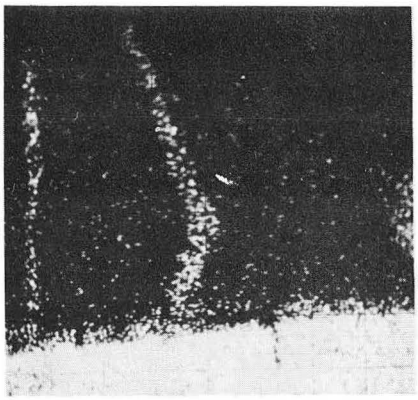


Fig. 12 Oscilloscope trace of a 6% FeO glass-NiCo interface, Ni radiation. (640×).

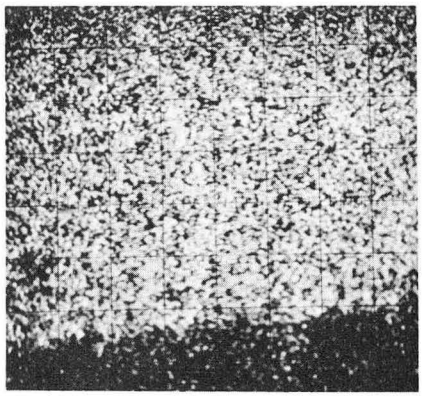


Fig. 13 Oscilloscope trace of a 6% FeO glass-NiCo interface, Fe radiation. (640×).

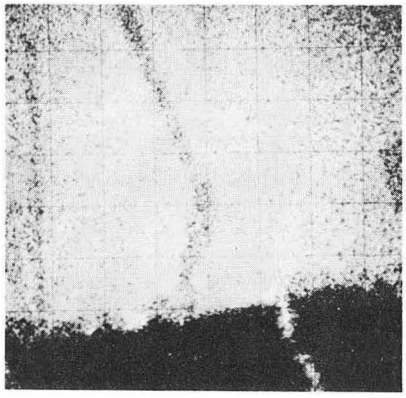


Fig. 14 Oscilloscope trace of a 6% FeO glass-NiCo interface, Si radiation. (640×).

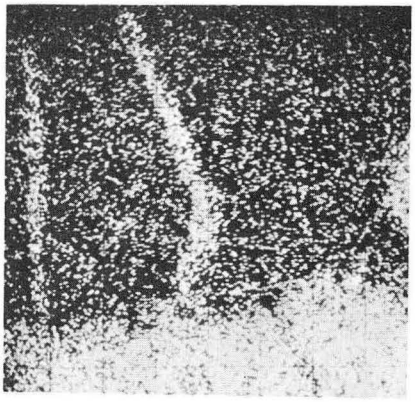


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Fig. 15 Oscilloscope trace of a 6% FeO glass-NiCo interface, Co radiation. (640×).

TABLE II

Contact Angles of Sodium Disilicate Glass
with Varying Amounts of CoO

Substrate \ Wt. % FeO →	0	1.96	5.66	9.1	15.25	19.35	25.4	Color of Oxide Containing Glass
Co Furn I	56°	48°	40°	5°	0°	0°	0°	blue
Adherence	poor	poor	poor	fair	good	very good	very good	
Co Furn II	60°			56°			24°	blue
Adherence	poor			poor			good	
Fe Furn I	55°	50°	40°	31°			21°	green
Adherence	poor	good	good	very good			very good	
Fe Furn II	60°			30°			24°	green-blue
Adherence	poor			very good			very good	
Ni Furn I	56°	10°	9°	10°	3°		0°	blue
Adherence	poor	poor	poor	poor	fair		good	
Ni Furn II	60°			56°			19°	blue
Adherence	poor			poor			poor	
FeNi Furn I	55°	46°	23°	0°			0°	blue-green
Adherence	poor	good	good	very good			very good	
FeNi Furn II	60°			45°			27°	blue-green
Adherence	poor			good			very good	
NiCo Furn I	57°	54°	50°	26°	10°		4°	blue
Adherence	poor	poor	poor	fair	fair		good	
NiCo Furn II	60°			50°			27°	blue
Adherence	poor			poor			fair	

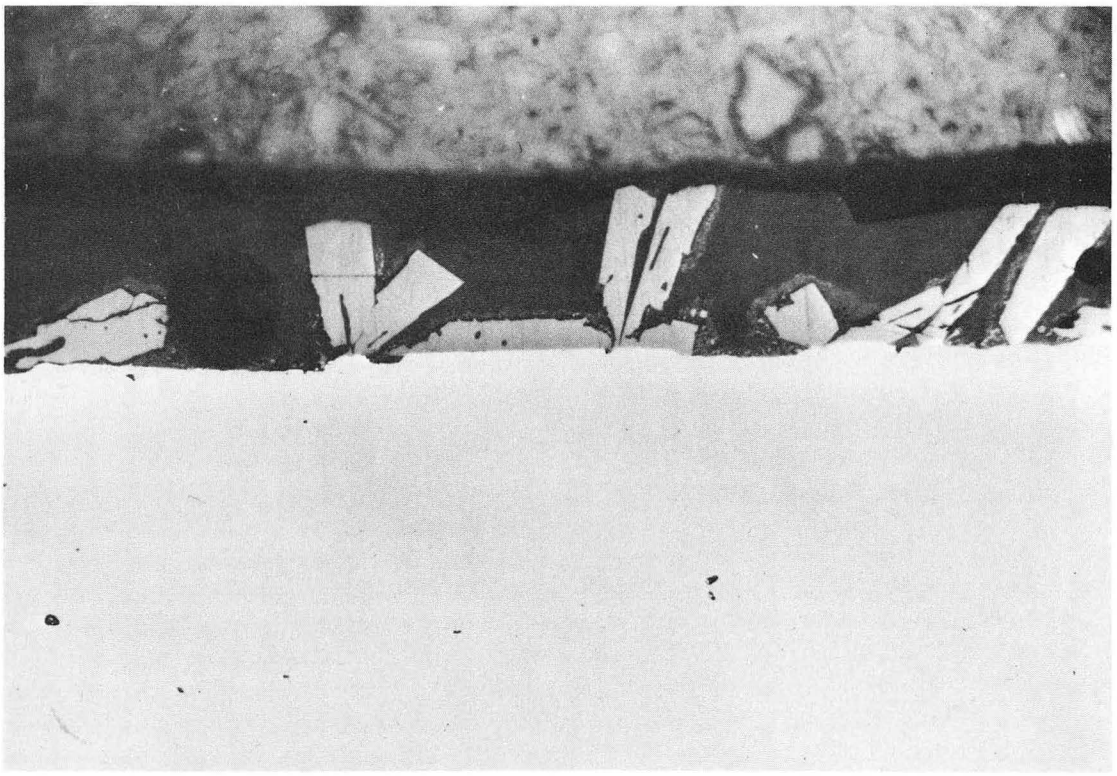

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Fig. 16 19.35% CoO glass-Co interface showing reaction product; Co substrate at bottom of photpgraph, glass in center, plastic at top. (250×).

