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REACTIONS BETWEEN METALLIC IRON AND COBALT OXIDE-BEARING SODIUM DISILICATE GLASS

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March 17, 1966

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ABSTRACT

Electrochemical reactions are shown to be initiated at a glass-metal interface if thermodynamic equilibrium, represented by saturation of the glass with the low valence oxide of the substrate metal, is not present. In the systems iron-sodium disilicate glass with and without cobalt oxide, oxidation of the metal occurred with an addition of atmospheric oxygen to the glass if heatings were made in platinum crucibles. Such gains in weight were not realized if heatings were made in alumina crucibles. With glasses containing ions of cobalt, whose potential for oxidation is lower than that of iron, electrochemical reactions occurred resulting in oxidation of iron at the interface and reduction of metallic ions in the glass with the formation of dendrites.

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At the time this work was done the writers were, respectively, research assistant, laboratory technician, and professor of ceramic engineering, Department of Mineral Technology, College of Engineering, and Inorganic Materials Research Division, Lawrence Radiation Laboratory. M. P. Borom is now associated with the Metallurgy & Ceramics Laboratory, Research and Development Center, General Electric Company, Schenectady, New York; J. A. Longwell, with Research & Development Department-Fairchild Semiconductor, Palo Alto, California.

The composition of a precipitating dendrite in all cases was found to be in thermodynamic equilibrium with the adjoining glass. A galvanic cell of "iron--glass--glass with cobalt oxide--cobalt" illustrated the electrochemical nature of the reactions by oxidation of iron at the iron-glass interface and reduction of cobalt ions at the cobalt-glass interface to form dendrites. In all cases fulfillment of local electroneutrality was largely satisfied by movement of the highly mobile sodium ions, which generally resulted in an uphill composition gradient for sodium because of the establishment of an electrochemical potential gradient.

I. INTRODUCTION

Recent studies have supported the theory that chemical bonding occurs between a glass and metal when thermodynamic equilibrium relative to the low valent oxide of the metal is present at the interface.[1-3] This requirement is exemplified by a condition wherein both phases at the interface are saturated with the metal oxide. The addition to the glass of oxides of metals whose potentials for oxidation are lower than that of the base metal (e.g., cobalt oxide in an enamel to be applied to iron) was shown by Borom and Pask to lead to the oxidation of the base metal, after solution of the surface oxide, thus tending to maintain the glass at the interface saturated with the base metal oxide.[3] The complexity of the glass compositions studied in the previous work, however, permitted only a qualitative discussion of the interfacial reactions in glass-metal systems. This report presents the results of a more quantitative and definitive study of the electrochemistry of a model glass-metal system, i.e., iron and sodium disilicate glass containing cobalt oxide.

II. EXPERIMENTAL PROCEDURE

A. Glass Preparation

Blocks of sodium disilicate glass from the Philadelphia Quartz Co. were heated for 6 hrs at approximately 1350°C in a platinum crucible. The glass was cast in 3/4 in. diam graphite molds, annealed, and sectioned into 1/2 in. lengths. Additional glass cylinders were similarly prepared from a mixture of crushed sodium disilicate glass and Co_2O_3. Chemical analyses of these two glass compositions showed respectively 67.5% SiO_2-32.5% Na_2O (glass A) and 4.8% CoO-64.2%

SiO_2-31.0% Na_2O (glass B).

B. Thermogravimetric Analyses

Glass-metal composites were prepared by placing one of the glass disks on a 3/4 in. diam by 1/8 in. thick Armco iron disk and placing the unit in an appropriate crucible (iron disk down). Prior to assembling the composite, the Armco iron disks had been given a high metallurgical polish, heated in a vacuum of 2×10^{-5} torr for 20 min at 950°C and oxidized for 10 min at 950°C in flowing argon saturated with water vapor at 25°C. The thickness of the oxide coating was calculated from weight gain measurements to be of the order of 2μ. The iron surface was oxidized to insure wetting of the disk by the glass.

Both recrystallized alumina and platinum crucibles were used in the thermogravimetric measurements. Composites placed in these crucibles were lowered under a vacuum of 5×10^{-4} torr into the hot zone of a controlled atmosphere, resistance-heated vertical tube furnace and held for 1-1/2 min. at temperature. Purified argon was then introduced to a pressure of 1 atm and the sample was held in the hot zone for another 8-1/2 min. to insure complete sealing of the iron disk in the crucible by the glass.

After sealing, the specimen was transferred to a thermobalance capable of detecting weight changes of 0.5 mg. The experiments were conducted in air at a number of constant temperatures and various times as indicated in Table I.

C. Galvanic Cell Experiment

In order to demonstrate the galvanic or electrochemical nature of some of these reactions, a composite arrangement of unoxidized

Fe and Co disks and cylinders of glasses A and B was placed in a platinum crucible, as shown in Fig. 1. To insure a good external electrical circuit, the two metal disks were connected by spot welding a platinum strip between them. This specimen was sealed under vacuum at 950°C as previously discussed and the heating was continued under a flowing atmosphere of purified argon for 3 hrs.

D. Electron Microprobe Analyses

Each of the above-mentioned specimens after heating was sectioned perpendicularly to the surface of the metal disk. The cross sections were given a high metallurgical polish, and a coating of graphite was vapor-deposited on the surface to make it conductive and suitable for electron microprobe analysis. The concentration distributions in the glass perpendicular to the glass-metal interface were determined by means of an ARL* electron microprobe. The analytical technique involved scanning a 2μ diam beam parallel to the interface at 96μ/min and making a 20 sec. integrated count of the K_α radiation of Na, Si, Fe, and Co. A concentration-vs-distance profile was constructed by taking a number of such measurements at known distances from the interface. Due to the wave length limitations of the spectrometers it was necessary to generate the profile by first simultaneously analyzing for Na, Si, and Fe and then repeating the steps and analyzing for Na, Si, and Co.

