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Abstract

The wetting of iron was investigated by the sessile-drop method using similar compositions in the soda-silica and soda-boric oxide systems, sodium disilicate glass with FeO and Fe_2O_3, and sodium disilicate glass with Fe^{+2} ions replacing some of the Na^+ ions. A qualitative measure of adherence was also obtained for these glasses.

A requirement for wetting of a metal by molten glass and for adherence by chemical bonding is a balance of bond energies at the interface, which is associated with a lower interfacial energy. This condition is achieved by lowering the internal energy of the glass until, in most cases, a crystalline phase appears. Adherence by van der Waal's bonding is possible when the interfacial energy is high, if the surface energy of the fractured glass is also correspondingly higher; work of adhesion in this case remains high. A certain amount of glass phase must be present for adherence to occur.

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I. Introduction

Previous work on glass-metal systems has shown that the development of good wetting and adherence depends upon the formation of a chemical bond rather than a van der Waal's bond across the glass-metal interface. Pask and Fulrath have proposed a theory that a chemical bond can be formed by adjusting the glass composition so that the internal energy of the glass is lowered until a balance of bond energies occurs across the interface.[1] In most cases, the internal energy of the glass must be reduced to some thermodynamically stable state as indicated by the precipitation of a crystalline phase. The internal energy of a glass is lowered by increasing its oxygen-silicon ratio either by adding oxides of the network-modifying cations to the composition or by solution of the substrate metal oxide before or during sealing, or by replacing noble-gas-type secondary cations by more polarizable cations of a non-noble-gas type. It has been shown a number

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*This work was done under the auspices of the U.S. Atomic Energy Commission.

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‡Professor of Ceramic Engineering.

of times that better adherence can be obtained by saturating the glass with sufficient substrate metal oxide to precipitate a crystalline phase.[2,3,4] This paper presents and discusses sessile-drop experiments that were designed to verify the proposed theory.

The degree of wetting of a metal by a glass can be measured by the contact angle of a sessile drop. Figure 1 shows the equilibrium configurations of liquids that (a) wet a solid, and (b) do not wet a solid. In the first case, the surface energy of the solid is reduced by the liquid; in the second case, it is increased by the liquid. In both cases, however, a glass-metal interface is formed because the basic driving force is toward a lower energy state for the over-all system.

The contact angle, θ, is dependent upon surface tensions as given by Young's equation:[5]

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} , \qquad (1)$$

where γ_{sv} is the surface tension of the solid-vapor interface, γ_{sl} is the surface tension of the solid-liquid interface, and γ_{lv} is the surface tension of the liquid-vapor interface. Necessary conditions for the applicability of Young's equation are: (1) the effect of adsorbed substances on the surface energies under test conditions must be known, and (2) no interfacial compounds should form as a distinct phase at the glass-metal interface.[6,7]

Seven soda-silica compositions were used to investigate the effect of the oxygen-silicon ratio of the glass on the wetting of iron. Iron was chosen because earlier work showed no adherence with sodium disilicate glass in vacuum. Thus, by using it, we could more readily evaluate and study the development of any adherence as well as the

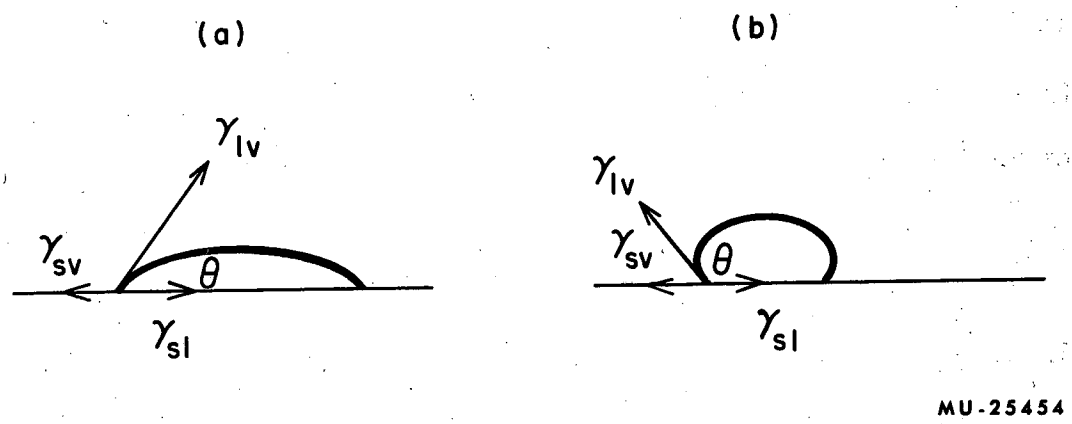

Fig. 1. Sessile-drop method for determining degree of wetting of solid by liquid. (a) Wetting, (b) nonwetting.

contributing factors. The effect of metal oxide was studied by saturating sodium disilicate glass with ferric oxide and ferrous oxide, respectively; intermediate compositions were made by adding 5 mol % of the respective oxide to sodium disilicate glass. Ferric ions in the glass react with the iron substrate, leading to an irregular interface, while ferrous ions do not react. Thus, an evaluation of the effect of an irregular interface on adherence becomes possible. The role of the network-modifying cation in promoting adherence was investigated by substituting Fe^{+2} ions for Na^{+} ions in a disilicate glass. The wetting of iron by five soda-boric oxide compositions was studied to determine the effect of the oxygen/network-former ratio in another type of glass system.

II. Experimental Procedure

1. Apparatus

The experiments were run in an enclosed strip furnace which served as a specimen holder as well as a source of heat. Current was carried to the dual-strip molybdenum heating elements by water-cooled copper electrodes. The electrode assembly in Figure 2 was shielded by removable radiation shields (the inner one of zirconium and the two outer ones of tantalum foil) held in place by a slotted alundum cylinder. The shields had holes cut on opposite sides for observation of the specimen. The radiation shield in the Figure has been cut in half to show the placement of the specimen.

The temperature was measured with an alumina-sheathed Pt/Pt-10% Rh thermocouple attached to the specimen holder with molybdenum wire. Because the thermocouple bead was situated at

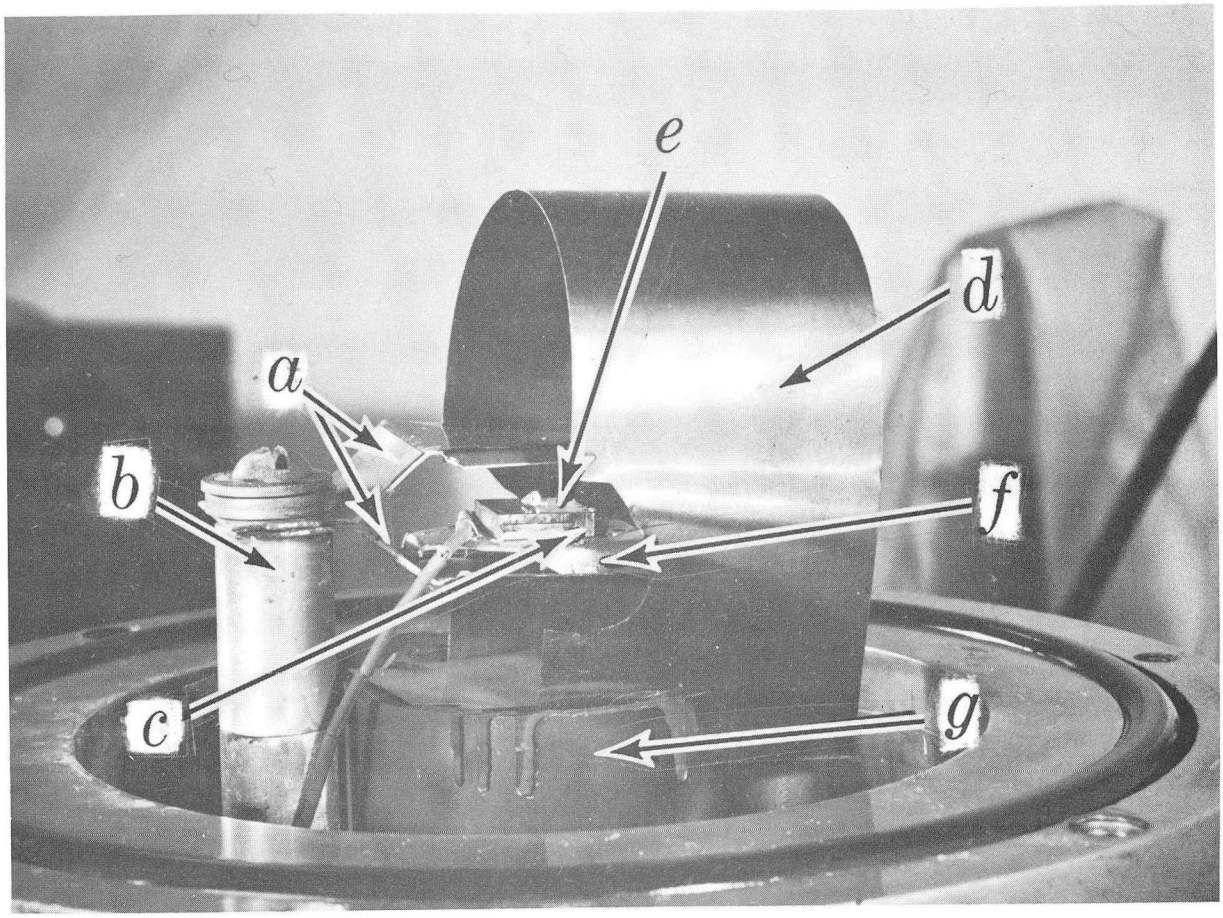

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Fig. 2. Electrode assembly, showing (a) heating elements, (b) water-cooled electrodes, (c) thermocouple bead, (d) radiation shield (cut in half), (e) iron specimen plate with glass specimen, (f) specimen holder, and (g) radiation shield holder.

the side of the iron plate rather than in contact with the glass, it was calibrated for a given phenomenon occurring on the iron plate. This objective was accomplished by fusing substances of known melting points on iron specimen plates, simulating the actual experimental conditions. The usual method of calibrating against a standard thermocouple does not yield useful data for this equipment because of the absence of black-body conditions. It was found that the emissivity of a substance and its reactivity with the iron plates were the important factors in its selection as a calibration standard. The final calibration curve was based on the use of KCl, NaCl, LiF, and MgF_2.[8]

The water-cooled brass furnace cap, shown in Figure 3, had two silica windows for observation of the specimen. Measurements were made at test temperatures with a telescope equipped with a filar-micrometer eyepiece and a graduated protractor. Angles could be read to ± 1 deg, when auxiliary lighting was placed behind the specimen.

