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CHEMICAL REACTIONS AND ADHERENCE AT GLASS-METAL INTERFACES

by

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ABSTRACT: Good adherence of glass to metal is obtained when a continuous electronic structure, or chemical bond, exists in the interfacial zone. This continuity is realized when both the substrate metal and glass are saturated at the interface with the metal oxide, resulting in a transition oxide-like layer. In the loss of this oxide layer by diffusion into the glass, under certain conditions oxidation-reduction reactions can occur which bring substrate metal ions into the glass at the interface, thus maintaining saturation and the chemical bond, with a corresponding reduction of some metal ions in the glass. Two types of reductions can occur. Metal ions whose oxidation potentials are lower than those of the substrate metal (e.g., cobalt oxide in glass on iron) can be reduced to form metallic dendrites in the glass in the interfacial zone. Metal ions in the glass whose oxidation potentials are higher than those of the substrate metal (e.g., sodium oxide in glass on iron) can be reduced if the temperature is above the boiling point of the reduced metal and the compositions of the reacting phases are favorable.

The subject of chemical reactions at glass-metal interfaces is of great fundamental importance since such reactions play a major role in the development of adherence of porcelain enamels to metals. There have

been many studies and reports either on or related to the general problem of adherence, both within and outside the field of porcelain enamels. Although interpretations of experimental results have varied, each study has made some contribution in the development of an overall understanding of the conditions under which adherence is achieved that succeeding workers have built on either knowingly or unknowingly.

No effort will be made to review, survey or specifically analyze the voluminous literature. A monumental contribution in this direction has been made by King, Tripp and Duckworth[1] at the time they reported on their extensive adherence studies. The objective of this lecture will be to discuss our present understanding of the nature of the interfaces with and without adherence, the types of reactions and the conditions under which they occur at glass-metal interfaces, and the role that these reactions play in the development of adherence. Primarily, model systems will be used to illustrate points because of the complexity of the porcelain enamel glasses; the fundamentals on derived principles, however, are applicable to the porcelain enamel systems. Early studies at Berkeley were made in collaboration with Fulrath,[2] Adams,[3] and Gaidos.[4] Particular attention to the nature of the chemical reactions and their effect on adherence was first made in studies with Borom[5] and with Borom and Longwell.[6] A further extension of these studies has been made in yet unpublished studies of Brennan[7] and Hoge.[8]

Nature of Interfaces

The nature of and conditions at the interface are all-important in realizing adequate adherence. In our discussion we will not be concerned with problems associated with introduction of strains due to thermal

expansion mismatches of the glass and metal phases at the interface; it will be assumed that such problems are under control. We will also not be concerned with the mechanical contribution to adherence realized by a highly irregular interface obtained by abrasion or chemical erosion of the metal surface, or by chemical erosion during the firing of the enamel. Although such roughening of the interface contributes adherence and provides a safety factor in terms of a transition zone and a greater contact area, it is theoretically not necessary if a chemical bond (i.e., metallic, ionic, and/or covalent) is attained throughout the interface. A chemical bond means that continuity of the electronic structure exists across the interface as well as a continuity of the atomic structure.

To realize the continuity of the atomic and electronic structures, a transition layer or zone is needed that is compatible or in equilibrium with both the metal and glass at the interface. This zone is the oxide of the metal and is retained <u>only</u> when both the metal and glass <u>at the interface</u> are saturated with the metal oxide. Figure 1 shows schematic atomistic models of cross-sections across the interface when an oxide layer is present and also when absent. In the former case (upper sketch) a layer of metal atoms must exist between the bulk metal and oxide that has both metallic and ionic-covalent characteristics which results in a cross-sectional continuity of the chemical bond. In the latter case (bottom sketch), the glass comes in direct contact with the metal resulting in atomic continuity but not in electronic structure continuity; a van der Waals type of bonding then exists which is considerably weaker than a chemical bond. Another schematic way of identifying this principle is shown in Fig. 2. This picturization also emphasizes that only

a single layer of the oxide is necessary to realize chemical bonding across the interfacial zone.

Thermodynamically, equilibrium compositions across the interfacial zone can be expressed as having equal activities or chemical potentials of the oxide. The activities of the oxide are one, or essentially one, when an oxide layer is present and the adjoining phases are saturated with the oxide at the interface, as shown schematically in Fig. 3. The figure represents the condition when a glass with no dissolved metal oxide is sealed to a metal with an oxide layer. The glass at the interface dissolves the equilibrium or saturation amount of metal oxide, and the oxide diffuses into the bulk glass since the driving force is for the whole system to move towards thermodynamic equilibrium which is a uniform activity of the oxide. The solution reaction is faster than the diffusion flux rate so that the interfacial glass composition remains saturated and its oxide activity is essentially one as long as oxide remains, as represented by time t_1 and t_2. When the oxide layer has been completely dissolved, the diffusion process continues resulting in a drop of the oxide activities at the interface, as represented by t_3 and t_4. Chemical bonding exists when the activity of the oxide is one, and the bonding transforms to the van der Waals type as the activity drops towards zero.

The practical problem is then one of attaining and maintaining oxide saturation at the interface, preferably with no discrete and identifiable oxide layer since its presence leads to a decrease in strength. The initial saturation is achieved by solution of the oxide layer formed on the metal either by separate preoxidation, atmospherically

or chemically, or during the heating up period before the applied enamel powder coating melts and forms a continuous liquid film which retards or essentially prevents the metal from further oxidation. When the oxide layer is dissolved, the maintenance of saturation can only be achieved by chemical reactions that oxidize the base metal and introduce the metal cation in sufficient quantities into the glass at the interface.

The balance of the lecture will deal with a discussion of the possible reactions and the resulting effect on the transition zone at the interface. Illustrative experimental data was obtained in our laboratories. The base glass used in most experiments was sodium disilicate (32.5 w/o Na_2O, 67.5 SiO_2 and designated as Glass A); Glass B had CoO added (4.8 w/o CoO, 31.0 Na_2O, 64.2 SiO_2); and a series of glasses were also used with additions to Glass A of FeO up to 43 w/o. A commercial enamel glass without "adherence oxides" was also used in some experiments (38.2 w/o SiO_2, 19.0 B_2O_3, 3.7 Al_2O_3, 18.2 Na_2O, 2.0 K_2O, 10.3 CaO, 4.7 BaO, 2.9 F_2, 1.0 P_2O_5 and designated as Glass C); Glass D had additions of CoO, NiO, MnO, and CuO (36.8 w/o SiO_2, 18.2 B_2O_3, 3.5 Al_2O_3, 17.4 Na_2O, 1.9 K_2O, 9.9 CaO, 4.5 BaO, 2.8 F_2, 1.0 P_2O_5, 0.7 CoO, 1.3 NiO, 1.7 MnO, 0.3 CuO). Two types of iron specimens were used: Armco iron (0.015 w/o C, 0.029 Mn, 0.005 P, 0.025 S, 0.003 Si, with an undetermined amount of precipitated oxide particles); and Marz iron (8 ppm C, 1.2 S, 7.0 N, 7.2 O).

Solution of Oxide by Glass

Any oxide that forms on the metal prior to the formation of the glass interface is first dissolved by the glass at the firing temperature. Dissolution and diffusion studies[9] were made using couples of iron-rich

wüstite and Glass A (sodium disilicate) in the temperature range of 900 to 1100°C (1653 to 2013°F). Concentration profiles of SiO_2, Na_2O and FeO into the glass from the oxide interface were obtained by electron microprobe analyses of the cross-sections. Such an analysis of a specimen couple heated at 909°C (1670°F) is shown in Fig. 4. The interfacial composition remained constant for heatings for 5, 10, 20 and 50 hrs indicating that this was the equilibrium composition in contact with FeO under the conditions of the experiment and that the dissolution reaction rate was faster than the diffusion flux rate.