Calibration curves for analysis of SiO_2, FeO, and CoO in the unknown glass were constructed from a selection of chemically analyzed

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* Manufactured by Applied Research Laboratory

standard glasses. Only qualitative information was gained from the sodium counts; however, a confidence of ±1-2% in the determination of the other oxide components permitted the determination of Na_2O by difference. The metallic dendrites precipitated from glass B during the experiments were found, by microprobe spectral scanning, to contain only Fe and/or Co. The actual compositions were analyzed with the microprobe using Fe and Co as standards. It was predicted and found that, with appropriate dead time and background corrections, the intensity of x-radiation from the metallic particles was a linear function of the percent of the element present. Percent Fe and Co determined by separate measurements on the various dendrites added to 100% ± 0.5%. In determining the concentration profile in the glass, specific attention was given to analysis of the glass compositions adjacent to analyzed dendrites. This information was used in the calculation of an equilibrium constant.

The solubility of ferrous oxide in sodium disilicate glass at 950°C is given by phase diagrams of Carter and Ibrahim[4] to be approximately 42 wt%, but no information is available on the solubility of CoO in this glass. In order to determine this value, a diffusion couple was prepared from a disk of Co metal which had been oxidized to a thickness of approximately 36μ (15 min. in air at 1000°C) and a cylinder of sodium disilicate glass. X-ray analysis showed the oxide to be predominantly CoO. The couple was given a diffusion anneal of 10 min. at 950°C and the profile and interfacial concentration of CoO in the glass was determined by microprobe analysis as described earlier. During the anneal the glass did not dissolve all of the oxide so that

the interfacial concentration of CoO represents the solubility limit at 950°C, which was found to be approximately 25 wt% CoO.

III. RESULTS AND DISCUSSION

It was pointed out in previous studies[3,5] that a driving force for reactions exists in a glass-metal system if thermodynamic equilibrium is not present. These reactions are initiated at the base metal-glass interface. In the system iron-glass-air if the glass at the interface is not saturated with ferrous oxide, then it attempts to reach this condition either by (a) oxidation of the iron by atmospheric oxygen which results in a weight increase of the assembly, or (b) by a redox type of reaction of an electrochemical nature between the iron and some constituent in the glass that has a lower oxidation potential, with no weight increase.

A. Glass-Metal Interfacial Reactions

The experimental conditions for the thermogravimetric experiments are indicated in Table I. In general, those runs conducted in platinum crucibles showed an appreciable gain, as seen in Fig. 2, with glass A in each case showing a slightly higher rate of weight gain. Those runs conducted in alumina crucibles, with both glasses, showed no net change in weight indicating no reaction with atmospheric oxygen. Examination of the concentration profiles for the experiments with glass B in alumina crucibles (Figs. 3 and 4), however, demonstrates that the total iron oxide content of the glass has increased with time. This increase is the result of internal redox reactions of an electrochemical nature arising from the demand for equilibrium within the system. These

reactions are associated with the appearance of dendrites.

Of the diffusion profiles shown in Figs. 3 and 4 the 10 min. specimen (Fig. 3) most closely approximates a typical profile for ferrous oxide dissolution;[6] but even in this short time the small amount of oxide on the iron surface had been completely dissolved and sufficient diffusion had occurred to drop the iron oxide content of the glass at the interface from the saturated value of 42% to about 28%. Also, the beginning of electrochemical interactions between the iron substrate and the cobalt ions in the glass was indicated by the appearance of small dendrites in the diffusion zone.

After dissolution of the iron oxide, iron continues to enter the glass by the following electrochemical reaction steps

$$\mathrm{Fe(substrate)} \rightarrow \mathrm{Fe^{2+}(glass\ I)} + 2e^- \qquad (1a)$$

and

$$2e^- + \mathrm{Fe^{2+}\ (glass\ II)} \rightarrow \mathrm{Fe(alloy)} \qquad (1b)$$

$$2e^- + \mathrm{Co^{2+}\ (glass\ II)} \rightarrow \mathrm{Co(alloy)} \qquad (1c)$$

resulting in the coupled reaction

$$\mathrm{Fe(substrate)} + x\mathrm{Fe^{2+}\ (II)} + (1 - x)\mathrm{Co^{2+}(II)} \rightarrow \mathrm{Fe^{2+}(I)} + \mathrm{Fe_xCo_{-x}(alloy)} \qquad (1d)$$

wherein glass I is in contact with the base iron and glass II is at the site of the Fe-Co alloy dendrite formation. This reaction depends on the substrate having a higher potential for oxidation than the metal being reduced from its ionic state in the glass. The mechanism involves a transport of electrons from the iron substrate (as Fe^{2+} enters the glass structure) to the ions in the glass whenever a proper combination

of conductive path and nucleation site is available. The conductive path in this case is probably provided by the dendrites themselves, although the possibility of some semiconductive mechanism in the glass close to the interface due to the presence of iron oxide cannot be discounted entirely. If a glass initially containing no iron ions is placed on a clean iron substrate, the very first iron enters the glass by a redox reaction, and the reduced cobalt precipitates out on the substrate iron and alloys with the iron.[3]

The material transport phenomena associated with these reactions can be observed in Figs. 3 and 4. All the iron which has been introduced as a glass oxide component (with the exception of the initial thin oxide layer on the substrate) must be accounted for by the amount of cobalt which has been precipitated as dendrites since there was no atmospheric oxidation as indicated by no gain in weight or heating. The boundary conditions in this case are an infinite supply of substrate metallic iron and a finite supply of cobalt ions in the glass. Since the oxygen content of the glass remains constant, an adjustment of the cation distribution must occur locally to maintain electroneutrality. As positions occupied by either Fe^{2+} and Co^{2+} within the iron diffusion zone adjacent to the substrate metal or by Co^{2+} beyond the diffusion zone are vacated by dendrite formation, they are filled by advancing cations from the interface zone with the result that the vacancy flux toward the base metal frees a position at the interface for the incoming Fe^{2+} formed by reaction (1a). The vacancies moving toward the base metal are equivalent to moving negative "holes", and the electrons released at the base metal move through the dendrites (and possibly

the transition-ion rich glass) to the precipitating site. The circuit is thus completed. The decrease in Co^{2+} content in the bulk glass due both to diffusion toward the interface and to precipitation of dendrites and the introduction of Fe^{2+} at the interface are thus counteracted by the diffusion of the highly mobile sodium ions from the glass-metal interface (as seen in Figs. 3 and 4). This uphill diffusion of Na^{+} with respect to its concentration gradient and in all probability also with respect to its activity gradient satisfies the need for maintaining local electroneutrality throughout the glass. Such uphill diffusion of Na^{+} can be explained on the basis that in the presence of an electrical potential gradient the diffusion flux of an ion must involve consideration of both the chemical and electrical potential gradients according to an expression[7] similar to

