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ROLE OF "ADHERENCE OXIDES" IN THE DEVELOPMENT OF
CHEMICAL BONDING AT GLASS-METAL INTERFACES*

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ABSTRACT

Adherence at glass-metal interfaces is dependent on chemical
bonding which results from achieving and maintaining equilibrium com-
positions at an interface. Reactions between iron and glasses with and
without "adherence oxides" were studied by the use of thermogravimetric,
microscopic and electron microprobe techniques. Presence of "adherence
oxides" enhances atmospheric oxidation of the metal and results in the
formation of alloys at the interface that are in equilibrium with the
adjoining glass. These reactions maintain equilibrium compositions at
the interface over an extended period of time. The occurrence of dendrites
in the bulk glass and the function of a "nickel flash" in porcelain enameling
are discussed in terms of these reactions.

I. INTRODUCTION

A knowledge of the physical chemistry of glass-metal systems is necessary for a fundamental understanding of how an interfacial chemical bond, which is a requirement for good adherence, is developed and maintained. This knowledge has been limited. Because of the needs of the porcelain enamel and glass-metal seal technologies, however, numerous empirical studies have been made with the practical achievement of satisfactory bonding.

Studies over many years at the University of California at Berkeley[1] have culminated in a theory of chemical bonding based on the concept that equilibrium compositions are necessary at the glass-metal interface and that, as a consequence, a balance of bond energies and a continuous electronic structure exist across the interface. This equilibrium occurs when the glass at the interface is saturated with the low-valent oxide of the base metal. A concurrent study at Battelle[2] also has shown that good adherence of porcelain enamels on iron is dependent upon saturation of the glass at the interface with FeO. Phenomenologically, the glass at the interface then has a structure related to the oxide and is both contiguous and in equilibrium with the metal. This report contributes to a further understanding of the thermodynamic equilibrium concept by illustrating more effectively that glass and metal interfaces develop a chemical bond when equilibrium compositions are present at the interface. Small amounts of certain transition metal oxides, primarily cobalt oxide, are generally used in porcelain enamels to achieve good adherence and are referred to as "adherence oxides". It is shown that

their function is to assist in maintaining the required equilibrium com-

positions at the interface.

II. THEORETICAL DISCUSSION

The experimental studies were carried out with normal porcelain

enamel glasses. However, since they contain many atomic constituents

whose structural relationships become quite complex, a model system

of $Na_2Si_2O_5$ glass, Fe and FeO^* can be used more effectively to illustrate

the potential reactions and the conditions under which thermodynamic

equilibrium occurs. This system can be represented within the com-

ponent tetrahedron of Na, Si, Fe, and O by the plane of Na_2O, SiO_2,

and FeO which has been determined by Carter and Ibrahim[3] for atmos-

pheric conditions and which is shown in Fig. 1. In actuality the "plane"

would have some varying thickness that would be dependent upon the

range of non-stoichiometry of the oxides. Figure 1 also includes an

isothermal section showing the equilibrium phase regions at 1000°C

Hagan and Ravitz[4] have shown that when $Na_2Si_2O_5$ glass is placed

in contact with Fe at elevated temperatures, a redox reaction occurs

between the Fe and Na with the formation of $Na_{(2-x)}Fe_{x/2}Si_2O_5$ (ignoring

the equilibrium formation of Fe^{3+}). This reaction should continue until

SiO_2 is precipitated; however, the final reation products in equilibrium with

iron have not been established. $Na_2Si_2O_5$ and Fe under normal

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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.

conditions in an open system are not at thermodynamic equilibrium because the kinetics of the overall reaction are too slow. [5]

On the other hand, when $Na_2Si_2O_5$ is placed in contact with Fe containing an FeO layer, solution of FeO occurs (forming $Na_2Fe_xSi_2O_{5+x}$) and results in an immediate saturation of the liquid at the interface with the oxide. The rate of further solution of the remaining oxide is dependent upon diffusion into the bulk FeO-unsaturated glass. Of interest, then, is the condition of the molten glass-Fe interface upon complete solution of the FeO layer. Because of the lack of information on the phase relationships involving elemental iron, within the Na-Si-Fe-O tetrahedron, this question can be best explored on the basis of either the activities or chemical potentials of iron oxide in the indicated phases.

Figure 2 is a schematic diagram of the activities of iron through the cross section of a glass-oxidized-iron interface at different time intervals. Curve t_0 represents the situation when the glass is just placed in contact with the oxidized iron; equal activities of iron in the metal and oxide at their interface indicates thermodynamic equilibrium between them. Curve t_1 shows equal activities of iron in the glass and oxide at their interface, which is representative of the condition when the glass at the interface is saturated and, thus, in equilibrium with the iron oxide; this condition is maintained as long as an oxide layer exists because the solution rate is higher than the diffusion rate. Curve t_2 represents the situation just at the time when the last discrete layer of the oxide has been dissolved and the glass at the interface still retains an oxide-like structure. It is apparent that at this point the activity of iron is the same in the iron, iron oxide, and the oxide-saturated glass at the interface and that these phases must

be in equilibrium. Curve t_3 represents the situation some time after the oxide has been completely dissolved and after the iron concentration in the glass at the interface has dropped because of diffusion into the bulk of the glass; equilibrium at the interface, thus, is lost since the redox reaction between iron and glass is too slow to provide sufficient Fe^{++} to maintain saturation. The situation indicated by condition t_2 is the critical one since no degree of latitude in time is indicated at this point which is necessary for successful practical applications.