The change in composition as represented by the increase in the O/Si ratio in the glass at the interface due to the dissolution of FeO should be noted. The dissolution is not completely a simple dilution of the sodium disilicate as indicated by a higher Na_2O/SiO_2 ratio at the interface; this intermediate state occurs because of the extension of the chemical interdiffusion of Na^+ and Fe^{+2} beyond the dilution zone, in this case at approximately 1500μ from the interface.

The actual solubility of iron oxide in a glass is dependent upon its composition. This type of experiment is most convenient and straightforward for determining dissolution rates and the solubility limits at a given temperature.

Oxidation of Metal at Interface

When the glass dissolves the existing oxide layer and comes in contact with the metal, a driving force then exists for the oxidation of the metal. It is important that the system realizes such electrochemical reactions that oxidize the metal, for they are the means by which the interfacial zone, and thus the glass, maintains the required saturation

with the oxide of the metal. The possible reactions can be categorized as (1) gaseous oxidation, (2) redox--reduction of cation valence, and (3) redox--reduction of cations to metallic state.

(1) Gaseous Oxidation

Some oxidation of the base metal can occur by atmospheric oxygen if the composition of the glass is favorable. Experiments of Glass A and Glass B (with CoO) in contact with Armco iron in air at 950°C up to 24 hrs showed no weight gain, which would be required if atmospheric oxidation did occur.

Eubanks and Moore[10] working with an enamel frit composition (51.0 w/o SiO_2, 16.1 B_2O_3, 5.7 Al_2O_3, 15.4 Na_2O, 3.5 K_2O, 8.3 CaF_2) on iron showed that no oxidation, roughening or adherence occurred in oxygen atmospheres without cobalt oxide. Roughening of the interface and development of adherence occurred with enamels containing cobalt oxide that were fired in oxygen. Glass C at 870°C for 24 hrs did not show a weight gain, but Glass D (with CoO, NiO, MnO, and CuO) did. It would be expected that the additional presence of NiO, MnO and CuO, most likely MnO, has contributed to the oxidation.

The presence of these additive oxides, thus have provided some mechanism (probably electronic conductivity) for oxidation of metallic iron at the interface by introduction of oxygen from the atmosphere at the glass surface. This mechanism has been referred to as galvanic corrosion. In any case, in addition to roughening the interface, such a reaction will lead to the enrichment of the liquid composition at the interface in iron oxide.

Another possible supply of oxygen is in the entrapped water vapor in the bubbles that are normally present in enamels. The source of the water is the decomposition of the bentonitic-type of clay that is used as a suspending agent in the preparation of enamel slurries.

(2) Redox--Reduction of Cation Valence

If a glass containing Fe_2O_3 is melted on iron, a reaction between the ferric ions in the glass and the iron can take place:

$$Fe_2^{+3}\ O_3(gl) + Fe(s) = 3Fe^{+2}\ O(gl) \qquad (1)$$

This reaction has a standard free energy of -12 kcal and thus readily proceeds. As an example, Glass A with 10% Fe_2O_3 on Armco iron for 2 hrs at 1000°C showed a reaction at the interface as indicated by roughening, as seen in Fig. 5. The color of the glass changed from yellow-brown to green-blue and some adherence developed as expected with an enrichment of FeO.

Glass A containing increasing amounts of FeO, when melted on iron, did not show any roughening at the interface.[3] Adherence, however, improved with increase of FeO and reached a maximum at the saturation amount (Glass A with 43 w/o FeO at 1000°C).

(3) Redox--Reduction of Cations to Metallic State

These redox reactions are of greatest interest, for they probably occur most extensively; the substrate metal is oxidized by giving up electrons that are transferred to a cation in the glass which is reduced to the metallic state. A reaction between iron and Glass A is an example:

$$xFe + Na_2Si_2O_5 = Na_{2-2x}Fe_xSi_2O_5 + 2xNa \qquad (2)$$

This reaction can be given in the following general form (where gls refers to glass, and int to interface):

$$M_I^o + M_{II}^{+2}O(gls) = M_I^{+2}O(gls) + M_{II}^o \qquad (3)$$

The step reactions for Eq. (3) are:

$$M_I^o + O^{-2}(gls) = M_I^{+2}O(int) + 2e \qquad (4)$$

$$2e + M_{II}^{+2}O(gls) = O^{-2}(gls) + M_{II}^o \qquad (5)$$

$$M_I^{+2}O(int) = M_I^{+2}O(gls) \qquad (6)$$

The mechanism of the reaction at the interface as represented by the step reactions is subject to interpretation. If M_IO forms directly in the glass, then step reactions (4) and (6) can be combined to form step reaction (7):

$$M_I^o + O^{-2}(gls) = M_I^{+2}O(gls) + 2e \qquad (7)$$

Then, Eq. (3) would consist of step reactions (4) and (7) instead of (4), (5) and (6). In any case, the activity of $M_IO(gls)$ would not be affected since the M_IO activity in the transition zone would always have

a driving force towards equilibration and thus would tend to be equal in the glass, interface, and metal. If $M_I O$ formed at the interface by (4) and the activity of $M_I O$ in the glass was less than one, then the glass would immediately dissolve the formed $M_I O$.

The free energy equation for Eq. (3) is given by:

$$\Delta F = \Delta F^{o} + RT \ln \frac{a(M_I O(gls)) \cdot a(M_{II})}{a(M_{II} O(gls)) \cdot a(M_I)} \tag{8}$$

Thermodynamically, the reaction takes place at a given temperature if ΔF is negative, i.e., the energy for the system is reduced. If the standard free energy, ΔF^{o}, is negative, then the reaction is favorable. On the other hand, if ΔF^{o} is positive, then the reaction can still take place <u>only</u> if the activity quotient $a(M_I O(gls)) \cdot a(M_{II}) / a(M_{II} O(gls)) \cdot a(M_I)$ is sufficiently less than one (since the log of a number less than one is negative) to result in a negative ΔF.

Reaction (3) thus takes place most readily when ΔF^{o} is negative. This situation occurs when the glass or enamel has oxides whose free energy of formation is larger than that of the oxide of the substrate metal or whose metallic element has a lower oxidation potential than that of the substrate metal. An example is a glass containing CoO applied on iron:

$$Fe + CoO(gls) = FeO(gls) + Co \tag{9}$$

The ΔF for this reaction is -9 kcal/mole at 1000°C. NiO and CuO in the glass can also be reduced when the glass is in contact with iron.

Many studies have been based on this reaction. Its nature is illustrated in Fig. 6. It shows the concentration profiles that formed when Glass B was heated in air at 950°C (1742°F) for 10 minutes in contact with Armco iron that had been preoxidized to form about a 2 μm thick oxide layer. This specimen, including one that had been heated for 9 hrs, did not show any gain in weight. Therefore, the profiles in the glass are the result of the solution of the oxide and the redox reaction represented by Eq. (9). The drop in SiO_2 and Na_2O content at the interface is primarily due to the initial dissolution of the oxide layer; subsequent introduction of iron is due to the reduction of cobalt oxide.