In furnace II, no reactions took place between the CoO glass and Co. The contact angle was determined solely by the three surface energy forces acting on the periphery of the drop as described previously. As the interfacial energy was reduced with increasing CoO content of the glass, the contact angle also was lowered with a corresponding increase in adherence. The best adherence was obtained when the glass was saturated with CoO.

Fe-CoO Glass

In this system the predominant reaction in furnace I is not the reaction to reduce the soda (reaction 7) but is instead a redox reaction between the CoO in the glass and the iron substrate.

$$CoO_{(gl)} + Fe_{(s)} = FeO_{(gl)} + Co_{(s)} \qquad \Delta F = -9 \text{ kcal} \qquad (12)$$

Borom[6] gave a detailed account of the reaction kinetics in this system. In short, the CoO in the glass is reduced by the Fe forming Co metal at the interface. FeCo dendrites then begin growing from the interface out into the glass, their composition being determined by the activities of the two oxides in the glass. Figure 17 shows the glass-metal interface (at the bottom of the photograph) for a glass drop originally containing 5.66% CoO heated in furnace I. Notice how the base metal has been corroded by reaction (12). The glass now contains very little CoO but the FeO content has increased from zero to 17%. Figure 18 shows that when a glass with 19.35% CoO dissolved in it was heated at 1000°C in furnace I for 2 hours, reaction (7) has also taken place. Notice the second phase interspersed between the metal dendrites. This second phase

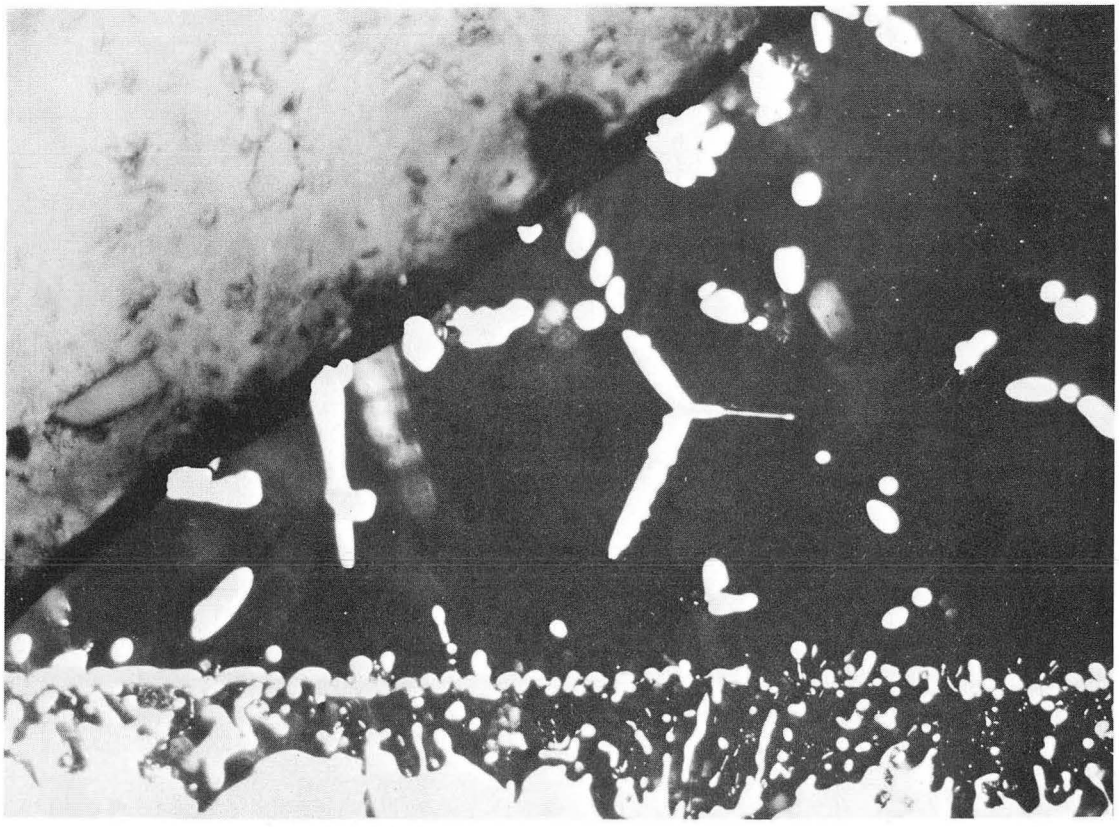

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Fig. 17 5.66% CoO glass-Fe interface showing CoFe dendrites; Fe substrate at bottom of photograph, glass at right, plastic at left. (32×).

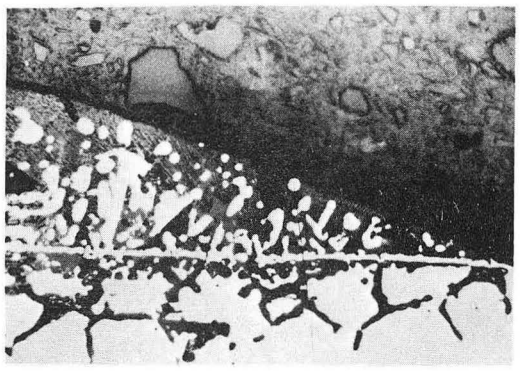

Fig. 18

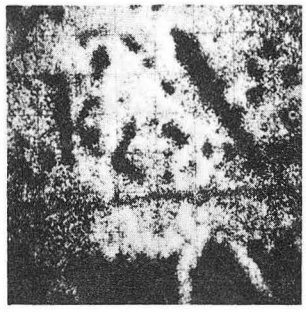

Fig. 19

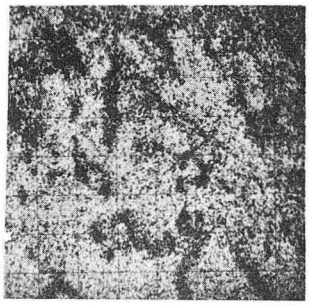

Fig. 20



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Fig. 21

Fig. 18. 19.35% CoO glass-Fe interface showing CoFe dendrites and reaction product; Fe substrate at bottom of photograph, glass in center, plastic at top. (32×).

Fig. 19 Oscilloscope trace of 19.35% CoO glass-Fe interface, Si radiation. (36×) 240μ square.

Fig. 20 Oscilloscope trace of 19.35% CoO glass-Fe interface, Fe radiation. (360×).

Fig. 21 Oscilloscope trace of 19.35% CoO glass-Fe interface, Co radiation. (360×).

is SiO_2 surrounded by Fe_2SiO_4 which precipitated out of the glass due to saturation of the glass with FeO and the simultaneous loss of sodium, as previously described. This glass now contains 33% FeO and 1% CoO with less than half of the starting sodium content remaining. Figures 19, 20, and 21 are oscilloscope traces of this interface. From these pictures it can be seen that the dendrites contain both Fe and Co and that the regions between the dendrites are a mixture of SiO_2 surrounded by Fe_2SiO_4 and FeO containing glass. The composition of the dendrites varies from 70% Fe-30% Co to 80% Co-20% Fe from the interface outward.