The system was evacuated with a mechanical forepump and an oil-diffusion pump. The pressure was measured with a cold-cathode ionization gauge. A liquid-nitrogen cold trap was used to condense vapors from the diffusion pump.

2. Specimen Preparation

The metal specimens were prepared by cutting 3/8-in.-square samples from 1/8-in.-thick Armco magnetic ingot iron (typical analysis: 0.015% C, 0.0285% Mn, 0.005% P, 0.025% S, and 0.003% Si).*

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*"Armco Magnetic Ingot Iron - for O-C Applications" catalogue, Armco Steel Corp., Middletown, Ohio, 1955.

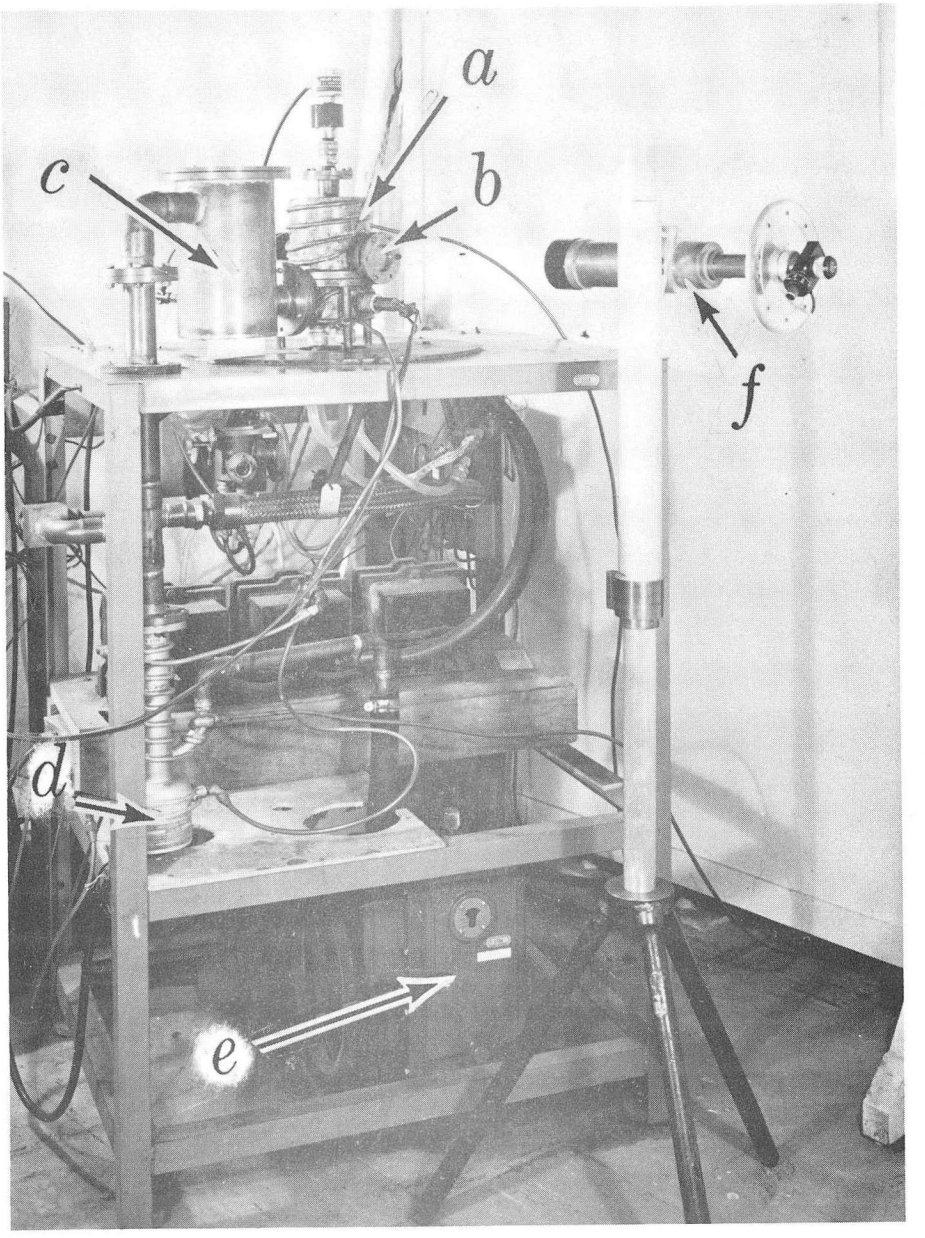

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Fig. 3. Furnace assembly, showing (a) the furnace, (b) silica window, (c) cold trap, (d) diffusion pump, (e) mechanical pump, and (f) telescope with graduated protractor.

The specimens were ground on belt grinders, polished on dry polishing papers, and given a final polish with a suspension of Linde A-5175.* They were then washed in distilled water, dried, sprayed with Krylon clear plastic to prevent tarnishing, and stored in a dessicator. The iron was cleaned just before a run by swabbing with acetone and then anhydrous ether.

The glasses in the soda-silica and soda-boric oxide systems had the same mol % compositions: 40, 50, 60, 66.7, and 80% SiO_2 or B_2O_3. (All percentages in the remainder of the paper are mol % unless otherwise stated.) In addition, the 55% and 75% SiO_2 compositions were made in the soda-silica system. The disilicate and diborate glasses were prepared first from sodium carbonate and silica flour or boric acid. The other compositions were then made from these base glasses by the necessary additions of sodium carbonate, silica flour, or boric acid. After the mixed powders were fused in a platinum crucible that was rotated in an inclined Globar-heated furnace, the molten glasses were poured into graphite molds and cooled. The cooled samples were stored in a dessicator. The test samples were made by pulling fibers from the glassy compositions and heating the tips to form balls; the nonglassy compositions were crushed to provide chunks of the proper size.

The ferric oxide glasses were made from sodium nitrate, ferrous ammonium sulfate, and silica flour in platinum crucibles in the Globar furnace.[9] The ferrous oxide glasses were made from

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*Alumina type of abrasive, Linde Co.

sodium disilicate, ferrous oxalate, and silica flour in iron crucibles in a vacuum furnace.[9]

The fusion temperatures for the glasses ranged from 1000 to 1300°C. All of the compositions were in a liquid state at the test temperature.

3. Test Procedure and Measurements

A clean iron specimen was placed on the molybdenum stand, and a glass ball or chunk was put on the iron. After the radiation shields were placed in the holder, the furnace was capped and evacuated. Heating was started when a vacuum of 2×10^{-5} mm Hg was reached. The rate of heating was manually controlled to keep the vacuum below 5×10^{-5} mm Hg.

The contact angles were measured at the test temperature, four readings being taken on each side to minimize any reading errors. Average values were calculated for the right and left sides, and these values were averaged to get the contact angle for the run.

Adherence at room temperature was tested by pushing against the glass with a blunt object. Good adherence and chemical bonding was associated with failure either of the glass or metal. Presence of van der Waals type of bonding was indicated when it was possible to remove the glass cleanly from the metal. Varying degrees of adherence were obtained with the latter type of bonding.

4. Preparation of Microstructures

The iron plate was wet-ground on a 120-grit belt down to the piece of glass. The plate was then mounted on edge in catalytic-setting plastic and ground down to the center of the glass. After wet-polishing with 400- and 600-grit SiC, the specimen was given a

final polish on a vibrating polisher, first with 1- to 5-μ and then 0- to 1-μ diamond paste. The cross sections of the interfaces were examined with a Bausch and Lomb bench metallograph.

III. Results

1. Soda-Silica Glasses

The experimental results for these glasses are summarized in Table I. The equilibrium-angle and color data were obtained when outgassing of the glass was completed. The experiments summarized in the other columns of the Table were made primarily to study the effect of time on adherence of the glass.

The contact angle decreased with increasing Na_2O content. After 10 minutes at the test temperature, the 75% and 80% SiO_2 glasses were essentially colorless, while the other compositions had various intensities of green or black caused by reaction with the iron plate. The color of the high-SiO_2 glasses, however, increased in intensity with longer periods of time, indicating a slower rate of reaction. Examination of cross sections showed greater attack and penetration by the glasses at the grain boundaries of the iron.