The reduction of the cobalt oxide leads to the precipitation of metallic cobalt first as a layer at the interface and then as dendrites. The nature of the reaction is shown in Fig. 7: the top photograph is of a cross-section of Glass C and Armco iron, and the bottom two photographs (middle one taken with reflected light, and bottom one with dark field illumination) are of Glass D and Armco iron.[5] Both specimens were heated at 900°C for 28 hrs in platinum crucibles and showed a similar weight gain; the top of the crucible in each case was to the right. The roughening of the interface in the top specimen was due to atmospheric oxidation with the platinum serving as a path for electrons from the iron to the glass surface where oxygen was introduced. The bottom photos show the additional effect of the presence of the adherence oxides.

An analysis of dendrites by electron microprobing indicates that their composition is determined by the adherence oxide composition in the glass at the point and time of precipitation. The compositions of the dendrites show Co, Ni, Cu and Fe and are variable; the ones close to the

interface where the iron oxide content in the glass is the highest (as seen from the Fe profile in Fig. 6) are richest in Fe. The mechanism for dendrite formation as illustrated schematically in Fig. 8 is based on a galvanic cell-type of reaction. A circuit is established with the electrons, that are released by Fe going into the glass, moving along the dendrite and reducing Co^{+2} ions as they deposit on the dendrite; the circuit is completed as the resulting negative holes move toward the Fe substrate and provide a site for the Fe^{+2} cations. The reaction proceeds even though the dendrite may not be in physical contact with the substrate providing the glass composition will allow the movement of electrons. The cation adjustment in the glass is based on diffusion gradients and a balance of charges, the oxygen content remaining constant. The dendrite grows into the regions where the cobalt oxide content is the highest since it is the most favorable composition in terms of having the smallest ΔF^{o} for the redox reaction.

It should be emphasized that this galvanic cell type of reaction by itself will not produce maximum adherence since it is impossible to attain the necessary saturation of the interfacial zone with iron oxide because of the small amount of so-called adherence oxides added to the glass. The reaction is of great importance, however, in a role of assisting in maintaining oxide saturation of the interface in cases where the glass at the interface had been enriched with the substrate metal oxide by some other oxidation mechanism or by solution of the oxide on a preoxidized substrate.

As described, reaction (3) can also take place even though ΔF^{o} is positive if its activity quotient (Eq. (8)) is sufficiently smaller than

one. This is the case with regard to Eq. (2) which can be written more simply as:

$$Fe + Na_2O(gls) = FeO(gls) + 2Na\uparrow \tag{10}$$

The free energy equation for this reaction is

$$\Delta F = \Delta F^{o} + RT \ln \frac{a(FeO(gls))\ (P_{Na})^2}{a(Na_2O(gls))} \tag{11}$$

At 1000°C, the standard free energy is +9.3 kcal/mole. The activity quotient, thus, has to be small for the reaction to occur. This requirement can be fulfilled by a sufficiently low activity of FeO and high activity of Na_2O in the glass at the interface, and low partial pressure of Na vapor. The latter factor is the most critical since this redox reaction is possible only because the boiling point of liquid Na (880°C or 1616°F) is below the test temperature. The Na vapor may diffuse to the atmosphere interface where the vapor pressure of Na is low and leave the system, or react with oxygen if present and stay within the system as Na_2O. Or, it may diffuse to the bubbles in the enamel where it could react with entrapped water vapor. In either case the Na vapor pressure within the glass would be kept small allowing the reaction to continue.

Reaction (10) can be followed by monitoring the changes in the glass composition: loss of $2Na^{+}$ for each Fe^{+2} gained expressed as the corresponding loss of Na_2O and gain of FeO. The effect of this change of composition in the model Glass A can be followed by examination of the

$FeO-Na_2O-SiO_2$ phase diagram, shown in Fig. 9. Any solution of FeO by NS_2 (sodium disilicate) corresponds to dilution of NS_2 and an increase in the O/Si ratio; the overall composition falls on the $FeO-NS_2$ join. Any one of these glasses in contact with Fe, on reaction have Na_2O replaced by FeO without changing the O/Si ratio. An example is shown on the phase diagram by the row of dots; as every $2Na^+$ in NS_2 continues to be replaced by a Fe^{+2}, the system becomes saturated with SiO_2 which is precipitated. If the initial glass in contact with Fe contains 15% or more of FeO, then the reaction of replacement of $2Na^+$ by Fe^{+2} continues until Fe_2SiO_4 (fayalite, F_2S) is precipitated. The occurrence of precipitates and their composition can be determined by obtaining electron microprobe oscilloscope traces of the specimen cross-section. As an example, Fig. 10 shows traces of the Fe radiation on the left and the Si radiation on the right for Glass A with 9.1% FeO after heating on an iron substrate for 2 hrs at 1000°C in a vacuum of very low partial pressure of oxygen, indicating that the precipitates are SiO_2.

Reaction studies[7,8] have shown that the redox reaction (10) resulting in introduction of the substrate metal oxide into the glass is sensitive to the glass and the substrate metal compositions because they affect the activity quotient. Under given conditions and for a given substrate, the reaction occurred more readily with an increasing addition of FeO to Glass A, or an increase of the O/Si ratio, indicating that the resulting increase in activity of Na_2O in the glass was greater than the increase in activity of FeO for a given addition of FeO. Also, under equivalent conditions and for a given glass composition, the reaction was found to occur more readily with NiFe alloy, NiCo alloy, Co, and Ni substrates

than Fe, indicating that the activities of the transition metal oxides in the substrate and thus in the glass at the interface were smaller.

Similar studies of redox reaction (10) using enamel glasses have not been made. It would be expected, however, that these glasses would in general be more reactive in the sense of having larger activities of Na_2O for a given amount of Na_2O in the composition because of the glass's lower refractoriness and more complex network-forming oxide composition. The reported dependence of the reaction behavior on the nature of the substrate also suggests that this may be the principal function of the commonly used nickel flash coating. The initially precipitated coating of Co at the interface as identified in the discussion relative to Fig. 7 probably also contributes to this type of redox reaction since both Ni and Co readily alloy with Fe. This Co reaction particularly would be enhanced if the substrate was preoxidized because its solution at the interface would make the glass more reactive.

Summary and Conclusions

An effort has been made to explore the conditions under which a chemical bond, and thus good adherence, are achieved at glass-metal interfaces. It was shown that this continuity of electronic structure was obtained when the interfacial zone was saturated with the oxide of the substrate metal and thus had equilibrium compositions relative to the oxide. This condition is easily achieved when the metal is properly preoxidized before the glass melts and wets the oxidized metal.

When the glass comes in contact with the unoxidized surface of the metal at any time, then a driving force for a chemical reaction occurs whose net effect is to oxidize the substrate. This oxidation enriches

the substrate oxide content of the glass at the interface; there is a counteracting depletion of the oxide going on at the same time because of chemical interdiffusion into the bulk due to the whole system moving towards chemical equilibrium. If the reaction rates are faster, then the interface remains saturated with the oxide with retainment of good adherence; any roughening of the interface that occurs in the course of the reactions contributes to the strength of the interface.

The reactions that can occur with the substrate under favorable conditions are: (a) atmospheric oxidation, when the glass composition provides a path for electrons from the metal to the surface; (b) redox reactions with the reduction of the valence of a multivalent cation, e.g., $Fe^{+3} \rightarrow Fe^{+2}$; (c) redox reactions with the reduction of an oxide in the glass whose metal has a lower oxidational potential than the substrate metal, e.g., Co and Fe; and (d) redox reactions with the reduction of an oxide in the glass whose metal is above its boiling point, e.g, Na.