$$J_i = -D_i \frac{C_i}{RT} \frac{\delta\mu_i}{\delta x} - D_i \frac{Z_i C_i F}{RT} \frac{\delta\phi}{x} \qquad (1e)$$

where

$\frac{\delta\mu_i}{\delta x}$ = chemical potential gradient for species i

$\frac{\delta\phi}{\delta x}$ = electrical potential gradient

J_i = diffusion flux

D_i = diffusion coefficient

Z_i = valence

C_i = concentration

F = Faraday constant

R = gas constant

T = absolute temperature

In this case a negative electrical potential gradient is supplied by reaction (1d) of sufficient magnitude to predominate in equation (1e) with the result that the sodium diffuses away from the substrate-glass interface. Such reactions would terminate with depletion of either Co^{2+} in the glass or complete oxidation of the base iron. At this point the whole system would move towards equilibrium by elimination of all concentration gradients by diffusion.

The experiments conducted in platinum crucibles showed not only weight gains but also extensive reaction and decomposition of both glasses A and B at the platinum-glass-air contact circle. The principal compounds formed were identified by x-ray diffraction as Na_2SiO_3 and its hydrates. The mechanism responsible for this reaction is illustrated by the diagram in Fig. 5. The platinum crucible acts as a path for electrons from the iron to the contact circle where the half-cell reaction for formation of O^{2-} anions from oxygen in air takes place. As iron gives up electrons, Fe^{2+} enters the glass displacing an adjoining cation which displaces a cation in turn until the surface anion is balanced. This displacement is accomplished principally by Na^+ because of its high mobility. Earlier discussions in regard to uphill diffusion of Na^+ also apply here. As a consequence the glass at the contact circle becomes sufficiently enriched in Na_2O to form the metasilicates. The lower gain in weight with glass B is attributed to the concurrent electrochemical reaction (1d) which lessens the need for atmospheric oxidation.

B. Dendrites

In the absence of the availability of oxygen but with a supply of Co^{2+} and Fe^{2+} in the glass, the mechanism for introducing additional iron into the glass at the interface is the precipitation of dendrites of Co or Co-Fe alloys by means of reaction (1d). Dendrites thus appear in glass B in regions that are both energetically favorable and accessible to available electrons. The dendrites appear initially at or near the iron surface and with time extend considerably beyond the limit of Fe^{++} diffusion into the glass. This extension was not observed in the previous study with a more complex glass indicating, as expected, that the nature of the glass structure is critical. In the case of the galvanic cell (Fig. 1), the dendrites appear at the cobalt metal surface but not along the platinum strip in contact with glass B, illustrating the necessity for both nucleation sites and available electrons.

In analyzing the composition of a dendrite and its adjacent glass, one obtains a measure of the equilibrium which is established at the cathode of the cell described by reaction (1d). The equilibrium at the cathode is regulated by a balance between equations (1b) and (1c) which yields

$$Fe(alloy) + Co^{2+}(II) = Fe^{2+}(II) + Co(alloy) \qquad (2a)$$

The equilibrium constant for Eq. (2a) may be given in terms of the activities of the individual species as

$$K_{eq} = \frac{a_{Co(alloy)} \cdot a_{Fe^{2+}(II)}}{a_{Fe(alloy)} \cdot a_{Co^{2+}(II)}} \qquad (2b)$$

If an equilibrium is established at the cathode, it is apparent from relation (2b) that the composition of the alloy precipitated from the glass will be determined by the ratio of iron and cobalt ions in the glass at the dendrite site.

The iron content of the dendrites of the 9-hr thermogravimetric specimen as a function of the distance from the interface is shown in Fig. 6 with the balance of the composition being cobalt. Table II lists these data and the data for glass compositions at corresponding distances, taken from Fig. 4, and the calculated equilibrium constants for redox reaction (2a) as given by Eq. (2b). For these calculations the activities of the various species were considered to be proportional to their respective weight fractions in the dendrites and the adjacent glass, respectively. From these values the equilibrium constant is then calculated to be 127 ± 11. The immediate establishment of electrochemical equilibrium at any point between the dendrite alloy and the adjacent glass is indicated by the fairly constant values for the equilibrium constant (Table II).

The value of K_{eq} at 950°C for reaction (2a) based on the thermodynamic functions given in Lewis and Randall[8] for the elements and the oxides is 46 (Table II footnote). The difference between this value and the calculated experimental value of 127 is not critical, particularly on the basis of further interpretations. The use of weight fraction as a measure of the activity values for the alloy serve as first-order approximations since Fe and Co have similar atomic weights and since the Fe-Co alloy system is almost ideal.[9] There is, unfortunately, no data for the activity coefficients of the components of the glass

expressed as oxides. As a further approximation, however, it can be assumed that the activities of the iron and cobalt oxides in the glass are proportional to the fraction of the oxide present in terms of the oxide in the glass at saturation (25% CoO and 42% FeO in sodium disilicate). The equilibrium constant is then calculated to be 76. Furthermore, the theoretical value of 46 was based on solid oxides and did not consider any differences in the free energy of mixing of the oxides in the glass. On the basis of relative solubilities of iron and cobalt oxides in sodium disilicate glass and the higher heat of fusion of cobalt oxide, one would predict the free energy of mixing of iron oxide in sodium disilicate glass to be more negative than that of cobalt oxide. Application of such a correction would result in a theoretical value higher than 46.

A K_{eq} of 76 requires that the standard free energy for the reaction be -10,560 cal/mole or 1,280 more negative than the theoretical value of -9280 cal/mole for Eq. (1d). This difference could easily be accounted for by the above complicating factors.

