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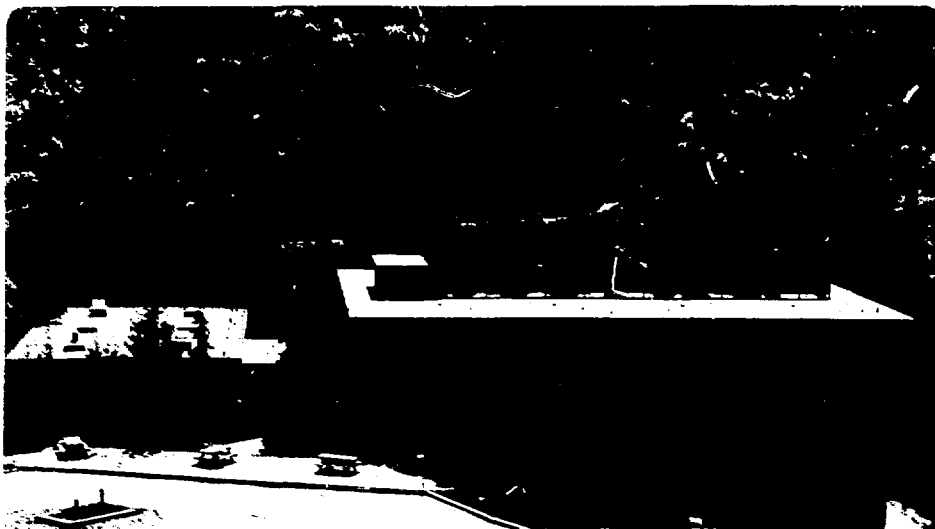
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WETTING, SPREADING AND REACTIONS AT LIQUID/SOLID INTERFACES

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ABSTRACT

Chemical (thermodynamic) stable equilibrium at glass-metal interfaces is established when the liquid glass becomes saturated with the low valence oxide of the metal. Stable or metastable equilibrium conditions at glass-metal interfaces result in a constant contact angle in a sessile drop experiment. If chemical equilibrium is absent, then a driving force exists for the occurrence of a reaction to attain equilibrium. All reactions that take place contribute to the maintenance of the necessary saturation of the liquid and solid at the interface with the solid substrate oxide in order to realize chemical bonding across the interface. Spreading always occurs when the solid metal is an active participant in these reactions. Examples showing the development of these principles are based on systems of sodium disilicate with Fe, Co, Ni, Fe-Ni alloys, Pt, Ag, Au, Cu, Ta, W, Mo, Nb, Zr and Cr. The final structure and composition of the glass-metal interfacial zone are determined by the kinetics and thermodynamics of the reactions that occur.

I. INTRODUCTION

A surface represents the discontinuity of the bulk structure; the resulting distortion and change in coordination number of the atoms at the surface causes a higher free energy over a corresponding plane and number of atoms in the bulk. This excess free energy is defined as surface energy or the solid/vapor interfacial energy, γ_{sv} . The same analysis applies to an interface between condensed phases, e.g. a solid and liquid; the excess free energy in the solid at the interface is then referred to as the solid/liquid interfacial energy, γ_{sl} , and in the liquid as γ_{ls} .

Research on surfaces has been a great deal more extensive because of the availability of sophisticated instruments that permit studies of their structure and composition. Studies on s/l and s/s interfaces, on the other hand, have been hampered because of the difficulties in directly examining the interface between two condensed phases, although there are currently significant efforts in this direction.

In applications such as protective coatings on metals and glass/metal seals an understanding of the interfaces is extremely important. Even though determination of specific values of their properties is difficult, some knowledge of their relative values is useful. Sessile drop experiments are informative in studies of such systems for they provide a means of studying wetting and spreading of a liquid on a rigid solid and a configuration that, on cutting perpendicular to the interface, lends itself to the potential study of any reactions that may occur at the interface.

II. WETTING AND SPREADING

Many studies of wetting, spreading and reactions of $\text{Na}_2\text{Si}_2\text{O}_5$ glass on metals have been made. Similarities of certain groups of metals are recognized

but reliable predictability and complete understanding is still lacking. At least part of the reason is the difficulty of finding an acceptable criterion for comparison and the complexity of the reactions that occur at the interface. It would be extremely important, especially from the technological point of view, to be able to predict wetting or spreading in different metal/glass systems and the conditions under which chemical bonding would occur.

It is unfortunate that specific values of γ_{sv} and γ_{sl} cannot presently be measured, or at least measured easily and reliably. Liquid surface energies, γ_{lv} , and contact angles, however, can be measured. Relative magnitudes or changes can thus be deduced which in many cases can be just as informative and useful as actual values. Let us, therefore, first explore the general relationships¹.