Reaction (7) did not take place in furnace II; no sodium was lost from the glass and no precipitates were formed. Reaction (12), however, did take place with the glass being enriched in FeO and CoFe dendrites being formed. The contact angles remain high in furnace I as well as in furnace II due to the predominance of reaction (12) over reaction (7). Once the dendrite metal network forms in the glass, the glass does not seem to be able to spread out over the metal substrate. Adherence was very good as soon as the dendrites formed even though the interface was not yet saturated with the oxide of the base metal. In this case the adherence was due mainly to mechanical interlocking of the glass with the metal dendrites.

Ni-CoO Glass

Sodium disilicate glasses containing dissolved CoO when melted on nickel substrates in furnace I rapidly attained a contact angle approaching zero. For example, a 25.4% CoO glass on Ni heated to 1000°C for 2 hours resulted in a final glass composition of 17% CoO, 7% NiO and a solid solution of NiO and CoO precipitating out at the interface. Over

half of the original soda content of the glass was reduced to sodium. In figure 22, the NiO·CoO solid solution can be seen as small needlelike crystals growing into the glass from the metal-glass interface at the bottom of the photograph. The blocky grains are nickel. It is apparent that reaction (10) took place in furnace I. Furthermore, preferential attack of the nickel substrate along grain boundaries apparently resulted in some of the grains breaking loose from the substrate and drifting out into the glass.

With less initial CoO in the glass, a cobalt nickel silicate was the precipitating phase. For example, when a 15.25% CoO glass was melted on Ni in furnace I for 2 hours, the contact angle dropped to 3°, the glass composition changed to 9% CoO and 4% NiO, and $(Co_{1.2}Ni_{0.8})SiO_4$ precipitated at the interface. It is apparent that in just about all of the NS_2-metal oxide/metal systems many precipitate-glass combinations are possible depending on the amount of sodium lost from the glass, species of oxides dissolved in the glass either initially or through reaction, and how much of each oxide leads to saturation.

In furnace II, reaction (10) did not proceed with the resulting glasses being devoid of base metal oxide (NiO). Therefore, the contact angles remained high and the adherence was poor.

NiFe-CoO Glass

This system is similar to the system CoO glass on Fe except that in furnace I the CoO reduced according to reaction (12) does not form dendrites in the glass, but instead, forms a thin layer of Co along the glass-metal interface for initial CoO contents of 9.1% or higher. The nickel did not enter into the reaction due to the much higher oxidation

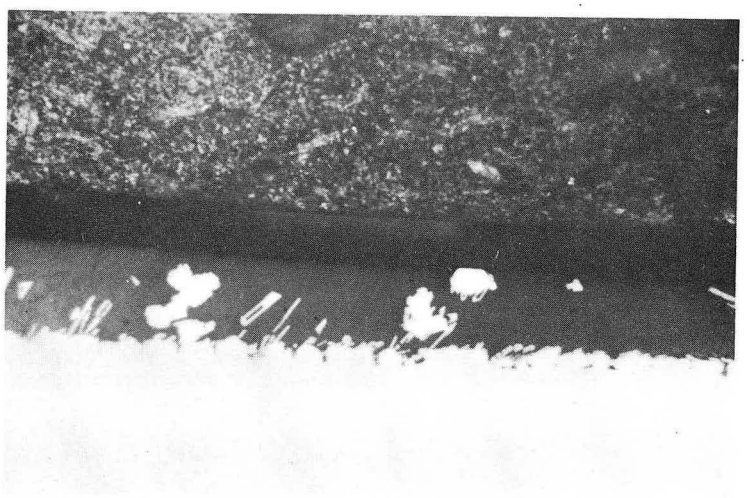

Fig. 22 25.4% CoO glass-Ni interface showing reaction product; Ni substrate at bottom of photograph, glass in center, plastic at top. (250×).

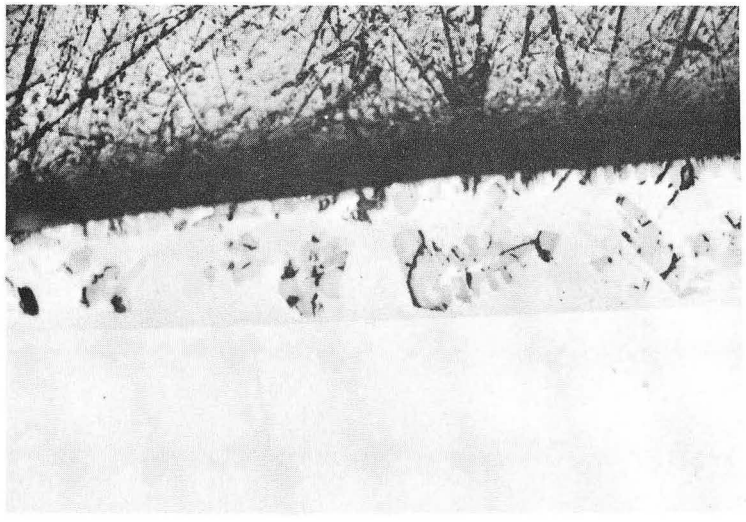

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Fig. 23 9.1% CoO glass-NiFe interface showing reaction product; NiFe substrate at bottom of photograph, glass in center, plastic at top. (250×).

potential of iron. With percentages of CoO less than 9.1 the reduced cobalt alloyed with iron from the base metal to form dendrites. For example, when a 1.96% CoO glass was melted on NiFe at 1000°C for 2 hours in furnace I, the CoO content dropped to 1/2%, the FeO content increased from zero to 4%, the contact angle remained high (46°), and FeCo dendrites formed in the glass. The adherence was good. Very little sodium was lost from the glass, indicating that reaction (7) did not proceed to any great extent. However, when a 9.1% CoO glass was melted on NiFe at 1000°C for 2 hours, the CoO content dropped to 1%, the FeO content increased from zero to 22%, the contact angle dropped to zero, Co formed as a layer along the interface, and silica precipitated out of the glass. The adherence was good, and over half of the sodium was lost from the glass. Figure 23 shows the interfacial area while Figs. 24, 25, 26, and 27 are oscilloscope traces showing the location of the elements, Fe, Ni, Si, and Co. In Fig. 27 the cobalt layer at the interface is clearly visible. It appears that at high percentages of CoO in the glass, reaction (7) proceeds at a faster rate than reaction (12). The rate of reaction (12) is evidently slowed down due to the presence of nickel in the alloy substrate.

In furnace II, the only reaction taking place is the redox reaction between the cobalt oxide in the glass and the iron in the substrate alloy. A 25.4% CoO glass melted on NiFe resulted in a final glass composition of 7% CoO and 19% FeO, a contact angle of 27°, good adherence, no loss of sodium from the glass, and the formation of FeCo dendrites extending from the base metal into the glass.

