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EFFECT OF COMPOSITIONS ON GLASS-METAL INTERFACE REACTIONS AND ADHERENCE

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ABSTRACT

Reduction-oxidation reactions and enhanced wetting or spreading of $Na_2Fe_xSi_2O_{5+x}$, $Na_2Co_xSi_2O_{5+x}$, and $Na_2Ni_xSi_2O_{5+x}$ glasses on substrates of Fe, Co, Ni, NiFe and NiCo were observed at 1000°C at low partial pressures of O_2 and Na vapors as the O/Si ratio of the glass was increased. Whtn the substrate metal had a higher oxidation potential than the metal of one of the cations in the glass, e.g., CoO containing glass on Fe, redox reactions resulted in the formation of metallic precipitates under all conditions. A third type of redox reaction based on reduction of the valence of a cation in the glass, e.g., Fe^{+3} to Fe^{+2}, also occurred. Adherence developed between substrates and glasses containing the substrate oxide. All redox reactions increased the substrate oxide content in the glass at the interface and thus improved adherence.

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I. Introduction

Equilibrium compositions and maximum adherence of glass to metal have been shown to occur at the interface when it is saturated with the oxide of the lowest valence cation of the substrate metal. If saturation does not exist, reactions can occur at the interface under certain conditions that introduce substrate oxide into the glass. These concepts have been discussed as applied to systems of iron substrates and sodium silicate glasses containing iron oxide in atmospheres of low partial pressures of oxygen.[1]

The purpose of this investigation was to extend and apply these concepts to other systems. Studies were made of the interfacial reactions, degree of wetting and the resulting adherence in systems of sodium disilicate (NS_2) glasses containing varying amounts of iron, cobalt, or nickel oxides in contact with Fe, Co, Ni, NiFe or NiCo substrates under several atmospheric conditions.

II. Experimental

(1) Materials

Three series of glasses were prepared. One composition series consisted of NS_2 with additions of 0, 2.9, 6.0, 9.1, 16.1, 28.0 and 44.5 w/o FeO. The preparation procedure for these glasses has been described.[1] The second series consisted of 0, 2.0, 5.7, 9.1, 15.3, 19.4 and 25.4 w/o additions of CoO to NS_2; the third, NS_2 with additions of 0, 1.1, 2.2, 3.2, 5.1, 6.5, 7.0 and 7.6 w/o NiO. These glasses were prepared from NS_2 powder (Philadelphia Quartz Co.) and reagent grade CoO and NiO powders. They were dry mixed and melted in platinum crucibles in air at 1400°C.

The specimens of Fe, Co and Ni were obtained from Materials Research Corp., Orangeburg, N.Y., and were approximately 99.995% pure. The NiFe and NiCo alloys of about 50-50 composition were made at the Lawrence Berkeley Laboratory* and had a purity of 99.99+%. All metal specimens were approximately 15 mils thick and were cut into 1/2 in. by 1/2 in. 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.

(2) Experimental Conditions

Two furnaces provided different atmospheric test conditions at the experimental temperature of 1000°C. Furnace I† consisted of a resistance heated graphite tube surrounded by a vacuum chamber, which has already been described.[1,2] Total pressures of 3×10^{-5} torr were attained at the test temperature. The P_{O_2} in this set up, taking into account leakages, was estimated to be less than about 10^{-20} atm due to the presence of carbon.

Furnace II consisted of a tantalum wire wound alumina tube inside of which was an alumina "dee" tube, surrounded by a vacuum bell jar. The total pressure at 1000°C was about 10^{-7} atm, and the P_{O_2} was approximately 10^{-10} atm.

Selected specimens, after vertical cross-sectioning, were subjected to electron microprobe analysis to determine the presence of any

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*High-purity metals laboratory under the direction of S. F. Ravitz.

†Furnaces will be referred to in the text by the designated numeral.

reaction products and their composition as well as the composition of the glass. X-ray fluorescence photos and photomicrographs of the interfacial zones were also taken. Qualitative information on the strength of interfacial bonding was obtained by subjecting representative sessile drop specimens to bending. Poor adherence was indicated by separation of the glass from the metal substrate; and good adherence, by fracturing of the glass.

III. Results

(1) $Na_2Fe_xSi_2O_{5+x}$ Glasses

The sessile drop contact angles of $Na_2Si_2O_5$ glasses with increasing amounts of FeO on substrates of Fe, Co, Ni, NiFe and NiCo, after 2 h at 1000°C, are plotted in Fig. 1.* In furnace I, reactions of the type

$$M_s + Na_2O(\text{glass}) = M_sO(\text{interface}) + 2Na\uparrow \quad (1a)$$

$$M_sO(\text{interface}) = M_sO(\text{glass}) \quad (1b)$$

$$M_s + Na_2O(\text{glass}) = M_sO(\text{glass}) + 2Na\uparrow \quad (1)$$

occurred between the glasses and the substrate metal (M_s), whose rates increased with the FeO content of the glasses: a rapid increase of reaction rates was associated with a rapid drop in contact angle and also with spreading; and after continued reaction, with the appearance of Na deposits in the cold parts of the furnace set-up, including the

*The values for the Fe substrate are taken from Hoge, Brennan and Pask.[1]

viewing ports, and of precipitates in the glass. The following limited observations were made relative to the reactions and adherence for each of the substrates:

(a) On Fe--with 2.9 wt% FeO glass: Na loss, and poor adherence; with 6.0% FeO: Na loss, and fair adherence; with 9.1% FeO: Na loss, precipitates of SiO_2 and 25% FeO in glass at edge of drop and 17% FeO in glass in center, and good adherence around the edge.

(b) On Co--with 2.9 wt% FeO glass: Na loss, and poor adherence; with 9.1% FeO: Na loss, no precipitates and 9% FeO, 15% CoO in glass, and poor adherence; with 28.0% FeO: Na loss, and precipitates of $(Fe_{1-x}Co_x)SiO_4$, and good adherence.

(c) On Ni--with 2.9 wt% FeO glass: Na loss, and poor adherence; with 6.0% FeO: Na loss, precipitates of $(Ni_{1-x}Fe_x)SiO_4$, and good adherence; with 9.1% FeO: Na loss, precipitates of $(Ni_{1.8}Fe_{0.2})SiO_4$ and 8% FeO, 7% NiO in glass, and good adherence.