CoO in the glass appears to play a role in three of these types of reactions. In addition to its participation in the well-documented redox reaction resulting in the formation of dendrites, it enhances atmospheric oxidation of the substrate. Also, by precipitating and alloying with Fe at the interface, it enhances the type of redox reaction in which Na is released. The Ni flash unto iron substrates appears to perform a similar function of enhancing the sodium-forming redox reaction.

It is obvious that the overall reaction pattern is complex and that it consists of a number of reactions going on simultaneously and/or in sequence. Most of the reactions that have been suggested in the

literature do take place, and under a given set of conditions one reaction may be dominant. The end result, however, of all these reactions is to enrich the interfacial zone in the oxides of the substrate metal. Studies are continuing in an effort to understand the mechanisms of these reactions better and to place them on a more quantitative basis.

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Figure Captions

Figure 1. Schematic atomistic representations of cross-sections across the interfacial zone (a) when an oxide layer is present (top sketch with metal-oxide-glass left to right), and (b) when no oxide layer is present.

Figure 2. Schematic representation of transition zones through metal-glass interfaces, showing conditions for chemical and van der Waals type of bonding: (a) chemical bonding with and without discrete intermediate oxide layer, and (b) van der Waals type of bonding.

Figure 3. Schematic picturization of the change in activity of iron oxide (a(FeO)) versus distance across the interfacial zone of a system containing a starting oxide layer after heating at a given temperature for a number of times.

Figure 4. Concentration profiles of FeO, Na_2O and SiO_2 in a cross-section of a FeO-sodium disilicate glass couple heated at 909°C for 50 hrs.

Figure 5. Cross-section of interface (bottom of photograph) between Fe substrate and sodium disilicate glass with 10 w/o Fe_2O_3 showing chemical attack of Fe after heating at 1000°C for 2 hrs (X).

Figure 6. Diffusion profiles of glass B-iron composite heated at 950°C in an Al_2O_3 crucible for 10 minutes.

Figure 7. Photomicrographs of cross-sections of glass-iron interfaces heated at 900°C for 28 hours: (top photo)--Glass C taken with reflected light, (middle photo)--Glass D taken with reflected light, and (bottom photo)--Glass D taken with dark field

illumination.

Figure 8. Schematic illustrating mechanism for dendrite formation, based on galvanic cell type of reaction.

Figure 9. $FeO-Na_2O-SiO_2$ phase diagram. Upper shaded region--fayalite (F_2S) and liquid in equilibrium at 1000°C; lower shaded region--SiO_2 and liquid in equilibrium.

Figure 10. Electron microprobe oscilloscope traces of cross-section of Glass A with 9.1 w/o FeO heated on iron substrate at 1000°C for 2 hours: left--Fe radiation, right--Si radiation (X).