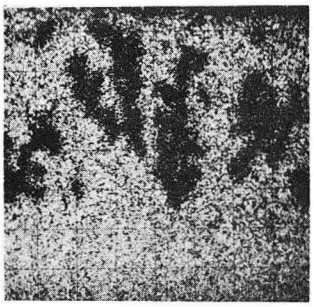

Fig. 24 Oscilloscope trace of 9.1% CoO glass-NiFe interface, Fe radiation. (640×).

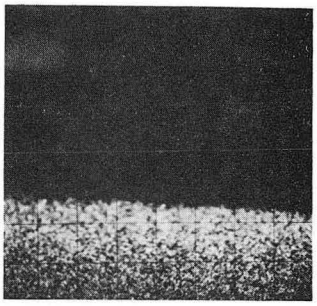

Fig. 25 Oscilloscope trace of a 9.1% CoO glass NiFe interface, Ni radiation. (640×).

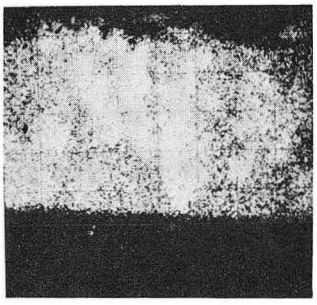

Fig. 26 Oscilloscope trace of a 9.1% CoO glass-NiFe interface, Si radiation. (640×).

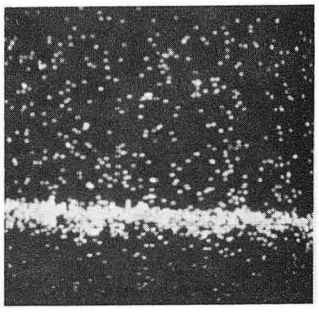

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Fig. 27 Oscilloscope trace of a 9.1% CoO glass-NiFe interface, Co radiation. (640×).

NiCo-CoO Glass

In this system, with the similarity in oxidation potentials of nickel and cobalt, both elements in the alloy take part in reaction (10) and reaction (11) in furnace I. For example, a 25.4% CoO glass melted on NiCo for 2 hours at 1000°C in furnace I resulted in a final glass composition of 22% CoO and 4% NiO, a precipitate phase of approximate composition $Co_{1.7}Ni_{0.3}SiO_4$ formed at the interface, loss of sodium from the glass, and good adherence. Figures 28 and 29 are oscilloscope traces showing the location of the Ni and Si. No oscilloscope trace using Co radiation was taken due to the fact that the amount of Co in the precipitating phase, the substrate, and in the glass was so similar that the phases could not be distinguished. Figure 30 is a photomicrograph of the same cross-section with the interface at the bottom showing the precipitate in greater detail.

In furnace II, reactions (10) and (11) did not proceed resulting in high contact angles and poor adherence until saturation of the glass with CoO was approached. At saturation (25.4% CoO) equilibrium existed across the interface; the adherence was due to chemical bonding due to a continuous electronic structure across the interface.

C. Nickel Oxide Containing Glasses

From Table III it can be seen that NiO glasses, like CoO glasses, exhibited low contact angles in furnace I on all substrates except iron. The angles for NiO glasses on Ni were not quite as low as the corresponding angles for CoO glasses on Co, however. In furnace II the contact angles remained relatively high on all substrates.

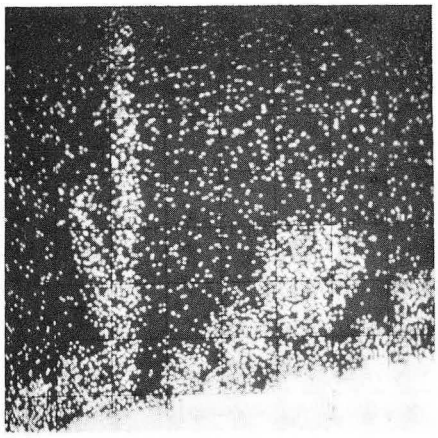

Fig. 28 Oscilloscope trace of 25.4% CoO glass-NiCo interface, Ni radiation. (640×).

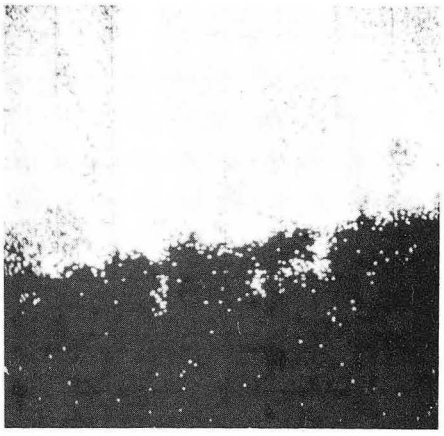

Fig. 29 Oscilloscope trace of 25.4% CoO glass-NiCo interface, Si radiation. (640×).

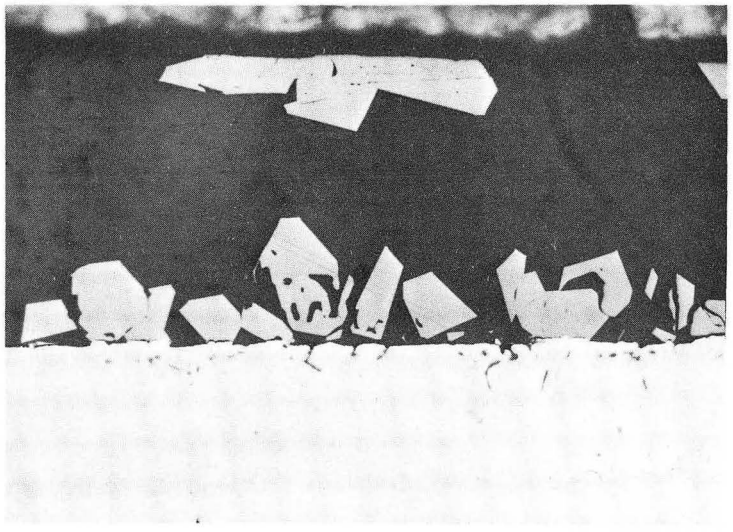

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Fig. 30 25.4% CoO glass-NiCo interface showing reaction product; NiCo substrate at bottom of photograph, glass in center, plastic at top. (250×).

