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WETTING BEHAVIOR IN THE IRON-SILVER SYSTEM

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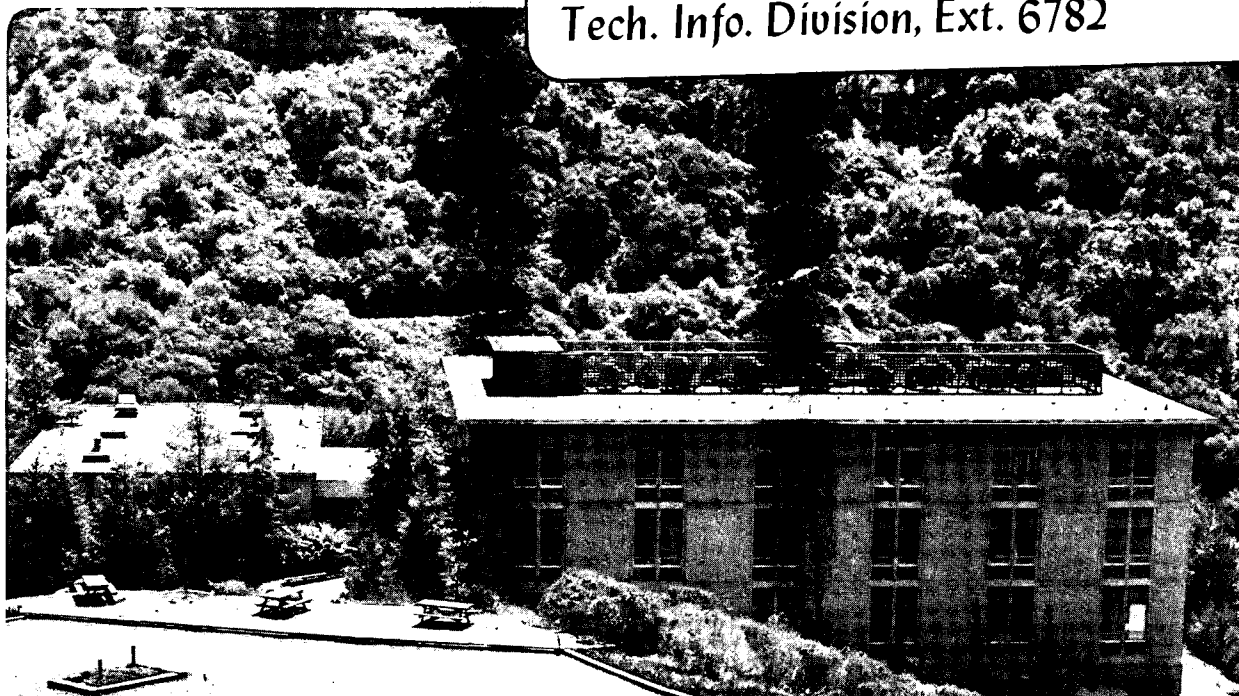
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## WETTING BEHAVIOR IN THE IRON-SILVER SYSTEM

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and Department of Materials Science and Mineral Engineering  
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### ABSTRACT

Sessile drop experiments of molten Ag on Fe at 1000°C and partial pressures of oxygen of  $10^{-5}$  and  $10^{-15}$  Pa show acute contact angles that vary with oxygen content of the Fe and experimental conditions. Surface energies of Fe, and correspondingly contact angles, are sensitive to the degree of saturation of the Fe with oxide and to the degree of adsorptivity of oxygen which is dependent on the activity of oxide in Fe and the  $p(O_2)$  in the ambient atmosphere. Obtuse angles form when surface energy of solid is sufficiently decreased by formation of oxide layer on the Fe surface. Adherence of chemical bonding type occurs when thermodynamic stable phase equilibrium is attained and maintained at the interface, represented by saturation of each phase by the other, which is the case for the Fe-Ag system in the absence of a discrete oxide phase.

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\* Visiting Scholar from Department of Materials Science and Engineering, Chekiang University, Hangchow, People's Republic of China.