The high- and low-SiO_2-content glasses adhered after short runs, while the intermediate glasses (55, 60, and 66.7% SiO_2) did not adhere. The intermediate compositions, however, adhered after running at 1000°C for longer periods. All compositions except the 75% and 80% SiO_2 showed the presence of a crystalline phase in the glass when adherence developed.

Twenty-hour runs on the 75% and 80% SiO_2 glasses decreased their adherence to iron. The glasses had a whitish precipitate at the

Table I. Contact angles, colors, and adherences of sodium silicate glass on iron at 1000°C

Glass composition		Time	Color	Adherence	Contact angle (deg)
Na_2O	SiO_2				
0.20	0.80	equilibrium[a]	blue-green	b	62
		1 hr	colorless	good	b
		9 hr	blue-green	good	b
		20 hr	black	poor	b
0.25	0.75	equilibrium	green	b	59
		1 hr	colorless	good	b
		20 hr	black	poor	b
0.33	0.67	equilibrium	green	b	59
		1 hr	light green	poor	b
		5.5 hr	black	good	b
		17 hr	black	very good	45
0.40	0.60	equilibrium	green	b	b
		< 1 hr	light green	poor	b
		1 hr	black	good	b
0.45	0.55	equilibrium	green	b	b
		< 1 hr	green	poor	b
		1 hr	black	good	29
		16.5 hr	yellow-grey	poor	b
0.50 (crystalline)	0.50	equilibrium	black	very good	20
0.50 (glassy)	0.50	equilibrium	black	very good	23
0.60	0.40	equilibrium	black	very good	0

[a]"Equilibrium" time refers to the time at which outgassing of the glass was completed.

[b]Not observed or obtained.

interface, which was identified as α-cristobalite by X-ray diffraction. A sodium disilicate specimen heated for 17 hours at 1000°C adhered strongly to the iron and was dislodged only by shearing in the metal. The 55% SiO_2 glass had a yellowish-grey color after heating for 17 hours at 1000°C and was removed with difficulty; there was no indication of shearing in the metal.

An equilibrium contact angle for the 55% SiO_2 composition was not obtained. As soon as the glass wetted the metal, it began traveling over the iron plate, making contact angle measurements difficult, but an angle of about 47 deg was indicated. After 1 hour at 1000°C, the glass became stationary with a contact angle of 29 deg. Cline et al[3] experienced a similar problem with sodium disilicate on oxidized iron.

The 40% and 50% SiO_2 glasses reacted with the iron plate before any visible softening occurred. The first indication of softening was in the dark reacted zone. In the 50% SiO_2 glass, this liquid zone bubbled violently upon formation and reacted with the remaining solid glass to form a melt. The glass was completely molten at approximately 960°C, about 120°C below the melting point of $Na_2O \cdot SiO_2$. The 40% SiO_2 liquid did not bubble as violently as the 50% liquid and spread uniformly upon formation. Vaporization of Na metal from the 40% SiO_2 composition became particularly evident, as indicated by its deposition on the furnace windows. Table I notations on these two compositions were limited to measurement of contact angles when outgassing was complete and to determination of adherence at room temperature.

2. Iron-Containing Glasses

The results of experiments with sodium disilicate glasses with

iron additions are summarized in Table II. The contact angle of glasses containing 5% iron oxide decreased from that of sodium disilicate, although ferric oxide was more effective in lowering the angle than ferrous oxide or substitution of ferrous ions for sodium ions. Saturating sodium disilicate glass with either form of iron oxide led to complete wetting of the iron plate by the glass. Replacing Na^+ ions with Fe^{+2} ions in the disilicate composition did not decrease the contact angle considerably, but adherence was improved.

All of the ferric oxide glasses had good adherence at all times. Sodium disilicate glass saturated with ferrous oxide had good adherence at equilibrium and after 15 hours at the test temperature; glass with 5% FeO had good adherence at equilibrium and poor adherence after 15 hours at the test temperature. The latter long-time run showed precipitation of fayalite at the interface. At equilibrium, good adherence was obtained for the disilicate glass in which Fe^{+2} ions replaced some of the Na^+ ions; after 15 hours at the test temperature, adherence decreased. The latter glass showed precipitation of α-cristobalite, particularly at the periphery. No contact angle was thus recorded for this run. Disilicate glasses saturated with ferrous or ferric oxide became completely molten only at temperatures above 1100°C.

The glasses containing ferric oxide reacted with the iron plate causing a considerably roughened interface. No such attack took place at the interface with the glasses containing ferrous ion.

3. Soda-Boric Oxide Glasses

The results with these glasses are summarized in Table III. The contact angles showed a small decrease with increasing Na_2O

Table II. Contact angles and adherence of iron-containing sodium disilicate glasses on iron

Glass composition		Time	Temperature (°C)	Contact angle (deg)	Color	Adherence
$(Na_2O \cdot 2SiO_2)_{0.61}$	$(Fe_2O_3)_{0.39}$	equilibrium[a]	1143	0	brown	good
$(Na_2O \cdot 2SiO_2)_{0.95}$	$(Fe_2O_3)_{0.05}$	equilibrium	1000	45	black	good
		15 hr	1000	41	black	good
$(Na_2O \cdot 2SiO_2)_{0.32}$	$(FeO)_{0.68}$	equilibrium	1138	5	grey	good
		5.5 hr	1138	0	yellow-black	good
$(Na_2O \cdot 2SiO_2)_{0.95}$	$(FeO)_{0.05}$	equilibrium	1000	54	green	good
		15 hr	1000	44	yellow-black	poor
$(Na_2O \cdot 2SiO_2)_{0.40}$	$(FeO \cdot 2SiO_2)_{0.60}$	equilibrium	1000	53	black	good
		15 hr	1000	--	yellow-black	poor
$Na_2O \cdot 2SiO_2$		equilibrium	1000	59	green	poor
		17 hr	1000	45	black	good

[a] "Equilibrium" time refers to the time at which outgassing of the glass was completed.

Table III. Contact angles and adherence of sodium borate glasses on iron at equilibrium

Glass composition		Temperature	Angle[a]	Color	Adherence
Na_2O	B_2O_3	(°C)	(deg)		
0.20	0.80	1000	67	colorless	good
		816	61	colorless	poor
0.33	0.67	1000	53	colorless	good
		763	49	colorless	good
0.40	0.60	1000	58	greyish	good
		875	51	greyish	poor
0.60	0.40	900	0	black	good

[a]Contact angles were measured at equilibrium, i.e., when outgassing was complete.

content up to about 50%; with 60% Na_2O, the angle was 0 deg. A greyish color developed in the 60% B_2O_3 glass; the glasses with higher B_2O_3 contents remained colorless. The 40% B_2O_3 samples showed some darkening from reaction with the iron before melting, analogous to the 40% SiO_2 composition; however, there was no deposition of sodium metal on the silica furnace windows as with the 40% SiO_2 composition.

Adherence was good for all glasses at 1000°C. Because this temperature was considerably higher than the liquidus temperatures for the 60 to 80% B_2O_3 compositions as compared with the 60 to 80% SiO_2 compositions, experiments were run at temperatures just above that of the liquidus. The contact angles for these runs were lower, and the adherence was poor with the exception of the diborate.

No data are presented for the 50% B_2O_3 composition because it sublimed under the normal test conditions. If the temperature was raised rapidly above the melting temperature without holding the vacuum below 5×10^{-5} mm Hg, the specimen first melted, then immediately evaporated.

IV. Discussion

The soda-silica compositions reacted with the iron plate as indicated by the development of color during testing. A cross section through an iron specimen after removal of the glass, as seen in Figure 4, shows the attack of the surface by the glass. The rate of reaction was more rapid with increasing Na_2O content. A greater reaction at the grain boundaries of the iron was indicated by observations of polished cross sections at higher magnifications and of iron surfaces from which the glass had pulled away. Figure 5 shows an example of