TABLE III

Contact Angles of Sodium Disilicate Glass
with Varying Amounts of NiO

Wt. % NiO → / Substrate	0	1.14	2.18	3.20	5.11	6.45	6.99	7.55	Color of oxide Containing Glass
Ni Furn I	56°	40°	34°	21°	19°	20°	17°	6°	brown
Adherence	poor	poor	poor	fair	fair	fair	good	very good	
Ni Furn II	60°			48°				33°	brown
Adherence	poor			poor				good	
Fe Furn I	55°	50°	44°	42°	40°	39°		37°	green
Adherence	poor	fair	good	good	very good	very good		very good	
Fe Furn II	60°			44°				36°	green-blue
Adherence	poor			good				very good	
Co Furn I	56°	23°	13°	5°	5°	5°		5°	blue
Adherence	poor	poor	fair	good	good	very good		very good	
Co Furn II	60°			52°				43°	blue
Adherence	poor			fair				good	
NiFe Furn I	55°	40°	32°	0°				0°	green
Adherence	poor	fair	fair	good				good	
NiFe Furn II	60°			47°				41°	green-blue
Adherence	poor			fair				good	
NiCo Furn I	57°	55°		12°		5°		5°	blue
Adherence	poor	fair		good		very good		very good	
NiCo Furn II	60°			49°				39°	blue
Adherence	poor			fair				good	

Ni-NiO Glass

This system was very similar to the CoO glass-Co and FeO glass-Fe systems except that the contact angle did not fall to zero when the glass was melted on Ni in furnace I. It is possible that the kinetics in this system are slower due to the lower oxidation potential of nickel compared to cobalt and iron. Also, the low solubility of NiO in NS_2 glass results in very little change in the oxygen to silicon ratio in the glass. This ratio is an important factor in determining the kinetics for the glass-metal reactions taking place in furnace I, as will be explained in a later section. However, for a 7.55% NiO glass melted on Ni for 2 hours at 1000°C, the kinetics of reaction (10) were fast enough so that sodium was visibly lost from the glass, the contact angle dropped to 6°, Ni_2SiO_4 precipitated from the glass, and good adherence was attained. The good adherence was due again to the saturation of the glass with the base metal oxide giving a continuous electronic structure across the interface.

In furnace II no reactions took place between the NiO glass and the nickel substrate. As the interfacial energy was reduced by addition of NiO to the glass the contact angle dropped and the adherence increased. The best adherence was obtained when equilibrium existed across the interface at the saturation point of the glass with NiO.

Fe-NiO Glass

This system is analagous to the system Fe-CoO glass in that the predominant reaction is the redox reaction between the metal oxide in the glass and the metal substrate:

$$NiO_{(gl)} + Fe_{(s)} = FeO_{(gl)} + Ni_{(s)} \qquad \Delta F^{\circ}_{1000} = -13 \text{ kcal} \qquad (13)$$

The NiO in the glass is reduced by the Fe. Simultaneously, the FeO produced by the oxidation of the base metal diffuses away from the interface into the glass. NiFe dendrites grow from the interface into the glass, their composition being determined by the activities of the two oxides in the glass. When the NiO in the glass is extremely reduced, the reaction and dendrite formation stop.

Figure 31 shows the dendrite formation in the glass for a 7.55% NiO glass melted on Fe in furnace I. Very little NiO remained in the glass while the FeO content increased from zero to 15%. For the FeO content to increase to 15% reaction (7) must also have taken place in furnace I. However, the FeO content had not risen sufficiently high nor had the amount of sodium lost from the glass been enough to precipitate a second phase. The composition of the dendrites formed in this specimen vary from 50% Ni-50% Fe away from the interface to 80% Fe-20% Ni near the interface.

In furnace II only reaction (13) took place with NiFe dendrites forming in the glass. A 7.55% NiO glass melted on Fe in furnace II resulted in a final glass composition of approximately zero NiO and 7% FeO with very good adherence and a contact angle of 36°. With only 7% FeO being dissolved in the glass, it is apparent that reaction (7) did not proceed in furnace II. Adherence is due to mechanical interlocking of the glass with the metal dendrites.

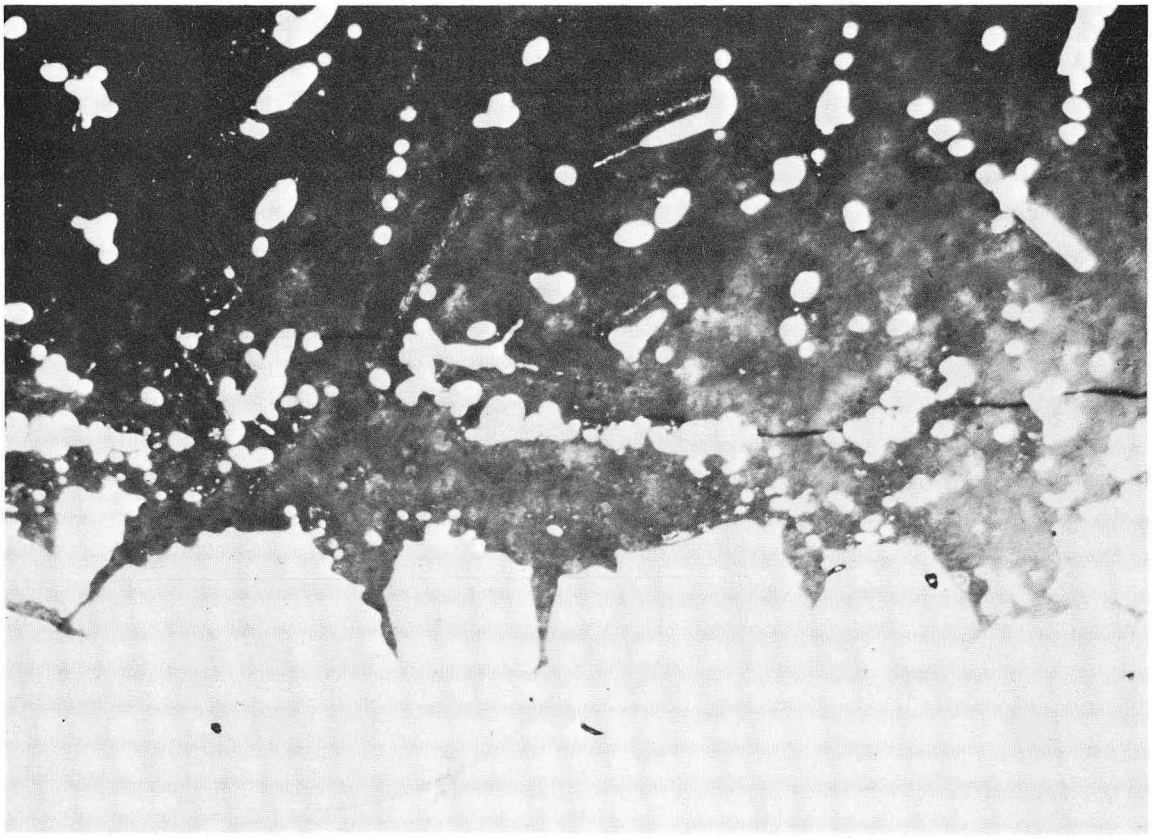

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Fig. 31 7.55% NiO glass-Fe interface showing extensive dendrite formation. (250×).

Co-NiO Glass

As in the system Fe-NiO glass, the base metal has a higher oxidation potential than the NiO dissolved in the glass leading to a redox reaction:

$$NiO_{(gl)} + Co_{(s)} = CoO_{(gl)} + Ni(s) \qquad \Delta F^{\circ}_{1000} = -4 \text{ kcal} \qquad] \quad (14)$$

The NiO in the glass is reduced by the cobalt substrate. NiCo dendrites then grow out into the glass. In this system, however, the negative free energy of reaction (14) is sufficiently small so that its rate is less than the rate of reaction (11) in furnace I after some CoO has been introduced into the glass from reaction (14). For glasses containing more than 3.20% NiO on Co reaction (11) proceeded at a fast enough rate so that the glass wetted the metal before the NiCo dendrites grew very far into the glass. For example, when a 7.55% NiO glass was melted on Co, the contact angle fell to 5°, sodium was lost from the glass, the adherence was good, and the final glass composition was approximately 1% NiO and 17% CoO. NiCo dendrites were also present in the glass near the interface. Figures 32, 33, and 34 are oscilloscope traces showing the location of the Ni, Co, and Si in the cross-section of this specimen. Figure 35 shows the interfacial zone in greater detail.