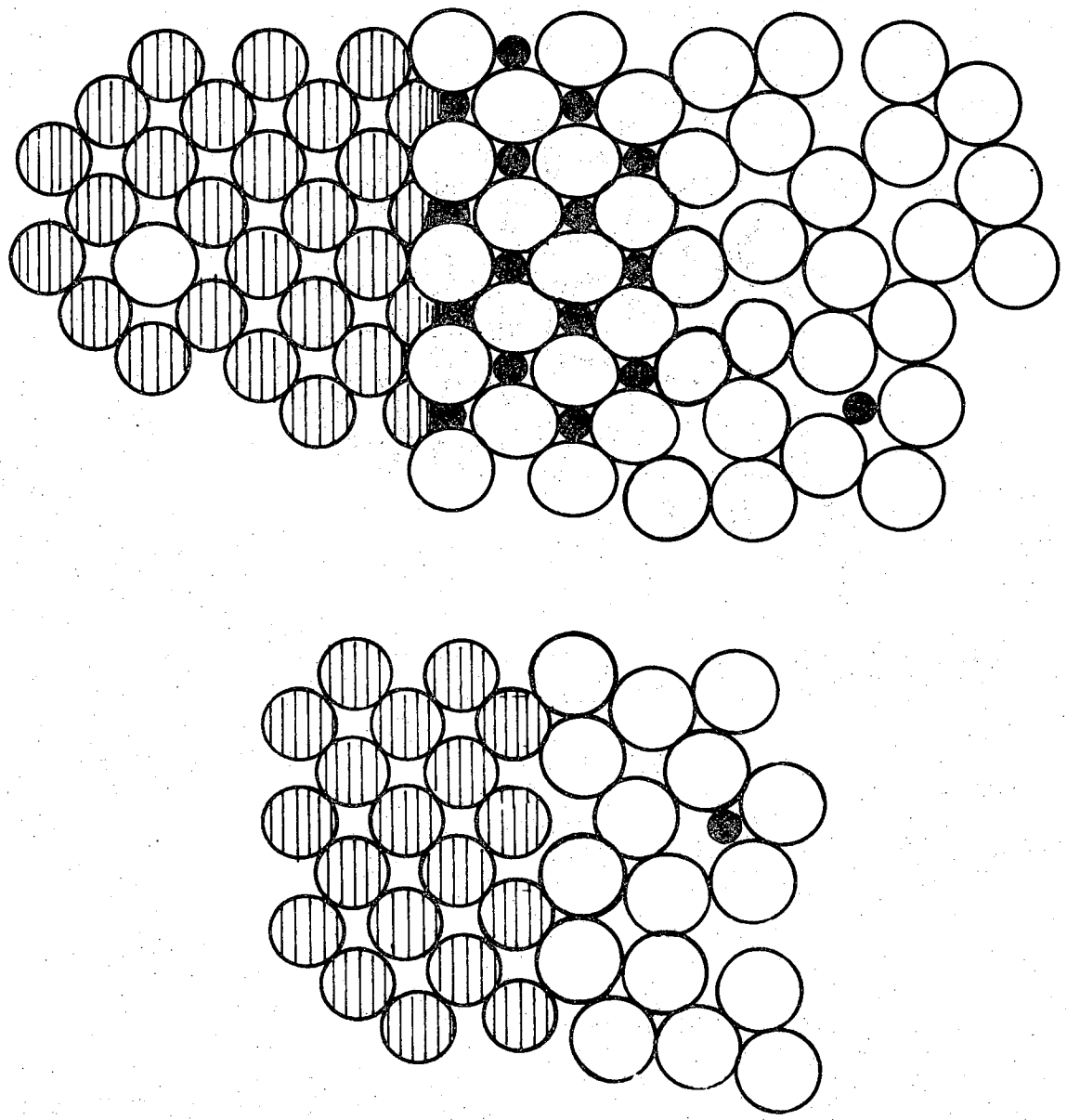

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Fig. 1

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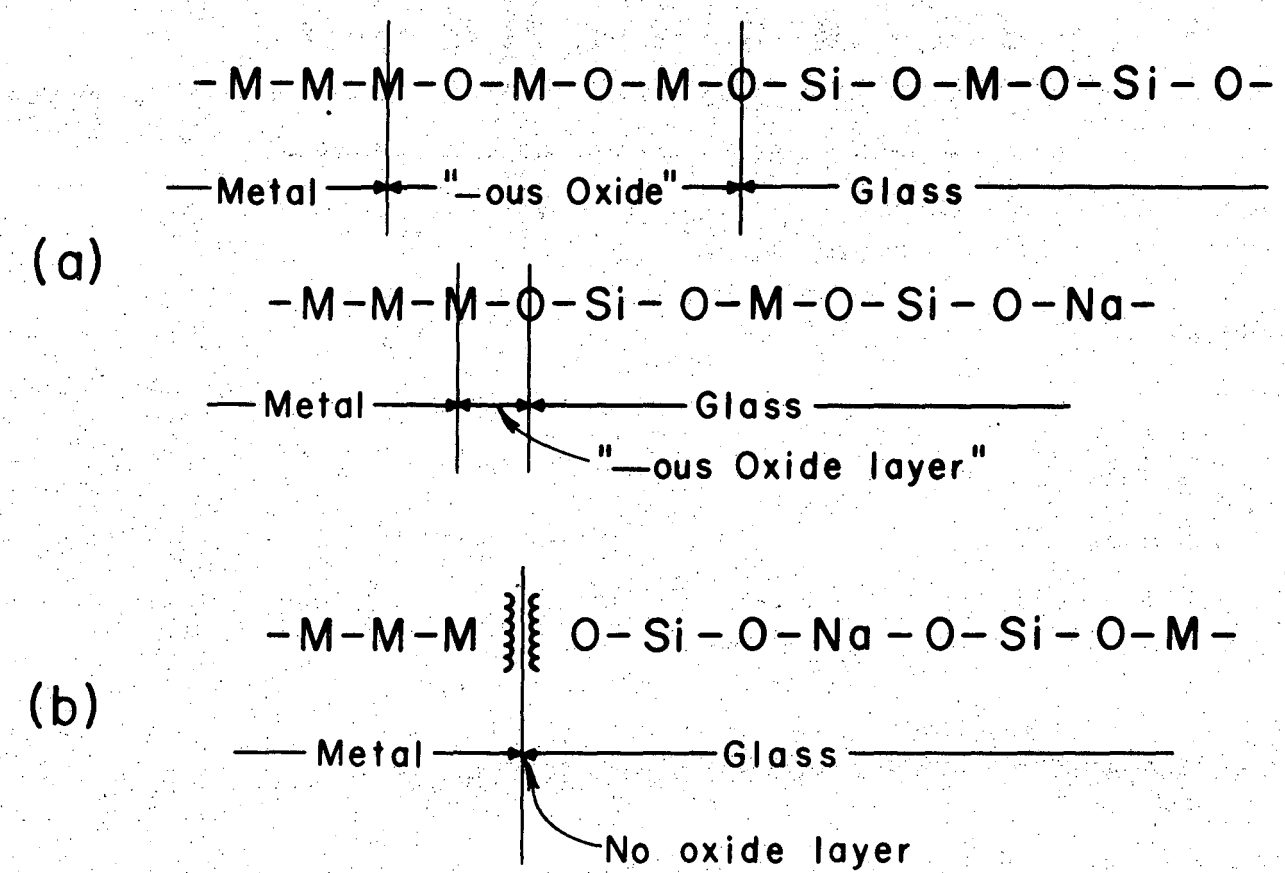

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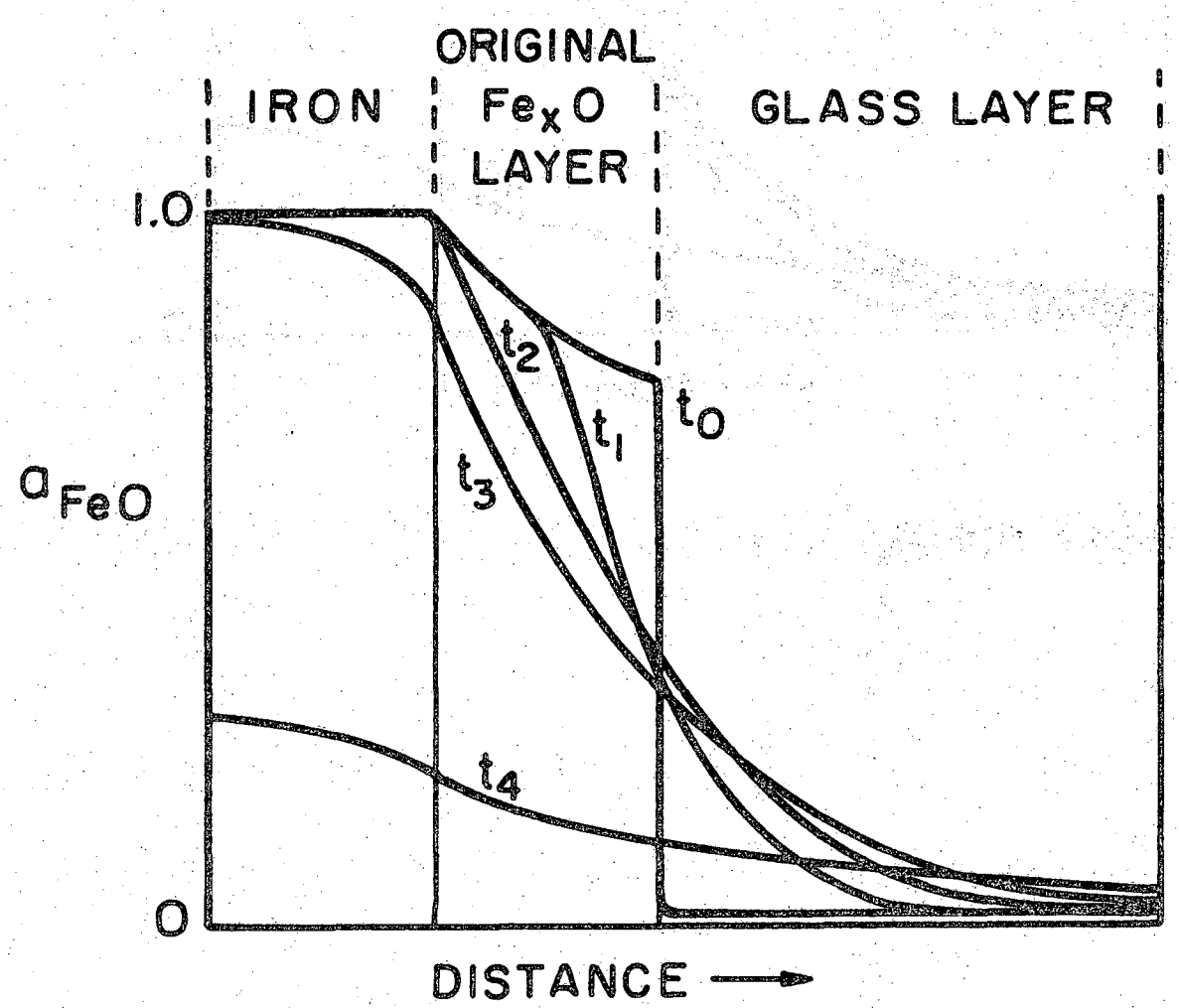
Fig. 2



