THE EFFECT OF ATMOSPHERE ON INTERFACIAL REACTIONS
AND WETTING BEHAVIOR OF GLASS-METAL SYSTEMS

Carl E. Hoge
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AND WETTING BEHAVIOR OF GLASS-METAL SYSTEMS

Carl E. Hoge

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
and Department of Materials Science and Engineering,
College of Engineering, University of California,
Berkeley, California

ABSTRACT

Interfacial reactions and wetting behavior of $\text{Na}_{2-2x}\text{Fe}_x\text{Si}_2\text{O}_5$ glasses on substrates of high purity iron (Marz) and impure iron (Armco) were studied using the sessile drop technique. Experiments were performed at 1000°C in high vacuum and at 1 atmosphere pressure of argon and a 10 to 1 mixture of CO-CO_2 . All vapors had low partial pressures of O_2 and Na.

Decomposition of FeO and Na_2O in the glasses was observed at the liquid-vapor interface. The oxidization of metallic iron by Na^+ occurred at the solid-liquid interface under high vacuum conditions, but not in argon or CO-CO_2 .

A thin oxide film is present on the surface of the iron substrates. This film, as well as any impurities in the bulk of the iron, affects the specific surface free energy f_v of the substrate. The wetting behavior of the glasses is mainly determined by changes in f_v . When the oxide film is desorbed from high purity iron (Marz), f_v increases and spreading by the liquid on the solid occurs. For impure iron (Armco), f_v is maintained at a low value due to the impurities present which results in the liquid attaining a finite wetting angle.

I. INTRODUCTION

The work of Pask and Fulrath has led to a theory of glass to metal bonding which requires that the glass be saturated at the glass-metal interface with the oxide of the lowest valence cation of the substrate material.¹⁻⁷ At equilibrium, such conditions lead to a balance of attractive forces exerted by the glass and metal on oxygen ions in the interfacial region. A transition zone is then established between the metallic bond of the substrate and the ionic-covalent bond of the glass. The bonding in such a region is assumed to be chemical rather than Van Der Waals in nature and therefore, very strong.

The sessile drop technique has been employed by several authors in an attempt to measure the relationship between wetting angle and the formation of a chemical bond at the glass-metal interface. Saturation of the glass with the oxide of the lowest valence cation of the substrate material has generally been associated with a reduction of the glass-metal interfacial energy, γ_{sl} , and a lowering of the wetting angle made by the glass on the metal.¹⁻⁷

Experiments by Brennan⁸ in the system glass ($\text{XFeO Na}_2\text{Si}_2\text{O}_5$) on iron substrates have indicated that the occurrence of interfacial reactions between the glass and base metal leads to a lowering of the wetting angle. His experiments also revealed that the composition of the vapor phase above the sessile drop influenced interfacial reactions and in turn affected the wetting angle.

A reaction between a glass and metal leads to compositional changes at their interface, causing the interfacial energy γ_{sl} to change. The degree to which γ_{sl} changes is a function of the rate of interfacial

reaction and the diffusivity of components in the two phases. With the existence of a non-steady state, the use of Young's equation becomes inappropriate. As components are introduced or removed from the two phases; across the interfacial region, the composition of the phases changes. These compositional variations can affect surface energies of the system-- f_s (solid-vapor energy) and f_v (liquid-vapor energy).

For a solid-liquid-vapor system, the free energy of the system, F_{system} , will tend toward a minimum. The rate with which the minimum of energy is reached is a function of kinetics of interfacial reactions and diffusivities of components in the phases. When $\delta F_{\text{system}} = 0$, a steady state is reached and an equilibrium wetting angle is attained.

The present work was initiated to continue the study of the effect that atmospheres have on interfacial reactions and wetting behavior. The glasses chosen for this investigation were $(\text{FeNa}_{2-2x}\text{Si}_2\text{O}_5)$. Glasses of such compositions have a constant O/Si ratio of 2.5 which results in a glass structure which, according to the network concept, remains approximately constant as Fe is substituted for Na. The substrates chosen were iron and platinum. Iron is known to react significantly with such glasses,⁹ whereas the degree of platinum reaction is slight. Several atmospheres were employed to study their effects on interfacial reactions and glass stability.

II. INTERFACIAL RELATIONSHIPS

Young's equation has been used by many researchers in analyzing sessile drop experiments. This relation has been the subject of criticism concerning its use. Johnson¹⁰ has shown that much of the controversy associated with it has resulted from confusion between surface tension and specific surface free energy. Surface tension is defined as

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T,P,n_i} \quad (1)$$

and specific surface free energy is defined as

$$f = \frac{F - (F_\alpha + F_\beta)}{A} \quad (2)$$

where T = absolute temperature

V = volume

n_i = moles of i th component

F = Gibbs free energy for the entire system

F_α = Gibbs free energy in the homogeneous part of the α -phase
multiplied by the volume

F_β = same for the β -phase

A = interfacial area

Surface tension and specific surface free energy are related by the equation

$$f = \gamma + \sum_i \mu_i \Gamma_i \quad (3)$$

where $\mu_i = \left(\frac{\partial F}{\partial n_i} \right)_{T,P,n} =$ chemical potential

Γ_i is the excess interfacial concentration of the i th component in a system over the concentration in the bulk. In reality, a surface or interface has a volume associated with it which can be defined as a region where physical and thermodynamic properties differ from properties of the bulk phase. Generally, such regions are several atoms in thickness. In most thermodynamic treatments, a surface volume is not considered. The calculations are much less difficult when considering only a surface area and the basic equations are still applicable to real systems.¹¹ It is important, however, to keep the physical meaning of a surface volume in mind when discussing interfacial phenomena.

When two phases form an interface, the change in free energy of the system is given by

$$\delta F_{\text{system}} = \delta \int_V dF_V + \delta \int_A dF_A \quad (4)$$

$$dF_V = VdP - S_V dT + \sum_i \mu_i dn_i^V \quad (5)$$

$$dF_A = \gamma dA - S_A dT + \sum_i \mu_i dn_i^{A*} \quad (6)$$

* Surface volume is considered zero.

$$\begin{aligned} \delta F_{\text{system}} = & \delta \int_V V dP - \delta \int_V S_V dT + \delta \sum_i \int_V \mu_i dn_i^V \\ & - \delta \int_A S_A dT + \delta \int_A \gamma dA + \delta \sum_i \int_A \mu_i dn_i^A \end{aligned} \quad (7)$$

at constant T, P, and n_i .

$$\delta F_{\text{system}} = \delta \int_A \gamma dA \quad (8)$$

For a three component system, solid-liquid-vapor,

$$\delta F_{\text{system}} = \delta \int_A s \gamma_{\ell} dA_{s\ell} + \delta \int_A s \gamma_v dA_{sv} + \delta \int_A \ell \gamma_v dA_{\ell v} \quad (9)$$

$$\text{since} \quad dA_{sv} = - dA_{s\ell} \quad (10)$$

$$\delta F_{\text{system}} = \delta \int_A (s \gamma_{\ell} - s \gamma_v) dA_{s\ell} + \delta \int_A \ell \gamma_v dA_{\ell v} \quad (11)$$