(d) On NiFe--with 2.9 wt% FeO glass: no Na loss, poor adherence; with 6.0% FeO: Na loss, precipitates of SiO_2 surrounded by Fe_2SiO_4 and 36% FeO, 0% NiO in glass, and good adherence.

(e) On NiCo--with 2.9 wt% FeO glass: no Na loss, poor adherence; with 6.0% FeO: Na loss, precipitates of $(Fe_{0.4}Ni_{0.4}Co_{1.2})SiO_4$ and 4% FeO, 2% NiO, 10% CoO in glass (Fig. 2), and fair adherence; with 16.1% FeO: reaction, precipitates, and good adherence.

In furnace II a continuous decrease in contact angle occurred in each series with an increase of FeO in the glass, the greatest decrease occurring for the series with Fe and NiFe substrates (Fig. 1). Adherence also developed in the latter two series; fair adherence started with

9.1% FeO glasses and reached excellent adherence with 44.5% FeO. Adherence was always poor with the Co, Ni and NiCo substrates. No reactions were observed in any of the series in furnace II.

(2) $Na_2Co_xSi_2O_{5+x}$ Glasses

The sessile drop contact angles of $Na_2Si_2O_5$ glasses with increasing amounts of CoO on substrates of Co, Fe, Ni, NiFe and NiCo, after 2 h at 1000°C, are plotted in Fig. 1. In furnace I, reactions of the type represented by Eq. (1) occurred with a similar behavior pattern. In addition, on Fe and NiFe substrates reactions of the type

$$Fe + CoO(glass) = FeO(glass) + Co \qquad (2)$$

also took place. The following limited observations were made relative to the reactions and adherence in these series:

(a) On Co--with 2.0 wt% CoO glass: slight Na loss, and poor adherence; with 9.1% CoO: Na loss, no precipitates and 15% CoO in glass, and fair adherence; with 19.4% CoO: Na loss, precipitates of Co_2SiO_4 and 22% CoO in glass, and good adherence.

(b) On Fe--with 5.7 wt% CoO glass: Na loss, Fe_xCo_y dendrites, no precipitates and 17% FeO, <1% CoO in glass, and good adherence; with 19.4% CoO: Na loss, $Fe_{0.7}Co_{0.3}$ to $Fe_{0.2}Co_{0.8}$ dendrites, precipitates of SiO_2 and Fe_2SiO_4 and 33% FeO, ∿1% CoO in glass (Fig. 3), and good adherence.

(c) On Ni--with 15.3 wt% CoO glass: Na loss, precipitates of $(Co_{1.2}Ni_{0.8})SiO_4$ and 9% CoO, 4% NiO in glass, and fair adherence; with

25.4% CoO: Na loss, precipitates of (Ni,Co)O and 17% CoO, 7% NiO in glass, and good adherence.

(d) On NiFe--with 2.0 wt% CoO glass: slight Na loss, Fe_xCo_y dendrites, no precipitates and 4% FeO, <1% NiO in glass, and good adherence; with 9.1% CoO: Na loss, $Co_xNi_yFe_z$ layer at interface, precipitates of SiO_2 and 22% FeO, 1% CoO, 0% NiO in glass (Fig. 4), and good adherence.

(e) On NiCo--with 25.4 wt% CoO glass: Na loss, precipitates of $Co_{1.7}Ni_{0.3}SiO_4$ and 22% CoO, 4% NiO in glass, and good adherence.

In furnace II, no reactions of the type represented by Eq. (1) were observed. Fe_xCo_y dendrites, however, formed in the glasses on Fe and NiFe substrates; for example, a glass with 25.4% CoO on NiFe, after reaction, showed no Na loss, 7% CoO and 19% FeO. Presence of dendrites led to development of adherence. Good adherence was also obtained in the combinations with the Co and NiCo substrates as the CoO content of the glass was increased to 25.4%. Poor adherence and no reactions were realized with the Ni substrate.

(3) $Na_2Ni_xSi_2O_{5+x}$ Glasses

The sessile drop contact angles of $Na_2Si_2O_5$ glasses with increasing amounts of NiO on substrates of Ni, Fe, Co, NiFe and NiCo are plotted in Fig. 1. In furnace I, reactions of the type represented by Eq. (1) occurred. Reactions of the type

$$Fe + NiO(glass) = FeO(glass) + Ni \qquad (3)$$

$$Co + NiO(glass) = CoO(glass) + Ni \qquad (4)$$

also took place. As before, reactions continued throughout the test period and steady state conditions were not reached; the angles in the figure thus represent estimates after 2 h at 1000°C. The following limited observations were made relative to the reactions and adherence in these series:

(a) On Ni--with 7.0 wt% NiO glass: Na loss, no precipitates, and good adherence; with 7.6% NiO: Na loss, precipitates of Ni_2SiO_4, and good adherence.

(b) On Fe--with 3.2 wt% NiO glass: slight Na loss, many Ni_xFe_y dendrites, no precipitates, and good adherence; with 7.6% NiO: Na loss, $Fe_{0.8}Ni_{0.2}$ to $Fe_{0.5}Ni_{0.5}$ dendrites, no precipitates and <1% NiO, 15% FeO in glass, and good adherence.

(c) On Co--with 3.2 wt% NiO glass: Na loss, some Ni_xCo_y dendrites, no precipitates, and good adherence; with 7.6% NiO: Na loss, Ni_xCo_y dendrites, no precipitates and 1% NiO, 17% CoO in glass (Fig. 5), and good adherence.

(d) On NiFe--with 2.2 wt% NiO glass: slight Na loss, Ni_xFe_y dendrites near interface, no precipitates and <1% NiO, 5% FeO in glass, and fair adherence; with 3.2% NiO; Na loss, Ni-rich layer at interface, no precipitates and 15% FeO in glass, and good adherence.

(e) On NiCo--with 3.2 wt% NiO glass: Na loss, some Ni_xCo_y dendrites, no precipitates, and good adherence; with 7.6% NiO: Na loss, Ni_xCo_y dendrites, no precipitates and 1% NiO, 14% CoO in glass, and good adherence.