XBL 718-7193

Fig. 3

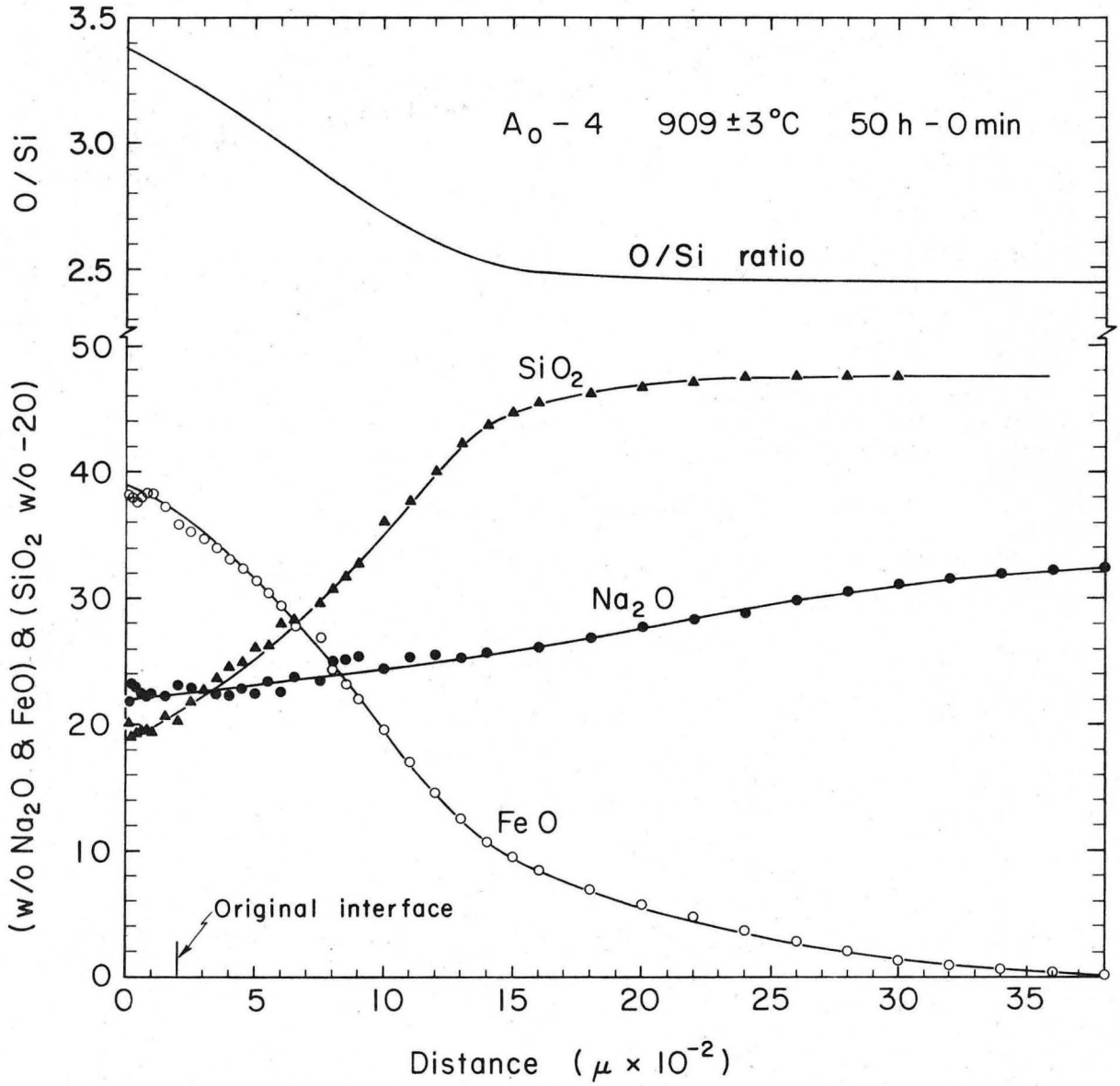
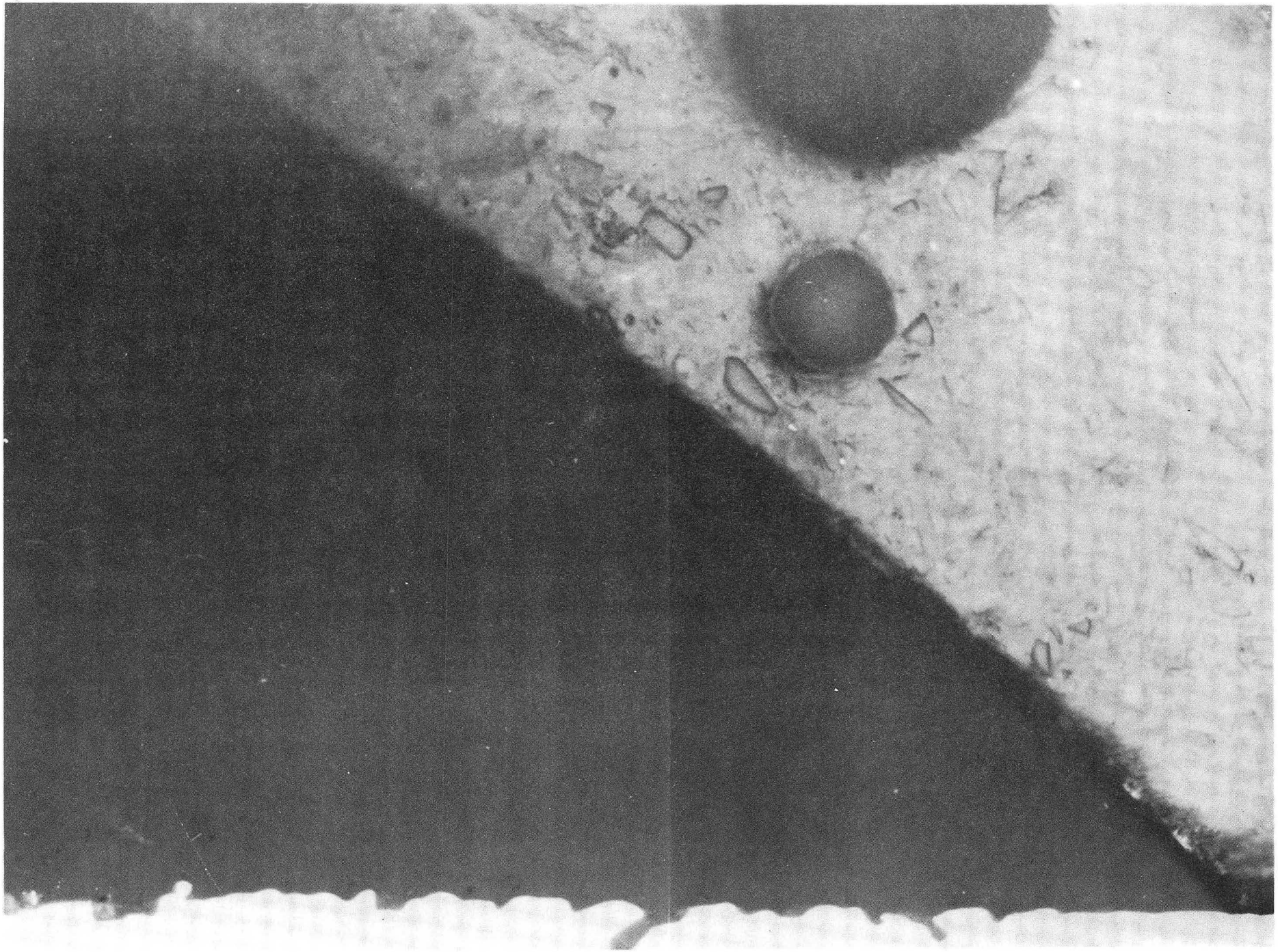

A₀ - 4 909 ±3°C 50 h - 0 min
O/Si ratio
O/Si
SiO2
Na2O
FeO
Original interface
(w/o Na2O & FeO) & (SiO2 w/o -20)
Distance (μ × 10⁻²)
MU-36278