Thermodynamically, if no reaction or mass transport of atoms occurs at the interface, i.e. if stable or metastable chemical equilibrium exists, the γ_{sl} specific value (ergs/cm²) lies between γ_{sv} and γ_{sl} and the amount of reduction of the larger γ never exceeds the smaller γ . Thus when $\gamma_{sv} > \gamma_{sl} > \gamma_{lv}$, e.g. ceramic liquid on metal, an acute angle forms and when $\gamma_{sv} < \gamma_{sl} < \gamma_{lv}$, e.g. metal liquid on ceramic, an obtuse angle forms. The solid phase being rigid determines the configuration and, in the acute angle case, the reduction of γ_{sv} by the liquid provides a driving force for wetting which acts on the periphery of the liquid drop, expressed as $(\gamma_{sv} - \gamma_{sl})$. The resisting force is due to the increase of the total liquid surface energy as the liquid surface area is increased. From a mechanics viewpoint, then, a balance of the horizontal components of the forces determine the contact angle and is expressed as $(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv} \cos \theta$.

This analysis is indicated schematically in Fig. 1. The actual magnitude of γ_{S1} will be smaller with the existence of a chemical bond instead of a van der Waals bond because the discontinuity will be less severe due to the presence of electronic continuity across the interface. With a smaller γ_{S1} the driving force for wetting is greater and a smaller contact angle forms, but in neither case does the driving force for wetting exceed γ_{1V} . Therefore, no spreading, or unrestrained extension of the liquid surface, occurs with no reaction at the interface.

Two special relationships of the interfacial energies should be considered for purposes of understanding the overall relationships. If experimental conditions are such that a true interface does not form between the condensed phases and each phase retains some of its surface characteristics, then $\gamma_{SV} < \gamma_{S1} > \gamma_{1V}$ resulting in a large obtuse angle and weak vdw bonding. On the other hand, if a reaction occurs at the interface in which a third phase does not form and the solid is an active participant (i.e. its composition changes), a dynamic situation exists in which there is a contribution to the reduction of the free energy of the surface of the solid by the free energy of the reaction per unit area at a given time, as a function of time. The dynamic driving force for wetting can then be expressed as $\gamma_{SV} - (\gamma_{S1}' + dG_R)$ at a given instant of time. As a result the contact angle decreases and if the driving force exceeds γ_{1V}' , spreading will occur. (The primes refer to the fact that the composition of the glass changes as the reaction proceeds.) When the reaction is completed, a steady state exists. However, in a reaction in which the solid is a passive participant (i.e. its composition does not

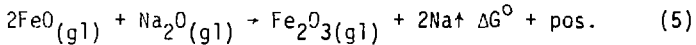
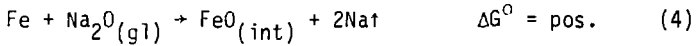
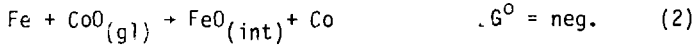
change but that of the liquid changes) the dG_R does not contribute to the driving force for wetting of the solid regardless of its magnitude and spreading does not occur².

III. REACTIONS AND BONDING

Chemical bonding is represented by the presence of a continuous electronic structure across the interface³. It is achieved by having stable chemical equilibrium across the interfacial zone. No difficulties exist in realizing this equilibrium continuity across metal/metal or ceramic/glass interfaces because of similarities in electronic structure in each couple. There are problems, however, with metal/glass or more generally metal/non-metallic interfaces. When dealing with oxide ceramics electronic continuity across a metal/glass interface can be realized if equilibrium relative to the low valent oxide of the metal exists at the interface. In addition the interface must be saturated with the metal oxide; the thermodynamic activity of the oxide in the metal and the glass then is one. Atomistically, this condition results in the presence of a monomolecular layer of the metal oxide at the interface, which is compatible and bonds with both phases.

A redox reaction is thus involved in making seals in which the metal atoms at the interface form an oxide by reduction of oxygen gas (atmospheric oxidation) or of cations in the glass. For illustrative purposes, sodium disilicate glass alone and with CoO , FeO or Fe_2O_3 in solution; and an iron substrate will be used in the examples^{2,4-6}.