It thus becomes evident that cobalt oxide and other "adherence oxides" must play some role in providing the needed latitude at condition t_2 which results in the maintenance of equilibrium compositions at the interface over an extended period of time. A possible role is the establishment of a mechanism for the introduction of Fe^{++} into the glass by atmospheric oxidation of the base metal. Another role can be participation of the glass in the formation of alloys at the interface whose compositions can easily adjust to that of the glass in order to maintain equilibrium. The objective of this study has been to experimentally investigate these possibilities.

III. EXPERIMENTAL PROCEDURE

(1) Preparation of Specimens

Commercial frits of the compositions shown in Table I., calculated from batch compositions, were resmelted at 1350°C in a platinum crucible until there was no further evidence of bubbles. Glass B with adherence oxides, as expected, develops good porcelain enamel adherence, whereas glass A without adherence oxides does not. One inch diameter rods

of the glasses were cast in graphite molds, and the rods were subse-
quently annealed. Sections 3/4 in. and 1/8 in. in thickness were cut
from the rods.

Disks 7/8 in. in diameter were cut from 20 gauge Armco iron,
cleaned in toluene, and rinsed in acetone. The disks were polished with
dry papers to remove any surface oxide and the cleaning and rinsing pro-
cedure was repeated. The disks to be oxidized were weighed on an
analytical balance, oxidized in a water vapor atmosphere for 5 min at
1000°C and reweighed to determine the amount of oxide formed. The
thickness of the layer was calculated by assuming that it consisted of
ferrous oxide.

The iron disks were sandwiched between the glass sections with
the 3/4 in. section on the top. The composites were placed in either a
platinum or a recrystallized alumina cylindrical crucible and sealed in
an argon atmosphere with a 10 min heating at the test temperature. The
samples were subsequently subjected to diffusion anneals either in an
air atmosphere in a thermobalance, which gave a continuous record of
weight change, or in an argon atmosphere in a conventional vertical
resistance heated furnace.

(2) Examination of Specimens

The reacted composite glass-metal samples were mounted in clear
casting resin, and a section perpendicular to the interface was cut from
the center of the sample with a diamond saw. This section was remounted
and given a high metallurgical polish. After photomicrographs of the
polished sample were made, it was coated with a film of vapor-deposited

carbon to make it conductive and was subjected to electron microprobe analysis.

The microprobe data was gathered:

(1) by scanning perpendicular to the glass-metal interface at the rate of 96 microns per minute in order to obtain a diffusion profile; the K-alpha radiation of both iron and cobalt were monitored and the intensities were automatically recorded,

(2) by scanning across dendrites which were located at various distances from the interface at a rate of 8 microns per minute, once again simultaneously recording the intensities of iron and cobalt radiation, and,

(3) by conducting a spectral scan of the dendrites in order to determine their overall compositions.

The reported microprobe data should be regarded as only semi-quantitative. No attempt has been made to apply the various corrections necessary for complete quantitative work (e.g., absorption, fluorescence, etc.). Olivine and garnet samples containing 8.7 and 25.6 wt% Fe, respectively, were used as approximate standards for the glass. Due to complex absorption and fluorescence effects and a lack of adequate standards, the composition of the dendrites was approximated by taking the absolute K-alpha peak intensities from the spectral scan, subtracting background, and normalizing the total to 100%.

IV. RESULTS

(1) Weight Changes

Weight gain vs. time data were obtained for oxidized and unoxidized

iron imbedded in glasses with and without adherence oxides heated in air at 870, 900, and 980°C. Figure 3 shows the curves obtained in platinum crucibles and Fig. 4, in alumina crucibles. The curves represent data corrected for weight losses that occurred on heating glass blanks at the respective test temperatures; these weight losses resulted from evolution of volatiles and exhibited a typical temperature-dependent parabolic relationship. The time period of the experiments was extended in order to exaggerate reactions for purposes of interpretation. The experimental conditions for the various runs, the total weight changes, and the iron content in the glasses at the interfaces are listed in Table II. Comparison of the data for the different conditions are possible since the size and weight of the iron specimens were equivalent and amounts of glass were approximately equivalent in each experiment.

The indicated gains in weight are due to atmospheric oxidation of the iron and should show parabolic weight vs. time curves.[6] The nature of the experimental curves, however, indicates a complex behavior involving several processes. A number of general relationships, nevertheless, are evident. The use of the glass containing adherence oxides, with other factors kept essentially constant, results in more rapid oxidation of the metal and in different shapes of the curves than those obtained with the glass without adherence oxides; these phenomena are particularly evident for the runs that used alumina crucibles instead of platinum. The degree of preoxidation of the iron also affects the shape of the curves, under comparable experimental conditions, particularly in the early stages.