At equilibrium $\delta F_{\text{system}} = 0$. Young's equation is then valid in terms of surface tensions.¹²

$$\gamma_v - \gamma_l = \gamma_v \cos \theta \quad (12)$$

If adsorption occurs, the change in bulk concentration is generally slight; therefore, n_i^v remains approximately constant for most cases. Thus at constant, T, P, n_i^v

$$\delta F_{\text{system}} \cong \delta \int_A \gamma dA + \delta \sum_i \int_A \mu_i dn_i^A \quad (13)$$

Since $\Gamma_i dA = dn_i^A$ (14)

$$\delta F_{\text{system}} = \delta \int_A \gamma dA + \delta \sum_i \int_A \mu_i \Gamma_i dA \quad (15)$$

$$\delta F_{\text{system}} = \delta \int_A (\gamma + \sum_i \mu_i \Gamma_i) dA \quad (16)$$

From (3)

$$\delta F_{\text{system}} = \delta \int_A f dA \quad (17)$$

For a solid-liquid-vapor system,

$$\delta F_{\text{system}} = \delta \int_A s^f_{\ell} dA_{s\ell} + \delta \int_A s^f_v dA_{sv} + \delta \int_A \ell^f_v dA_{\ell v} \quad (18)$$

From (10)

$$\delta F_{\text{system}} = \delta \int_A (s^f_{\ell} - s^f_v) dA_{s\ell} + \delta \int_A (\ell^f_v) dA_{\ell v} \quad (19)$$

Under nonequilibrium conditions,

$\delta F_{\text{system}} < 0$. Therefore

$$\delta \int_A (s^f_{\ell} - s^f_v) dA_{s\ell} + \delta \int_A \ell^f_v dA_{\ell v} < 0 \quad (20)$$

$$\delta \int_A \ell^f_v dA_{\ell v} < - \delta \int_A (s^f_{\ell} - s^f_v) dA_{s\ell} \quad (21)$$

$$\delta \int_A \ell^f_v dA_{\ell v} < \delta \int_A (s^f_v - s^f_{\ell}) dA_{s\ell} \quad (22a)$$

or from (3)

$$\delta \int_A (\ell \gamma_v + \sum_i \mu_i \Gamma_i^{\ell v}) dA_{\ell v} < \delta \int_A (s \gamma_v + \sum_i \mu_i \Gamma_i^{sv} - s \gamma_{\ell} - \sum_i \mu_i \Gamma_i^{s\ell}) dA_{s\ell} \quad (22b)$$

Due to the small volume of surfaces, diffusion rates of components are unimportant, adsorption is generally rapid. Thus δF_{system} approaches zero quickly giving rise to an equilibrium wetting angle.

When a chemical reaction occurs between two phases at their interface, the free energy of the reaction (F_R) must be included in Eq. (19).

$$\delta F_{\text{system}} = \delta \int_A (f_{s\ell} - f_{sv}) dA_{s\ell} + \delta \int_A f_{lv} dA_{lv} + \delta F_R \quad (23)$$

At constant T, P

$$dF_R = \sum_j \mu_j dn_j^V + \sum_j \mu_j dn_j^A + \gamma dA \quad (24)$$

since an interface is present when the reaction occurs

$$\gamma dA = 0$$

In Eq. (19), the changes in properties of the bulk were neglected since it was assumed that, for the adsorption case, they would remain approximately constant. The wetting of a liquid on a solid is dependent on changes in surface properties, not bulk properties. Unless the viscosity of the liquid is high, the wetting angle attained by the system will reach a steady state before the bulk properties change appreciably. Therefore, when discussing wetting behavior for short times, changes in the free energy of the system will be due mainly to changes in the surfaces. n_j^V can be assumed constant. For long times this is not true and n_j^V varies. However, for the long time case, the surfaces have reached a

steady state and no longer contribute towards lowering the free energy of the system.

At constant T, P, n_j^V (24) becomes

$$dF_R = \delta \sum_j \int_A \mu_j dn_j^A \quad (25)$$

From (14)

$$\delta F_R = \delta \sum_j \int_A \mu_j \Gamma_j dA_{sl} \quad (26)$$

Substituting into (23)

$$\delta F_{\text{system}} = \delta \int_A (s_{sl}^f - s_{sv}^f) dA_{sl} + \delta \int_A \ell_{sv}^f dA_{\ell v} + \delta \sum_j \int_A \mu_j \Gamma_j dA_{sl} \quad (27)$$

$$\delta F_{\text{system}} = \delta \int_A (s_{sl}^f - s_{sv}^f + \sum_j \mu_j \Gamma_j) dA_{sl} + \delta \int_A \ell_{sv}^f dA_{\ell v} \quad (28a)$$

or from (3)

$$\delta F_{\text{system}} = \delta \int_A (s_{sl} \gamma_{sl} + \sum_i \mu_i \Gamma_i^{sl} + \sum_j \mu_j \Gamma_j^{sl} - s_{sv} \gamma_{sv} - \sum_i \mu_i \Gamma_i^{sv}) dA_{sl}$$

$$+ \delta \int_A (\ell_{sv} \gamma_{sv} + \sum_i \mu_i \Gamma_i^{sv}) dA_{\ell v} \quad (28b)$$

when $\delta F_{\text{system}} < 0$

$$\delta \int_A (s^f_{\ell} - s^f_v + \sum_j \mu_j \Gamma_j) dA + \delta \int_A \ell^f_v dA_{\ell v} < 0 \quad (29)$$

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$$\delta \int_A \ell^f_v dA < \delta \int_A (s^f_v - s^f_{\ell} - \sum_j \mu_j \Gamma_j) dA_{s\ell} \quad (30)$$

When these equations are applied to real systems where bulk properties change, one must remember that they give only the change in free energy of the surfaces. If one limits the boundaries of the system under consideration to include only the surface volumes of each phase, the equations may be used to explain wetting behavior. If one includes the bulk phases within the boundaries of the system, the equations do not apply.

Consider the application of Eq. (10) to a solid-liquid-vapor system. Figure 1 represents a hypothetical three phase system involving no interfacial reactions which has reached equilibrium, $\delta F_{\text{reaction}} = 0$. Figure 2 is the same system as Figure 1 except that an interfacial reaction is allowed to occur between the solid and liquid.

ℓ^f_v = free energy of the liquid-vapor interface

s^f_v = free energy of the solid-vapor interface

$s^f_{\ell}^A$ = free energy of the solid-liquid interface of Fig. 1

$s^f_{\ell}^B$ = free energy of the solid-liquid interface of Fig. 2

$$\delta \int_A s_v dA_{sv} + \delta \int_A s f_l^A dA_{sl} + \delta \int_A l f_v dA_{lv} = 0$$

$$\delta F_{\text{SYSTEM}} = 0$$

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Figure 1. Solid-Liquid-Vapor system in state A. No chemical reaction at the solid-liquid interface.

$$\delta \int_A s f_v dA_{sv} + \delta \int_A s f_l^B dA_{sl} + \delta \int_A l f_v dA_{lv} < 0$$

$$\delta \int_A l f_v dA_{lv} < \delta \int (s f_v - s f_l^B) dA_{sl}$$

$$\delta F_{\text{SYSTEM}} < 0$$

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Figure 2. Solid-Liquid-Vapor system in state B. A chemical reaction occurs at the solid-liquid interface.