In furnace II, no reactions of the type represented by Eq. (1) were observed. Good adherence was obtained on a Ni substrate as the NiO content of the glass increased to 7.6%. All other substrates containing Fe and Co reacted with glasses containing NiO according to Eqs. (3) and (4) to form dendrites which in most cases resulted in adherence. For example, a glass with 7.6% NiO on Fe, after reaction, showed no Na loss, <1% NiO and 7% FeO.

(4) $Na_2Si_2O_5$ + 10% Fe_2O_3 Glass

The sessile drop contact angle of this glass on Fe in furnace II was 34° and fair adherence was obtained. A reaction occurred as indicated by the roughening at the interface in Fig. 6, as previously reported,[3] according to the reaction represented by:

$$Fe + Fe_2O_3(glass) = 3FeO(glass) \qquad (5)$$

The Fe in the glass, calculated as FeO, was found to be 15%. In furnace I on Fe, an additional reaction of the type represented by Eq. (1) occurred as indicated by a loss of Na and appearance of SiO_2 precipitates after 2 h. The contact angle dropped to a nominal 0° in about a minute.

The glass reacted with Co in furnace I resulting in a contact angle of about 0° in a few minutes. After 2 h, FeO in the glass, as calculated from the Fe content, was 12% and CoO was 10%; precipitates of $(Fe_{1-x}Co_x)SiO_4$ also formed.

IV. Discussion

(1) Reactions

The observed reactions are of the oxidation-reduction type and can be classified into three categories: the first two involving the reduction of a cation in the glass to the atomic state, and the third to a lower valence. The first two types can be represented in general by Eq. (6)

$$M_s + MO(gl) = M_sO(gl) + M \qquad (6)$$

and can be differentiated on the basis of whether ΔF^o (the standard free energy) is positive or negative. The third type is represented by Eq. (5), which has a negative ΔF^o.

(A) Reduction to Atomic State, Positive ΔF^o: This type is represented by Eq. (1) which is the summation of step reactions (1a) and (1b). ΔF^o is positive because the oxidation potentials of the substrate metals, M_s, are lower than that of Na which is the reduced cation in the glass. The standard oxidation potentials in volts at 25°C of interest are: $Na \rightarrow Na^+$, +2.71; $Fe \rightarrow Fe^{2+}$, +0.44; $Co \rightarrow Co^{2+}$, +0.28; $Ni \rightarrow Ni^{2+}$, +0.23: $Fe^{2+} \rightarrow Fe^{3+}$, -0.77. This type of reaction becomes feasible only when the activity quotient (equilibrium constant) for reaction (1a), shown in Eq. (7) is sufficiently smaller than one to result in an overall negative ΔF. This occurrence can be realized when the experimental temperature is above

$$\Delta F = \Delta F^o + RT \ln \frac{a(M_sO)_{int}(P_{Na})^2}{a(Na_2O)_{gl}} \qquad (7)$$

the boiling point of the elemental product. An examination of Fig. 1 indicates that for equivalent systems the reactivity is greater in furnace I than II (because of a lower P_{O_2}), and for a given series the reactivity increases with amount of M_sO (corresponding to an increase of the O/Si ratio of the liquid). In any case, the P_{Na} at the interface must be sufficiently low; it will remain low if there is a sink for atomic Na within the glass or the diffusion path through the glass layer is short and the ambient atmosphere has a low P_{Na} and a low total pressure. A low P_{O_2} (less than the equilibrium P_{O_2} of M_sO) results in an increase of the surface energy of M_s and a reaction of the Eq. (1) type. The equilibrium P_{O_2} at 1000°C for $Fe_{0.95}O$ is 1.52×10^{-15} atm, for CoO--1.38×10^{-12} atm, and for NiO--3.47×10^{-11} atm; all of which are between the estimated P_{O_2} in furnace I of $\sim 10^{-20}$ atm and $\sim 10^{-10}$ atm in furnace II. The dependence of the rate of this reaction on the P_{O_2} indicates that the controlling step of the reaction is Eq. (1a). At equilibrium $a(M_sO)_{int}$ will equal $a(M_sO)_{gl}$ as previously discussed.[1]

The increased reactivity with increasing O/Si ratio indicates that the $a(M_sO)_{int}/a(Na_2O)_{gl}$ ratio is remaining favorable, probably due to an increasing $a(Na_2O)_{gl}$ to counteract the increasing $a(M_sO)_{gl}$, and that ΔF^o is also becoming less positive. The $a(M_sO)_{gl}$ becomes one when $Na_2Si_2O_5$ liquid becomes saturated with M_sO; at 1000°C the saturation value for $Fe_{0.95}O$ is 46 w/o, CoO--28 w/o, and NiO--7.8 w/o.[4]

Reaction (1) results in a replacement of $2Na^+$ in the liquid with M_s^{2+} with no change in the O/Si ratio; the resulting Na vapor was observed to deposit on the cold parts of furnace I. This reaction continues until the liquid becomes saturated with a phase that begins to

precipitate. The reaction for the system Fe substrate-$Na_2Fe_xSi_2O_{5+x}$ can be followed on the $FeO-Na_2O-SiO_2$ phase diagram (Fig. 1 in ref. 1). Phase diagrams for corresponding $CoO-Na_2O-SiO_2$ and $NiO-Na_2O-SiO_2$ systems are not available, but in all three cases the observed reaction precipitates are SiO_2 in the liquids with the smaller O/Si ratios, isomorphous orthosilicates for the larger O/Si ratios, and isomorphous oxides for compositions just short of saturation. The primary phase fields at the interface with the 100% liquid region, however, would be expected to be smaller in the systems with CoO and NiO because of their lower saturation amounts in $Na_2Si_2O_5$. If a crystal is precipitated from a liquid containing several transition metal cations (Fe^{++}, Co^{++}, Ni^{++}), then solid solutions form whose compositions are determined by the composition of the liquid at the crystallization site according to Eq. (8), the equilibrium constant being indicated by Eq. (9) when the crystal is either an orthosilicate ($M_s{}_2SiO_4$) or an oxide (M_sO).