(2) Analyses of Cross-Sections

Cross-sections were made of the composites after the gravimetric
experiments. Photomicrographs of the cross-sections from runs II-A
and II-B taken with reflected light are shown in Fig. 5; Figure 6 shows
the same sections under dark field illumination. An important feature
in run II-B, relative to II-A, is the presence of metallic layers at approxi-
mately the position of the original metal surfaces, which will subsequently
be referred to as the "barrier layers". Figure 6 also shows the presence
of dendrites throughout the iron diffusion zone in the glass. The metal
surfaces undergoing reactions in all cases, except experiment III_a-A,
showed roughening, but it was more pronounced for the surfaces facing
the open end of the crucible and for the surfaces in contact with the glass
containing adherence oxides. Figures 5 and 6 are typical of all the
experiments including the ones conducted in argon, with the exception of
III_a-A.

The cross-section of sample III-B indicated that all of the iron,
including the "barrier layer," had reacted with the glass leaving only a
broad zone containing dendrites whereas specimens II-B and V-B, which
showed a similar gain in weight of about 80 mg, still had some of the
original base iron present. Complete oxidation of the iron disk by
atmospheric oxygen would have resulted in a gain of weight of about 400 mg.
This data provides further evidence that complex reactions are taking
place in the glass-iron system that do not result in weight gains.

Figure 7 shows the iron and cobalt diffusion profiles from the
sections of Figs. 5 and 6 obtained with the electron microprobe. The
profile for the glass containing "adherence oxides" shows that the

"barrier layer" and dendrites are alloys whose composition depends upon their distance from the original interface. Table III. gives the surface compositions of these dendrites as well as the iron content of the glass at the interfaces. An examination of the larger dendrites also indicated a variation in composition through their cross-sections with the Fe content decreasing toward their centers.
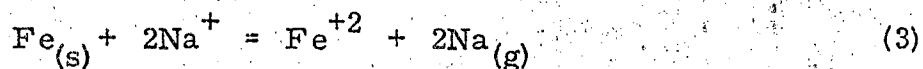
V. DISCUSSION

(1) Reactions

The interpretation of the experimental data is based on the concept that when a glass-metal heterogeneous system is not at thermodynamic equilibrium, reactions occur at the interface in an attempt to attain and to maintain the compositions of the phases representing thermodynamic equilibrium. The realization of this objective, in turn, is dependent upon the kinetics of the reactions involved. With preoxidized iron, as pointed out earlier, a sufficient amount of oxide is first dissolved to saturate the glass at the interface with iron oxide. With diffusion of the iron into the bulk glass because of a lack of thermodynamic equilibrium in the over-all system, a driving force for replenishment of the iron at the interface develops which leads to further solution of the oxide. After solution of all the iron oxide, equilibrium can potentially be maintained by atmospheric oxidation of the iron or by some redox reaction with one of the constituents of the glass. The data further indicate, however, that in systems with glasses that contain adherence oxides the establishment or maintenance of equilibrium is assisted by an adjustment of both the metal and the glass compositions at the interface. The drive

for chemical equilibrium in the latter case may also lead to the incidental formation and growth of dendrites which, however, contribute to the roughening of the interface.
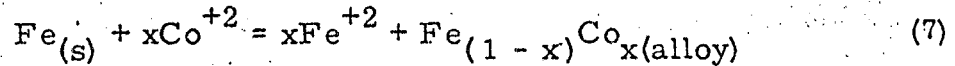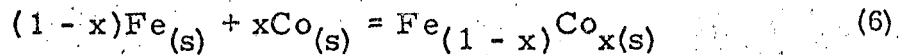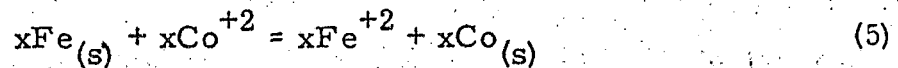
Analysis of specific cases will become more significant after first examining the various reactions that can take place. For simplicity the following possible reactions consider the presence of only one adherence oxide in the glass, that of cobalt, and iron as the substrate metal. With additional adherence oxides, as in the case of glass B used in this study, the reaction would be similar but complicated by the presence of additional metal ions and the formation of more complex alloys.

The possible reactions of iron in contact with glass without cobalt oxide are represented by Eqs. (1), (3), and (4).

$$Fe_{(s)} = Fe^{+2} + 2e^- \tag{1}$$

$$\frac{1}{2}O_2 + 2e^- = O^= \tag{2}$$

$$Fe_{(s)} + 2Na^+ = Fe^{+2} + 2Na_{(g)} \tag{3}$$

$$Fe_{(s)} + 2Fe^{+3} = 3Fe^{+2} \tag{4}$$

Of these, Eq. (1) at the interface in association with Eq. (2) at the surface represents atmospheric oxidation and is the only one that would show a gain in weight. Equation (3) should cause a loss in weight, unless the sodium atoms are retained in the structure, but is not significant in any case because of its slow rate.[4] Equation (4), which would show no change in weight, does not apply in the absence or limited amount of Fe^{+3}.