$s f_{\ell}^B$ is less than $s f_{\ell}^A$ by the contribution of the free energy of the interfacial reaction

$$s f_{\ell}^B = s f_{\ell}^A + \sum_j \mu_j \Gamma_j \quad (31)$$

Substituting into Eq. (28)

$$\delta F_{\text{system}} = \delta \int_A (s f_{\ell}^B - s f_v) dA_{s\ell} + \delta \int_A \ell f_v dA_{\ell v} \quad (32)$$

A reaction at the solid-liquid interface will cause a compositional change which will lead to diffusion from the interface into the solid and liquid. If diffusion of any component n_i is slow in both phases compared to the fluidity of the liquid, and if the rate of reaction at the interface is rapid compared to diffusion, $s f_v$ and ℓf_v will stay approximately constant and $s f_{\ell}^B$ will be reached rapidly. $s f_v - s f_{\ell}^B$ will be greater than $s f_v - s f_{\ell}^A$. Therefore, system B can attain a lower energy state than system A by replacing solid-vapor area with solid-liquid area. Increasing the solid-liquid interface by $\delta A_{s\ell}$ means that the liquid-vapor interface must increase its area by $\delta A_{\ell v}$ (Fig. 3). Increasing the liquid-vapor interfacial area will raise the free energy of system B over system A by $\delta \int_A \ell f_v \delta A_{\ell v}$ if the contribution of the interfacial reaction toward lowering $s f_{\ell}^B$ is great enough, then $\delta \int_A (s f_v - s f_{\ell}) dA_{s\ell}$ will counterbalance the increase in free energy due to creation of liquid-vapor interface $\delta \int_A \ell f_v dA_{\ell v}$ and the entire system will be in a lower energy state. If

$\delta \int_A (s f_v - s f_l) dA_{sl}$ reduces the free energy of the system

if $(s f_v - s f_l) > (1 f_v)$ spreading will occur

XBL 709-6640

Figure 3.

$$({}_s f_v - {}_s f_\ell) > {}_\ell f_v \quad (33)$$

δF_{system} will be negative until a zero degree wetting angle is attained, i.e., spreading results. If $({}_s f_v - {}_s f_\ell)$ is less than ${}_\ell f_v$ a finite wetting angle will result.

Now consider the case where a reaction occurs at the solid-liquid interface and diffusion is slow in the solid compared to kinetics of reaction, but fast in the liquid. Since the composition of the liquid is changing, ${}_\ell f_v$ will change to ${}_\ell f_v^1$.

$${}_\ell f_v^1 = {}_\ell f_v + \sum_j \mu_j \Gamma_j \quad (34)$$

If

$$({}_s f_v - {}_s f_\ell^B) > {}_\ell f_v^1 \quad (35)$$

spreading will occur. However, the change in composition in the liquid can cause the viscosity to increase or decrease. If the viscosity decreases and Eq. (35) is valid, spreading will occur. If the viscosity increases, the rate of flow of liquid over the solid may be slow compared to the time of the experiment causing a slowly decreasing non zero wetting angle. Generally ${}_\ell f_v$ is in a very low energy configuration because mobility of atoms in the liquid permits rearrangement of the surface to a low energy state, i.e., adsorption. The change in composition due to a reaction should not affect ${}_\ell f_v$ appreciably. Therefore, ${}_\ell f_v$ and ${}_\ell f_v^1$ are often approximately equal. Equation (33) may often be

used instead of Eq. (35).

If a reaction occurs at a liquid-solid interface, and if diffusion in the solid is comparatively rapid, the composition of the solid surface will change. (Fig. 4). f_v can either increase or decrease, a larger value of f_v will make $(f_v - f_l^B)$ greater. If the conditions of Eq. (33) are fulfilled, spreading will result. A decrease in f_v can cause Eq. (33) to be unfavorable, resulting in a finite wetting angle, even though there is an interfacial reaction.

In most configurations, the volume of the solid can be considered infinite compared to the liquid. Therefore, the solid will be an infinite sink or source for any component n_i . The liquid, on the other hand being finite, can be depleted or saturated. A reaction at the solid-liquid interface or diffusion from the liquid into the solid across the interface will lead to depletion of component n_i from the liquid. As this occurs, the activity of n_i in the liquid is reduced. Eventually the rate of introduction of n_i into the solid will approach zero. As n_i diffuses into the bulk, it will also be depleted from the solid-vapor interface (Figs. 5A and B). If the presence of n_i at the solid surface reduced f_v , diffusion of this component away from the surface into the bulk will cause an increase in f_v . The change in f_v can cause Eq. (33) to become operative only after the liquid has been depleted of n_i . Thus spreading is delayed (Fig. 5A). If the introduction of n_i into the solid surface increases f_v , causing spreading, the diffusion of n_i into the bulk will decrease f_v . Equation (33) becomes unfavorable, and

$$(f_v - f_l^B) < f_v \quad (36)$$

Case where s_v^f increases

s_v^f increases due to the compositional change in the solid surface associated with diffusion of component n_i from the solid-liquid interface. If the conditions of Eq. (33) are met by this change, the system can lower its free energy by creating solid-liquid interfacial area. The rate of spreading will be determined by the rate of diffusion of n_i in the solid.

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Case where s_v^f decreases

s_v^f decreases due to the compositional change in the solid surface. If the difference $s_v^f - s_l^f$ is reduced sufficiently, the conditions of Eq. (33) are no longer met. Thus no spreading occurs even though there is a reaction at the solid-liquid interface.

Figure 4.

Figure 5A. Diffusion of n_i away from the solid surface causes $s f_v$ to increase. If the increase is great enough, the conditions of Eq. (33) are met and spreading occurs.

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Figure 5B. Diffusion of n_i away from the solid surface causes $s f_v$ to decrease. If the decrease is great enough, the conditions of Eq. (33) become unfavorable resulting in pull-back of the liquid.

pullback of the liquid will result (Fig. 5B).

If a reaction occurs at the solid-vapor interface, that is adsorption or desorption of a gas from the solid surface, f_v will be affected. If adsorption occurs, f_v will be reduced. This can lead to unfavorable conditions for Eq. (33) resulting in a finite wetting angle even though f_l^B is being reduced by the other interfacial reaction at the solid-liquid interface. If desorption occurs, f_v will be increased. This increase in f_v can cause Eq. (33) to be operative. Spreading may be delayed until desorption is complete even though the solid-liquid interfacial reaction affects f_l^B immediately.

III. REACTIONS AT INTERFACES IN THE SYSTEM METALLIC IRON AND FeO-Na₂O-SiO₂ GLASSES AT 1000 DEGREES CENTIGRADE

1. Case I

There is no reaction at the glass-iron interface other than equilibration of activities of components of each phase at the interface.

This case is governed by: (1) relative diffusion rates in the two phases of the ion under consideration; (2) the saturation limit of the ion in each phase; (3) the rate of transfer of the ion across the interface.