$$M_sO^{I}(\text{glass}) + M_sO^{II}(\text{crystal}) = M_sO^{II}(\text{glass}) + M_sO^{I}(\text{crystal}) \qquad (8)$$

$$K = \frac{a(M_sO^{II})_{gl} \cdot a(M_sO^{I})_{cr}}{a(M_sO^{II})_{cr} \cdot a(M_sO^{I})_{gl}} \qquad (9)$$

It should be noted that all combinations of substrate metals and $Na_2Si_2O_5$ glasses containing relatively small additions of transition metal oxides showed reactions involving loss of Na under conditions of furnace I. This reaction was generally associated with a rapid drop in

contact angle and spreading due to the contribution of the reaction to the driving force for wetting.[5] It is of further interest to note that glasses with small additions of iron oxide are more reactive on the Ni, Co, NiFe and NiCo substrates than Fe, as would be expected because of their lower $a(M_sO)_{int}$ values due to the absence of M_sO in the glass at the start of the reaction. In the case of alloys, the element with the highest oxidation potential takes part in the reaction more extensively: both Ni and Co in NiCo were oxidized, and in NiFe essentially only Fe was oxidized. The critical composition variable, however, is the O/Si ratio of the liquid.

(B) Reduction to Atomic State, Negative $\Delta F°$: The second type of redox reaction is represented generally by Eq. (6) and specifically by Eqs. (2), (3) and (4). $\Delta F°$ is negative because the oxidation potential of M_s is higher than that of one of the cations in the glass. Since the reduced cations become metallic precipitates and the reactions are essentially independent of the ambient atmosphere, the activity quotient for these reactions is generally close to one. The reactions thus proceeded spontaneously in furnaces I and II. Metallic precipitates were therefore observed in the glass at the interface after reactions of glasses containing CoO with Fe and NiFe substrates, and glasses containing NiO with Fe, Co, NiFe and NiCo substrates.

Equations (2), (3) and (4) represent the initial reaction, but just as soon as substrate cations are introduced into the glass, the precipitates become alloys since these elements form solid solutions readily because their ΔF of formation is negative. The composition of the dendrites, as described by Borom et al.[6,7] is determined by the

composition of the glass adjoining the precipitate according to the equilibrium constant indicated in Eq. (10).

$$K = \frac{a(M_s O^{II})_{gl} \cdot a(M_s{}^{I})_{den}}{a(M_s O^{I})_{gl} \cdot a(M_s{}^{II})_{den}} \tag{10}$$

In a binary alloy substrate in which one of the elements has a higher oxidation potential and the other lower than the element of the cation that is reduced, only the former element is oxidized, e.g., NiFe with CoO(gl) reaction to form Fe_xCo_y precipitates.

In furnace I redox reactions of the first type also occurred in which M_sO was introduced into the glass by reduction of Na_2O(gl). The configuration of the metallic precipitates appeared to be dependent upon the relative rates of the two types of reactions, as indicated by the series of glasses with increasing CoO or NiO on NiFe substrate. At lower CoO or NiO contents the reaction rates resulted in the formation of dendrites in the glass, but at higher amounts of oxide when the reaction rates for the first type were faster a layer precipitate formed at the interface; in furnace II all of the glasses of both series formed dendrites. It is significant to note that Na reduced at the interface diffusing through the glass does not take part in the second type of reaction in the absence of nucleation sites.

It is of interest that the contact angles for the CoO series of glasses on Fe and the NiO series on Fe (Fig. 1) in furnace I did not drop and that no spreading occurred, as all of the other series did in furnace I. Observations indicated that the reaction forming the dendrites at the interface was relatively so much faster that the dendrites

formed a barrier to the spreading glass. It should also be noted that the ΔF of the metallic precipitate forming reaction in furnace II did not contribute to wetting since the internal energy of the substrate was not being affected.[5]

(C) Reduction in Valence State, Negative ΔF^{o}: The third type of redox reaction is represented by Eq. (5). For glass with Fe_2O_3 on Fe, ΔF^{o} is negative because the oxidation potential for Fe is greater than for Fe^{2+}. The reaction thus occurred in both furnaces, but in furnace I a reaction of the first type also occurred leading to the precipitation of SiO_2. On a Co substrate the precipitates were iron-cobalt orthosilicates.

The contact angle behavior was similar to that of the other series. In furnace II just the third type of reaction occurred that did not affect the internal energy of the substrate; therefore, the ΔF of the reaction did not contribute to the driving force for wetting. In furnace I, there was a contribution to wetting and spreading by a reaction of the first type.

(2) Adherence

In the absence of any extensive reactions maximum adherence was realized only when the starting glass composition approached saturation with the oxide of the substrate ($a(M_sO)_{gl} \rightarrow 1$), e.g., FeO containing glass on Fe or NiFe, NiO glass on Ni, because a chemical bond then forms across the interfacial transition zone. All of the FeO glasses on Ni, Co, or NiCo exhibited poor adherence; also, the contact angles for the glasses in these series did not decrease as much with FeO additions as with the Fe and NiFe substrates because the interfacial energies were

higher.

Good adherence can also be realized with a sufficient increase of the activity of the substrate oxide in the glass at the interface by the introduction of the substrate oxide by any of the redox reactions, the degree of adherence being proportional to the degree of saturation of the glass with the substrate oxide. The roughening of the interface by any of these reactions also contributes to the adherence because of an increase in the interfacial area.

Extensive dendrite formation, firmly attached to the substrate, also contributes to the development of adherence because of any mechanical interlocking that may occur. It is difficult, however, to determine the extent of this contribution since the redox reactions of the second type that cause the dendrites also bring in substrate oxide into the glass thus increasing the $a(M_sO)_{int}$ value which is necessary to develop a chemical bond across the interfacial zone.