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### I. INTRODUCTION

The conditions that determine wetting and spreading of a liquid on a solid are not only of basic scientific interest but are also of importance in understanding the development of a metal/metal bond during welding, soldering and brazing; glass/metal bonds in protective coatings on metals and seals for electronic applications; and liquid-phase sintering, melting of metals in metal containers, etc. Many investigators have studied the principles which govern wetting and spreading in metal-metal systems at temperatures at which one is a liquid. Sessile drop experiments provide a method for studying these phenomena; they also provide information on relative values of surface and interfacial tensions/energies during kinetic changes and at equilibrium.

In a sessile drop experiment wetting corresponds to the reduction of the surface energy of the solid by the liquid ( $\gamma_{sl} < \gamma_{sv}$ ) with the formation of a steady state acute contact angle; spreading corresponds to the continuing extension of the liquid drop periphery

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with availability of liquid, the contact angle being nominally zero. [1] On this basis, a slow and measurable approach to an equilibrium contact angle because of kinetic factors would not be considered to be spreading, and spreading in itself should not be defined as good wetting which would correspond to a steady state small contact angle. Unfortunately, in many cases the words "wetting" and "spreading" have been used interchangeably without reporting values of contact angles. This situation exists in the case of the iron (Fe)-silver (Ag) system at temperatures above the melting point of Ag (962°C).

Bailey and Watkins in 1951 [2] have concluded that the prerequisites for good wetting are some mutual solubility and/or the formation of intermetallic compounds. Thus, the observed "dewetting" (appearance of droplets of liquid) in the system Fe-Ag was explained as being due to lack of compound formation and solid solution. In 1952 Bondi reported [3] a much earlier experiment performed by Tamman in 1935, which was described as very slow spreading at 1000°C under hydrogen. More than 30 years later, Adams [4] also reported that silver spreads on iron and claimed that solubility is not a necessary criterion for spreading. Eremenko and Lesnik [5] during studies of infiltration of molten Ag into porous Fe, measured the contact angle between Armco Fe and Ag in hydrogen atmosphere. They found that at the melting point of Ag the equilibrium value of the angle was 23°; it decreased to 10° at 1100°C. In 1967, Klein-Wassink wrote that it is well known that iron is readily wetted by copper but badly wetted by silver [6]. His theoretical calculations based on Young's equation

indicated that  $\gamma_{sl}$  for the Fe-Ag interface is probably about 1200 ergs/cm<sup>2</sup> which is sufficiently large to restrict wetting. Westwood and Lye [7] in describing the Klein-Wassink results, wrote that this behavior supports Bailey and Watkins' criteria for wetting, in that Cu and Fe are mutually soluble (to the extent of 5 a/o) whereas Ag and Fe are practically insoluble in each other.

The present study was undertaken to systematically examine the wettability of molten Ag on Fe from several sources under different experimental conditions. As seen from the literature survey a great deal of confusion exists in regard to terminology and the reported wetting behavior of Ag on Fe.

## II. EXPERIMENTAL INFORMATION

### A. Materials

Silver shot of 99.99% purity was obtained from Apache Chemical Company (C-12 ppm/wt, O&N-10). A second type of Ag in the form of small droplets of 99.9999% purity was received from Cominco American Inc. (C- 3 ppm/wt, O&N-5).

Marz iron foil of 99.995% purity was obtained from Materials Research Corporation. The major impurities were carbon (8 ppm) and oxygen (60 ppm). A second iron specimen, Armco, was received in the form of sheet of 1 mm thickness with a typical analysis of 0.015% C, 0.025% Mn, 0.005% P, 0.025% S, 0.002% Si and an unspecified amount of oxygen. Metallographic analysis revealed presence of FeO. Oxygen content, as measured in our laboratory by SIMS, showed 0.12 wt.% of oxygen ( $\pm 0.02\%$ ). A third iron, APT, was prepared by vacuum sintering and then melting of Fe powder of 99.999+% purity obtained from SPEX Industries. This specimen was cold-rolled in a tungsten envelope and then homogenized at 1000°C at  $\sim 1.3 \times 10^{-4}$  Pa vacuum. Finally, the Fe sheet was hydrogen annealed for 60 minutes at 1100°C. This prepared Fe was analyzed and showed O -  $5 \pm 4$  ppm, C - 7, N - 8, Co - 2, S - 3, Al - 4, all other impurities  $< 0.1$  ppm each. The oxygen content was measured immediately after hydrogen annealing. Thus, the order of relatively increasing O content in the Fe specimens was APT, Marz and Armco.