Glass containing cobalt oxide in contact with iron can first undergo the reactions represented by Eqs. (5), (6), and (7).

$$xFe_{(s)} + xCo^{+2} = xFe^{+2} + xCo_{(s)} \tag{5}$$

$$(1-x)Fe_{(s)} + xCo_{(s)} = Fe_{(1-x)}Co_{x(s)} \tag{6}$$

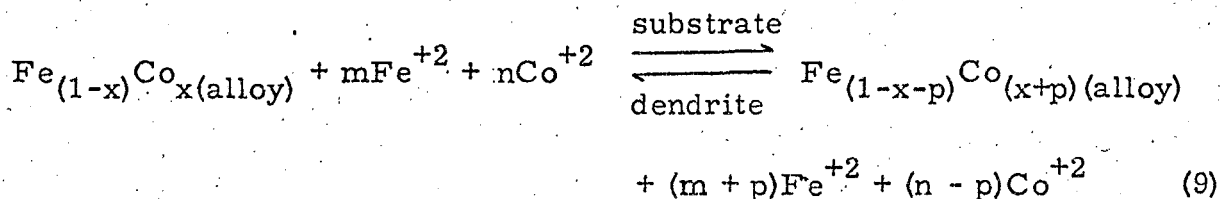$$Fe_{(s)} + xCo^{+2} = xFe^{+2} + Fe_{(1-x)}Co_{x(alloy)} \tag{7}$$

Equation (5) becomes possible because the oxidation potential of cobalt is less than that of iron; and Eq. (6), because cobalt forms a continuous solid solution with iron. These equations are the steps for the overall alloy reaction indicated by Eq. (7) which occurs at the interface and which determines the activity of iron in the alloy.

Further possible reactions of the base metal with cobalt-containing glass are represented by Eqs. (8) and (9). The drop of activity or chemical potential of the iron in the glass at the interface due to diffusion into the bulk unsaturated glass can be counteracted by having more iron brought into the glass either through reaction (1) (in the early stages) or through reaction (8) after alloy formation has begun.

$$Fe_{(1-x)}Co_{x(alloy)} = Fe_{(1-x-p)}Co_{(x-q)(alloy)} + pFe^{+2} + qCo^{+2} + (p+q)2e^{-} \tag{8}$$
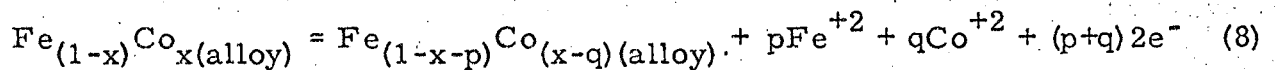
For simplicity in Eq. (8), the summation of the subscripts for the alloy on the right is not intended to be equal to one. The half-cell reactions (8) plus (2) then represent atmospheric oxidation. Preferential or selective oxidation is indicated by use of the subscripts p and q. If an equilibrium is not maintained by means of reaction (8) and with continued diffusion of cobalt to the interface, a further adjustment of compositions at the substrate interface to re-establish equilibrium can be represented by Eq. (9)

to the right. Equilibrium compositions, at the interface, or equal

activities of iron oxide and of cobalt oxide in the two phases, are thus

maintained by the necessary adjustments in the compositions of the phases

$$Fe_{(1-x)}Co_{x(alloy)} + mFe^{+2} + nCo^{+2} \xrightarrow[\text{dendrite}]{\text{substrate}} Fe_{(1-x-p)}Co_{(x+p)(alloy)}$$

$$+ (m + p)Fe^{+2} + (n - p)Co^{+2} \qquad (9)$$

by means of these two reactions. The extent to which each of these

reactions will occur will be affected by the amount of preoxidation of the

substrate metal and the relative kinetics of the various reactions.

As the iron diffuses from the glass-substrate metal interface, com-

positions are realized in the glass along the diffusion profile such that the

activities of iron and cobalt ions in the glass are equivalent to those in a

specific mixed oxide of these metals. This mixed oxide, in turn, would

be in equilibrium with a specific alloy of iron and cobalt. In the presence

of available electrons, and with a suitable nucleation site, it becomes

thermodynamically more favorable for the appearance of the metallic dendrite

instead of the mixed oxide. The dendrites can form and grow according

to Eq. (10).

$$mFe^{+2} + nCo^{+2} + (p + q)2e^- = Fe_pCo_q + (m - p)Fe^{+2} + (n - q)Co^{+2} \qquad (10)$$
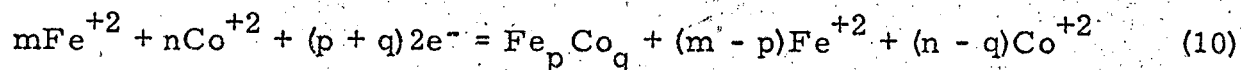
The electrons are supplied either by reaction (8) at the interface, or by

reaction (11) within the glass. The electrons are transported to the dendrite

site through the glass as discussed in the next section.

$$Fe^{+2} = Fe^{+3} + e^- \quad or \quad Co^{+2} = Co^{+3} + e^- \qquad (11)$$
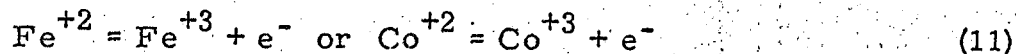
The reverse direction of Eq. (9), on the other hand, expresses a possible

adjustment of the alloy compositions that can occur at a dendrite to re-establish

equilibrium which is lost as a result of the increase in iron concentration in the adjacent glass due to the advancing Fe concentration gradient from the interface and a corresponding decrease in cobalt concentration.