C. Galvanic Cell Reactions

The concentration distributions shown in Fig. 7 were determined by microprobe analysis of a cross section of the galvanic cell shown in Fig. 1. Not shown by the graph is the existence of dendrites growing from the cobalt-glass interface (Fig. 8). The concentration profiles are due to the electrolytic process in which the iron base metal supplies Fe^{2+} to the glass while Co^{2+} ions are reduced to dendrites according to the electrochemical reaction

$$Fe(substrate) + Co^{2+}(II) \rightarrow Fe^{2+}(1) + Co(dendrite) \quad (3)$$

The material balance is simplified since no metallic precipitates can occur in the iron diffusion zone and those in the cobalt side of the cell are cobalt. On a molar basis, $[Fe^{2+}]$ introduced = $[2Na^{+}]$ (iron side) displaced = $[2Na^{+}]$ (cobalt side) enriched = $[Co^{2+}]$ precipitated. This material balance is unaffected by the interdiffusion occurring at the liquid junction interface between the cobalt-free and cobalt-bearing sodium disilicate glasses. The needed transfer of electrons from the iron to the cobalt disk to complete the circuit was achieved by the external connector between the disks. The external circuit is necessary since electronic conductivity through sodium disilicate glass, as indicated by the thermogravimetric experiments, is negligible or non-existent.

Of particular interest is the achievement of a material balance with the nonexistence of either a Na_2O or SiO_2 gradient over a distance of more than 11,000μ within glass A. This fact suggests a mechanism of "domino-like" mass transport which results from the shorting of the galvanic cell and associated establishment of an electrical potential gradient.

It should also be noted that the specific data in Fig. 7 do not show an exact balance between the loss in Co^{2+} and the gain in Fe^{2+} in the glass or between the loss in Na^{+} in glass A and the gain in glass B. In actuality, such balances do exist on an integrated basis. An appreciable amount of convection observed in the cross section of the specimen at the iron end accounts for this unbalance. A composition traverse at another point would thus show a reverse unbalance.

The maximum concentration of iron which can be introduced under these conditions, i.e., without addition of oxygen, is limited to the equivalent concentration of sodium available for displacement. Saturation of the glass with respect to iron oxide at the glass-iron interface thus can never be achieved by this cell; likewise, with respect to cobalt oxide at the glass-cobalt interface. As a result, chemical bonding did not occur at either glass-metal interface and no adherence was observed. This fact is particularly interesting in view of the extensive dendrite formation in the cobalt-bearing glass.

IV. CONCLUSIONS

It has been shown that reactions may occur in glass containing reducible oxides-metal systems that are not at equilibrium, which are galvanic or electrochemical in nature and thus require both electronic and ionic transport mechanisms. The principal points are:

(1) When an electronic path is provided, reactions at the base metal-glass interface are coupled with other reactions occurring elsewhere, e.g., absorption of atmospheric oxygen or formation of metallic dendrites.

(2) The formation of dendrites is associated with the establishment of a galvanic circuit wherein electrons released at the base metal by formation of metallic ions travel by way of the dendrite to the site where the low oxidation potential ions are being precipitated, and the return current is provided by the vacancy flux, or movement of negative "holes", toward the base metal as the cations move toward the precipitating site. Dietzel[10] was one of the first who proposed

a theory of adherence involving galvanic reactions at the interface, but the proposed cell reactions required atmospheric oxygen which in this study with sodium disilicate glass was found not to be the case.

(3) An adjustment of charges and an electrovalent balance is maintained over relatively long distances by electrolytic transport of cations, principally the highly mobile sodium ions. In all of the cases studied, Na^+ diffusion occurred against both sodium concentration and chemical potential gradients. These uphill diffusion gradients were caused by the electrochemical potential gradient imposed by reaction (1d) which resulted in a lowering of the free energy for the entire system.

(4) The composition of the dendrites that precipitated was that required for thermodynamic equilibrium with the adjoining glass, and the equilibrium constant was independent of the distance from the metal surface. The glasses at the dendrite surfaces, however, were not saturated with respect to either oxide.

(5) In the experiments on the galvanic cell the glass composition at either interface did not reach saturation with respect to the corresponding metal oxide, and glass-metal adherence was therefore poor at both interfaces. The presence of dendrites at the cobalt interface did not produce adherence.

(6) Saturation of the glass at the glass-metal substrate interface with the oxide of the metal can be achieved only by solution of an oxide formed by preoxidation of the metal. The concentration of the cations at the interface can be subsequently maintained by means of redox reactions of an electrochemical nature between the

substrate metal and atmospheric oxygen or cations, in the glass, of metals whose potentials for oxidation are lower than that of the substrate metal, resulting in dendrites. In the systems reported here the latter mechanism was dominant.

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Table I. Experimental Conditions for Thermogravimetric Experiments in Air

Substrate	Glass used	Time	Crucible Material	Net wt. Change, mgm.	Temp., °C
Fe disk	A	3 hrs	Pt	65	900
with about	B	"	"	50	"
2μ oxide	A	"	"	70	1000
layer	B	"	"	63	"
"	A	3 hrs	Al_2O_3	0	950
	B	10 min	"	0	"
	B	9 hrs	"	0	"
	B	24 hrs	"	0	"

Table II. Calculation of K_{eq}. †

Distance μ	Co wt%	Fe wt%	FeO wt%	CoO wt%	K
100	24	76	20.5	0.05	130
200	39	61	18.5	0.1	118
400	60	40	15.6	0.2	117
600	79	21	13.5	0.4	127
800	89	11	11.4	0.8	115
1000	94	6	9.2	1.1	131
1200	96	4	6.9	1.4	118
1400	98	2	4.8	1.7	138
					127 average*

† Data taken from curves of wt% Fe (in dendrites) and wt% oxides (in glass) vs distance after heating at 950°C for 9 hrs.

$$0.947\ Fe + CoO = Fe_{0.947}O + Co$$

$$\Delta F^{\circ}_{1223^{\circ}K} = -9280;\ K_{eq} \cong 46$$

*With no corrections; value of 76 with correction for saturation contents of the oxides in the glass.

FIGURE CAPTIONS

Fig. 1. Schematic cross section of galvanic cell.

Fig. 2. Weight gain vs time for glass-iron composites heated in Pt crucibles. A = sodium disilicate glass with iron disk; B = A plus 4.8% CoO with iron disk; Blank = sodium disilicate glass. Weight loss during the initial minutes is due to degassing of the glass.

Fig. 3. Diffusion profiles of glass B-iron composite heated at 950°C in an Al_2O_3 crucible for 10 min.