## B. Experimental Equipment

Sessile drop experiments were performed in two furnaces providing two different oxygen partial pressures which were described previously. [8] The first one, which will be identified as the "alumina" furnace, is based on a one-inch diameter, eight-inch long kanthal-wound alumina tube. The second one, which will be identified as the "graphite" furnace, is based on a graphite tube resistance heating element. In such cases the cores were inside a large chamber that had a vacuum capability of  $1.3 \times 10^{-4}$  Pa. The temperatures were determined with calibrated Pt - Pt 10% Rh thermocouples with an accuracy of  $\pm 2^\circ\text{C}$ . The contact angles were measured through a port-hole in the vacuum chamber by a telegoniometer. Leak valves on the vacuum chamber allowed gettered helium to be introduced into a furnace. Helium was 99.998% pure with the average composition (in ppm)  $\text{H}_2\text{O} - 0.3$ ,  $\text{N}_2 - 1.0$ ,  $\text{O}_2 - 0.2$ ,  $\text{CO}_2 - 0.05$ ,  $\text{Ar} - 0.05$ ,  $\text{Ne} - 8.8$ . The oxygen partial pressure, as measured at  $1000^\circ\text{C}$  by a solid state oxygen probe, was  $2.5 \times 10^{-5}$  Pa in the alumina surface and  $5.3 \times 10^{-14}$  Pa in the graphite furnace.

## C. Experimental Runs

For each experiment an Fe substrate with a Ag drop was placed on an alumina D-tube and introduced into the center of the furnace. Before heating to the experimental temperature, the vacuum chamber was pumped to less than  $1 \times 10^3$  Pa, flushed with helium, and pumped with a cold-trapped diffusion pump to  $\sim 1.3 \times 10^{-4}$  Pa. The furnace was then

heated to 400°C in ten minutes, and the chamber was filled with helium slightly below atmospheric pressure. The temperature was then increased to 1000°C in either 20 minutes (slow heating) or 10 minutes (fast heating). After holding the temperature for a specified time, usually 30 minutes, the samples were furnace-cooled. In some specific experiments the helium backfilling temperature was varied.

Surfaces of Fe and Ag were examined by Auger Electron Spectroscopy and SIMS. Selected sessile drop specimens were cut with a diamond saw perpendicular to the interface. A sectioned half was mounted in Bakelite and polished. The interfaces were examined with SEM, and Auger x-ray line scans were made with a Kevex unit on the SEM. Several samples were prepared for Auger depth profiles by thinning either the Ag or Fe part of the assembly parallel to the interface down to ~ 2-3  $\mu\text{m}$  from the interface.

### III. RESULTS

The contact angles in sessile drop experiments of molten Ag drops on Fe substrates at 1000°C in a He atmosphere were sensitive to the history of the specimens in terms of their preparation and of their exposure to environmental conditions both before and during the experiments. Both Fe and Ag showed this sensitivity, although variations in the Fe resulted in greater variability of results. Perhaps of greatest significance is the fact that the sessile drop test provided information on changes in surface adsorptivity, and correspondingly surface energies, under conditions that are currently unworkable with LEED and other more sophisticated approaches to surface studies. Of particular interest is the generation of information in regard to changes in interfacial energies.

#### A. Ag on Armco Fe

In all cases under normal procedures of slow heating the initial contact angle on melting of the Ag drop was larger than at equilibrium which was reached within ~ 3 and maintained for 30 minutes. In the graphite furnace, the range of the initial angle for 13 experiments was 80 to 55° and the equilibrium or steady state angle 67 to 48° with averages of 62 and 57°, respectively. In the alumina furnace, the range of the initial angle for 4 experiments was 62 to 54° and the equilibrium angle 58 to 48° with corresponding averages of 57 and 53°. The periphery of the drop after cooling was always regular and circular.