The diffusivity of FeO (oxygen) in γ -Fe at 1000°C has been reported to be 6.67×10^{-7} cm²/sec.¹³ Borom¹⁴ has reported the apparent diffusivity of Fe⁺⁺ in Na₂Si₂O₅·xFeO at 1000°C to vary from 6 to 12×10^{-8} cm²/sec depending on the FeO concentration in the glass. These data indicate that the diffusivity of FeO is approximately the same in both phases. The solubility of FeO in γ -iron is approximately 40 ppm.¹³ The solubility of FeO in the glass varies from 20 to 44 wt. % at 1000C, depending on the O/Si ratio.¹⁵ Experiments indicate that the dissolution of FeO in the glass is rapid compared to diffusion rates and therefore is not rate determining.³⁻⁵

If an interface forms between a glass and iron, with the glass having a higher activity of FeO than the iron, diffusion will proceed from the glass into the metal. Since the diffusivities are about the same, FeO will not diffuse into the metal faster than it is introduced at the glass-metal interface. Due to the large difference in solubilities, the glass will have to lose only a fraction of an atomic percent to bring the activity of FeO in the metal up to the value of FeO in the glass.

The loss of a fraction of a percent of FeO will not appreciably change the activity of FeO at the interface from that of the glass. Therefore, Eq. (37) is valid.

$$a(\text{FeO})_{\text{interface}} = a(\text{FeO})_{\text{glass}} \quad (37)$$

If the iron is saturated with FeO but the glass is unsaturated, diffusion will proceed from the metal into the glass. Since the diffusivities are about the same, FeO will not diffuse into the glass faster than it is introduced at the interface. Due to the large difference in solubilities, the metal will have to lose only a few ppm of FeO in order to lower its activity. The pickup of this amount by the glass will be a fraction of a percent and will not noticeably change the activity of FeO in the glass. Therefore,

$$a(\text{FeO})_{\text{interface}} = a(\text{FeO})_{\text{glass}} \quad (37)$$

2. Case II

The reaction $\text{Fe} + \text{Na}_2\text{O} = \text{FeO} + 2\text{Na}$ occurs at the glass-metal interface.

The results of Case I still apply. As an interface forms between the glass and iron, reaction (37) occurs. In addition, it is known that metallic iron can be oxidized by sodium in the glass.⁸ The reaction

may proceed at the interface. This reaction is very sensitive to the partial pressures of Na and O₂ in the vapor (Fig. 6). If the sodium pressure is high enough, the reaction will not proceed as written. If the oxygen pressure is high enough, FeO will oxidize to Fe₂O₃ or Fe₃O₄ which are stable at higher oxygen pressures.

At 1000°C, taking the standard states for reactions (38) as pure solid iron, pure liquid sodium oxide, pure solid iron oxide, and sodium gas at one atmosphere pressure, the Standard Free Energy ΔF° ¹⁶ is given by

$$0 - 52,500 = -43156 + 0 \quad (40)$$

$$\Delta F^\circ = +9344 \text{ cal/mole} \quad (41)$$

Under nonequilibrium conditions

$$\Delta F = \Delta F^\circ + RT \ln(a_{\text{FeO}})(P_{\text{Na}})^2/(a_{\text{Na}_2\text{O}}) \quad (42)$$

$$\Delta F = 9344 + RT \ln(a_{\text{FeO}})(P_{\text{Na}})^2/(a_{\text{Na}_2\text{O}}) \quad (43)$$

Reaction (38) is favored by low activities of FeO and Na and by high activities of Na₂O. No explicit data are available for activities in this reaction but activity data are available for FeO in glasses which have a greater O/Si ratio than glasses used in this study.¹⁷ Assuming

XBL 709-6642

Figure 6. The equilibrium activity of Na₂O versus the equilibrium pressure of Na gas at several activities of FeO for the reaction, at 1000°C.

$a(\text{FeO}) = 0.043$, and $a(\text{Na}_2\text{O}) = 0.3$, ΔG can be calculated if an estimate is made for the pressure of Na gas. This pressure will not be the pressure of Na in the vapor. Na gas has experimentally been observed to emerge from the glass in the form of a bubble. The bubble has to nucleate and break through the glass vapor interface in order to escape into the atmosphere. An internal pressure of Na must build up above the pressure of the ambient atmosphere before this can happen. Neglecting density and gravitational effects, the pressure necessary to nucleate a spherical bubble is given by

$$p - p_0 = 2\gamma/r \quad (44)$$

p_0 = the external pressure on the liquid. (The pressure over a 2cm radius liquid glass bead is approximately equal to the pressure over a flat surface of liquid and can be taken as the pressure in the furnace.)

p = the Na vapor pressure in the bubble.

γ = the surface tension of the liquid. (Assume 400 ergs/cm^2 for the liquid glass.)

r = radius of the bubble. ($r = 0.5 \text{ mm}$)

then

$$\begin{aligned} p - p_0 &= 2 \times 400 / .05 \\ &= 0.016 \text{ atm} \end{aligned} \quad (45)$$

The free energy for reaction (41) may now be calculated. Assume first the conditions of high vacuum. Let $p_o = 10^{-8}$ atm.

$$p = p_o + 0.016$$

$$p = 10^{-8} + 0.016$$

$$p \approx 0.016$$

Substituting this value into Eq. (43), $\Delta F = -6156$ cal/mole. When such a bubble forms, it escapes into the atmosphere releasing sodium gas. As the reaction continues at the glass-metal interface, sodium gas pressure builds up until another bubble is nucleated. Thus Fe^{++} is introduced into the glass and Na gas is released to the atmosphere. The activity of FeO at the interface increases causing diffusion of Fe^{++} into the glass.*

Assume now a total pressure of one atmosphere, $p_o = 1$ atm. Therefore, from Eq. (45), $p = 1.016$ atm. Substituting this value into Eq. (43) $\Delta F = +4474$ cal/mole. This free energy corresponds to the formation of a bubble in an atmosphere where the total pressure is 1 atmosphere. The free energy becomes positive before a bubble can nucleate. Therefore, the reaction ceases at the glass-metal interface before sufficient Na gas is present in the glass. The introduction of Fe^{++} into the glass by reaction (38) will be very slight.

3. Case III

The reaction $Na_2O = 2Na + 1/2 O_2$ occurs at the liquid-vapor interface.

*Since the solubility of oxygen in Fe metal is slight, very little will diffuse from the interface into the metal.

If the activity of Na_2O in the glass is higher than the equilibrium value corresponding to a particular vapor, the reaction

will proceed at the liquid-vapor interface. Taking the standard states for this reaction as pure liquid Na_2O , and Na and O_2 gases at one atmosphere pressure, the standard free energy for the reaction is + 52,500 cal/mole at 1000C. Under non equilibrium conditions,

$$\Delta F = 52,500 + RT \ln(P_{\text{Na}})^2 (P_{\text{O}_2})^{1/2} / (a_{\text{Na}_2\text{O}}) \quad (47)$$

This reaction is favored by a high activity of Na_2O and low pressures of Na and O_2 . Figure 7 is an equilibrium plot of activity of Na_2O versus pressure of Na at several oxygen pressures. No bubble nucleation is required for this reaction since it occurs at the liquid-vapor interface.

4. Case IV

The reaction $\text{FeO} = \text{Fe} + 1/2\text{O}_2$ occurs at the liquid-vapor interface.

If the activity of FeO in the glass is higher than the equilibrium value corresponding to a particular vapor, the reaction

will proceed at the liquid-vapor interface. Taking the standard states for this reaction as pure solid FeO, pure solid Fe and oxygen at one atmosphere, the standard free energy is + 43156 cal/mole, at 1000C.