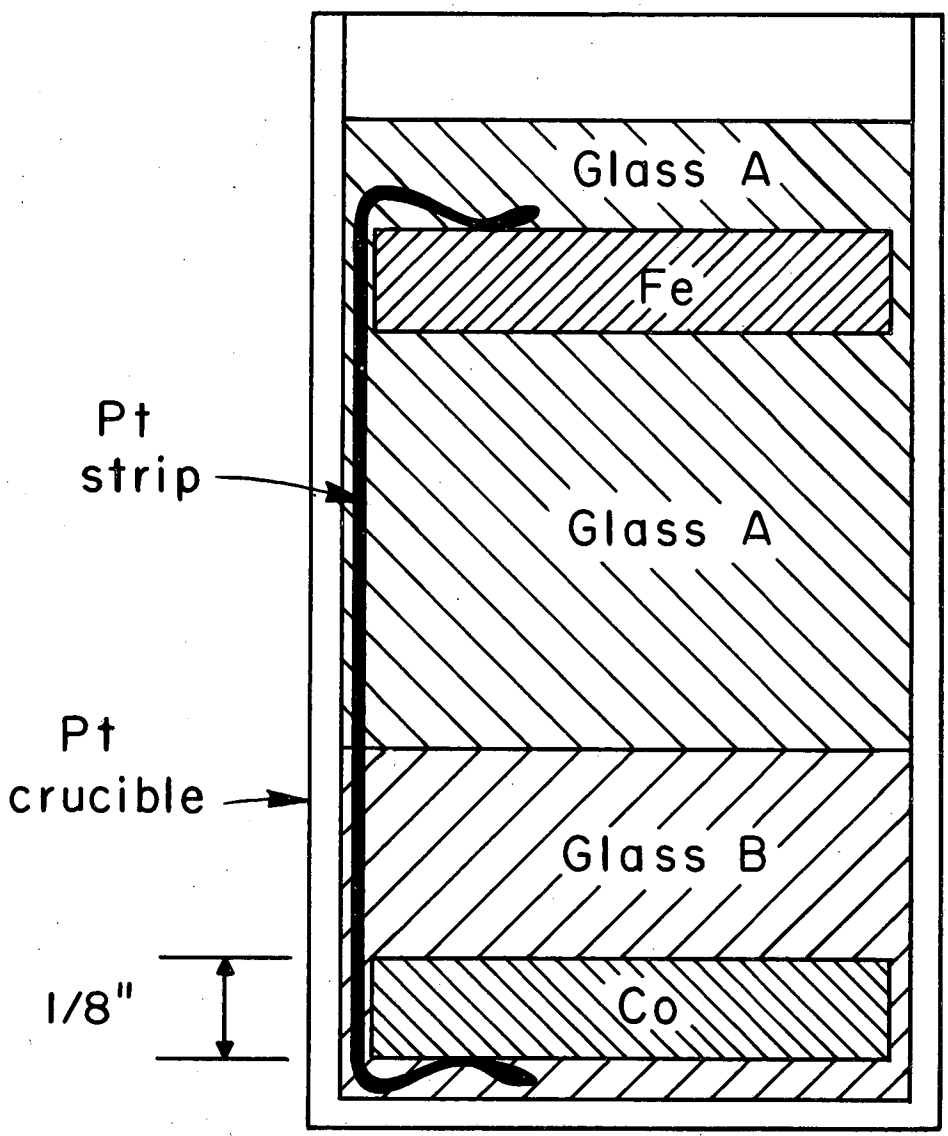
Fig. 4. Diffusion profiles of glass B-iron composite heated at 950°C in an Al_2O_3 crucible for 9 hrs.

Fig. 5. Mechanism for the reaction occurring at the platinum-glass-air contact circle.

Fig. 6. Iron content of dendrites vs distance from blass B-iron interface for specimen in Fig. 3b; the balance of composition is Co.

Fig. 7. Diffusion profile of the galvanic cell sketched in Fig. 1 after 3 hrs at 950°C.

Fig. 8. Dendrites growing from the cobalt-glass interface of the galvanic cell shown in Fig. 1 after 3 hrs at 950°C.