Oxygen content of the starting Ag was of concern. Several specimens of Ag received at different times with different reported purities, however, showed no significant trends in the values of the equilibrium angles. Ag remelted in oxygen at 1000°C for 24 hrs showed equilibrium angles that were only ~ 8° smaller in both furnaces. Light preoxidation of Armco Fe (30 minutes at 250°C) and fast and slow heating rates to 1000°C also showed no significant changes in contact angle.

B. Ag on Marz Fe

Under normal procedures of slow heating in the graphite furnace, the range of the initial contact angle for 20 experiments was 110 to 47° and the equilibrium angle, generally reached within ~ 5 minutes and maintained for 30, ranged from 76 to 17° with averages of 73 and 45°, respectively. The initial larger angles and the time for their reduction to the smaller equilibrium acute angle, which experimentally showed a range of 5 to 20 minutes, were dependent on the heating rate to 1000°C and the temperature at which He was introduced. Slower heating rates and one or more backfillings with He at temperatures > 400°C resulted in smaller and shorter-lasting initial angles. When He was introduced at 100°C, an initial angle took 20 minutes to reach equilibrium; when He was backfilled at 650°C, the larger initial angle lasted for only 30 seconds and at lower heating rates the final equilibrium angle was obtained immediately on reaching temperature.

Examination of a specimen that still retained an obtuse angle showed a black halo around a regularly-shaped drop. The halo had a width of 2-3 mm, a thickness of  $\sim 1 \mu\text{m}$ , and lightened in color rapidly away from the Ag periphery. Specimens heated further to form the acute angle indicated that the Ag had broken through the halo ring and was avoiding the discolored areas resulting in an irregularly shaped drop. Auger depth analysis identified the halo to be an iron oxide.

In the alumina furnace under normal procedures, the range of the initial contact angle for 5 experiments was 68 to 56° and the equilibrium angle, reached within a minute also ranged from 68 to 56° with averages of 62° for both initial and final values. An obtuse angle was formed only when He was introduced at 100°C and the heating rate was fast; the Fe surface was then covered with an oxide layer  $\sim 0.5 \mu\text{m}$  thick. The Fe surface remained bright when He was introduced at  $> 150^\circ\text{C}$ .

On using modified Ag specimens on Marz Fe in the graphite furnace significant differences were observed. Ag remelted on alumina in the graphite furnace showed an acute contact angle of 32° immediately whereas as-received Ag showed an initial obtuse angle of 110° which decreased to 48° in 20 minutes. Correspondingly steady state or final angles on Marz Fe specimens which were annealed in the graphite furnace at 1150°C for 16 hours to remove oxygen were 17 and 45°, respectively. Ag aged at room temperature for 1 year behaved similarly to as-received Ag. Ag remelted in oxygen for 16 hours at 1000°C showed an acute angle of

86° on slow heating which changed to its equilibrium angle of 44° in 2 minutes. Marz Fe that had been aged for 1 year behaved similarly to Armco Fe, i.e. always showing an initial acute angle with all Ag specimens which did not change significantly with time.

C. Ag on APT Fe

General similarity but definite variability in results with two additional lots of Marz Fe prompted the preparation of specimens in our laboratory which are being referred to as APT Fe.

Under normal procedures with both slow and fast heating in the graphite furnace and using a number of Ag specimens, the range of the initial contact angle for 18 experiments was 112 to 40° and the equilibrium angle reached within ~5 minutes and maintained for 30, ranged from 50 to 26° with averages of 76 and 36°, respectively. The obtuse contact angle was most often obtained with aged Ag when He was introduced at < 400°C. Furthermore, an obtuse angle was always associated with the formation of a black halo around the silver drop, but it always disappeared after some minutes with the formation of an acute angle. The high reactivity of a vacuum -melted and H<sub>2</sub>-annealed APT Fe specimen relative to the atmosphere was illustrated by measuring an equilibrium contact angle of 6-9's Ag on nonaged Fe of 45°, 41° after 1 week of aging, 37° after 2 weeks, and 28° after 3 weeks of aging of the iron.