XBL 709-6643

Figure 7. The equilibrium activity of Na_2O versus the equilibrium pressure of Na gas at several pressures of O_2 at 1000°C for the reaction

Under nonequilibrium conditions,

$$\Delta F = 43,156 + RT \ln(P_{O_2})^{1/2} (a_{Fe}) / (a_{FeO}) \quad (49)$$

This reaction is favored by a high activity of FeO, and a low pressure of O₂. Figure 8 is a plot of the equilibrium activity of FeO versus pressure of O₂. Since the decomposition proceeds at the liquid-vapor interface, no bubble nucleation occurs. Metallic iron will be deposited at the surface of the liquid as the reaction proceeds.

XBL 709-6644

Figure 8. Equilibrium activity of FeO versus pressure of O₂ at 1000°C,
for the reaction

IV. EXPERIMENTAL

A. Glass Preparation

Glasses for this study were prepared in the ternary system $\text{FeO}-\text{Na}_2\text{O}-\text{SiO}_2$, Fig. 9. Compositions ranged from $\text{Na}_2\text{Si}_2\text{O}_5$ (NS_2) to saturation with respect to SiO_2 at 1000C, holding the O/Si ratio constant at 2.5, ($\text{Na}_{2-2x}\text{Fe}_x\text{Si}_2\text{O}_5$). One glass was prepared which precipitated FeO at 1000C having its composition on the NS_2 -FeO tie line.

NS_2 glass rods were purchased from Corning Glass Works. They were cut into discs and stored in a dessicator prior to use. All other glasses contained Fe^{++} and were prepared from NS_2 powder obtained from Philadelphia Quartz Co. and from Baker's reagent grade Fe, Fe_2O_3 , and SiO_2 powders. These components were mechanically mixed and packed into iron crucibles. The powders were then heated in a Kanthal wound resistance heated mullite tube furnace for 24 hours at 1000C. An atmosphere of one part CO to one part CO_2 was allowed to flow through the furnace in order to maintain an oxygen pressure of 10^{-15} atm. At this oxygen partial pressure, solid FeO is stable. At temperature, the reaction

proceeds. FeO is then dissolved into the liquid NS_2 . After 24 hours at temperature, the glasses were cooled to room temperature, removed from the iron crucibles and stored in a dessicator. All glasses containing Fe^{++} were bluish in color. The glass precipitating into the FeO phase field had dendrites of FeO (wustite) dispersed throughout the glassy phase. These precipitates formed during cooling. A metallic

XBL 711-124

Figure 9. Glass compositions used indicated by dots.

residue was observed at the surface of the glass indicating that some metallic Fe did not react with Fe_2O_3 to form stoichiometric FeO as reaction (50) is written. It is certain that some Fe^{+++} was present in all the glasses containing iron. However, the equilibrium activity of Fe^{+++} in an oxygen partial pressure of 10^{-15} atm. is so low that the effect of the trivalent ion can be neglected.

B. Metal Preparation

Marz Grade Iron in 20 mil thick foils was obtained from Materials Research Corporation, Orangeburg, N.Y. A processing description and impurity content are given in Table I. The foil was cut into $1/2$ " squares and stored in a dessicator. Armco iron was obtained from LRL Berkeley in the form of $5/8$ " diameter rods. These rods were cut into $1/8$ " thick discs and stored in a dessicator. An impurity content is given in Table II. 99.99% pure platinum foils 20 mils thick were obtained from LRL Berkeley. They were cut into $1/2$ inch squares and stored in a dessicator. All specimens were given a high metallurgical polish prior to use.⁸

C. Furnace Description

Two furnaces were used in this study. One, designated furnace A was a Kanthal wound resistance heated mullite tube with glass fittings joined to either end of the tube, Figure 10. The glass joints were connected to a roughing pump, gas-in and gas-out valves, a zirconia oxygen probe connection,¹⁷ and thermocouple connections. An alumina dee was placed in the central region of the furnace. Heat shields were located at either end of the dee. At 1000C a 6° gradient existed between the thermocouples. The roughing pump permitted evacuation of the system

Table I. Typical analysis of Marz grade material

Impurity	Content (ppm)	Impurity	Content (ppm)
C	8	Mo	0.2
H	<0.1	Na	0.08
O	7.2	Nb	0.03
N	7.0	Ni	1.2
Ag	<0.04	Pb	<0.015
Al	--	Pd	<0.08
Bi	<0.008	Pt	<0.025
Ca	2	Rh	<0.03
Cd	<0.08	S	1.2
Co	0.3	Si	0.5
Cr	0.6	Sn	<0.02
Cu	<0.02	Ta	<1
Fe	--	Ti	0.5
Hf	0.025	V	<0.1
K	0.2	W	<0.1
Mg	8	Zn	<0.8
Mn	0.1	Zr	<0.06

Table II. Typical analysis for Armco iron

0.015%C, 0.0285% Mn, 0.005% P, 0.025% S, 0.003% S, Undisclosed amount of oxygen.

Figure 10. Furnace A

XBL 709-6646

which could then be sealed off and backfilled with the desired gaseous atmospheres. During experimentation, gas was continuously passed through the furnace. A zirconia oxygen probe was located near the dee to act as a continuous monitor of oxygen partial pressure.

The other furnace designated furnace B^{*} consisted of a resistance heated graphite tube surrounded by a vacuum chamber (Fig. 11). A specimen was placed on an alumina dee which was inserted into the graphite tube. Temperatures were monitored by a Pt-Pt 10% Rh thermocouple located next to the specimen. At temperature, a total pressure of 3×10^{-6} torr was attained. Visual observations of the specimen during the experiment were possible through two sighting ports pointing down the axis of the graphite tube.

D. Test Procedure

Furnace A. Glass chips were placed on highly polished metal substrates. Six specimens were inserted into the central region of the furnace simultaneously. The system was then evacuated, sealed off and backfilled with argon or CO-CO₂ mixtures. Gases were passed through the furnace during the entire experiment. All specimens were heated to 1000C, held there for a specified time and then furnace cooled. At temperature, the oxygen partial pressure was monitored with a zirconia oxygen probe.

Furnace B. Glass chips were placed on highly polished metal substrates and inserted into the central region of the graphite tube. The furnace was then evacuated to a total pressure of 3×10^{-6} torr and heated to 1000C. After a specified time at temperature, the specimens

*Called furnace 1 in a previous study.⁷

MUB-12306

Figure 11. Furnace B

were furnace cooled.

E. Analysis of Experiments

The specimens were sectioned, polished and subjected to optical and microprobe analysis. Photomicrographs, X-ray fluorescence pictures and backscattered electron pictures were taken of selected interfacial regions.

V. RESULTS AND DISCUSSION

A. Furnace A

1. (10/1 CO/CO₂ atmosphere)

Glass compositions of 0, 7.2, 11.3, 14.5, 17.3, and 19.2 weight percent FeO with the balance Na₂O and SiO₂ were run on pure iron substrates for 2 hours. The O₂ partial pressure above the specimens was 9.6×10^{-17} atm. The wetting angles of all compositions were approximately the same, 55 degrees. There was no evidence of precipitation in the glass. The reaction

proceeded to some extent since NS₂ glass was a bluish color after the experiment. This coloration was due to the introduction of Fe⁺⁺ into the glass. This reaction is sensitive to sodium pressure. Under test conditions, the total pressure necessary to nucleate a bubble of Na gas in the glass, was greater than one atmosphere. The free energy for Eq. (38) became positive before a bubble could nucleate. Therefore, the oxidization of metallic iron by sodium oxide was slight. When no bubble formation occurs, the rate at which (38) proceeds is determined by the rate of permeation of Na through the glass.