In furnace II the only reaction taking place is the redox reaction, Eq. (14), which resulted in high contact angles and good adherence. Again, adherence in both furnaces is due primarily to mechanical interlocking between the metal dendrites and the glass.

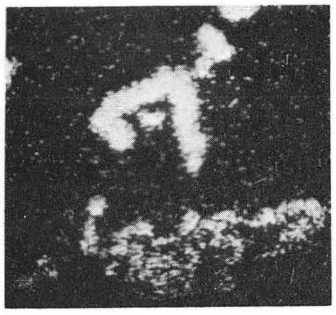

Fig. 32

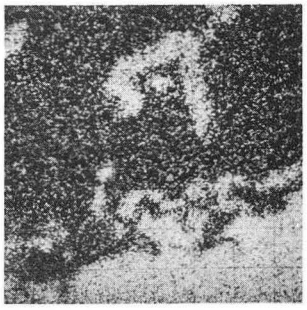

Fig. 33



Fig. 34

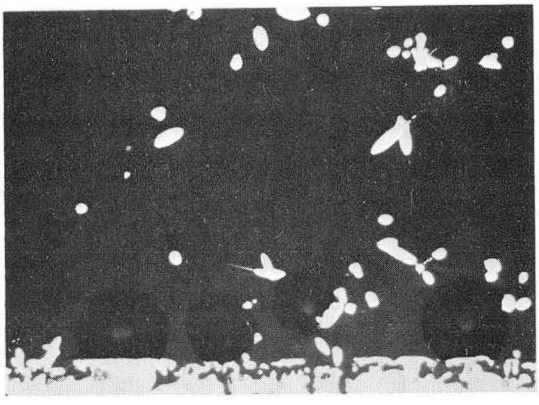

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Fig. 35

Fig. 32 Oscilloscope trace of a 7.55% NiO glass-Co interface, Ni radiation. (640×).

Fig. 33 Oscilloscope trace of a 7.55% NiO glass-Co interface, Co radiation. (640×).

Fig. 34 Oscilloscope trace of a 7.55% NiO glass-Co interface, Si radiation. (640×).

Fig. 35 7.55% NiO glass-Co interface showing dendrite formation. (250×).

NiFe-NiO Glass

This system parallels the system NiFe-CoO glass in that the nickel reduced by reaction (13) formed as a thin layer along the glass-metal interface for NiO contents of 3.20% or higher in furnace I. At lower percentages of NiO than 3.20 the nickel formed as dendrites alloyed with iron. For example, a 2.18% NiO glass on NiFe melted for 2 hours at 1000°C resulted in a 32° contact angle, fair adherence, NiFe dendrites in the glass near the interface, and a final glass composition of approximately 0% NiO and 5% FeO. Very little sodium was lost from the glass, indicating that reaction (7) did not proceed to any great extent. However, a 3.20% NiO glass melted on NiFe resulted in a zero contact angle, good adherence, loss of sodium from the glass, an Ni layer at the interface, and 15% FeO in the glass. Reaction (7) was evidently proceeding at a faster rate in this case than reaction (13) which had been retarded due to the presence of nickel in the alloy substrate.

In furnace II the only reaction taking place is the redox reaction between the NiO and the Fe in the substrate alloy resulting in NiFe dendrites in the glass, good adherence, and high contact angles.

NiCo-NiO Glass

This system is very similar to the Co-NiO glass system in that a redox reaction occurred between the NiO in the glass and the Co in the substrate (Eq. (14)) resulting in NiCo dendrites that grew from the interface into the glass. Again, however, the negative free energy of reaction (14) is sufficiently low so that the rate of this reaction was less than the rate of reaction (11) in furnace I after some CoO had been dissolved in the glass from reaction (14). In other words, the sodium

in the glass was more easily reduced than the nickel. For glasses containing more than 3.20% NiO reaction (11) proceeded at a fast enough rate so that the glass wetted the metal before the NiCo dendrites grew very far into the glass. For example, a 7.55% NiO glass melted on NiCo resulted in a final contact angle of 5°, loss of sodium from the glass, formation of NiCo dendrites in the glass near the interface, and a final glass composition of approximately 14% CoO and 1% NiO. The adherence was good as soon as the dendrites formed. Figures 36, 37, and 38 are oscilloscope traces of this interface while Fig. 39 is a photomicrograph of the same interfacial area. The NiCo dendrites extending into the glass from the base metal are clearly visible.

In furnace II only reaction (14) proceeded with NiCo dendrites forming in the glass. High contact angles and good adherence were obtained.

D. FeO, CoO, and NiO Containing Glasses on Gold and Platinum

A few contact angles were determined in both furnaces for NiO, CoO, and FeO glass on the noble metals, gold and platinum. All glasses, regardless of amount or specie of oxide, when melted on gold resulted in a 60° contact angle and poor adherence in both furnace I and II. Volpe, et al.[13] found that the contact angle of NS_2 glass on gold at 1000°C was unaffected by the presence of either oxygen, carbon dioxide, water vapor, or hydrogen in the furnace atmosphere and remained at 60° for as long as 10 hours. It is apparent that the oxidation potential of gold is so low that a reaction similar to reactions (7), (1) and (11) does not take place in furnace I. The contact angle is determined solely by the surface energy forces acting on the periphery of the drop and represents a steady state condition. All glasses retained their

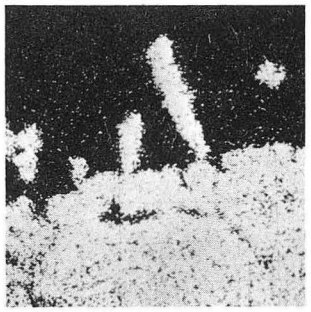

Fig. 36

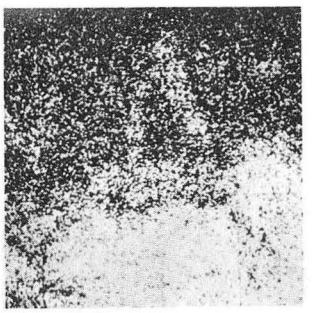

Fig. 37

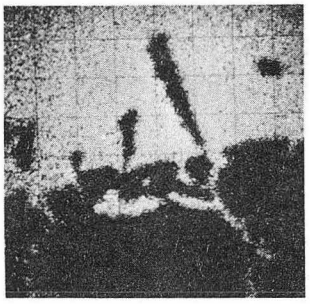

Fig. 38

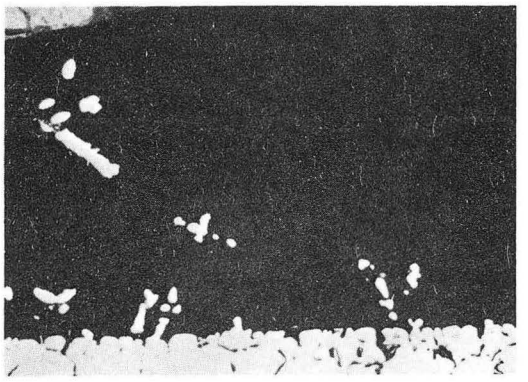

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Fig. 39

Fig. 36 Oscilloscope trace of a 7.55% NiO glass-NiCo interface, Ni radiation. (640×).