Fig. 4



XBB 697-4560

Fig. 5

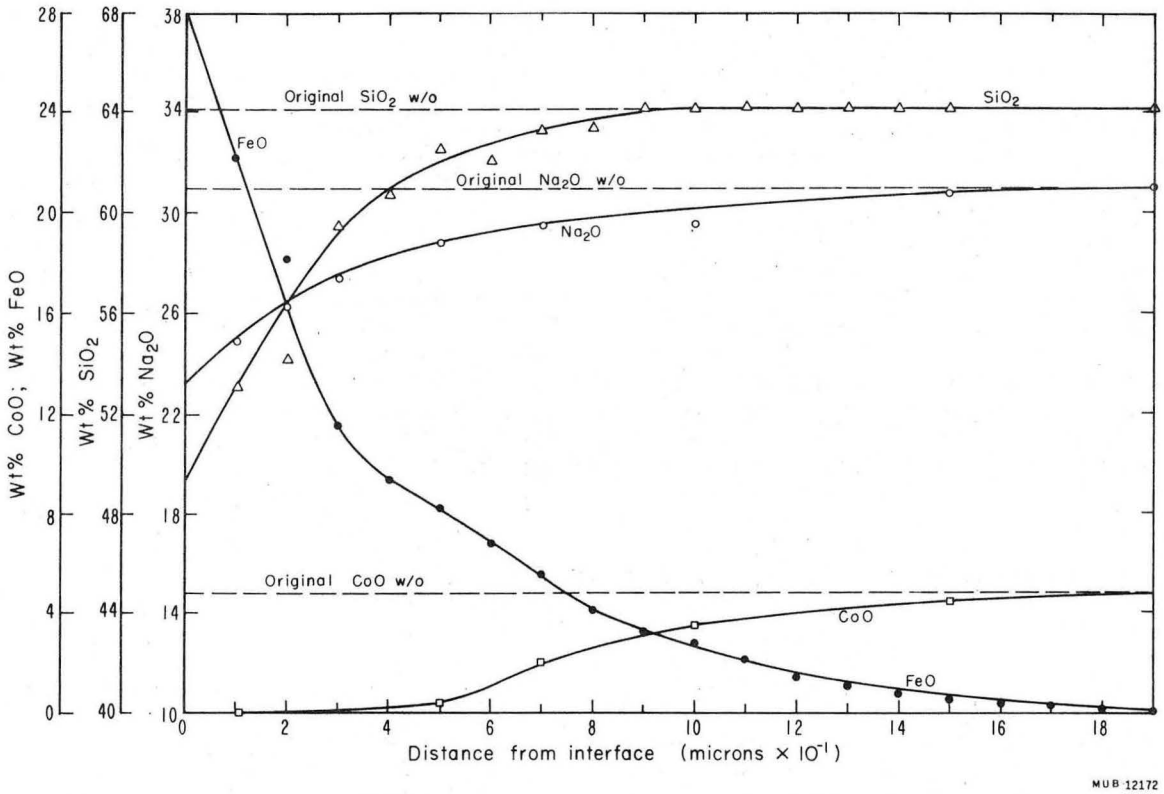
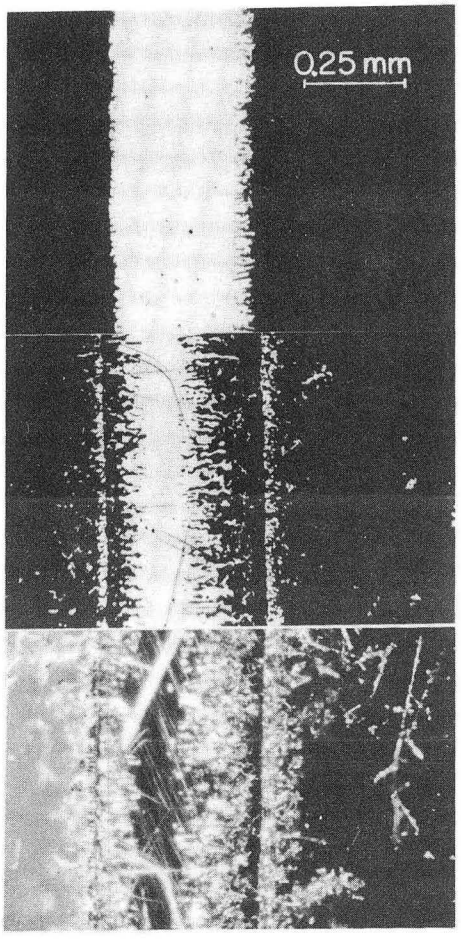
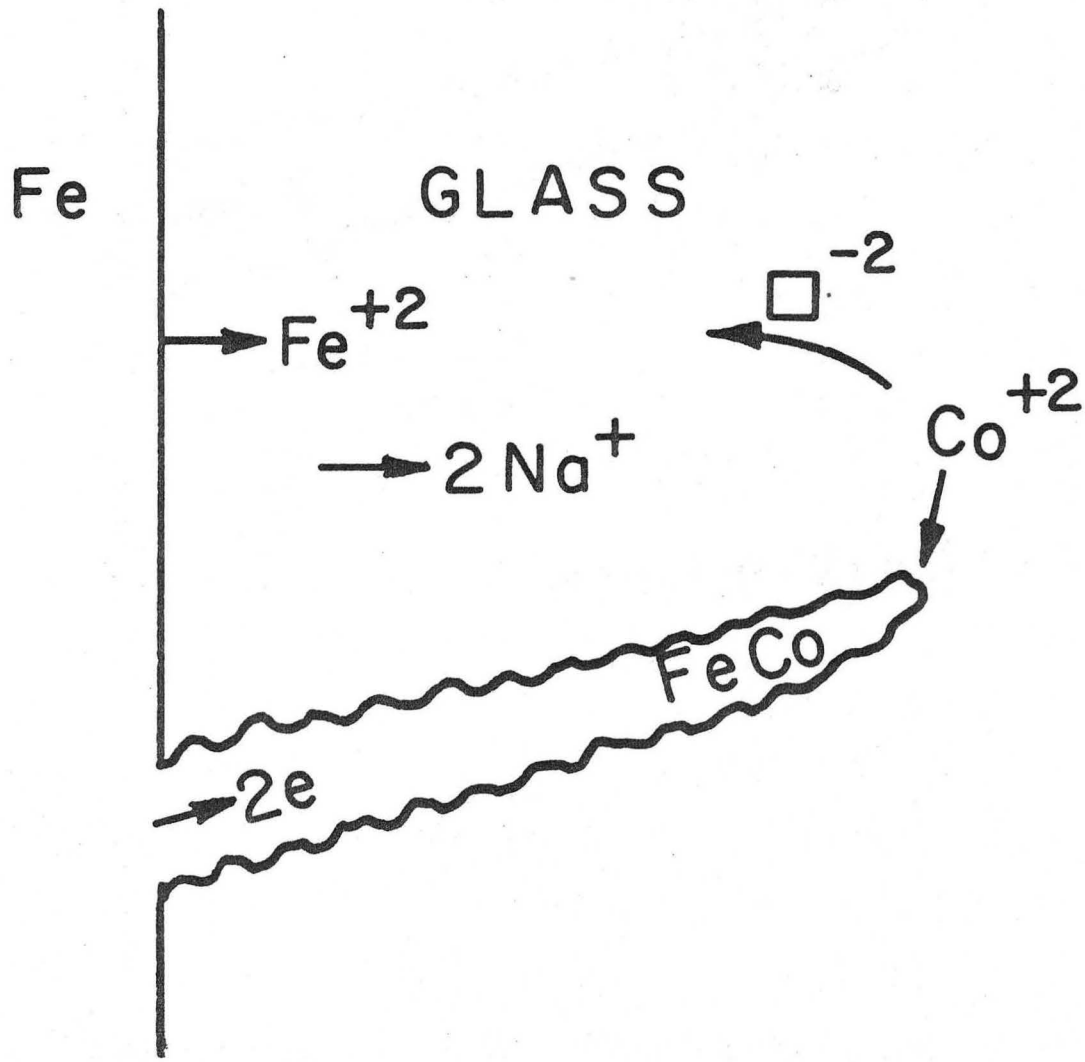