There was no evidence of FeO decomposition in the glass. FeO is stable to an activity of about 10^{-1} in the oxygen partial pressure used for this experiment (Fig. 8). Reaction is slow and occurs only at the liquid-vapor interface. The glasses with higher percentages of FeO (>11%) probably would show decomposition if held at temperature longer.

It is not known whether Na_2O in the glass decomposed since the sodium pressure in the furnace was not known. As can be seen from Fig. 7, a low Na pressure as well as low O_2 pressure is necessary for decomposition to occur.

2. Argon + Graphite Getter on Armco and Marz Iron

The same glass compositions were used for these experiments as were used in the CO/CO_2 atm experiments. Initially pure CO was used as an atmosphere. But the precipitation of carbon

on the metal and glass surfaces introduced an additional variable. Instead, the specimens were placed in a graphite tube which was inserted in the furnace. Argon was allowed to flow over the specimens. Reaction (51) proceeded to the left controlling the oxygen partial pressure in the furnace. This pressure was dependent on the flow rate of argon and varied from $(4 \text{ to } 7) \times 10^{-19}$ atm. Experiments were run for 2, 5, and 44 hours. All specimens exhibited wetting angles between 55 and 60 degrees. There was evidence in some glasses of a precipitate at the liquid-vapor interface. Sessile drops run for 2 hours had precipitates in the 14.5, 17.3, and 19.2 wt% FeO glasses. Those run for 5 and 44 hours revealed precipitation in all glass compositions (i.e. ≥ 7.2 wt% FeO) except NS₂, Fig. 12. Microprobe analysis indicated the precipitates were metallic iron, Fig. 13.

The reaction

Plastic Holder

7.2 wt.% FeO glass

Glass-vapor interfaces;
glasses on Armco iron were
run for 5 hours in Furnace A.
(Magnification, 160X)

14.5 wt.% FeO glass

19.2 wt.% FeO glass

XBB709-4036

Figure 12.

Micrograph of glass-vapor
interface. 160X

Backscattered electrons
700X

Fe-K α radiation

Si-K α radiation

XBB709-4032

Figure 13. Electron microprobe analysis. Liquid-vapor interface of an 11.3 wt.% FeO glass on Armco iron run for 44 hours in Furnace A. The precipitate at the surface is metallic iron.

occurred at the liquid-vapor interface. Figure 8 indicates that FeO will decompose, in the partial pressure of oxygen achieved in the furnace $(4-7) \times 10^{-19}$ if its activity is $> .05$. It is not known if Na_2O decomposition occurred. The blue coloration of NS_2 was due to reaction (38). This reaction proceeds only slightly as in the CO/CO_2 atmosphere.

All specimens run in CO/CO_2 or argon + graphite exhibited wetting angles between 55 and 60 degrees. Metallic iron has a surface tension of about 2000 dynes/cm¹⁸ and $\text{FeO-SiO}_2\text{-Na}_2\text{O}$ glasses have surface tensions between 300 and 500 dynes/cm, depending on glass composition (Fig. 14). The high wetting angles of the sessile drops indicate that $(\gamma_{sv}^f - \gamma_{sl}^f)$ was a small value. It is unreasonable to assume a value anywhere near 2000 dynes/cm for γ_{sl}^f . Although the iron substrates received a high metallurgical polish prior to use, a surface layer of oxide was undoubtedly present. Chemisorbed oxide layers are generally strongly bonded to the solid surface and will not readily desorb.¹⁸ The effect of oxygen and other impurities can be seen, from Fig. 15, to have a marked effect on γ_{sv}^f . Although this plot is for liquid Fe, the same trend can be expected for solid iron but at much lower impurity levels.¹⁸ Thus the value of γ_{sv}^f is appreciably lower than the value for a clean surface, due to the positive Γ 's. Impurities in the atmosphere act as an additional means of affecting Γ by which the iron can lower its surface free energy further. Since the extent of interfacial reaction at the solid-liquid interface is negligible, its contribution toward lowering γ_{sl}^f will be insufficient to induce spreading. Increasing the Fe^{++} content of the glass causes the bond between the glass and the metal

XBL 709-6653

Figure 14. Surface tensions vs silica contents for binary silicate melts. (From P. Kozakevitch, ref. 19, pp. 259.)

XBL 709-6652

Figure 15.

(From P. Kozakevitch, Ref. 19, pp. 257.)

to be more continuous⁸ thus lowering f_{ℓ} . The octahedral coordination of Fe^{++} in the glass will reduce the screening ability of oxygen on silicon ions, thus increasing f_v . Since all wetting angles were quite similar, the reduction in f_{ℓ} with increasing Fe^{++} contents in the glass was apparently counterbalanced by an increase in f_v .

B. Furnace B

1. Vacuum + Graphite Heating Element

The total pressure measured in this furnace was 10^{-9} atm at the test temperature. Under these conditions, the equilibrium O_2 partial pressure is 10^{-34} atm, (Eq. (51)). Due to the effects of residual leaks, outgasing of the furnace walls, and nonequilibrium conditions, (dynamic vacuum), it is assumed that the oxygen partial pressure is many orders of magnitude higher than this value. The low heat capacity of the furnace and high current flow through the graphite heating element made use of the zirconia oxygen probe impossible.

Glasses varying in composition from NS_2 to saturation with SiO_2 (0, 7.2, 11.3, 14.5, 17.3, 19.2 wt% FeO), were run on Armco iron and Marz iron. The wetting angles were dependent on the time of the experiment and nature of the iron substrate. Precipitation in the glass resulted after sufficient time at the test temperature.

A glass containing 14.5 wt% FeO on Marz iron exhibited an acute wetting angle (approximately 30 degrees) for one half hour while at temperature; spreading then occurred. During this time, bubbling of the glass was appreciable. After one hour at temperature, precipitates had formed around the periphery of the glass drop. Microprobe analysis indicated them to be SiO_2 (Fig. 16).

Plastic Holder

Glass with precipitates of SiO₂

Crack between glass and substrate

Fe-K_α radiation

14.5 wt.% FeO glass on Marz iron
run in Furnace B for 1 hour.
Top picture is an oscilloscope
trace of backscattered electrons.

Si-K_α radiation

XBB709-4034

Figure 16. Electron Microprobe Analysis.

As the glass and metal first formed an interface, the conditions of Eq. (37) were fulfilled. Then reaction (38) became operative, with Eq. (45) determining the Na pressure necessary to nucleate a bubble of Na gas. Introduction of Fe^{++} into the glass altered its composition. When sufficient Na^+ was replaced by Fe^{++} , SiO_2 precipitated (Fig. 9). In the early stages of the experiment, the wetting angle remained acute. Equation (33) was not operative. Although the contribution of the interfacial reaction lowered f_{ℓ} , the difference $(f_v - f_{\ell})$ was insufficient to overcome the gain in free energy of the system necessary to create a liquid-vapor interfacial area to result in spreading (Fig. 3). After sufficient time at temperature (about 30 minutes), spreading occurred. In this period of time, the combination of dynamic vacuum and low oxygen pressure caused f_v to be increased. This increase was undoubtedly due to the desorption of an oxide layer from the iron surface. As f_v increased, $(f_v - f_{\ell})$ became larger. The conditions of Eq. (33) became operative and spreading resulted.