Fig. 37 Oscilloscope trace of a 7.55% NiO glass-NiCo interface, Co radiation. (640×).

Fig. 38 Oscilloscope trace of a 7.55% NiO glass-NiCo interface, Si radiation. (640×).

Fig. 39 7.55% NiO glass-NiCo interface showing dendrite formation. (250×).

original colors when melted on gold in either furnace.

When the oxide containing glasses were melted on platinum, the contact angles observed were in the range 12-18° in both furnaces and the adherence obtained was quite good. Even the sodium disilicate glass with no oxide additions exhibited a 16° contact angle and good aherence. It has been found previously[13,14] that platinum has a strong affinity for oxygen and that the solubility of oxygen in platinum, although not known, must be quite high. It is possible that in both furnaces, with their low oxygen pressures, platinum is unsaturated with respect to oxygen. The oxygen is then obtained from the glass through a reaction similar to reactions (7), (10) and (11):

$$Na_2Si_2O_{5(gl)} + Pt_{(s)} \quad PtO_{(s)} + 2SiO_{2(gl)} + 2Na_{(g)} \uparrow \qquad (15)$$

The platinum oxide formed is not stable in the bulk phase at 1000°C;[15] however, it could exist as a dissolved constituent in the metal or in the glass. No data is available concerning the solubility of (PtO) in NS_2 glass; however, it should be extremely small. Thus, the glass interface becomes saturated with (PtO) very quickly giving the observed good adherence.

IV. DISCUSSION OF REACTIONS IN FURNACE I

When glasses with additions of transition metal oxides were heated on the metals iron, cobalt, nickel and their alloys in furnace I, an overall reaction of the form

$$Na_2O_{(gl)} + M_{(s)} = MO_{(gl)} + 2\ Na_{(g)} \uparrow \qquad (16)$$

was frequently observed as indicated by a loss of sodium from the glass which appeared as a deposit on cdd portions of the vacuum chamber and an enrichment of the glass with the oxide of the substrate metal. This reaction was also associated with an increased wetting of the metal by the liquid glass and, in many cases, with a spreading of the glass on the metal. This enhancement in wetting can be attributed to a reduction of the interfacial energy by a contribution from the free energy of the reaction, the actual amount being dependent on the magnitude of the free energy and the rate of reaction.

Reaction (16) did not take place in furnace II, however. Conditions in furnace I thus apparently played a role in the development of a driving force for the reaction to proceed. The operating difference in the two furnaces is the nature of the atmosphere. Furnace I, with the presence of a carbon heating element, has a very low oxygen pressure (10^{-19} atm, at 1000°C) and an atmosphere consisting mainly of carbon monoxide due to the reactions:

$$C_{(s)} + 1/2\ O_{2(g)} = CO_{(g)} \qquad \Delta F^{\circ}_{1000} = -53.7 \text{ kcal} \qquad (17)$$

and

$$C_{(s)} + CO_{2(g)} = 2CO_{(g)} \qquad \Delta F^{\circ}_{1000} = -12.7 \text{ kcal} \tag{18}$$

From Eq. (18) the equilibrium CO_2 and CO pressures were calculated. From these values an activity of MO (or oxygen) in the metal substrate was determined from the equation:

$$MO(\text{in } M)_{(s)} + CO_{(g)} = CO_{2(g)} + M_{(s)} \tag{19}$$

A sample calculation for the activity of FeO in Fe is shown in the Appendix. The following activity values were calculated at 1000°C: for FeO in Fe, 4×10^{-10}; CoO in Co, 9×10^{-12}; and NiO in Ni, 3×10^{-12}. The essentially pure metal substrates were thus unsaturated with respect to their metal oxides and a driving force therefore existed for the formation of metal oxide.

Equation (16) is an overall equation determined by the step reactions:

$$Na_2O_{(gl)} + 2e^{-} = O^{=} + 2Na_{(g)} \uparrow \tag{20}$$

$$M_{(s)} + O^{=} = MO_{(s)} + 2e^{-} \tag{21}$$

$$MO_{(s)} = MO_{(gl)} \tag{22}$$

which on summation result in the indicated equation. The metal oxide that forms at the interface between the metal and glass by Eqs. (20) and (21) can either be dissolved by the glass or by the metal, both of which are unsaturated relative to the metal oxide. Experimentally, it has been shown that essentially all of the oxide is dissolved by the glass (Eq. (22)) as would be expected on the basis that diffusion rates are generally considerably faster in liquids than solids. It is also possible that the solution by the glass is energetically more favorable. The metal then remains unsaturated and the reaction continues with Eq. (21) as the continuing driving force. Undoubtedly, any enrichment of the base metal with the oxide is counteracted by a reaction with the atmosphere according to Eq. (19). A dynamic situation prevails so that, if the reaction rates are fast enough, reaction (16) continues until all the sodium in the glass is reduced.

The Na_2O in the sodium disilicate glass does not exist as molecular Na_2O but is incorporated into the glass structure as Si-O-Na bonds. On addition of small amounts of metal oxide to the glass (3-9%) the oxygen-to-silicon ratio and the number of non-bridging oxygens are increased. The metal ions coordinate with more oxygens than do the sodium ions thus resulting in a greater screening effect on the silicon. This structural change results in a weakening of the Si-O-Na bonds, and at some point reaction (16) proceeds. No data is available concerning the activity of Na_2O in NS_2 glass and how this activity varies with oxygen to silicon ratio. However, it appears that the activity of the Na_2O is increased considerably with small oxide additions to the glass. From the equilibrium constant for reactions (20) and (21):

$$K = \frac{a(MO)_s \ (PNa)^2_g}{a(M)_s \ a(Na_2O)_{gl}}$$

it can be seen that increasing the activity of the Na_2O in the glass decreases the equilibrium constant, thus increasing the rate of reaction. Correspondingly, an increase in the activity of MO in M decreases the tendency for reaction.

The presence of the carbon heating element in furnace I was responsible for the above reactions since it allowed reactions (17), (18) and (19) to take place. In furnace II the $P(O_2)$ of 10^{-16} atms is sufficient to maintain saturation of the metal with its oxide, i.e., an oxide activity of one or close to one in the metal. This analysis was verified by an experiment where a 9.1% FeO glass was heated on Fe to 1000°C for 2 hours in furnace II in the presence of a few small pieces of carbon in the hot zone. The glass wet the metal (θ=5°) after approximately 30 minutes and SiO_2 began to precipitate out of the glass after one hour. Condensed sodium was found on the cold parts of the furnace.