MUB-10043

Fig. 1

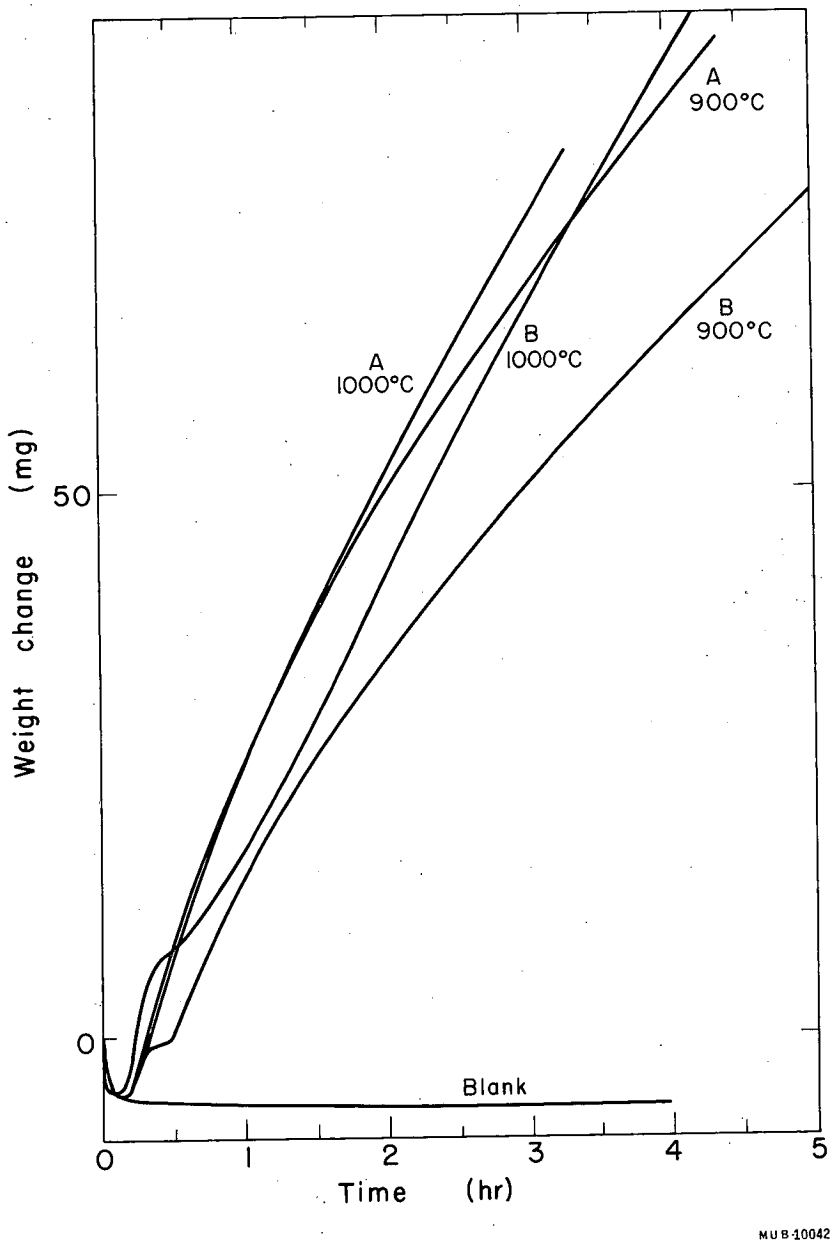

A
900°C
B
900°C
B
1000°C
A
1000°C
Blank
Weight change (mg)
50
0
0
1
2
3
4
5
Time (hr)
MUB-10042

Fig. 2

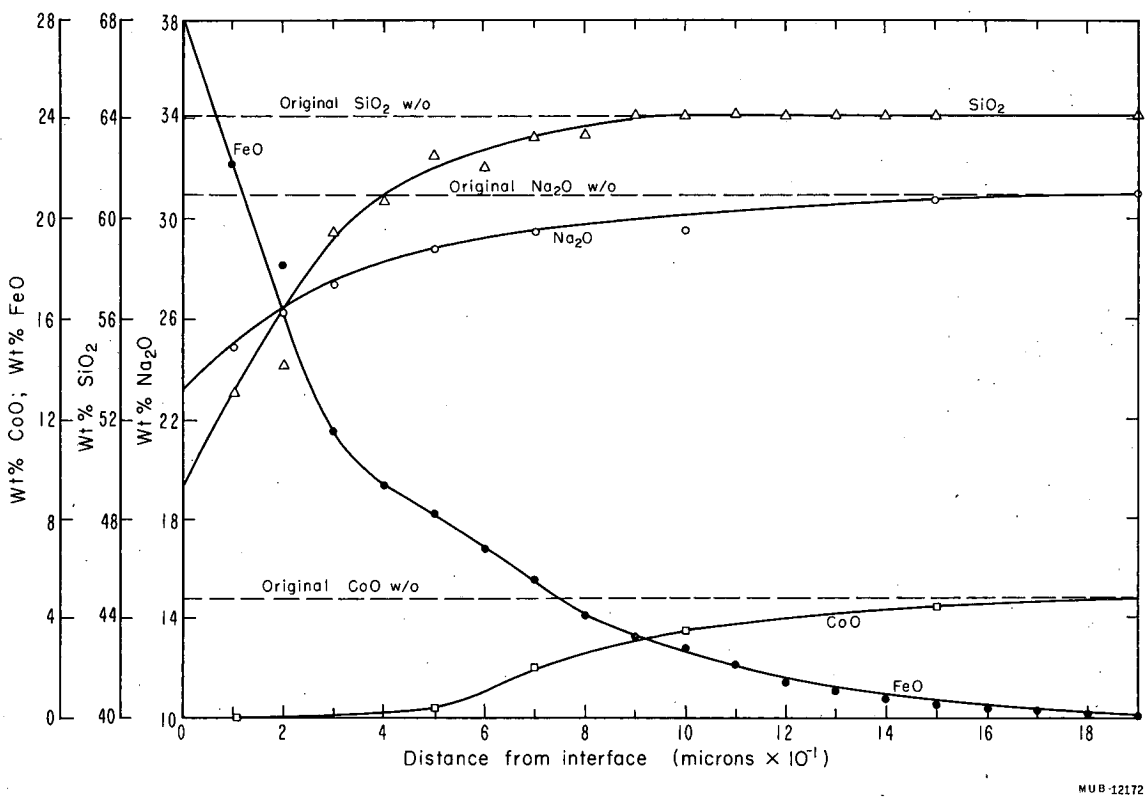

Wt% CoO; Wt% FeO
Wt% SiO2
Wt% Na2O
Original SiO2 w/o
Original Na2O w/o
Original CoO w/o
SiO2
Na2O
CoO
FeO
FeO
Distance from interface (microns × 10⁻¹)
MUB-12172