In the alumina furnace under normal procedures, the range of the initial contact angle for 8 experiments was 98 to 82° and the equilibrium angle, reached within a minute, ranged from 96 to 78° with averages of 91 and 89°, respectively. Iron surface in all cases had an adsorbed film as determined by Auger analysis. A photograph of a drop with an obtuse angle is shown in Fig. 1. Significant features of the specimen as observed in the photo are the presence of islands of a thin black iron oxide film on the surface of the drop, a whitish appearing zone around the periphery of the drop which is actually the black halo observed visually, and small Ag droplets around the Ag sessile drop evolved with the sudden emission of gases from the Ag on melting.

With acute contact angles the adherence was always excellent for all three types of iron specimens. With obtuse angles adherence was good in the center of the drop, but the interfacial zone close to the periphery of the drop separated easily when the Fe plate was bent. The bottom surface of the Ag drop of such a specimen is shown in Fig. 2. The visible periphery zone was always covered with a thin black film which was identified as iron oxide by Auger analysis; many bubbles are also visible at the interface.

#### D. Ag on Hematite

Several experiments were run with 6-9's Ag on hematite ( $\text{Fe}_2\text{O}_3$ ). In the graphite furnace the initial contact angle was an average of 121°, and the equilibrium angle was an average of 104° which was reached over a period of 10 to 60 minutes. In the alumina furnace an

equilibrium angle of  $\sim 112^\circ$  was reached immediately. Adherence was excellent in both bases with fracture occurring in the oxide. The obtuse angles indicate that the surface energy of the Ag is greater than that of the oxide. The decrease in contact angle in the graphite furnace was due to the presence of the lower  $P_{O_2}$  and indicates the development of an oxygen deficiency with a corresponding increase of the surface energy of the oxide.

In air the contact angle was  $75^\circ$  indicating a lower surface energy for Ag than that for the oxide. Udin [9] has shown that the surface energy of Ag drops significantly with increase of  $P_{O_2}$ . The Ag drop exhibited no adherence with separation at the interface; the Ag surface was roughened and the bottom of the drop was clean with no traces of Fe as determined by KEVEX analysis.



#### IV. DISCUSSION

Sessile drop experiments are significant since they provide information on relative values of surface and interfacial tensions under realistic changes in environments and materials. An acute contact angle indicates that for pristine materials  $\gamma_{SV} > \gamma_{Sl} > \gamma_{LV}$  and that the solid is wet by the liquid; it also indicates that the driving force for wetting is  $(\gamma_{SV} - \gamma_{Sl})$  and that the resisting force is the energy necessary to extend the liquid surface. The balance of the horizontal components of these forces at the periphery of the drop, represented by the Young equation, fixes the contact angle measured inside the drop [10];

$$\gamma_{SV} - \gamma_{Sl} = \gamma_{LV} \cos \theta$$

This equation is based on the formation of a true interface with a common plane, and no occurrence of a reaction at the interface, i.e. the existence of stable or metastable thermodynamic chemical equilibrium. It can be seen that if  $\gamma_{Sl}$  and  $\gamma_{LV}$  remain essentially constant, any adsorption or desorption on the solid substrate would decrease or increase  $\gamma_{SV}$  and correspondingly increase or decrease  $\theta$ . Furthermore, if decrease of  $\gamma_{SV}$  by continuing adsorption causes it to become less than  $\gamma_{Sl}$ ,  $\theta$  will increase continually through  $90^\circ$  up to an obtuse angle, and vice versa with desorption. Also, absence of a reaction means that no spreading of the liquid drop will occur [10].