(2) Weight Gain vs. Time Data

The total gain in weight data in Table II. indicates that the nature of the crucible used to hold the specimens is significant. Glass A and iron heated in alumina crucibles in air, experiments III-A, IV-A, and V-A, showed insignificant gains indicating that Eqs. (1) and (2) were limited by slow conduction and/or diffusion rates through the glasses. Corresponding heatings in platinum crucibles, experiments I-A and II-A, on the other hand, showed significant gains in weight, indicating that the crucible provided a conductive path for electrons thereby facilitating atmospheric oxidation of the iron. This interpretation, instead of some catalytic effect, was supported by showing that no significant gain in weight was experienced by a specimen with glass A and iron heated in an alumina crucible which had been fitted with a platinum ring that contacted the glass only at the surface. A similar type of electron transfer mechanism has been observed in thermally activated power cells. [7]

Table II. also indicates that the presence of "adherence oxides" in the glass enhances atmospheric oxidation as can be seen by comparison of weight gain data obtained under comparable conditions for glass A and glass B specimens, e.g., I-A and I-B, III-A and III-B. This effect is emphasized in the experiments with alumina crucibles in the absence of the conductivity mechanism provided through the use of platinum crucibles. In this case, then, the multivalent cations must play some role in facilitating the transfer mechanisms through the glass. The strong temperature

dependence of these transfer mechanisms is indicated by comparison of
data for IV-B and V-B. Recent work has indicated that certain oxide
glasses containing multivalent cations, such as iron, cobalt, nickel,
exhibit electronic conductivity. [8]

Data in Table II. further indicates that reactions can occur in the
absence of oxygen. The presence of 8 to 10% iron in the glass at the
interface in specimens I_a-B, III_a-B, and III_{a1}-B can only be accounted
for by reactions (8), (9), and (10); cross sections from these experiments
were also similar in appearance to those of glass B over iron heated in
air. However, the lower iron content than that obtained on heating speci-
mens with glass B in air indicates that atmospheric oxidation, as repre-
sented by Eq. (8) with (2), plays a significant role in maintaining thermo-
dynamic equilibrium at the interface. A lower iron concentration in the
glass in contact with an alloy in comparison with that in the glass in
contact with FeO could be attributed to the differences in the activities
of the iron in the substrate surfaces.

Equilibrium compositions having first been established at the
interface, normally by the solution of the preoxidized coating on the iron,
may thus be maintained by concurrent reactions at the interface illustrated
by Eq. (9) and by Eqs. (8) plus (2) (atmospheric oxidation). The relative
rates of these reactions will be determined by the experimental conditions,
and the relative demands of the system. As an example, the importance
of the amount of preoxidation on the rates is indicated by comparing data
for experiments III-B and IV-B, and I-B and II-B, listed in Table II.

The salient features of the reactions presented in section V-A
can be demonstrated by examining the results of experiments II-A and

II-B in greater detail. In these experiments the effects of atmospheric
oxidation were amplified by the use of platinum crucibles. The weight
gain vs. time curves are shown in Fig. 3. Photomicrographs of the cross
sections of the specimens are pictured in Figs. 5 and 6, and the iron and
cobalt concentration profiles perpendicular to the interface of the cross
sections are shown in Fig. 7.

Light preoxidation of the iron disk, as in these cases, results in
a high flux of iron away from the interface at the point of complete solution
of the oxide and in a corresponding tendency to move the interfacial com-
positions rapidly from their equilibrium values. The effect is a strong
initial driving force for equilibrium. It is satisfied in specimen II-B by
means of Eqs. (8) plus (2) after possibly an initial reaction of (1) plus
(2) as indicated by the rapid weight gain during the first hour. During
this period reaction (9), however, was also proceeding concurrently due
to the diffusion of adherence cations to the interface with the resultant
formation of an alloy which was becoming continuously richer in adherence
metals. This alloy began to act as a "barrier layer" to continued
atmospheric oxidation as it became more noble in nature, and the rate
of weight gain slowed down. Reaction (9) then predominated in maintaining
equilibrium at the interface and remained operative until the supply of
adherence cations to the interface became inadequate. At this time the
atmospheric oxidation processes represented by Eqs. (8) and (2) once
again became dominant and proceeded most readily along high energy
sites such as grain boundaries. As the reaction, consequently, moved
deeper into the metal, regions richer in iron were exposed and the rate
of reaction was further accelerated because of the higher oxidation

potential of the base metal. This transition corresponds to the increase in the rate of weight gain for curve II-B at about 6 hr and is associated with the bypassing of the "barrier layer" which remains as a marker of the original metal surface, as seen in Figs. 5 and 6. The area under the iron concentration profile of II-B, shown in Fig. 7, indicates the extensive oxidation of the iron disk which has occurred in an effort to maintain equilibrium compositions. . The lesser attack and lower iron concentration at the interface on the bottom side of the disk is due to a virtually complete depletion of adherence oxides from the thinner layer of glass and to a reduced participation in atmospheric oxidation because of poorer accessability to oxygen.

Heavy preoxidation of the iron disk, as in experiment I-B, reduces the early demand for additional oxidation and also reduces the rate at which the cobalt content increases in the alloy formed at the interface. This system, therefore, is able to maintain equilibrium for a longer period of time and does not exhibit the early demand for atmospheric oxidation as shown by comparing its weight gain vs. time curve in Fig. 3 with that for experiment II-B.