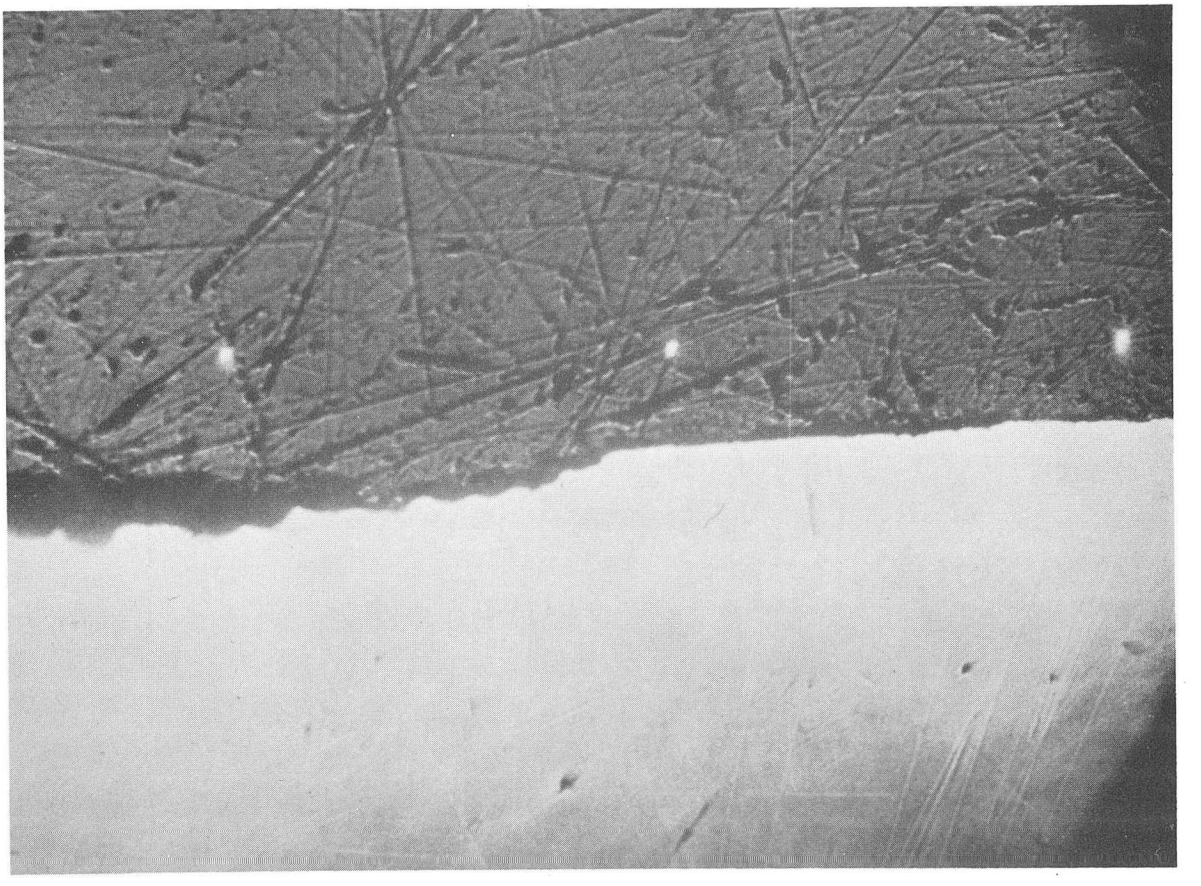

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Fig. 4. Cross section through $(Na_2O)_{0.40}(SiO_2)_{0.60}$ glass-iron test specimen, after glass had pulled away from left side of iron piece, shows attack by glass. No glass was in contact with the right side of the iron piece. 100×.

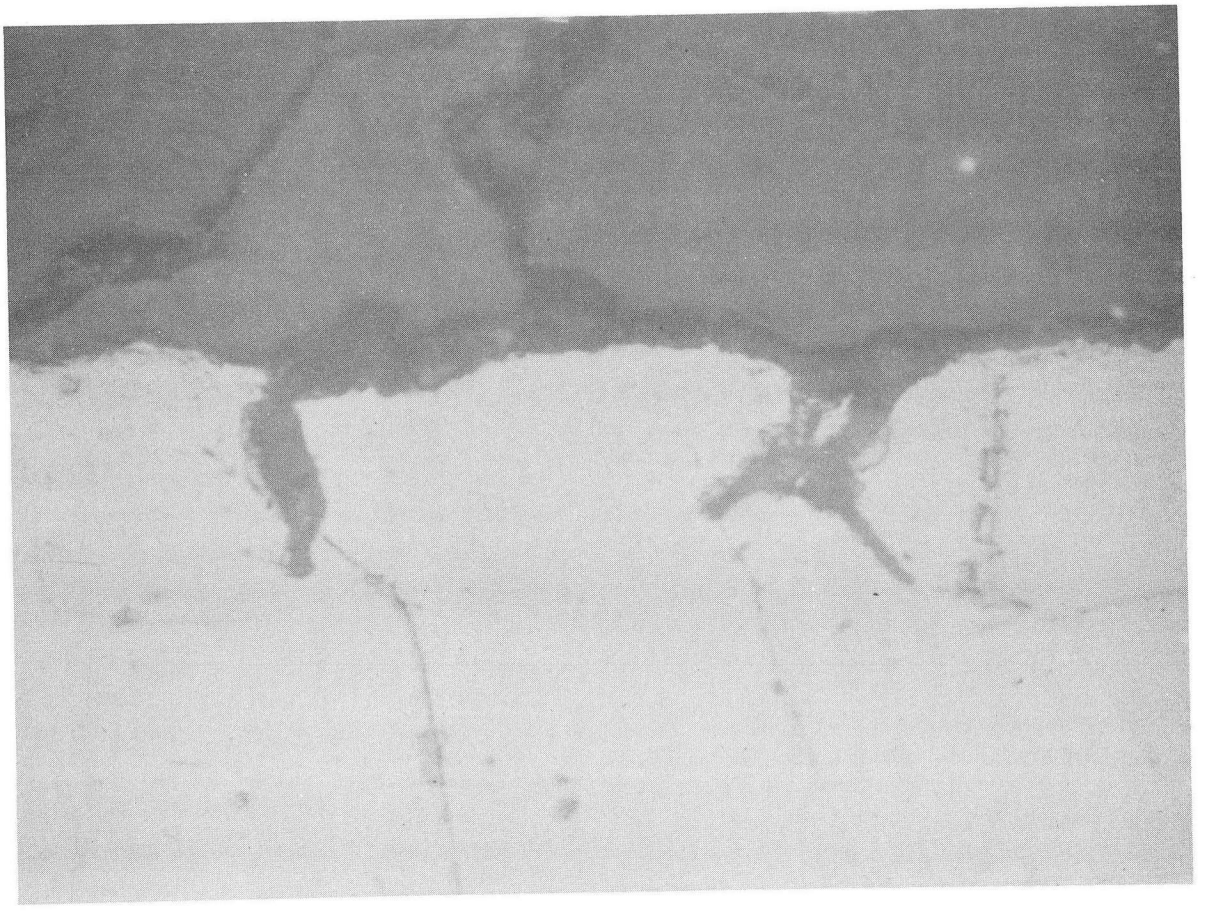

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Fig. 5. Cross section shows $(Na_2O)_{0.60}(SiO_2)_{0.40}$ glass penetrating iron (lower portion of photograph) along grain boundaries. Two FeO crystals are visible in the glass (upper right). 1000×.

such an attack. With no oxygen in the system, the reaction that takes place is:[10, 11]

$$Fe_{(s)} + 2\,Na^{+} = 2\,Na_{(v)} + Fe^{+2}\,. \qquad (2)$$

The oxygen-silicon ratio thus remains constant during this reaction. Such a reaction is favored, because the more polarizable Fe^{+2} ions allow the O^{-2} ions to better screen the Si^{+4} potential fields and lower the internal energy of the glass.[12] Ions of the noble-gas type, such as Na^{+}, compete more strongly with the Si^{+4} ions for the O^{-2} ions. A lower internal energy in the glass results in a better balance of bond energies at the interface, which causes a lower interfacial energy.

The contact angle decreases with increasing Na_2O content. Adding Na_2O to a glass increases the oxygen-silicon ratio. The Si^{+4} ions are thus more effectively screened, because there is less sharing of O^{-2} ions between the Si^{+4} ions. The resultant lowering of the internal energy of the glass promotes the formation of a chemical bond by a better balance of bond energies at the interface. The interfacial energy is then reduced, and better wetting occurs.

The addition of iron oxide to sodium disilicate glass decreased the contact angle from that of the sodium disilicate, Fe_2O_3 being more effective than FeO. Five percent FeO decreased the contact angle 5 deg, while 5% Fe_2O_3 decreased the contact angle 14 deg from that of the disilicate. The greater effectiveness of Fe_2O_3 is primarily due to the larger amount of O^{-2} ions added to the glass structure for an equivalent mole percentage of oxide, although the smaller number of network-modifying cations for an equivalent number of oxygen ions (Na^{+}: O = 2, Fe^{+2}: O = 1, Fe^{+3}: O = 0.67) probably also has a

favorable effect. The importance of the amount of oxygen is illustrated by the experiment in which Fe^{+2} ions replace 60% of the Na^{+} ions in the disilicate structure, where the contact angle was decreased only 6 deg from that of sodium disilicate. This reduction is comparable to adding 5% FeO to the disilicate structure, whereas the addition of 5% Fe_2O_3 decreased the contact angle 14 deg. However, in all of these cases, the internal energy of the glass is lowered because the O^{-2} ions can better screen the Si^{+4} potential fields in the presence of iron ions. Complete wetting occurred when sodium disilicate was saturated with iron oxide. This saturation lowered the internal energy of the glass to some thermodynamically stable state, because any further additions of oxide resulted in the precipitation of a crystalline phase.

The contact angles also decreased with increasing Na_2O content in the soda-boric oxide system. In this case, increased wetting is also attributed to improved screening of the B^{+3} ion, the network-former, because fewer O^{-2} ions are shared between B^{+3} ions. The sublimation of the 50% B_2O_3 glass is not understood.

In general, the oxygen—network-former ratio is an indication of the internal energy of the glass, being inversely proportional to the internal energy. With a low internal energy in the glass, a better balance of bond energies, and consequently a lower interfacial energy, occurs at the interface. A low interfacial energy is associated with the development of a chemical bond between the glass and the metal. On the basis of Young's equation, if the surface tension of the liquid glass does not change significantly with composition for a series of glasses, lower contact angles indicate lower interfacial energies. The oxygen—network-former ratio then tends to be proportional to the

degree of wetting and inversely proportional to the interfacial energy. This set of conditions is necessary only in the portion of the glass adjoining the interface.