Identical experiments run on Armco iron substrates revealed acute wetting angles for the duration of the experiment. Bubbling of the glass was in evidence but the degree of precipitation in the glass appeared to be less. As the glass and metal first formed an interface, the conditions for Eq. (38) were fulfilled. Reaction (38) occurred with the sodium pressure determined by (45).

Armco iron can be expected to have the same oxide layer on the surface as Marz iron. In addition, there are precipitates of FeO in the bulk plus other impurities. When the oxide layer is desorbed, f_v should increase. However, the effect of oxygen and other impurities in the bulk

allows f_v of Armco iron to remain at a lower value than f_v of Marz iron. These impurities give rise to nonzero values of Γ which directly affect f_v , Eq. (3) (Fig. 15). The difference $f_v - f_l$ remains small, causing Eq. (33) to be inoperative. Eventually f_v increases; however, precipitation in the glass causes it to become too viscous for the effect to be noticed.

The greater degree of precipitation in glasses in contact with Marz iron than with Armco iron results from two factors. After spreading occurs on Marz iron, the solid-liquid interfacial area is greater than on Armco iron at any comparable time. This additional area provides more reaction surface. Secondly, as spreading occurs, the diffusion path for Fe^{++} from the solid-liquid interface to the liquid-vapor interface is shorter than for conditions where no spreading occurs. Thus the glass on Marz iron is able to saturate faster.

When Armco iron was heated for 20 hours at 1100°C in furnace B and then run in a sessile drop experiment for 2 hours with a NS₂ glass with 9.1 wt% FeO (glass used in a previous study in this laboratory⁸), a wetting behavior similar to that for Marz iron was revealed. The 20 hour anneal caused the iron to be sufficiently depleted of impurities that they could no longer significantly affect f_v . Thus, after desorption of the oxide layer, the solid-vapor energy was sufficiently raised to cause Eq. (33) to be operative. As the interfacial reaction continued, precipitation of fayalite resulted (Fig. 17). From the phase diagram, it would be expected that this glass would precipitate SiO₂ if reaction (38) were operative (Fig. 9). The occurrence of F₂S indicates that in very low oxygen pressures the fayalite phase field must extend to lower FeO

Oscilloscope trace of backscattered electrons showing glass with precipitates of fayalite.

Substrate

Fe-K α radiation

A 9.1 wt.% FeO glass was run on Armco iron for 2 hours. The iron substrate was annealed in a high vacuum for 20 hours at 1100C prior to the sessile drop experiment.

Si-K α radiation

XBB709-4029

Figure 17. Electron Microprobe Analysis

concentrations in the glass than shown in Fig. 9.

In addition to reactions at the metal-glass interface, Na_2O decomposition at the glass-vapor interface occurred in all experiments. Under test conditions, the O_2 and Na pressures are both sufficiently low for reaction (46) to proceed (Fig. 7). The rate of this reaction seems to be slower than reaction (33). FeO decomposition is too slow to be of any significance in these experiments.

When precipitates begin to form in the glass, its viscosity goes up. Bubble nucleation becomes more difficult. Since there is a pressure difference between the bulk of the glass and the liquid-vapor interface, Na gas will permeate through the glass to its surface. The rate at which reaction (38) proceeds at the glass-metal-interface will be determined by the rate of permeation of Na gas. This effect is only significant when the viscosity of the glass is high.

NS_2 on Armco iron and Marz iron substrates was run for 20 hours at temperature. Wetting angles on both substrates differed. On Marz iron the glass exhibited an acute wetting angle for the early part of the experiment (30-45 min.) and then spread over the substrate. Precipitation occurred in the glass. NS_2 on Armco iron exhibited an acute contact angle for the entire time of the experiment. Precipitation also was observed (Fig. 18). During the early part of the experiment the glasses bubbled. Electron microprobe analysis revealed that the precipitates were SiO_2 (Fig. 19). Wetting behavior and reactions for NS_2 on Armco and Marz irons are similar to other glass compositions except that longer times are necessary to precipitate SiO_2 .

XBB709-4031

Figure 18. NS_2 on Armco iron (top) and NS_2 on Marz iron (above) run for 20 hours in Furnace B. 160X.

Oscilloscope trace of backscattered electrons showing glass with precipitates of SiO_2 . 700X

Iron substrate

Fe-K α radiation

NS_2 run on Armco iron for 20 hours in Furnace B. (See Figure 18.)

Si-K α radiation

XBB709-4035

Figure 19. Electron Microprobe Analysis.

2. Experiments with $\text{Na}_2\text{Si}_2\text{O}_5$ + 44.5% FeO

NS_2 glass with 44.5% FeO was run on Armco iron and Marz iron for various periods of time. All specimens exhibited similar wetting angles and reaction behavior. The glasses bubbled for 2-3 minutes at temperature. Then bubbling ceased. No wetting angles could be determined since the glasses had devitrified (by the time bubbling ceased) in several minutes. Figure 20 is a micrograph of the 44.5% FeO glass before the experiment. It contains precipitates of wustite which formed as the glass became supersaturated with FeO during cooling. Figure 21 shows micrographs of the 44.5% FeO glass on Armco iron run for 5, 10, and 120 min. For the early stages of the experiment, FeO dendrites dissolved in the glass. Notice how the small dendrites originally present in the glass gave way to larger precipitates with time, and how the degree of interfacial roughening increased with time. Figure 22 is a microprobe analysis of the interfacial region of the 10 minute experiment showing large precipitates of Fe_2S and smaller FeO dendrites.

The introduction of FeO at the glass-metal interface, according to reaction (38) causes the composition of the glass to shift toward the Fe_2S phase field. From the phase diagram (Fig. 9) it is evident that the FeO dendrites which did not dissolve in the glass will grow as the reaction proceeds.

XBB709-4039

Figure 20. 44.5 wt.% FeO glass; precipitates of FeO formed in the glass during cooling. 160X

5 minutes

10 minutes

120 minutes

Glass-metal interfaces between
44.5 wt.% FeO glass and Armco
iron. 160X

XBB709-4038

Oscilloscope trace of backscattered electrons showing glass with precipitates of fayalite and FeO.

Iron substrate

Fe-K α radiation

44.5 wt.% FeO glass on Armco iron run for 10 minutes in Furnace B. (See Figure 21.)
700X

Si-K α radiation

XBB709-4033

Figure 22. Electron microprobe analysis.

When the fayalite phase field is reached,

Therefore, FeO dendrites will be surrounded by fayalite. Microprobe analysis was ineffective in detecting such precipitate combinations since the FeO dendrites were quite small. However, it is logical to expect that nucleation of Fe_2S is kinetically simpler at the dendrite than homogeneously nucleating in the glass.

As precipitates formed in the glass, its viscosity increased causing the nucleation of Na bubbles to be increasingly difficult. After only several minutes at temperature bubbling ceased. Sodium was lost from the system by permeation of the gas from the glass-metal interface to the glass-vapor interface and by the decomposition of Na_2O at the glass vapor interface. As reactions (53) and (54) proceeded, the glass became poorer in Na^+ and Fe^{++} and richer in SiO_2 (Fig. 9).