Since the experiments were performed with molten Ag at 1000°C in ambient atmospheres with  $P_{O_2}$  below the stability range of Ag-oxides, it is expected that any changes that may occur in  $\gamma_{\ell v}$  for Ag under the various experimental conditions would be minor. Similarly, changes in  $\gamma_{s\ell}$  for a given type of Fe specimen after the formation of a true interface by removal of adsorbed oxides by the Ag also would be expected to be minor. EDAX line scans for Ag and Fe across an interface of a sessile drop after 1 hour at 1000°C are shown in Fig. 3; no oxygen was detected. The profiles indicate a slight solubility of Fe in Ag and essentially no solubility of Ag in Fe. However, because the 3 solid Fe specimens have decreasing amounts of oxygen (in the order of Armco, Marz and APT) and the dissociation  $P_{O_2}$  of FeO at 1000°C ( $\sim 10^{-10}$  Pa) is straddled in the 2 furnaces, values of  $\gamma_{sv}$  will be sensitive to the history of the Fe specimens and the experimental conditions. A summary of the average contact angles observed are as follows:

	<u>Graphite Furnace</u>		<u>Alumina Furnace</u>	
	<u>Initial</u>	<u>Equilibrium</u>	<u>Initial</u>	<u>Equilibrium</u>
Armco Fe	62	57	57	53
Marz Fe	73	45	62	62
APT Fe	76	36	91	89

The experimental conditions and results support the deduction that the degree of chemisorption of oxygen by an Fe specimen determines its surface energy which in turn determines the contact angle. In the

graphite furnace ( $P_{O_2} = \sim 10^{-15}$  Pa) since no adsorbed oxide will persist or form after desorption, the increase of the equilibrium or steady state angle indicating a decrease of  $\gamma_{sv}$  from APT Fe to Armco Fe must be due to an increasing  $a(FeO)$  in the bulk metal which means that  $\gamma_{sv}$  of the iron even in the absence of essentially no adsorption of oxygen from the ambient atmosphere is determined by the  $a(FeO)$  in the iron. The initial angle is dependent upon the amount of adsorbed oxygen (acquired in preparation, aging and early stages of the experiment) that the specimen retains by the time it reaches  $1000^\circ C$ . Subsequently, this oxygen is desorbed with time with an increase of  $\gamma_{sv}$  causing a decrease in contact angle as it approaches the final equilibrium value; this kinetic decrease of angle is not spreading since the interface does not undergo a reaction and a steady state angle is reached. Of interest is the fact that the initial angle for APT Fe is greater than for Armco Fe, which is saturated with oxide and whose  $a(FeO)$  is 1, suggesting that the initial chemisorption of oxygen is stronger for an Fe with a lower  $a(FeO)$  with a correspondingly greater decrease of  $\gamma_{sv}$ .

In the alumina furnace ( $P_{O_2} = \sim 10^{-5}$  Pa) the significant factors are that the initial contact angle shows the same trend as in the graphite furnace and that the equilibrium or final value shows an opposite trend. Furthermore, the initial and equilibrium angles for a given Fe specimen are essentially the same indicating that desorption in the alumina furnace does not take place because of the atmospheric  $P_{O_2}$  of

$\sim 10^{-5}$  Pa; the higher reactivity of APT Fe (lower  $a(\text{FeO})$ ) resulted in a more effective adsorption with a correspondingly lower  $\gamma_{\text{SV}}$ .

Another important comparison is the values of the contact angles in both furnaces. Armco Fe does not show a significant difference whereas APT Fe shows larger contact angles in the alumina furnace. These data support the above statements that the extent of adsorption of oxygen is dependent upon the  $a(\text{FeO})$  in the iron.

The appearance of an initial obtuse angle when as-received Ag on Fe is heated rapidly is an interesting phenomenon. The rapid evolution of entrapped oxygen with the melting of Ag, probably associated with the droplets of Ag, in the presence of He causes the formation of the oxide halo and Ag droplets observed in Fig. 1. Slow heating, on the other hand, permits dissipation of the evolved oxygen and a reduction of the halo. Premelting of Ag in vacuum removed the oxygen and eliminated the halo in subsequent sessile drop experiments. In this case, the  $\gamma_{\text{SV}}$  of the oxide halo is less than that of the liquid  $\gamma_{\text{LV}}$ , as a result  $\gamma_{\text{SV}} < \gamma_{\text{SL}} < \gamma_{\text{LV}}$  and an obtuse angle forms. The obtuse angle was verified by sessile drop experiments on iron oxide in both furnaces. As the oxide halo is desorbed in the graphite furnace,  $\gamma_{\text{SV}}$  increases relative to  $\gamma_{\text{SL}}$  causing the contact angle to become acute although  $\gamma_{\text{SL}}$  probably also increases as Ag displaces the iron oxide to form an Fe-Ag interface at stable equilibrium; the overall effect, however, is still an increase of  $(\gamma_{\text{SV}} - \gamma_{\text{SL}})$ , the driving force for wetting.