Five types of redox reactions have been identified. Four lead to the formation of substrate metal oxide on the metal at the interface directly:



The most common technological procedure is to preoxidize the metal according to eq. 1; the oxide is subsequently dissolved by the applied glass - ideally, just leaving one molecular layer which consummates the chemical bond as described. Other reactions that occur spontaneously because ΔG° is negative are represented by Eqs. 2 and 3. In Eq. 2 Co^{2+} in the glass that makes electronic contact with the Fe is reduced and Fe^{2+} forms at the interface because Fe has a higher oxidation potential than Co; the reduced Co forms metallic precipitates in the glass or at the interface. Equation 3 occurs if Fe^{3+} is present in the liquid glass because Fe^{3+} has a lower oxidation potential than Fe^{2+} .

If no spontaneously reducible cations relative to the substrate metal are present in the glass, a redox reaction of the type represented by Eq. 4 would have to take place. The conditions, other than standard, under which ΔG for this reaction becomes negative are indicated by its equilibrium constant or activity quotient as deduced from the following free energy equation for Eq. 4:

$$\Delta G = \Delta G^\circ + RT \ln \frac{a(\text{FeO})_{\text{int}} \cdot (p\text{Na})^2}{a(\text{Na}_2\text{O})_{\text{gl}}} \quad (6)$$

The ratio in the latter term has to be sufficiently smaller than one for the term to overcome the positive ΔG° , i.e. basically $a(\text{FeO})_{\text{int}}$ and the p_{Na} have to be less than one and $a(\text{Na}_2\text{O})$ has to be larger than the numerator. The pressure of the Na vapor that is formed has to exceed the ambient pressure to form bubbles of Na vapor at the interface and escape; therefore this reaction is potentially more favorable in vacuum. The $a(\text{Na}_2\text{O})$ in the glass is dependent on the glass composition, i.e. the availability of Na_2O for reaction. The $a(\text{FeO})$ at the surface or interface is dependent on the p_{O_2} in the ambient atmosphere and the amount of dissolved FeO in the starting Fe. ΔG for Eq. 1 is zero at 1000°C when p_{O_2} is 1.2×10^{-15} atm. At pressures above this value the surface remains saturated with FeO and the $a(\text{FeO})_{\text{int}}$ is one, and at pressures below this value the oxide does not form and any oxide present dissociates with a decrease of $a(\text{FeO})_{\text{int}}$ below one.

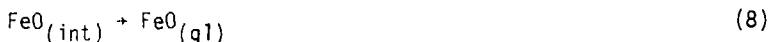
Another important redox reaction that occurs is represented by Eq. 5, indicating a reduction of Na^+ and oxidation of Fe^{2+} to Fe^{3+} in the glass. The standard free energy, ΔG° , is positive; therefore the reaction occurrence under other conditions is dependent on a favorable equilibrium constant as indicated in Eq. 7.

$$\Delta G = \Delta G^\circ + RT \ln \frac{a(\text{Fe}_2\text{O}_3)_{\text{gl}} \cdot (p_{\text{Na}})^2}{a(\text{FeO})_{\text{gl}}^2 \cdot a(\text{Na}_2\text{O})_{\text{gl}}} \quad (7)$$

The requirements for this reaction are a low p_{Na} , a high $a(\text{Na}_2\text{O})_{\text{gl}}$, and a small ratio of $a(\text{Fe}_2\text{O}_3)_{\text{gl}}/a(\text{FeO})_{\text{gl}}$. This reaction is important and interesting because it does not require a low p_{O_2} in the atmosphere to

achieve a low $a(\text{FeO})_{\text{int}}$ as in Eq. 4 and can proceed if a sink for Na, such as a dynamic vacuum or favorable side reaction, is available. This reaction is readily followed by the one represented by Eq. 3 which introduces FeO into the interface by reaction of $\text{Fe}_2\text{O}_3(\text{gl})$ with the substrate.

The first four reactions in each case represent the first step of the overall reaction. The formed $\text{FeO}_{(\text{int})}$ is spontaneously dissolved by the glass (Eq. 8), if it is not saturated with FeO, because of a negative ΔG° .