In summary, the unsaturated metal substrate in conjunction with an increased oxygen to silicon ratio in the glass due to added metal oxides created a driving force for the oxidation of the substrate metal and the reduction of soda in the glass. The rates of the reactions appear to be the fastest for the iron substrate systems and slowest for the nickel systems as would be expected on the basis of the respective oxidation potentials.

As the reactions proceed, the Na ions in the glass are replaced by the transition metal ions. If sufficient Na ions are present, the glass first becomes saturated with the substrate metal oxide and then a crystalline phase is precipitated. This phase is either silica or an orthosilicate as determined by the ternary Na_2O-SiO_2-MO phase diagram. If an orthosilicate is precipitated in the presence of more than one divalent cation, then its composition is determined by the following equation and its equilibrium constant.

$$(MO)^{I}_{(gl)} + (MO)^{II}_{cr} = (MO)^{II}_{gl} + (MO)^{I}_{cr} \qquad (22)$$

where

$$K = \frac{a(MO)^{II}_{gl}\, a\,(MO)^{I}_{cr}}{a(MO)^{II}_{cr}\, a(MO)^{I}_{gl}}$$

In addition to reaction (16) the reactions observed in furnace II that are independent of the oxygen pressure in the system also take place in furnace I. These are represented by Eqs. (9) and (12). The first one is a redox reaction involving the reduction of the valence of a dissolved ion by the base metal. The second is also a redox reaction that is dependent upon the existence of a negative standard free energy and is represented by a condition wherein the oxidation potential of the substrate metal is greater than that of the metal of a dissolved oxide in the glass. The latter reaction results in the formation of

metallic precipitates in the glass which are usually in the form of dendrites although layer precipitates are sometimes formed at the interface. The kinetics of the three types of reactions both individually and when they occur concurrently, and the factors controlling the morphology of the crystalline precipitates, have not been determined.

V. CONCLUSIONS

The following conclusions have been drawn regarding the systems explored in this study:

1. The low oxygen pressure and large CO/CO_2 ratio established by the presence of a carbon heating element in the furnace unsaturates the metal substrates Fe, Co, Ni, and their alloys with respect to oxygen which provides a driving force for the overall reaction:

$$Na_2Si_2O_{5(gl)} + M_{(s)} = MO_{(gl)} + 2SiO_{2(gl)} + 2Na_{(g)} \uparrow$$

leading to saturation of the glass with the base metal oxide and subsequent formation of precipitates if sufficiently extensive.

2. Saturation of the sodium disilicate glass at the interface with the base metal oxide, whether through reaction or initial addition to the glass, results in good adherence due to chemical bond formation across the glass-metal interface.

3. The addition of trivalent ions to the glass, such as Fe^{3+}, results in the reaction:

$$M^{3+}_{(gl)} + M_{(s)} = 2M^{2+}_{(gl)}$$

and also contributes to a weakening of the non-bridging oxygen bonds which results in a greater activity of sodium oxide, due to the screening effect of the trivalent ions.

4. When the substrate metal has a higher oxidation potential than the metal oxide in the glass, a redox reaction of the form

$$(MO)^{I}_{(gl)} + M^{II}_{(s)} = (MO)^{II}_{(gl)} + M^{I}_{(s)}$$

takes place with the formation of metal dendrites whose composition is determined by the metal oxide composition at the precipitation site. Good adherence is obtained through mechanical interlocking of the metal dendrites with the glass.

5. The wetting and adherence of sodium disilicate glass on the noble metals, gold and platinum, is determined by their oxygen solubilities. Platinum has a high oxygen solubility resulting in an unsaturated condition which leads to wetting and good adherence. Gold has an extremely low oxygen solubility resulting in saturation which leads to high contact angles and poor adherence.

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to Dr. Joseph A. Pask for his advice in carrying out this investigation; to George Dahl for his assistance in polishing and photographing specimens; to George Georgakopoulous for his assistance with the electron microprobe; and to the staff and personnel of the Inorganic Materials Research Division of the Lawrence Radiation Laboratory for their support.

This work was done under the auspices of the United States Atomic Energy Commission.

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APPENDIX

Sample calculations of activity of FeO in Fe in Furnace I.[19]

$$C + CO_2 = 2CO \qquad \Delta F^{\circ}_{1000} = -12.7 \text{ kcal}$$

$$\Delta F_T = \Delta F^{\circ}_T + RTmK$$

At equilibrium $\Delta F_T = 0$

$$\therefore F^{\circ}_T = -RTlnK$$

$$-12.7 = -5.82 \ln \frac{(P_{CO})^2}{P_{CO_2}}$$

$$\frac{(P_{CO})^2}{P_{CO_2}} = 10^{2 \cdot 2} = 159 \quad (1)$$

Since total pressure of system is $\sim 10^{-8}$ atm and consists mainly of CO with some CO_2 and O_2, one can write:

$$P_{CO} + P_{CO_2} + P_{O_2} = 10^{-8} \text{ atm}$$

P_{O_2} and P_{CO_2} are so small compared to P_{CO} they can be neglected, therefore

$$P_{CO} \sim 10^{-8} \text{ atm} \rightarrow$$

From Eq. (1) above

$$P_{CO_2} = \frac{(10^{-8})^2}{159} \sim 10^{-18} \text{ atm}$$

Now, one can set up the relation:

$$FeO(\text{in Fe}) + CO_{(g)} \rightarrow Fe + CO_{2(g)} \qquad \Delta F^{\circ}_{1000} = 2.1 \text{ kcal}$$

$$2.1 = -5.8 \ln \frac{(P_{CO_2})}{(P_{CO})(A\ FeO)}$$

using previously determined values for P_{CO_2} and P_{CO} one obtains

$$A\ FeO(\text{in Fe}) = 4 \times 10^{-10}$$

So one can consider the activity of FeO in Fe as being 4×10^{-10}

TABLE IV

Standard Free Energies of Formation from the Elements at 1000°C (1273°K)

$Na_{(g)}$	-	0[16]
$Na_2O_{(\ell)}$	-	-52.0 kcal/mole[17]
$Na_2Si_2O_{5(gl)}$	-	-440 kcal/mole[18]
$SiO_{2(s)}$	-	-155.5 kcal/mole[17]
$Fe_2SiO_{4(s)}$	-	-244 kcal/mole[16]
$Fe_xO_{(s)}$	-	-43.15 kcal/mole[17]
$Fe_3O_{4(s)}$	-	-169.3 kcal/mole[17]
$Fe_2O_{3(s)}$	-	-117.9 kcal/mole[17]
$Co_2SiO_{4(s)}$	-	-225 kcal/mole (estimated)
$CoO_{(s)}$	-	-34.6 kcal/mole[17]
$Co_3O_{4(s)}$	-	-102.8 kcal/mole[17]
$Ni_2SiO_{4(s)}$	-	-216 kcal/mole (estimated)
$NiO_{(s)}$	-	-30.4 kcal/mole[17]

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