For the shorter times, thus, the low-SiO_2 glasses had low contact angles with good adherence, and glasses with 55% to 66.7% SiO_2 had higher contact angles with no adherence. The results with the 75% and 80% SiO_2 glasses, however, were unexpected in that adherence occurred with still higher contact angles. Furthermore, adherence occurred before the glass had reacted with any appreciable amount of iron. As indicated by Young's equation, a high contact angle with a low interfacial energy would be possible if the surface tension of the liquid glass were sufficiently high. However, reported surface-tension data for the soda-silica glasses show decreasing values with increasing SiO_2 concentration.[13] Then, for these high-SiO_2 glasses, adherence occurred even though the interfacial energy increased with increasing contact angle. Similarly, the contact angles of the soda-boric oxide glasses increased with increasing B_2O_3 content at 1000°C while adherence was retained. Because surface tension decreases with increasing B_2O_3 content,[14] adherence again occurred with increasing interfacial energy.

The cross section of the 80% SiO_2 glass-metal interface in Figure 6 shows that little penetration of the iron by the glass occurred as compared with the disilicate-iron system in Figure 7, and that the glass pulled away from the interface during the preparation of the section. Similarly, the 80% B_2O_3 glass pulled away from the interface during the preparation of its cross section. These observations suggest that the existing adherence with high interfacial energies was due to the

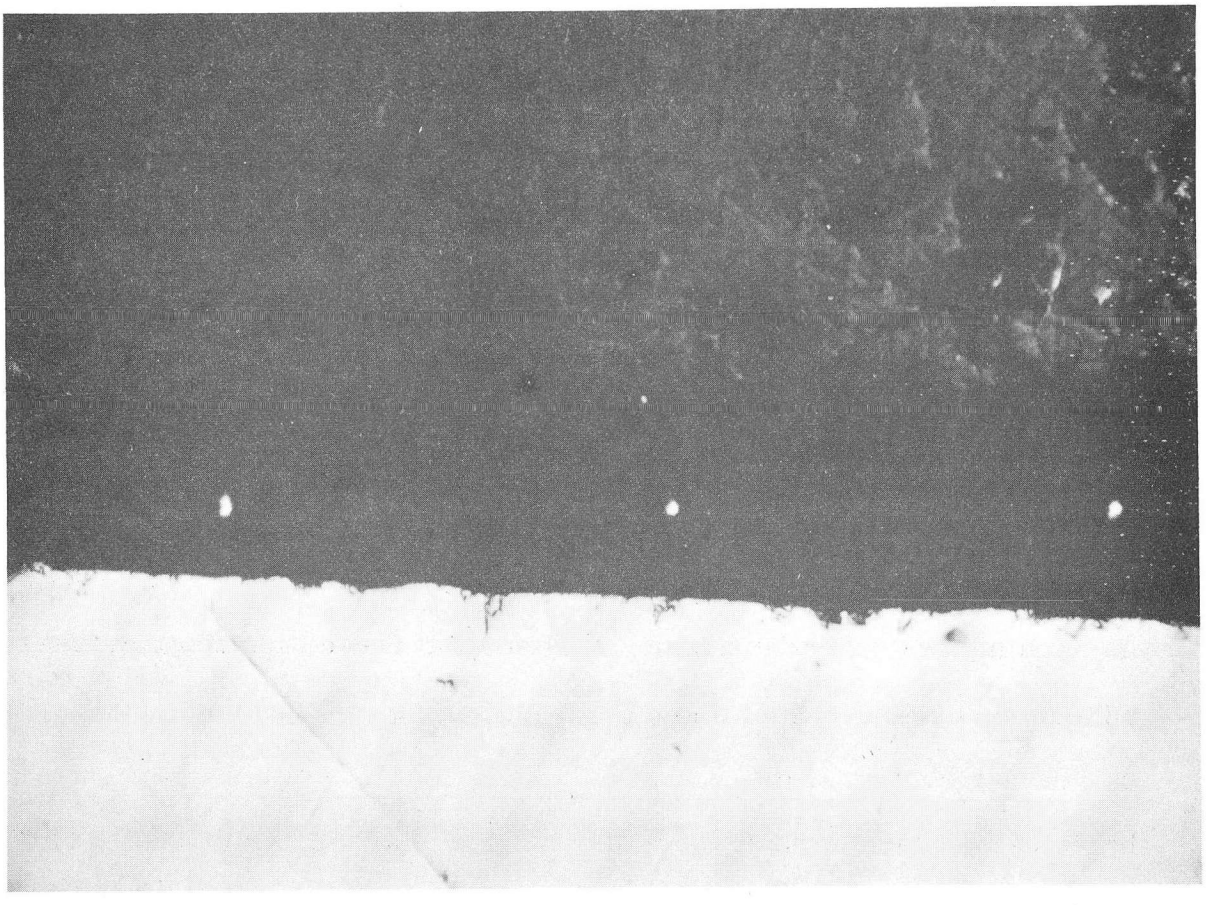

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Fig. 6. Cross section shows $(Na_2O)_{0.20}(SiO_2)_{0.80}$ glass pulled away from the interface, leaving a void (black area). The iron surface is relatively smooth. 250×.

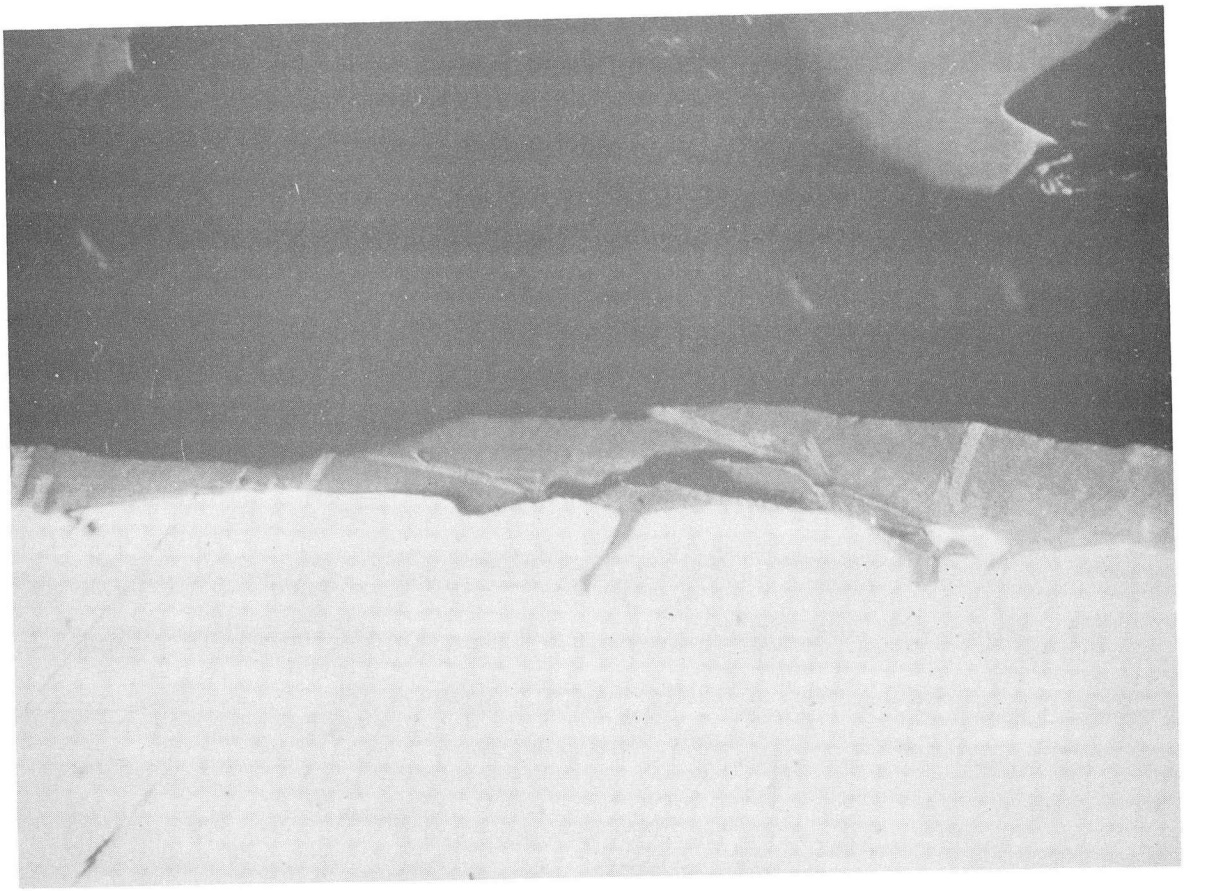

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Fig. 7. Cross section shows $Na_2O \cdot 2SiO_2$ glass on iron after long heating. The iron was attacked by the glass; and a crystalline phase is present in the glass along the interface. The glass was broken above the interface leaving a void. 250×.

development of strong van der Waal's bonding.