Fig. 3

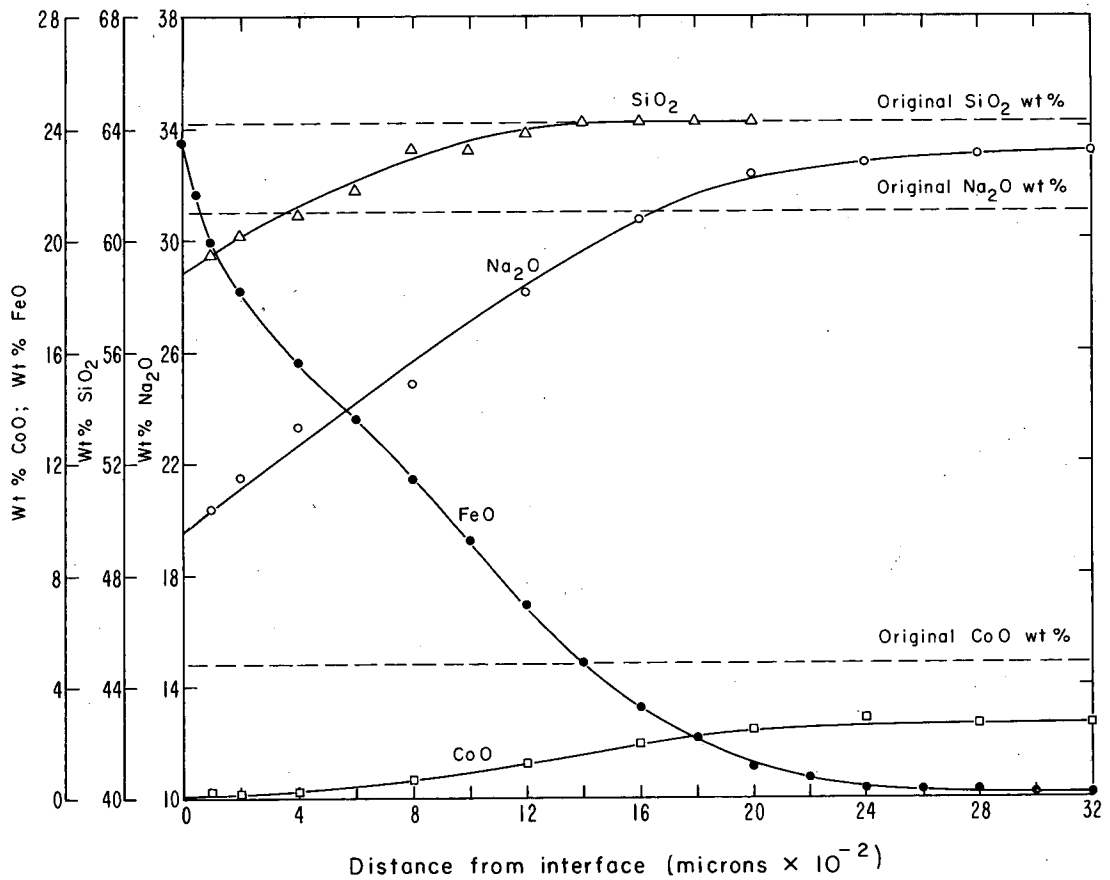
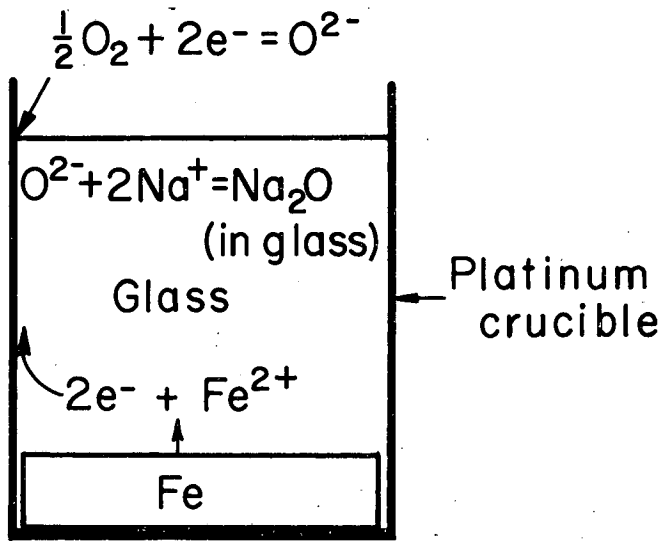

Wt % CoO; Wt % FeO
Wt % SiO2
Wt % Na2O
SiO2
Original SiO2 wt %
Original Na2O wt %
Na2O
FeO
Original CoO wt %
CoO
Distance from interface (microns × 10^-2)
MUB-10044

Fig. 4



MUB-10041

Fig. 5

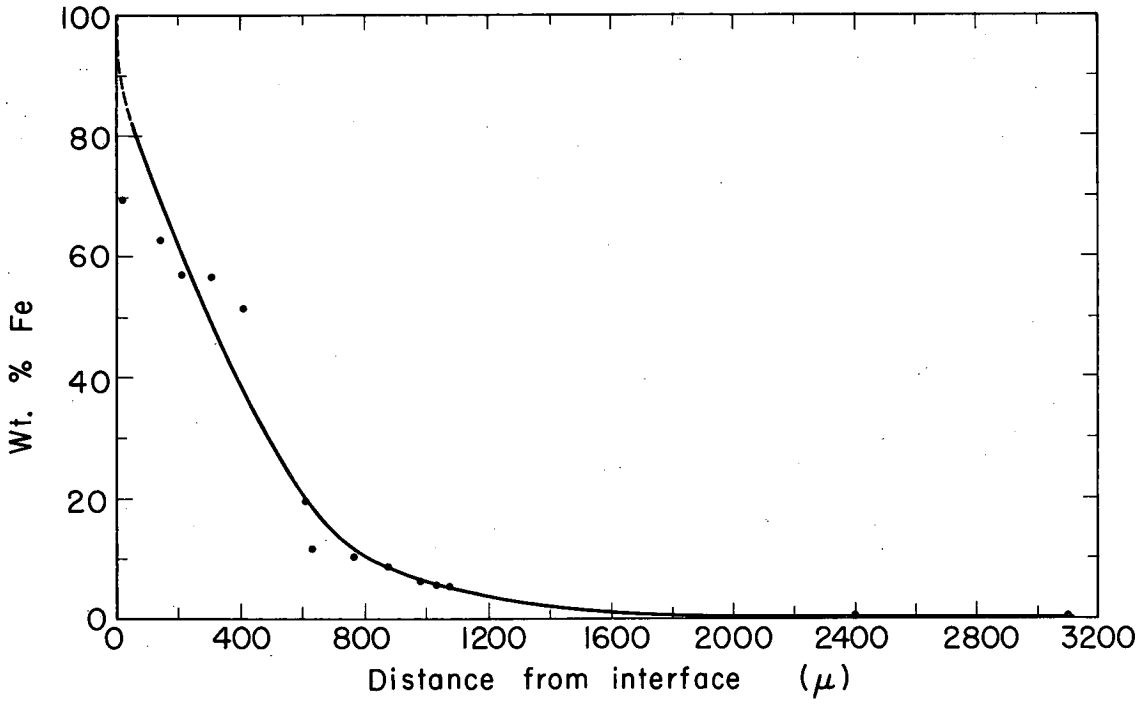

100
80
60
40
20
0
Wt. % Fe
0
400
800
1200
1600
2000
2400
2800
3200
Distance from interface (μ)
MUB-10040