In specimen II-A, on the other hand, because of the absence of "adherence oxides", the driving force for equilibrium, after solution of the oxide, was met only by atmospheric oxidation of the iron according to Eqs. (1) and (2). The corresponding gains in weight within the first hour shown by the curves for II-A and II-B in Fig. 3 again emphasize the effectiveness of the "adherence oxides" in providing a transport mechanism for the oxidation of the iron. Absence of reactions (8) and (9) in specimen II-A accounts for the lack of a "barrier layer". The weight loss curve

approaches a parabolic shape since atmospheric oxidation dependent on diffusion is the only reaction which is active. The observed roughening of the metal surface in experiment II-A (viz. Fig. 5) is probably due to faster oxidation rates along grain boundaries.

Similar analyses can readily be applied to other weight gain curves. Critical factors under consideration would be glass composition, crucible material and amount of preoxidation of the metal.

(3) Dendrites

Dendrites isolated from the base metal were observed throughout the diffusion zone for all experiments using glass with adherence oxides including those in argon for short times; dendrites occurring in experiment II-B are seen in Figs. 5 and 6. Their variable composition in relation to the adjoining glass compositions, as shown in Fig. 7 and Table III., is particularly significant for it indicates that it is possible for thermodynamic equilibrium to be readily maintained at the glass-metal interfaces by adjustment of the compositions (and, thus, the chemical potentials of the various elements involved) in the two phases.

Sites for heterogeneous nucleation of the dendrites can be provided by defects, such as bubbles. The nuclei form as a result of local supersaturation due to small compositional fluctuations in the glass. The dendrite formation is represented by Eq. (10). After a dendrite is formed, it experiences a constantly changing glass composition as a result of diffusion processes. The dendrite then becomes a site for further growth. The diffusion of the "adherence cations" in the glass is faster than the diffusion of metal atoms in the dendrites; therefore, each dendrite exhibits a composition profile which reflects the dendrite's adjustment

to its changing environment by growth. Those dendrites far removed
from the substrate, for instance, grow with the precipitation of phases
which become continuously richer in iron and leaner in "adherence metals".
It is assumed that the necessary electrons for reaction (10) are supplied
primarily by the base metal through reaction (8) and not by oxidation of
cations in the glass by reaction (11) since no dendrites were observed in
the specimens of glass B in contact with FeO_o A type of galvanic cell is
thus established with both electrons and cations flowing from the substrate
metal to the dendrites. Since this cell only requires a balance of positive
and negative charges and since each of the interfaces would attempt to main-
tain equilibrium compositions, an exact replacement of the types of cations
reduced at the dendrite is not necessarily made at the substrate interface.
Although adjustment of compositions at the dendrite surfaces can also
be effected by means of reaction (9) to the left, it undoubtedly plays a
minor role since its operation should result in essentially no growth or
zoning of the dendrites.

The more extensive interfacial roughening by glass B compared with
glass A can be attributed to the increased corrosion of the base metal
resulting from both transfer of materal to isolated dendrites and enhanced
atmospheric oxidation. Some of this roughening, however, can also be
attributed to the establishment of galvanic cells between points of different
compositions on the substrate surface. Transport of material then would
occur from site to site along the interface by means of reactions (8) and
(10). Although such roughening contributes to mechanical adherence and
provides a safety factor, the primary consideration should be the develop-
ment of chemical bonding which results from the attainment and mainte-
nance of equilibrium compositions at the interfaces.

(4) Function of the "Nickel Flash"

A common practice in industry is to apply a "nickel flash" to the iron to be enameled. On the basis of this study, nickel must play a role in the maintenance of the equilibrium compositions at the glass-metal interface. With the proper amount of nickel an Fe-Ni alloy forms readily and is not completely oxidized during the heating up period. This surface in contact with enamel glass now has additional degrees of freedom in the drive towards the maintenance of equilibrium compositions at the interface. Reactions of the type represented by Eqs. (7), (8), and (9) will continue to be operative but they will be more complex since the substrate metal initially in contact with the glass is now a nickel-iron alloy instead of iron.

An excessively thick nickel coating, however, would be undesirable because the nickel-iron alloy which would form under normal porcelain enamel heating conditions would not extend to the surface of the nickel layer. A glass saturated with nickelous oxide would then be necessary at the interface to form a chemical bond to nickel. The cobalt oxide in the normal enameling glasses, in this case, would not readily take part in the development of adherence, i.e., in the reactions represented by Eqs. (7), (8), and (9), since its free energy of formation (-80 kcal/mole O_2 at 700°C) is lower than that for nickel (-76 kcal/mole O_2).. Extensive discussions of such redox reactions have been reported.[2]

VI. CONCLUSIONS

This study supports the concept that there always exists at a glass-metal interface a driving force towards thermodynamic equilibrium, the

achievement of which is the necessary condition for chemical bonding across the interface. Chemical reactions occur if nonequilibrium exists; their effectiveness in maintaining equilibrium compositions at the interface is determined by the relative rates of the reactions and diffusion of various elements in the bulk glass. The function of "adherence oxides" in porcelain enamels is to play a favorable part in attaining and maintaining equilibrium compositions at the interfaces at the operating temperatures employed. They play a role in providing a mechanism for atmospheric oxidation of the metal but their most important function is to participate in the formation of alloys whose compositions can readily adjust themselves to maintain equilibrium with the changing compositions of the adjoining glasses, i. e., the chemical potentials or activities of the respective components in both phases become equal.