Although the interfacial energy of a glass-metal system may be high, indicating the absence of chemical bonding, consideration of the total energy of the system at the interface leads to the conclusion that adhesion could occur with a van der Waal's type of bond, if the surface energy of one of the newly formed surfaces is correspondingly higher. The adherence of glass to metal can be expressed by the amount of work or energy necessary to cleanly remove the glass from the surface of the metal. Energy is used to create new metal and glass surfaces, but the excess energy already present at the interface because of the structural discontinuity reduces the necessary work of separation.[1]

This situation can be expressed by Dupre's equation:

$$E_{ad} = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} . \qquad (3)$$

The energy values must be those at the time of separation. Thus, the surface energy of the glass, γ_{lv}, must be the value for the newly formed glass surface in the solid state. Surface-energy measurements are usually made on glasses in a softened or molten state. When a new surface is formed at high temperatures, the ions are mobile and can reorient themselves to an arrangement of lowest energy. On the other hand, if a new glass surface is formed at room temperature by fracturing, the surface will have a higher energy because the ions will not be able to move and screen their potential fields as well as in the molten state. The "fracture" surface energy of a soda-lime-silica glass calculated by Mould and Southwick,[15] based on strength measurements and the Griffith theory, is considerably higher than the value for the softened or molten state. This surface energy for glasses, γ_{lv}, would

also be expected to increase with increase of the network-former oxide content, because the potential fields of the network-former ions will not be screened as effectively.

If we assume values on this basis for surface energies of the "fractured" glass surfaces, γ_{lv}^{*}, and a value of 1600 ergs/cm^2 for the surface energy of solid iron, Figure 8 shows the calculated relationships that result between the interfacial energies of the soda-silica glass—iron system. Values for γ_{lv} in the molten state are those reported in literature;[13] these values and the contact-angle measurements (Table I) were used to calculate the interfacial energies, γ_{sl}, from Young's equation. With these assumptions and calculations, the work of adhesion, E_{ad}, is shown to be higher for both low- and high-SiO_2 compositions than that for the intermediate-SiO_2 compositions. The resulting adherence, however, for the low-SiO_2 glasses is due to the development of chemical bonding because of relatively low interfacial energies and, for the high-SiO_2 compositions, a van der Waal's type of bonding because of the higher interfacial energies.

Adherence was poor for the 60% and 80% B_2O_3 compositions at the liquidus temperatures at 875 and 816°C, respectively. The development of adherence at 1000°C suggested that possibly some increased chemical reaction occurred at this higher temperature, but examination of cross sections showed smooth iron surfaces at the interfaces. The color of the glass was the same as that at the lower temperature; and no crystals were present in the glassy phase. However, the bond strength was not too high because, in the preparation of the cross sections, the glass pulled away from the iron. Also, the adherence of the diborate at the lower temperature as opposed to the lack of

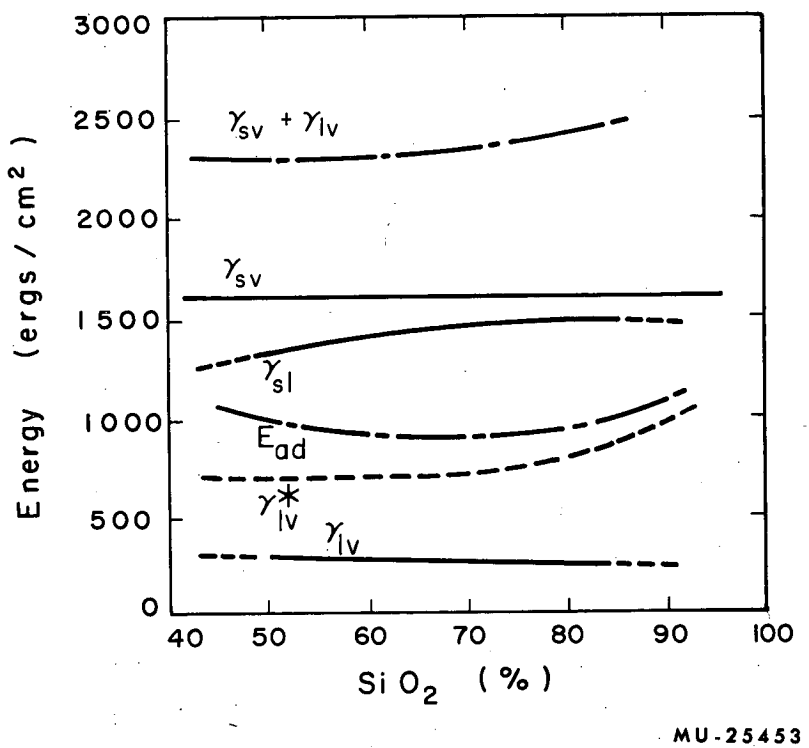


Fig. 8. Surface energy relationships in the soda–silica glass–iron system. The notations are identified in the text.

——— experimental values
----- assumed or extrapolated values
- — - calculated values

adherence for the 60% and 80% B_2O_3 glasses cannot be explained on the basis of strains induced by differences in the thermal expansions. Calculations with thermal-expansion data[16] show the same percentage mismatch with iron for the diborate and 80% B_2O_3 compositions at both temperatures; no expansion data for the 60% B_2O_3 composition are available. Further study is needed for an understanding of the wetting of iron by the soda-borate system.

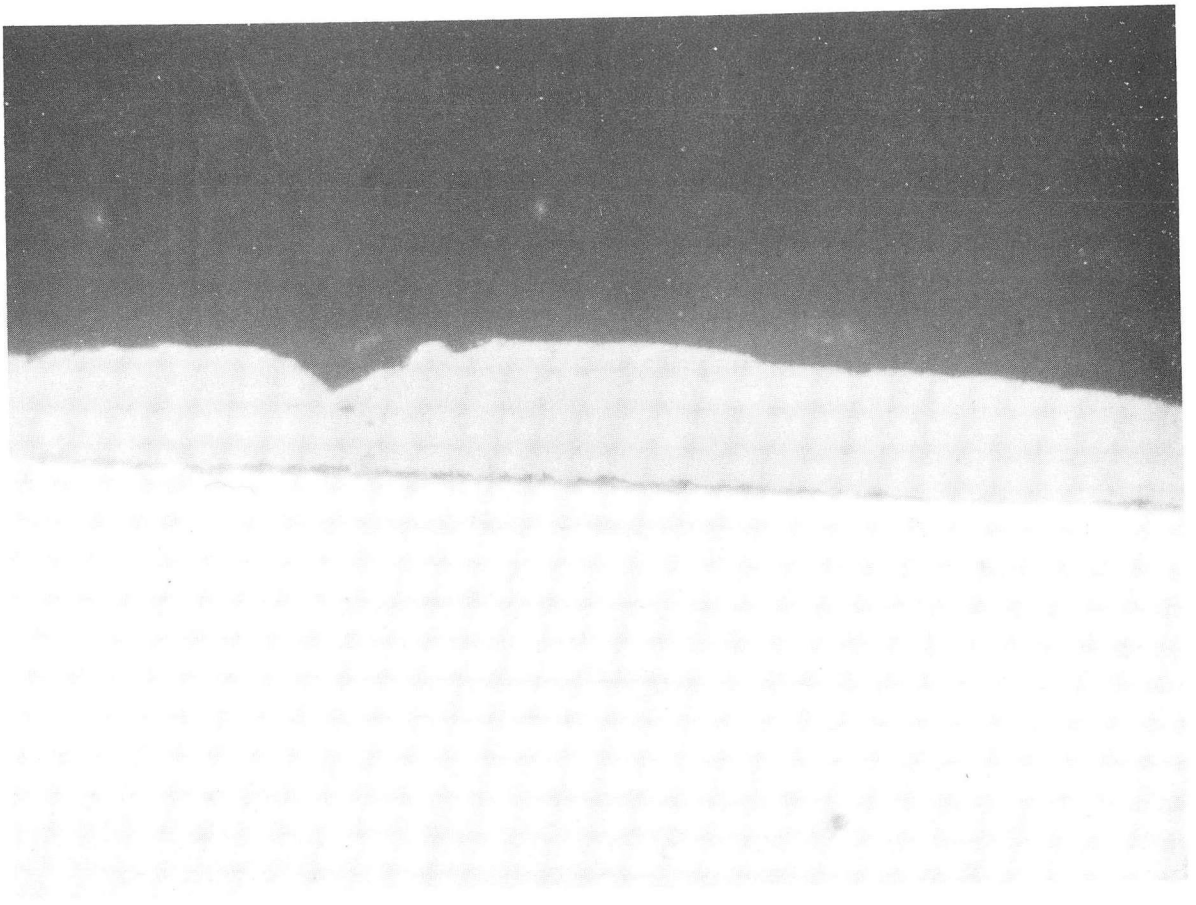
If Fe^{+3} ions are present in the glass, the following reaction occurs between the glass and the iron plate:

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

This reaction leads to considerable roughening of the iron plate. If iron is present as Fe^{+2} ions in the glass, this reaction does not occur. Figures 9 and 10 show examples of interfaces formed with ferrous oxide glass and with ferric oxide glass.