V. Conclusions

Three types of oxidation-reduction reactions are potentially possible at glass-metal interfaces, all of which introduce substrate cations into the glass when the system is not at thermodynamic equilibrium. Reactions involving the reduction of a cation in the glass, e.g., Na^+, even though their standard free energies were positive, take place at temperatures above the boiling point of the reduced element under conditions when the P_{Na} at the interface remained low, the glass compositions had relatively higher O/Si ratios, and the P_{O_2} was low. Reactions involving the formation of metallic precipitates, e.g., CoFe and NiFe dendrites, or reduction of multivalent cations to a lower

valence, e.g., Fe^{3+} to Fe^{2+}, whose standard free energies are negative, take place under all experimental conditions.

Maximum adherence was obtained in the absence of reactions when the $a(M_sO)$ at the interface approached one, i.e., the substrate oxide content in the glass approached saturation. In the absence of saturation, all redox reactions contributed to the development of adherence because they introduced substrate cations into the interface, i.e., increased the $a(M_sO)_{int}$. Redox reactions that led to the formation of dendrites at the interface also contributed to adherence because of mechanical interlocking.

Addendum

It is always of interest to apply fundamental information to an applied problem, in this case, adherence of porcelain enamels. The enamel glass composition is complex and normally has many bubbles that contain oxidizing vapors due to the steps taken in the application of the coating to the substrate metal. The glass composition includes the "adherence oxides" CoO, NiO, CuO and Mn_2O_3.

The complex and low melting composition undoubtedly makes the glass a great deal more reactive in comparison with the glasses used in this study. Redox reactions of the first type can then occur under normal enameling conditions if sinks for Na released at the interface can be provided. The P_{Na} can thus be kept low by the Na reacting with the oxidizable gases in the bubbles at the bubble surfaces and the resulting Na_2O being incorporated into the glass where it again becomes available for subsequent redox reactions. The P_{Na} can also be kept low by the Na

participating in redox reactions with transition metal oxides in the glass leading to the formation of dendrites at nucleation sites provided by the bubble surfaces. These dendrites are isolated from the interface and do not in themselves contribute to adherence like the dendrites growing from nucleation sites on the substrate interface.

This study shows that one of the functions that the "nickel flash" commonly used in porcelain enameling practice performs is to increase the redox reactivity at the interface. The initial redox reaction of the second type at the interface also increases the overall reactivity at the interface by the formation of metallic alloy precipitates (dendrites or interface layer) that are more reactive than Fe. The characteristic features of the adherence oxide metals (Co, Ni and Cu) are their lower oxidation potential than Fe and their capability of forming alloys with Fe which leads to lower ΔF^{o} values for the reactions of the first type.

The transition metal oxide additions whose elements do not form alloys with iron, such as Mn, take part in the third type of redox reaction which involves a reduction of the Mn valence. This reaction also results in the introduction of substrate oxide into the glass at the interface.

All of the redox reactions involve the increase of the substrate oxide content, and thus the $a(M_sO)_{gl}$, at the interface which results in the formation of a chemical bond and good adherence. In the course of these reactions, the roughening of the interface and the formation of dendrites of the type firmly attached to the substrate result in a mechanical contribution to adherence. The kinetics of the various reactions determine the extent of the respective contributions.

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Figure Captions

Fig. 1. Contact angles on Fe, Ni, Co, NiFe and NiCo substrates on $Na_2Si_2O_5$ glasses containing increasing amounts of (a) FeO, (b) CoO, and (c) NiO, in furnaces I and II.

Fig. 2. Electron microprobe oscilloscope traces of a cross-section of a $Na_2Si_2O_5$ glass with 6% FeO on a NiCo substrate: (a) (upper left) Ni radiation, (b) (upper right) Fe radiation, (c) (lower left) Si radiation, and (d) (lower right) Co radiation. (640X)

Fig. 3. Electron microprobe oscilloscope traces of a cross-section of a $Na_2Si_2O_5$ glass with 19.4% CoO on a Fe substrate: (a) (upper left) backscattered electrons, bottom--substrate, middle--glass, and top--plastic (32X), (b) (upper right) Si radiation, (c) (lower left) Fe radiation, and (d) (lower right) Co radiation. (640X).

Fig. 4. Electron microprobe oscilloscope traces of a cross-section of a $Na_2Si_2O_5$ glass with 9.1% CoO on a NiFe substrate: (a) (upper left) Fe radiation, (b) (upper right) Ni radiation, (c) (lower left) Si radiation, and (d) (lower right) Co radiation. (640X).

Fig. 5. Electron microprobe oscilloscope traces of a cross-section of a $Na_2Si_2O_5$ glass with 7.6% NiO on a Co substrate: (a) (upper left) Ni radiation, (b) (upper right) Co radiation, (c) (lower left) Si radiation (640X), and (d) (lower right) backscattered electrons showing Ni_xCo_y dendrite formation (250X).

Fig. 6. Polished section of $Na_2Si_2O_5$ glass with 10% Fe_2O_3 on Fe in furnace II.