An "adherence oxide" is one whose metal has an oxidation potential equal to or less than that of the base metal to be enameled so that Eq. (5) will have a negative free energy change. In addition, this metal should form a continuous solid solution with the base metal so that Eq. (6) and the overall Eq. (7) will have negative free energies. It thus becomes possible for small fluctuations in glass composition at the glass-metal interface, which upset the chemical equilibrium, to be compensated by an equivalently small change in alloy composition. Cobalt oxide in the enamel glass fulfills these requirements for enameling on iron. Copper oxide alone in the glass, however, is not a satisfactory "adherence oxide" for use with iron even though it satisfies the requirement of Eq. (5). Since copper forms only limited solid solutions with iron, compositions can be realized in which a small

change in the glass composition will result in large changes in the alloy

composition. In this case, the kinetics for the readjustment of the alloy

composition would not be rapid enough to maintain equilibrium in a dynamic

system. In combination with other "adherence metals", however, as in

the case of glass B, the range of solubility in the metal alloy phase may be

broadened. Those oxides which assist in adherence but fit neither of the

above requirements (e. g., Mn) possibly aid, by virtue of their multivalent

nature, in the maintenance of equilibrium compositions by facilitating

atmospheric oxidation through provision of a mechanism for transfer of

electrons from the interface to the surface of the glass.

It is now apparent that another "barrier layer" has been reached

in the quest for a fundamental and quantitative understanding of glass-

metal interfaces. Additional knowledge is needed on the structure of

glass in order to have a better understanding of conductivity and transfer

mechanisms, and nature of bonding. Also, and perhaps of greater im-

portance, a knowledge is needed of the chemistry of glass-metal systems

involving equilibrium constants, composition stabilities, and activity

coefficients. With such knowledge a more specific and quantitative

application of the equations presented, as well as the more complex ones

involving all the "adherence oxides", will be possible.

ACKNOWLEDGEMENTS

REFERENCES

1. a)   J. A. Pask and R. M. Fulrath, "Fundamentals of Glass-to-
        Metal Bonding: VIII. Nature of Wetting and Adherence,"
        J. Am. Ceram. Soc. 45 [12] 592-596 (1962).

   b)   J. A. Pask, "Glass-Metal 'Interfaces' and Bonding," in
        Modern Aspects of the Vitreous State, Vol. 3. (Butterworths,
        Washington, 1964) pp. 1-28.

2.   B. W. King, H. P. Tripp, and W. H. Duckworth, "Nature of
        Adherence of Porcelain Enamels to Metals," J. Am. Ceram.
        Soc., 42 [11] 504-525 (1959).

3.   P. T. Carter and M. Ibrahim, "The Ternary System
        Na_2O-FeO-SiO_2," J. Soc. Glass Technol. (Trans.), 36 142-163
        (1952).

4.   L. G. Hagan and S. F. Ravitz, "Fundamentals of Glass-to-Metal
        Bonding: VI. Reaction between Metallic Iron and Molten Sodium
        Silicate," J. Am. Ceram. Soc., 44 [9] 428-429 (1961).

5.   M. P. Borom, "Diffusion of Iron into Sodium Disilicate Glass,"
        (M. S. Thesis), Lawrence Radiation Laboratory Report UCRL-11116,
        January 1964, plus additional unpublished data.

6.   H. G. Lefort and A. L. Friedberg, "Quantitative High-Temperature
        Oxidation of Porcelain Enameled Iron," J. Am. Ceram. Soc.,
        41 [6] 216-226 (1958).

7.   B. W. King, W. A. Hedden, A. B. Tripler, Jr., D. J. Bowers,
        and B. O. Austin, "Thermally Activated Power Cells," Bull.
        Am. Ceram. Soc., 43 [2] 117-121 (1964).

8.   J. D. Mackenzie, "Semiconducting Oxide Glass: General
        Principle for Preparation," J. Am. Ceram. Soc., 47 [5]
        211-214 (1964).

Table I. Frit Glass Compositions

	Glass A wt%	Glass B wt%
SiO_2	38.2	36.8
B_2O_3	19.0	18.2
Al_2O_3	3.7	3.5
Na_2O	18.2	17.4
K_2O	2.0	1.9
CaO	10.3	9.9
BaO	4.7	4.5
F_2	2.9	2.8
P_2O_5	1.0	1.0
CoO	-	0.7
NiO	-	1.3
MnO	-	1.7
CuO	-	0.3