The net reaction involving Na evolution in both cases is the same and can be represented by

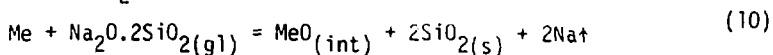


In case 1 the step reactions are Eq. 4 + Eq. 8, and in case 2 the step reactions are Eq. 5 + Eq. 3 + Eq. 8. It is thus necessary to consider the step reactions in order to fully understand the nature of the reactions and to correctly interpret their kinetics.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Analysis of the conditions for the occurrence of different types of reactions at interfaces provides a basis for comparison of metals. Sessile drop experiments were made of $\text{Na}_2\text{Si}_2\text{O}_5$ glass on a number of metals at 1000°C and an ambient pressure of 2×10^{-9} atm in two furnaces: "alumina furnace" with a $p\text{O}_2$ of $\sim 10^{-10}$ atm and a "graphite furnace" with a $p\text{O}_2$ of $\sim 10^{-20}$ atm. The metals are listed in Table 1 in increasing order of stability of their oxides, indicated by decreasing values of the $p\text{O}_2$, the dissociation pressure. As an example, let us consider the initial redox reaction, to be represented by Eqs. 4 or 5, which consists of reduction of

Na₂O in the glass by FeO. Because of the kind of available thermo-dynamic data⁷, the reaction with a metal (Me) can be assumed to be carried on hypothetically to the point indicated by Eq. 10 for purposes of calculation. ΔG⁰ for this reaction for each of the listed metals is included in Table 1. Using these values in Eq. 11, setting ΔG = 0, and assuming the oxide activities equal to 1, the values for pNa were calculated. These are seen (Table 1) to increase as the values for the equilibrium pO₂ for the oxides decrease.



$$\Delta G = \Delta G^0 + RT \ln \frac{a(\text{MeO})_{\text{int}} \cdot (\text{pNa})^2}{a(\text{Na}_2\text{O})_{\text{gl}}} \quad (11)$$

On the basis of this data, an Eq. 10 type of reaction can occur in both furnaces with all of the listed metals, except Au and Pt, since their calculated pNa is greater than the ambient pressure in the furnaces. This reaction can be monitored by measuring the weight change of the sessile drop assembly due to loss of Na; the percent of the total Na in the glass lost after 2 hrs at 1000°C in both furnaces is listed in Table 1. In addition, as indicated in Eqs. 6 and 11, a low value for a(MeO)_{int} should make the reactions of Eqs. 4 and 10 more favorable. Therefore, the metals whose oxides have equilibrium pO₂ values in between the pO₂ values in the two furnaces should have an increased reactivity in the "graphite furnace" due to the reduction of MeO and thus a decrease of a(MeO)_{int} below 1. An examination of Table 1 supports this prediction and also indicates an increase of reactivity with increase of stability of the metal oxides for equivalent experimental conditions

(i.e. $\text{Ni} < \text{Co} < \text{Fe}$); an increase of the driving force for wetting (i.e. a decrease of contact angle) also occurs with increase of reactivity. In the case of Fe in the "graphite furnace," the force exceeded γ_{1V} and spreading occurred (0 in this table represents spreading). Mo and W, although within this group, did not follow this expected pattern since they are involved with additional reactions. The appearance of a white reaction product at the interface at room temperature is due to the formation of Na_2MoO_4 and Na_2WO_4 which at the test temperature of 1000°C were molten since they melt at $\sim 690^\circ\text{C}$; spreading of the drop results because the metal is an active participant in these reactions.

The third group of metals in the table have oxides with values for the equilibrium $p\text{O}_2$ that are less than the $p\text{O}_2$ in both furnaces; their $a(\text{MeO})_{\text{int}}$ should thus be 1 and the reactions should be similar in both furnaces. It is seen that this expectation was not fulfilled and that the reactions in the "graphite furnace" were more intense on the basis of assuming that all of the weight loss was due to loss of Na from the glass. The lower $p\text{O}_2$ must therefore initiate some other reaction(s) also associated with a weight loss; Cr is a significant example since the total weight loss is greater than the total amount of Na in the starting glass. Similar calculations can also be performed assuming that reactions of the type represented by Eq. 5 were occurring when applicable. The nature of the specific step reactions and their interplay, however, have not been determined.

V. CONCLUSIONS

In conclusion, it should be emphasized that in sessile drop experiments no spreading occurs and true contact angles are observed only in

the absence of chemical reactions at the interface, i.e. with the existence of stable or metastable bulk thermodynamic equilibrium. The presence of a chemical reaction in which the substrate is an active participant results in a contribution to the driving force for wetting. If this contribution is large enough so that the driving force exceeds γ_{lv} , spreading will occur. The corollary is that the presence of spreading is a positive indication of a reaction at the interface initiated by the solid. It may be so limited to the interface, however, that the reaction may not even be easily perceptible. In such cases, considerable ingenuity may have to be employed to recognize and identify the reaction. Furthermore, additional complications may be introduced because the reactions may be sufficiently two-dimensional so that chemistry and thermodynamics knowledge and understanding based on three-dimensional phases may not be completely applicable. Reactions that introduce an additional rigid phase at the interface at temperature introduce additional complications. Nevertheless, a development of an understanding of all reactions that may occur is necessary. Experiments, such as those described here, thus are in progress for purposes of achieving this understanding.