Fig. 6

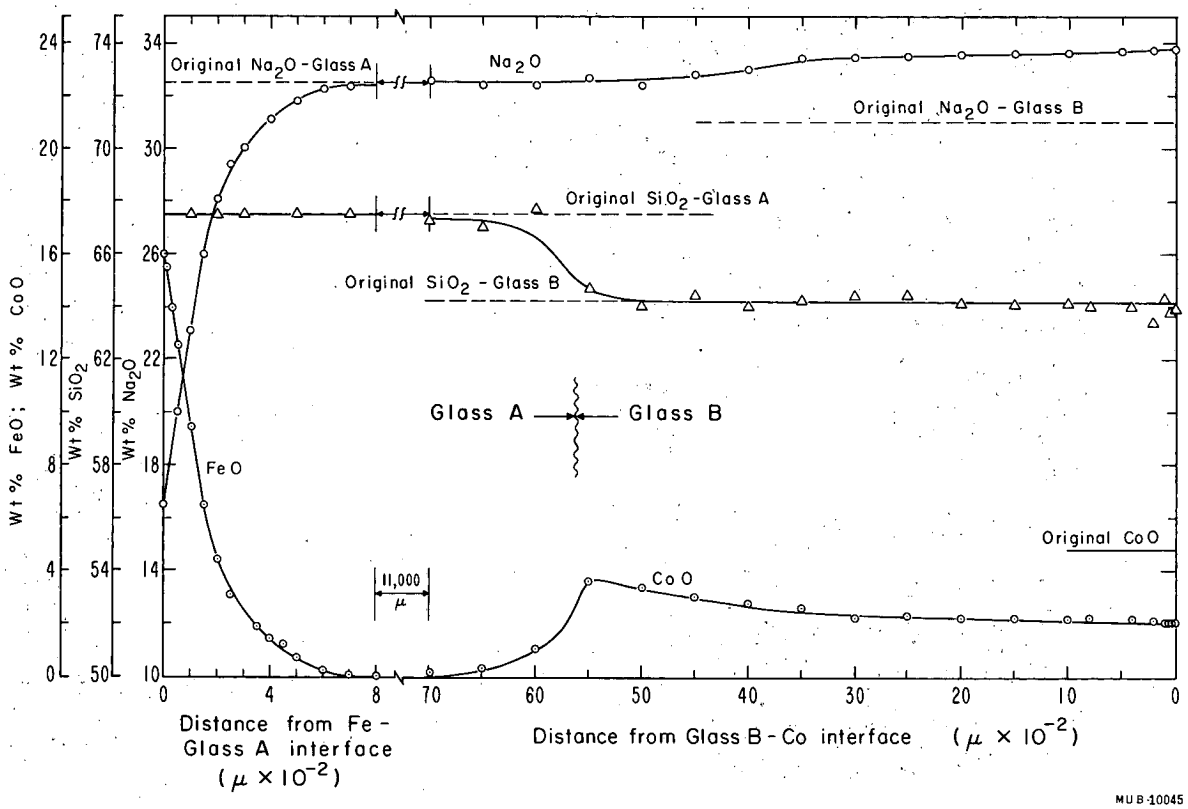
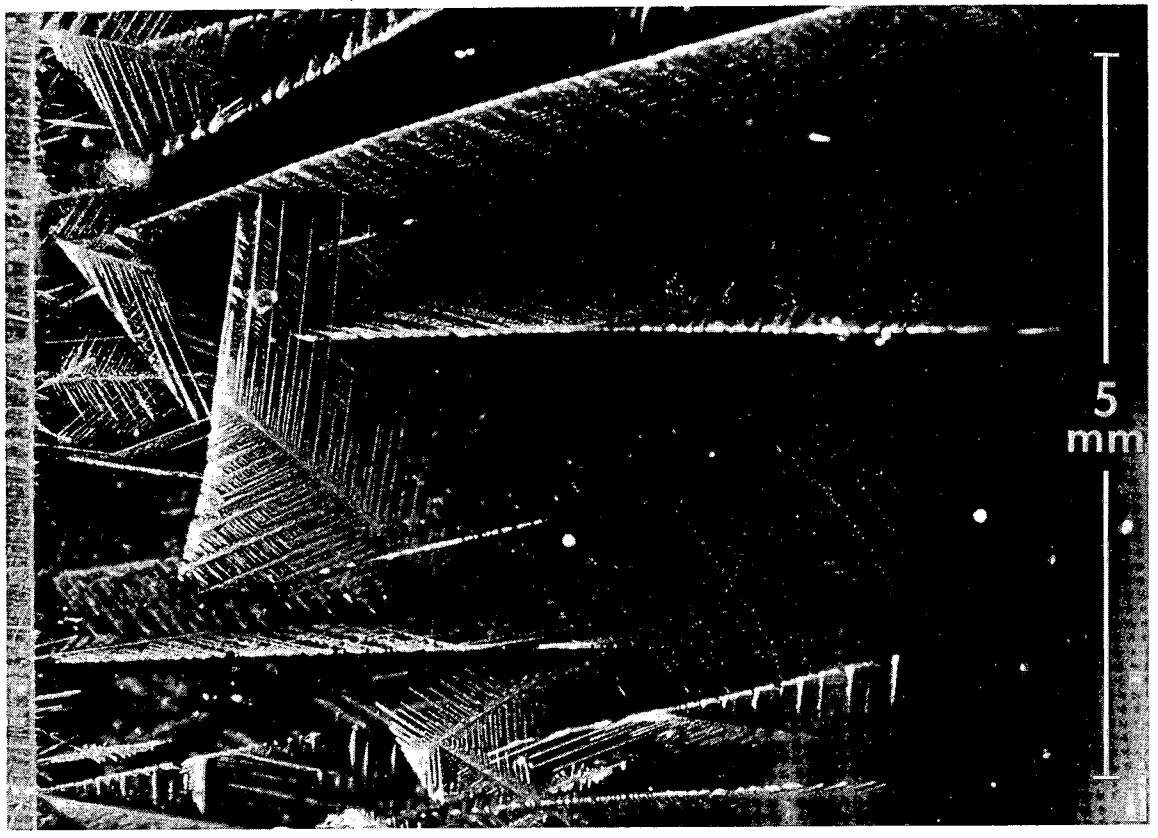

Original Na_2O - Glass A
Na_2O
Original Na_2O - Glass B
Original SiO_2 - Glass A
Original SiO_2 - Glass B
Glass A
Glass B
FeO
CoO
Original CoO
11,000 μ
Wt % FeO; Wt % CoO
Wt % SiO_2
Wt % Na_2O
Distance from Fe - Glass A interface ($\mu \times 10^{-2}$)
Distance from Glass B - Co interface ($\mu \times 10^{-2}$)
MUB-10045

Fig. 7



ZN-5758

Fig. 8

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