Original SiO_2 w/o
SiO_2
FeO
Original Na_2O w/o
Na_2O
Original CoO w/o
CoO
FeO
Wt% CoO; Wt% FeO
Wt% SiO_2
Wt% Na_2O
Distance from interface (microns × 10^{-1})
MUB-12172

Fig. 6



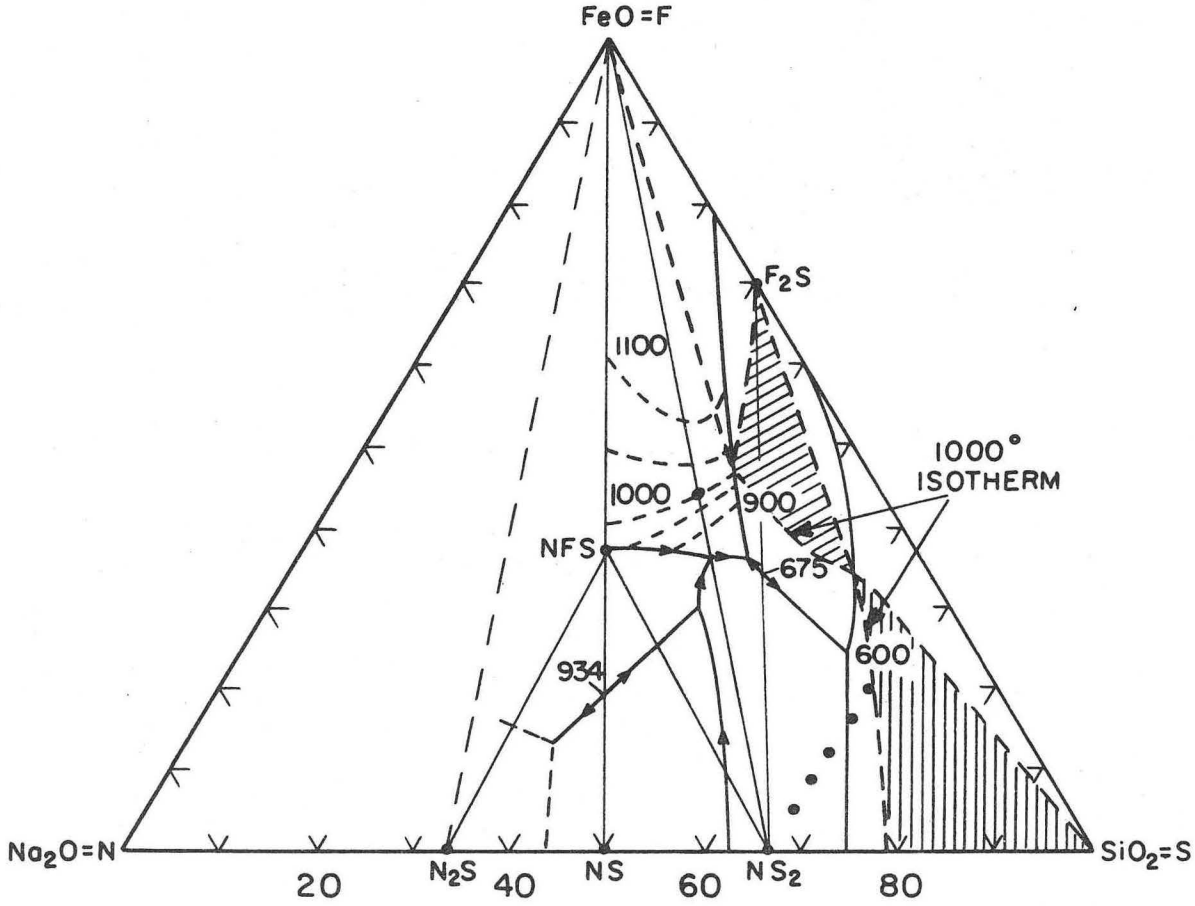
IM 976

Fig. 7



XBL718-7194

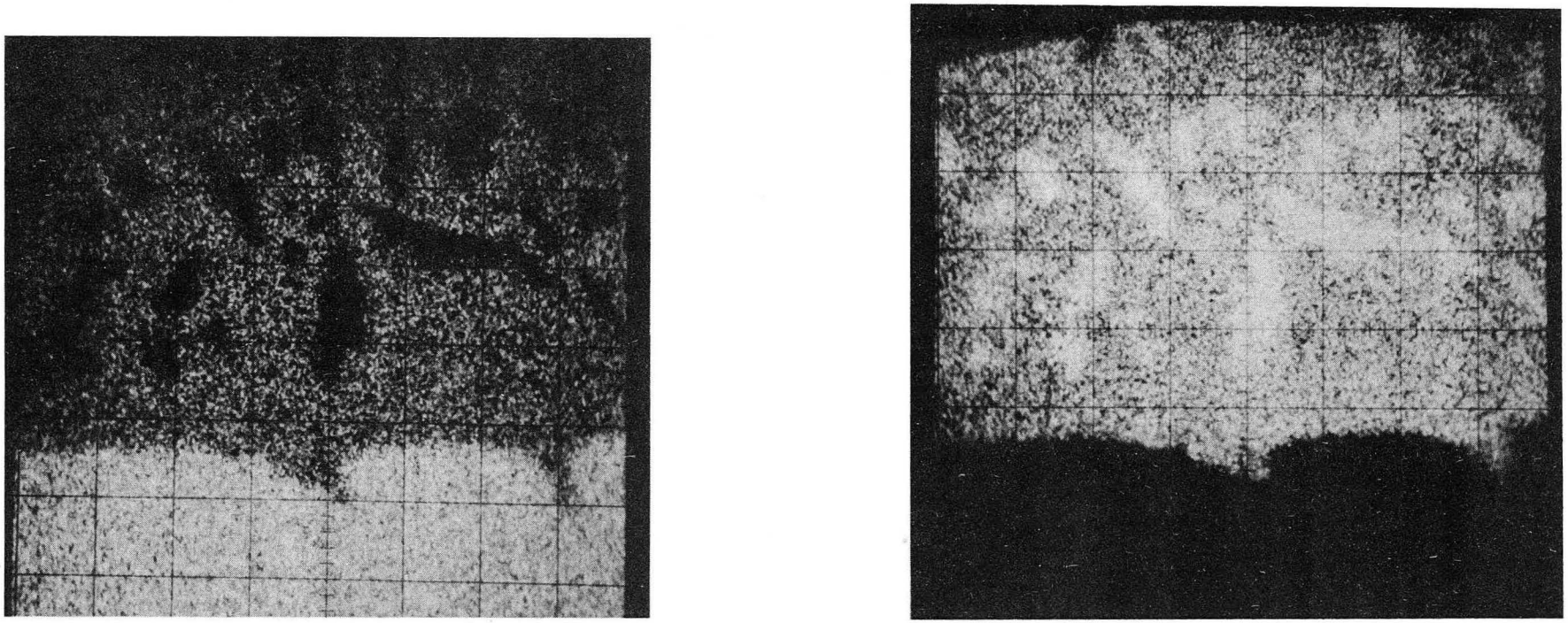
Fig. 8



XBL 711-124

Fig. 9

0 0 0 0 3 6 0 7 1 9 1



XBB 697-4572

Fig. 10

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