Experiments run on Marz iron were similar to those on Armco iron. Figure 23 gives micrographs of 5 and 120 minute experiments. Figures 24 and 25 show a microprobe analysis revealing large precipitates of Fe_2S .

All experiments performed with the 44.5% wt FeO glass revealed rapid devitrification of the glass. Thus spreading was unable to occur because of the high viscosity of the glass. Since the solid-liquid interface is "frozen in" differences in s_v between Armco and Marz irons are of little consequence. From examination of the micrographs of glass on Armco iron (Fig. 20) and glass on Marz iron (Fig. 22) it is quite evident that the rate of reaction at the solid-liquid interface is

5 minutes

XBB709-4027

120 minutes

Figure 23. Iron-glass interfaces of 44.5 wt.% FeO glass on Marz iron run in Furnace B. 160X

Oscilloscope trace of backscattered electrons showing precipitates of fayalite in the central region of the glass.

Fe-K α radiation

44.5 wt.% FeO glass on Marz
iron run for 120 minutes in
Furnace B. 700X

Si-K α radiation

XBB709-4028

Figure 24. Electron Microprobe Analysis.

Oscilloscope trace of backscattered electrons showing glass with precipitates of fayalite, near glass-metal interface.

Iron substrate

Fe-K_α radiation

Glass-metal interface of 44.5 wt.% FeO glass on Marz iron run for 120 minutes in Furnace B. (See Figure 24.) 700X

Si-K_α radiation

XBB709-4037

Figure 25. Electron Microprobe Analysis.

similar and fast for both irons. If the viscosity of the glass is less, then the differences in $f_{s/v}$ between Armco and Marz irons do lead to different wetting and different degrees of precipitation as a function of time.

3. FeO-Na₂O-SiO₂ Glass on Platinum Substrates

Several experiments were performed on Pt substrates with FeO containing glass. It is not known to what extent, if any, Pt reacts with iron-soda-silica glasses. No phase diagram has been determined for the system. It is assumed the solubility of platinum oxide is small. The presence of colloidal Pt has been reported in certain Pb and Ba containing glasses in contact with the metal, and phosphate glasses have been reported to contain some platinum ions.²⁰

A 14.5 wt% FeO glass on a Pt substrate was run for 48 hours at 1000°C. The wetting angle was approximately 5-6 degrees. Precipitates were in evidence at the liquid-vapor interface. Figure 26 is a microprobe analysis of the specimen. The precipitates were identified as SiO₂. No Pt (above background radiation) was detected in the glass. Also, no precipitates or roughening were in evidence at the solid-liquid interface. If reaction between Pt and the glass occurred, it was beyond the limit of detection.

The formation of SiO₂ precipitates indicates that the composition of the glass shifted such that it became saturated with SiO₂. The loss of Na₂O from the glass, by reaction (46) will cause such a compositional change. This reaction occurs at the liquid-vapor interface and is favored by low O₂ and Na pressures (Fig. 7).

Oscilloscope trace of backscattered electrons showing glass with precipitates of SiO_2 .

Fe-K_α radiation

14.5 wt.% FeO glass on platinum run for 48 hours in Furnace B. No platinum radiation was detected in the glass above background radiation. 700X

Si-K_α radiation

XBB709-4030

Figure 26. Electron microprobe analysis.

The only components leaving the system are Na and O₂. The kinetics of this reaction seem to be slow since experiments run for shorter times with the same glass composition on Pt revealed no precipitation. (Due to the low heat capacity of the furnace, cooling was rapid. Precipitation of SiO₂ could not have occurred during the cooling process.)

The small wetting angle exhibited by the specimens (5-6 degrees) is due to the large difference between s^f_v and s^f_l . The oxide of platinum is stable in air up to 400°C and then decomposes.²¹⁻²³

Low partial pressures of O₂ favor decomposition. Therefore, it can be assumed that there is little or no oxide layer on the surface of the Pt, above 400. This metal is known to be sensitive to certain gaseous elements which adsorb on its surface.²¹⁻²³ The high vacuum conditions of Furnace A keep impurity gases in the atmosphere at a minimum. The low O₂ pressure aids reaction (49). Therefore, under test conditions, s^f_v of platinum will approach the surface free energy (characteristic of a pure metal) at 1000°C which is about 2000 dynes/cm.¹⁸ It is believed that the wetting of platinum by the glass is due to this large value of s^f_v .

IV. CONCLUSIONS

The vapor phase present above the sessile drop affects the stability of the glass and the degree of glass-metal interfacial reaction.

1. A vapor phase having a total pressure of one atmosphere with low partial pressures of Na and O_2 causes decomposition of FeO and Na_2O at the glass-vapor interface.

2. Na gas is liberated at the glass-iron interface by the reaction

which will proceed as written if the pressure of Na is sufficiently low. Na gas formed at the interface nucleates into a bubble and then escapes from the glass into the atmosphere. The pressure necessary to nucleate a bubble is given by Eq. (44).

$$P = P_o + 2\gamma/r$$

If P_o is 1 atm, the free energy for reaction (38) becomes positive before a bubble can nucleate. The rate of reaction is then determined by the rate of permeation of Na through the glass, and is slow.

If P_o corresponds to high vacuum conditions (10^{-8} atm), the free energy for reaction (38) remains negative allowing bubble nucleation to occur. As Fe^{++} is substituted for Na^+ , the composition of the glass changes. If the reaction is allowed to proceed long enough, SiO_2 , FS_2 or FeO will precipitate from the glass. The starting composition of the glass determines which phase will appear.

3. Wetting behavior of $Na_{2-2x}Fe_xSi_2O_5$ on Marz iron and Armco iron is governed mainly by changes in f_v . In a high vacuum, Marz iron loses the thin oxide film present on its surface after approximately 30 min. at test temperature. Then spreading occurs. The loss of the film increases f_v giving rise to favorable conditions for spreading (Eq. (33)). Impurities present in the bulk of Armco iron keeps f_v at a low value even after the oxide film is desorbed, leading to unfavorable conditions for spreading and a resultant nonzero wetting angle. Although reaction (38) proceeds on both types of irons, the contribution of the free energy of the interfacial reaction toward lowering f_l alone is insufficient to induce spreading.

4. Spreading by the liquid on Marz iron as contrasted to the formation of an acute wetting angle on Armco iron, leads to an increase in solid-liquid interfacial area and a shorter diffusion distance from the solid-solid interface to the liquid-vapor interface. Thus, more rapid saturation of the glass with Fe^{++} occurs on Marz iron than on Armco iron.

5. Armco iron was heated at $1100^\circ C$ for 20 hours in a high vacuum prior to the sessile drop experiment. Liquid glasses revealed a similar wetting behavior to those run on Marz iron. During the 20 hour anneal, sufficient impurities were vaporized from Armco iron to cause its surface

region to become essentially the same as Marz iron, and therefore exhibit similar wetting behavior.

6. In one atmosphere total pressures of argon or 10 to 1 CO/CO₂ mixtures the wetting angles of Na_{2-2x}Fe_xSi₂O₅ on Marz iron and Armco iron were approximately the same, 55-60°. Impurities present in the vapor and the absence of vacuum conditions retarded the desorption of the oxide layer on both irons causing f_v to remain a low value giving rise to unfavorable conditions for spreading and a resulting finite wetting angle.

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