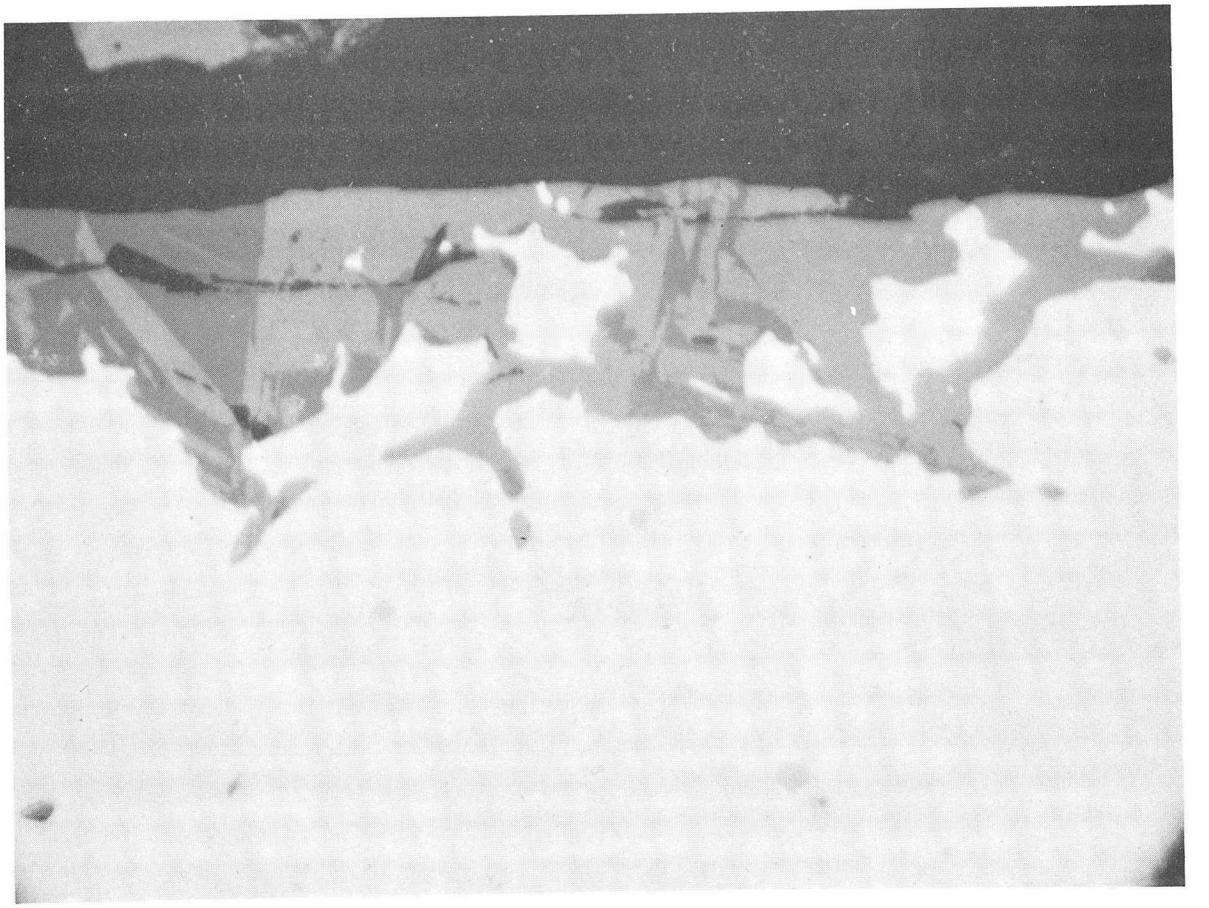
Polished cross sections of glasses that adhered to iron, illustrated in Figures 7 and 10 through 13, are characterized by the presence of a crystalline phase in the glass. Figures 11 and 12 show the development of such a phase at the test temperature with increase of time. The Fe-Na^+ reaction caused a change in the 40% SiO_2 composition with the appearance of FeO as the primary crystalline phase, as seen in Figure 13. Its appearance is similar to that of the crystals in a 50% FeO glass shown by King et al.[2]

Adherence in most cases is associated with the appearance of a crystalline phase, which indicates that the glass itself is at some stable energy state. Such a condition leads to a better balance of bond energies and chemical bonding at the interface and, in turn, to adherence. On



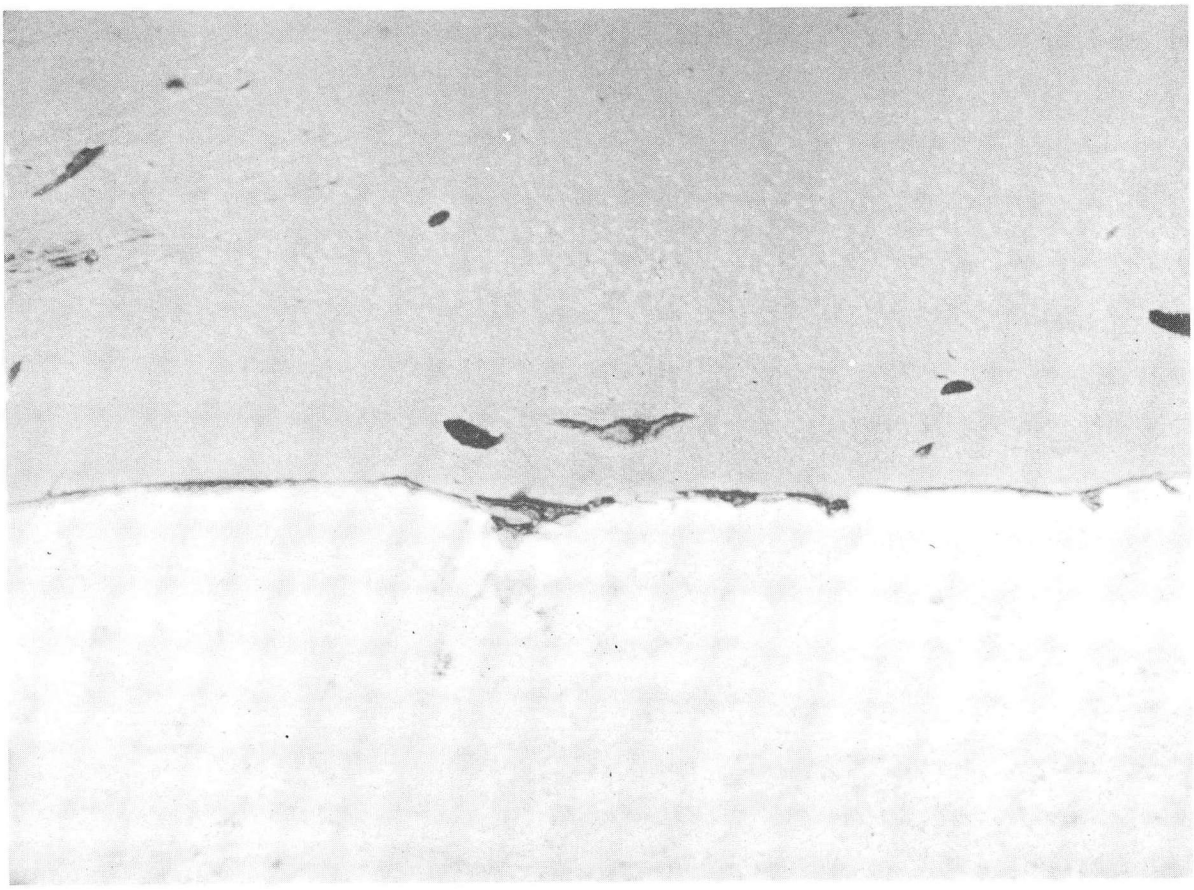
ZN-3000

Fig. 9. Cross section shows lack of reaction between $(Na_2O \cdot 2SiO_2)_{0.32}(FeO)_{0.68}$ glass and iron plate. 250×.