ACKNOWLEDGMENTS

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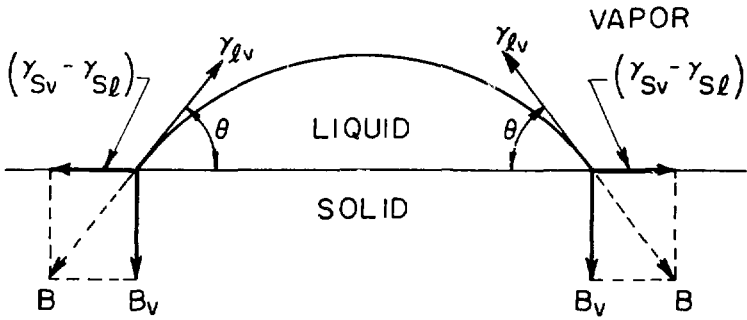
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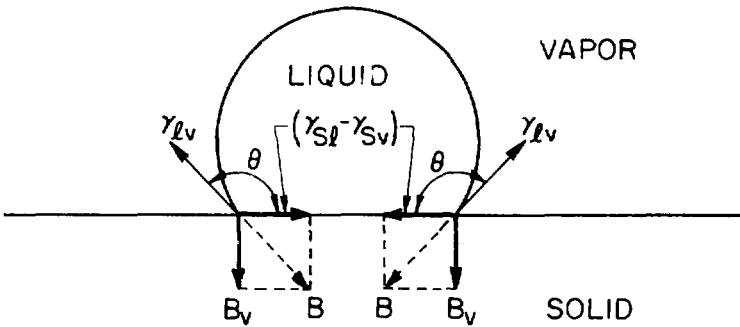
| METAL | GRAPHITE FURNACE $P_{O_2} = 10^{-20}$ atm. | | ALUMINA FURNACE $P_{O_2} = 10^{-10}$ atm. | | $\Delta G^\circ_{1,000^\circ C}$ For Reaction 1 cal/mol O_2 | EQUILIBRIUM P_{O_2} BULK Me/MeO (atm.) | %G 1000°C For Reaction 10 cal/mol O_2 | EQUILIBRIUM P_{Na} For Reaction 10 (atm.) |
|-------|---|---|--|---|---|--|---|---|
| | CONTACT ANGLE | WEIGHT LOSS OF Na/TOTAL Na mass % | CONTACT ANGLE | WEIGHT LOSS OF Na/TOTAL Na mass % | | | | |
| Au | 56 | 0.0 | 60 | 0.0 | 41,266 | $10^{7.08}$ | 400,795 | 3.4×10^{-12} |
| Pt | 15 | 0.0 | 16 | 0.0 | 6,700 | $10^{2.30}$ | 119,665 | 5.3×10^{-11} |
| Ni | 29 | 10.5 | 40 | 4.0 | -60,156 | 4.7×10^{-11} | 82,877 | 7.7×10^{-8} |
| Co | 13 | 42.0 | 20 | 15.7 | -75,722 | 1.5×10^{-12} | 75,079 | 3.6×10^{-7} |
| Fe | 0 | 95.4 | 10 | 57.3 | -86,850 | 1.2×10^{-15} | 69,526 | 1.0×10^{-6} |
| Mo | 0 | 40.8 | 0 | 17.2 | -86,375 | 1.5×10^{-15} | 139,555 | 1.0×10^{-6} |
| W | 0 | 70.1 | 0 | 39.7 | -92,290 | 1.4×10^{-16} | 132,940 | 1.9×10^{-6} |
| Cr | 13 | > 100.0 | 38 | 39.7 | -139,601 | 1.1×10^{-24} | 129,493 | 1.9×10^{-4} |
| Ta | 57 | 22.6 | 45 | 12.7 | -143,368 | 2.4×10^{-25} | 206,383 | 2.8×10^{-4} |
| Ti | 45 | 31.8 | 55 | 17.1 | -190,000 | 2.0×10^{-33} | 17,780 | 0.0297 |
| Zr | 55 | 28.9 | 72 | 4.7 | -201,794 | 2.2×10^{-35} | 24,136 | 0.0920 |

Table 1. Reactivity of sodium silicate glass with a number of metals.

(a)



(b)



XBL738-1699

Fig. 1. Equilibrium forces on the periphery of a sessile drop along a vertical plane through the center of the drop for an (a) acute angle and (b) obtuse contact angle.