Table II. Tabulation of experimental conditions

Expt. No. - type glass		Thick. of preoxidized layer (microns)	Temp(°C)	Time(hr-min)	Crucible material	Atmos.	Net wt gain(mg)	Final conc. Fe at interface (wt%)	
								top side	bottom side
I	A	150	870	24 - 0	Pt	air	36	19.1	-
	B	110	"	"	"	"	41	-	-
II	A	3	900	27 - 30	"	"	60	13.8	9.4
	B	3	"	28 - 0	"	"	85	19.8	12.0
III	A	0	870	24 - 0	Al_2O_3	"	0	1.2	1.2
	B	0	"	"	"	"	80	-	-
IV	A	130	"	"	"	"	0	5.6	-
	B	130	"	"	"	"	0	15.3	-
V	A	110	980	8 - 0	"	"	2	-	-
	B	110	"	"	"	"	80	-	-
I_a	B	140	900	24 - 0	Pt	argon	-	10.0	-
III_a	A	0	"	0 - 10	Al_2O_3	"	-	1.2	-
	B	0	"	0 - 10	"	"	-	8.4	-
III_{a1}	B	0	"	24 - 0	"	"	-	9.1	-
FeO	A	∞	900	0 - 30	"	"	-	25.8	-
FeO	B	∞	"	"	"	"	-	24.5	-

note: glass B = glass A + adherence oxides. (see Table I.).

Table III. Approximate metallic content of dendrites and associated iron content in adjacent glass analyzed from experiment II-B

Distance from original substrate interface to dendrite (microns)	Approximate alloy composition wt%				Wt% Fe in glass adjacent to alloy
	Co	Ni	Cu	Fe	
0 ("barrier layer" facing open end of crucible)	3	8	2	87	19
730	14	36	9	41	16
1860	13	60	9	18	11
2500	7	68	13	12	6

FIGURE CAPTIONS

Fig. 1 Na_2O-SiO_2-FeO phase diagram showing an approximate isothermal cut at 1000°C.

Fig. 2   Hypothetical iron activity vs penetration distance diagram for oxidized iron-glass contact zone showing ferrous iron activity in the oxide and the glass relative to metallic iron as the standard state.

Fig. 3   Net weight gain vs time curves for oxidized iron-glass composites heated in platinum crucibles. Experimental conditions are given in Table II.

Fig. 4   Net weight gain vs time curves for metal-glass and oxidized metal-glass composites heated in recrystallized alumina crucibles. Experimental conditions are given in Table II.

Fig. 5   Photomicrographs of the glass-metal interfaces of experiments II-A (left) and II-B (right) taken with reflected light (X 100).

Fig. 6   Photomicrograph of glass-metal interface from experiment II-B taken with dark field illumination showing extensive dendrite formation (X 100).

Fig. 7   Concentration vs penetration distance profiles for samples II-A and II-B.

Legend: (1), (2): base-metal-glass interface at conclusion of experiments II-A and II-B, respectively.

(3):   "barrier layers" associated with experiment II-B.

(4):   spikes indicate position and iron content of dendrites referred to in Table III.

System Na₂O-FeO-SiO₂ showing 1000°C isothermal cut
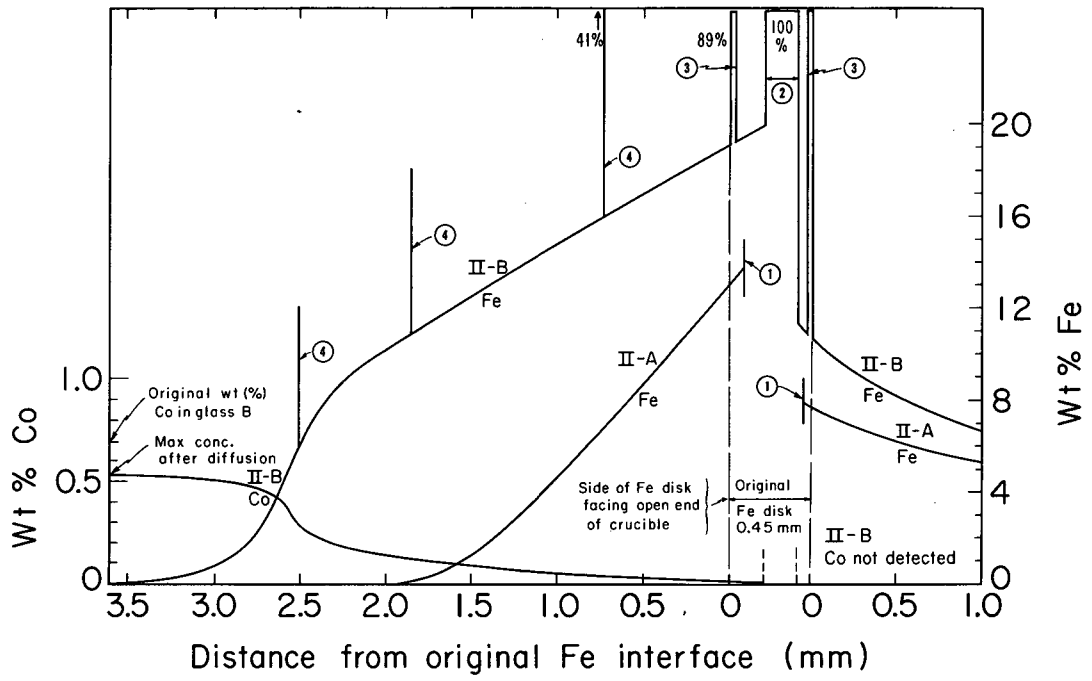
MU-33825

Fig. 1

Fig. 2

MUB-5125

Fig. 3

MUB-5126

Fig. 4

MUB-5127

ZN-4695

Fig. 5

ZN-4696

Fig. 6

Fig. 7

MUB-5124