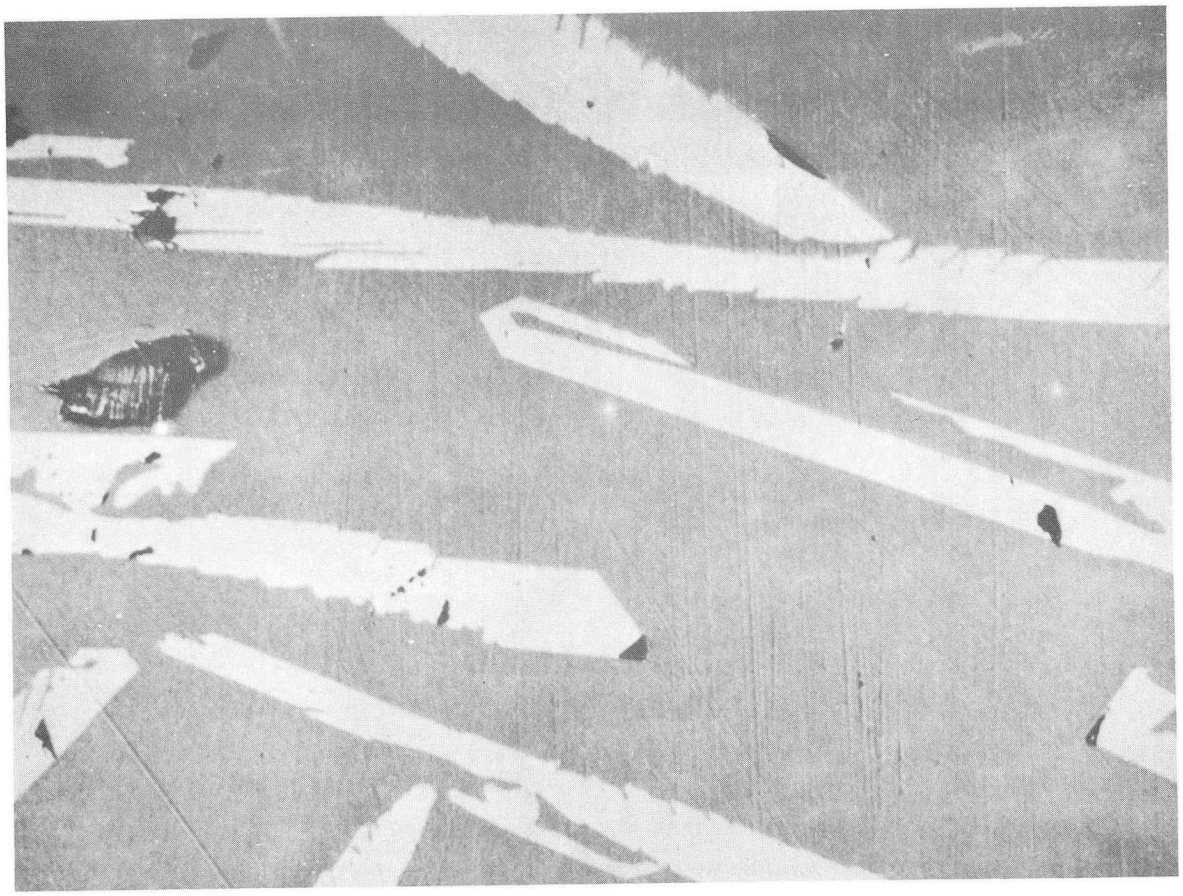
ZN-3001

Fig. 10. Cross section shows considerable reaction between $(Na_2O \cdot 2SiO_2)_{0.61}(Fe_2O_3)_{0.39}$ glass and iron plate, and the appearance of a crystalline phase in the glass. 250×.



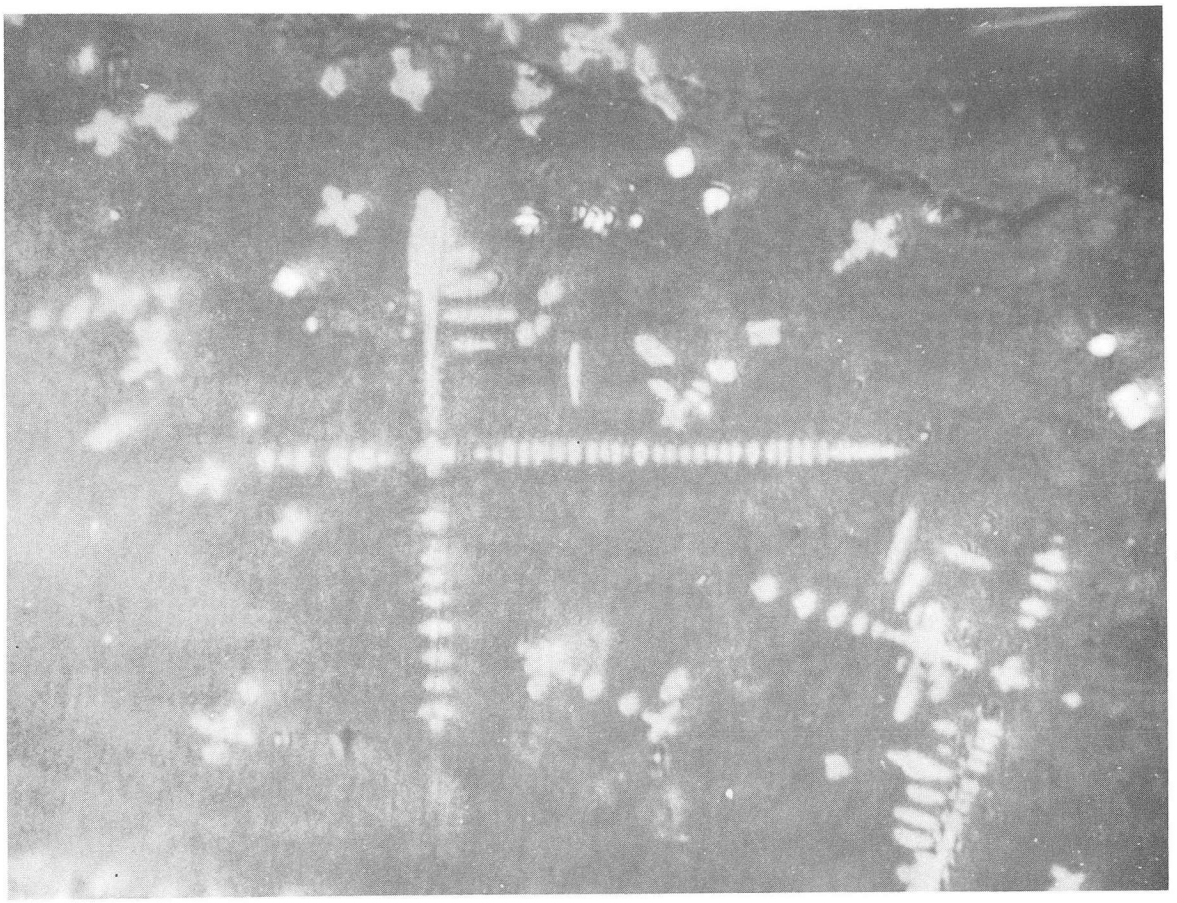
ZN-3002

Fig. 11. $(Na_2O)_{0.40}(SiO_2)_{0.60}$ glass heated at 1000°C for 1 hr. Note start of a crystalline phase (light dots). 250×.



ZN-3003

Fig. 12. $(Na_2O)_{0.40}(SiO_2)_{0.60}$ glass heated at 1000°C for 2-1/2 hr. Note increased development of crystalline phase in comparison with 1-hr run shown in Fig. 11. 250×.



ZN-3004

Fig. 13. $(Na_2O)_{0.60}(SiO_2)_{0.40}$ glass shows crystals of FeO similar to those shown by King et al.[2] Bright squares are α-iron crystals. 250×.

the other hand, several glasses did not adhere when the interface appeared to become all crystalline. A certain amount of glass phase is necessary for adherence, because its short-range order structure can adjust itself more easily to the atomic structure of the iron and, in most cases, a certain amount of this phase must be retained on cooling. A crystal structure has a rigid long-range order which, generally, does not match the structure of the metal epitaxially, resulting in a poor bond.

V. Summary and Conclusions

The wetting of iron by molten glass was investigated by the sessile-drop method. Selected compositions in the soda-silica and soda-boric oxide systems, sodium disilicate glass with varying amounts of ferrous oxide or ferric oxide, and a disilicate glass with Fe^{+2} ions replacing some of the Na^{+} ions were used. A qualitative measure of adherence was obtained by attempting to dislodge the glass from the metal with a blunt object.

A requirement for good wetting of metal by glass (low contact angles) and for adherence by chemical bonding is a balance of bond energies at the interface, which is associated with a lower interfacial energy. This condition is achieved by lowering the internal energy of the glass until, in most cases, some thermodynamically stable state is reached. The internal energy of a glass can be lowered by increasing its oxygen-silicon ratio, for example, by adding Na_2O to SiO_2. The addition of O^{-2} ions from the Na_2O decreases the number of O^{-2} ions shared by the Si^{+4} ions. The potential field of the Si^{+4} ions can then be more effectively screened, lowering the internal energy of

the glass. In general, the internal energy of a glass will be lowered when the oxygen—network-former ratio is increased. A soda-silica glass can also lower its internal energy by replacing Na^+ ions with Fe^{+2} ions. The polarizable Fe^{+2} ions do not compete with the Si^{+4} ions for the O^{-2} ions as strongly as do the noble-gas-type Na^+ ions. The Si^{+4} ions are thus again more effectively screened.

The low-SiO_2 glasses had low contact angles on iron and adhered apparently by chemically bonding with the iron. The intermediate glasses had higher contact angles and did not adhere initially. Adherence by chemical bonding was developed when the internal energy was sufficiently lowered by Fe^{+2} ions replacing Na^+ ions in the glass at the interface. The high-SiO_2 glasses had high contact angles and adhered in this case apparently by means of a van der Waal's bond. Adherence was lost when the base of the glass specimen appeared to become essentially crystalline.

The addition of ferrous or ferric oxide to sodium disilicate glass decreased the contact angle from that of the sodium disilicate, Fe_2O_3 being more effective than FeO. Complete wetting and adherence occurred when sodium disilicate was saturated with either form of iron oxide; the saturation lowered the internal energy of the glass to some stable lower value. Such a saturation is also associated with the appearance of a crystalline phase in the glass.

A certain amount of glass phase must be present for adherence to occur. A glass phase with its mobility at the time the interface is formed can adjust its structure to that of the metal and retain such an interface on cooling, unless the difference in the coefficients of expansion is too great. A crystalline phase, because of its long-range

order, may not be able to adjust itself epitaxially to the structure of the iron.

Adherence by van der Waal's bonding, as indicated by a high interfacial energy, is possible if the surface energy of fractured glass is also correspondingly higher. Such a situation results in a higher work of adhesion according to Dupre's equation.

Some work was done on soda-boric oxide glasses in contact with iron. General agreement of results with those of the soda-silica system was obtained, but additional study is necessary for more detailed understanding.

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