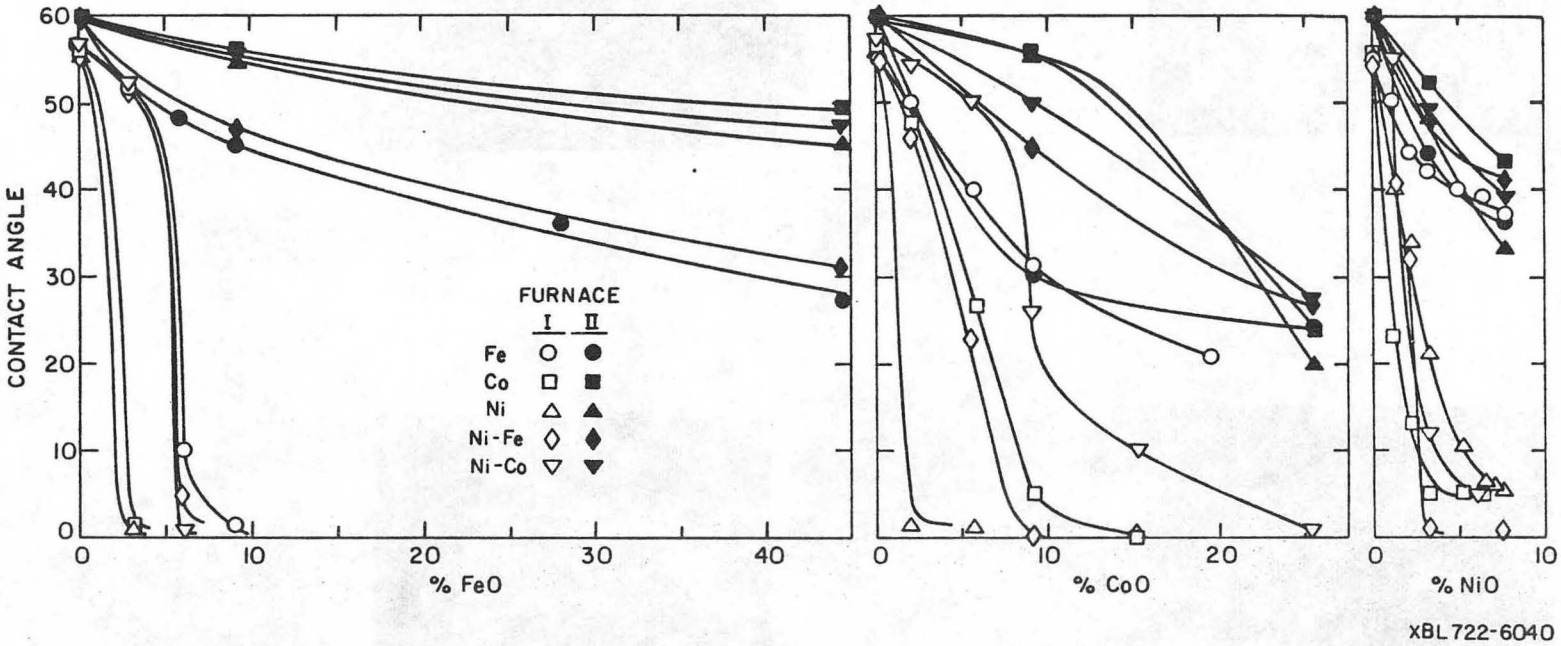
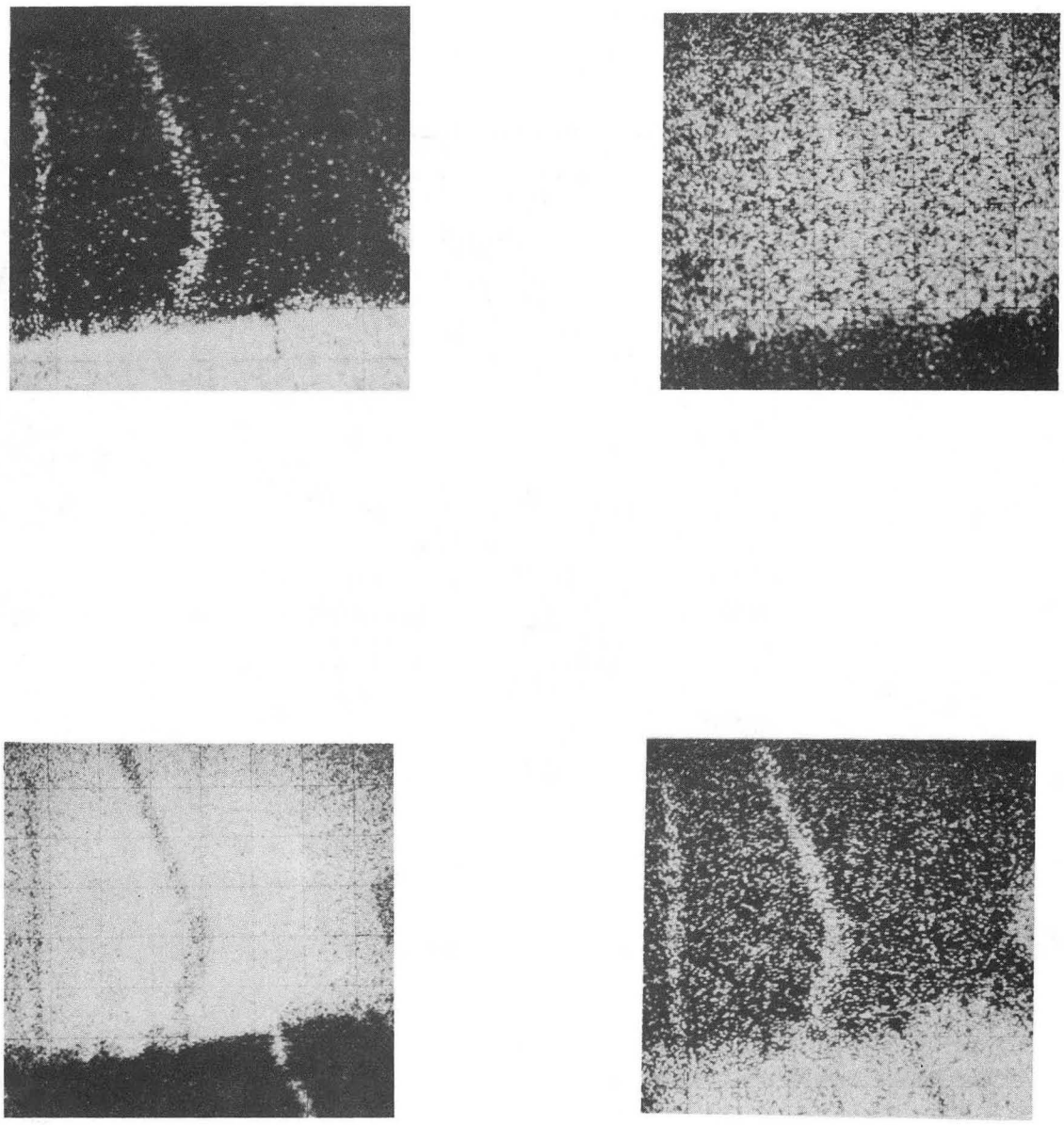
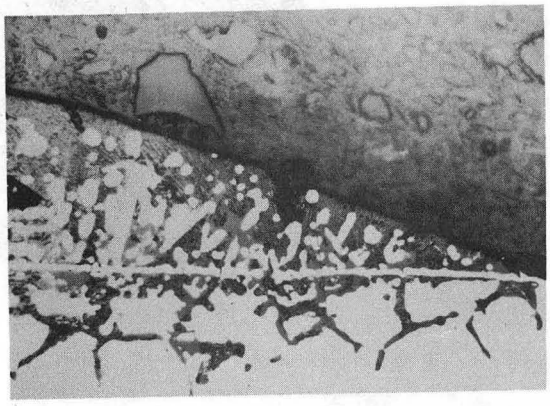

CONTACT ANGLE
60
50
40
30
20
10
0
0
10
20
30
40
% FeO
FURNACE
I II
Fe
Co
Ni
Ni-Fe
Ni-Co
0
10
20
% CoO
0
10
% NiO
XBL722-6040

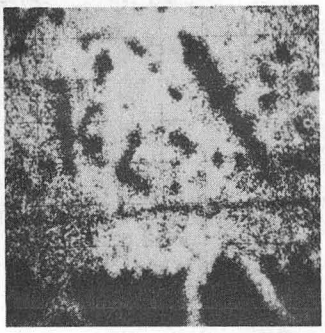
Fig. 1

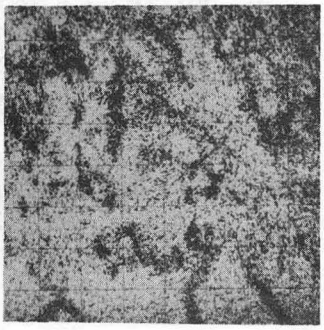


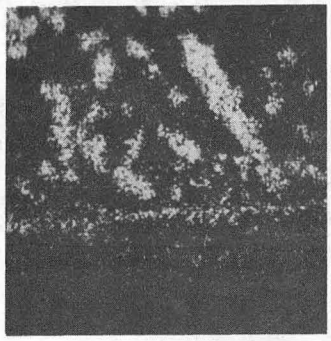
XBB 697-4571

Fig. 2



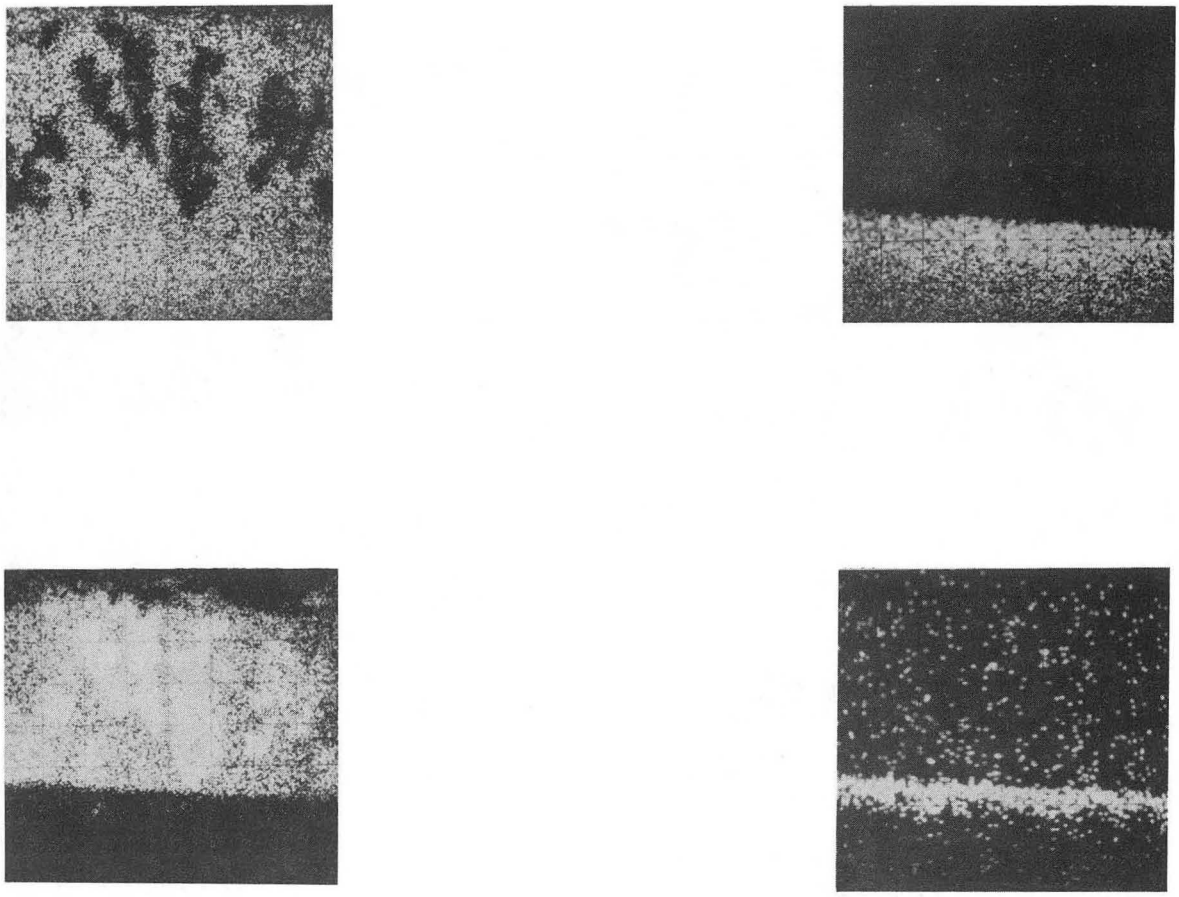






XBB 697-4569

Fig. 3



XBB 697-4565

Fig. 4

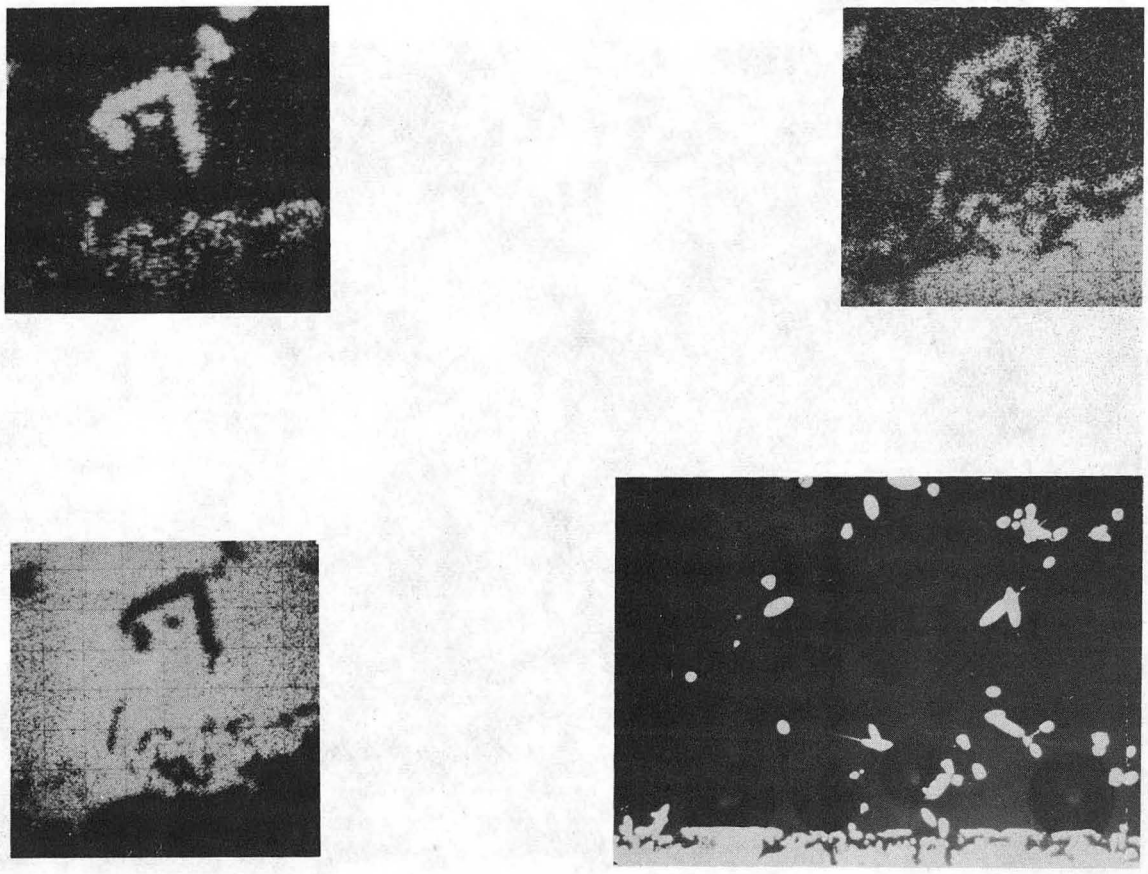


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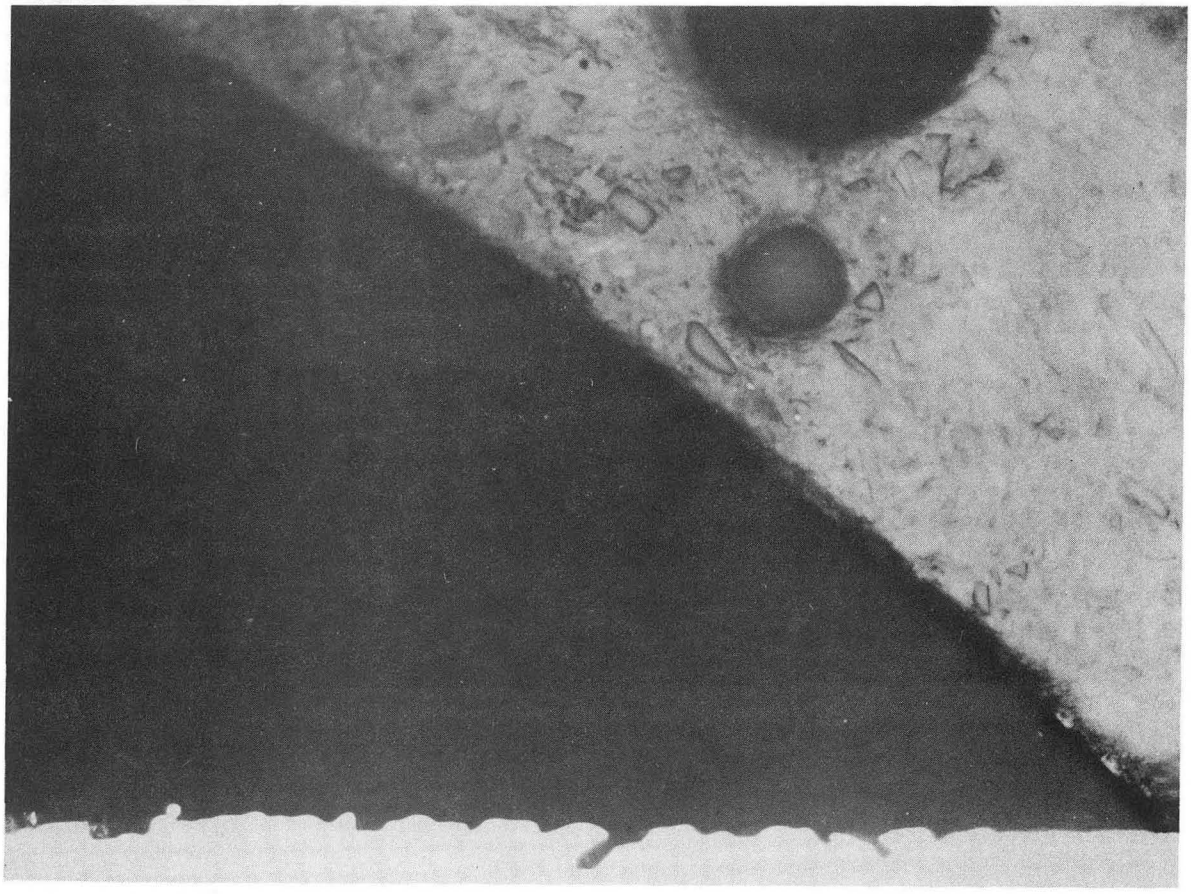
Fig. 5



XBB 697-4560

Fig. 6

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