Adherence was always excellent when an acute angle was formed with the formation of a true Fe-Ag interface associated with the development of thermodynamic chemical equilibrium, and thus a chemical bond, at the interface [8]. Because of the very limited solubility of Ag in Fe the free energy of the solution reaction per unit area and unit time is negligible and thus makes a minimal contribution to the driving force for wetting before equilibrium compositions are achieved at the interface; if the reaction was extensive and had occurred rapidly, the free energy contribution would have been large enough to cause spreading. In the case of an obtuse angle a discrete oxide layer was still present at the interface resulting in a  $\gamma_{\ell V} > \gamma_{SV}$ . On distortion, the oxide layer adhered strongly to the Ag but failure occurred in the oxide layer close to the interface resulting in poor adherence for the system.

The contact angle of Ag on hematite ( $\text{Fe}_2\text{O}_3$ ) specimens in both furnaces was obtuse ( $\gamma_{\ell V} > \gamma_{SV}$ ) and adherence was excellent. In this case the adherence was postulated to be due to a compatibility of both phases with FeO, i.e. presence of an oxygen-deficient surface on  $\text{Fe}_2\text{O}_3$  because of the low  $p(\text{O}_2)$  in the furnaces and some solubility of FeO in Ag. In air, the contact angle was acute and adherence was very poor. The  $\gamma_{\ell V}$  of oxygen-saturated Ag has been reported to be considerably reduced over oxygen-free Ag [9] resulting in  $\gamma_{SV} > \gamma_{\ell V}$ . Poor adherence is attributed to lack of thermodynamic stable phase equilibrium at the interface due to lack of reaction between the  $\text{Fe}_2\text{O}_3$  surface and oxygen-saturated Ag. The metastable phase

equilibrium, however, is associated with a reduction of the surface energy of the solid by the liquid creating a driving force for wetting

$$(\gamma_{sv} - \gamma_{sl}).$$

## V. CONCLUSIONS

At 1000°C and at low partial pressures of oxygen the surface energy of Fe is greater than that of Ag ( $\gamma_{sv} > \gamma_{lv}$ ) resulting in wetting of the Fe. The acute contact angle is sensitive to any changes of  $\gamma_{sv}$  which are sensitive to the  $a(\text{FeO})$  in the Fe and to the degree of chemisorption of oxygen. Adsorptivity occurs more effectively and extensively, with a corresponding decrease of  $\gamma_{sv}$ , on irons unsaturated with oxide, i.e. with decrease of  $a(\text{FeO})$  in Fe. Other factors that affect adsorptivity of oxygen directly or indirectly, are the history of the specimens, nature of ambient atmospheres and heating rates. At some higher partial pressure of oxygen in the vicinity of the Fe, oxidation occurs forming an oxide layer whose  $\gamma_{sv}$  is less than  $\gamma_{lv}$  of Ag unsaturated with oxygen resulting in an obtuse contact angle. This overall complexity accounts for the apparently inconsistent variations in sessile drop experimental results in this study and those reported in literature. These variations, however, are subject to explanation and understanding if the various basic principles are fully understood and applied.

Adherence of the chemical bond type is developed when thermodynamic stable phase equilibrium is present at the interface. With the formation of an interface and in the absence of stable equilibrium a reaction can occur resulting in equilibrium compositions at the interface, e.g. in this case an interface of molten Ag saturated with Fe and Fe saturated with Ag. The specimens with acute contact angles

always fulfilled this requirement; those with obtuse angles, only when there was no oxide layer at the interface.



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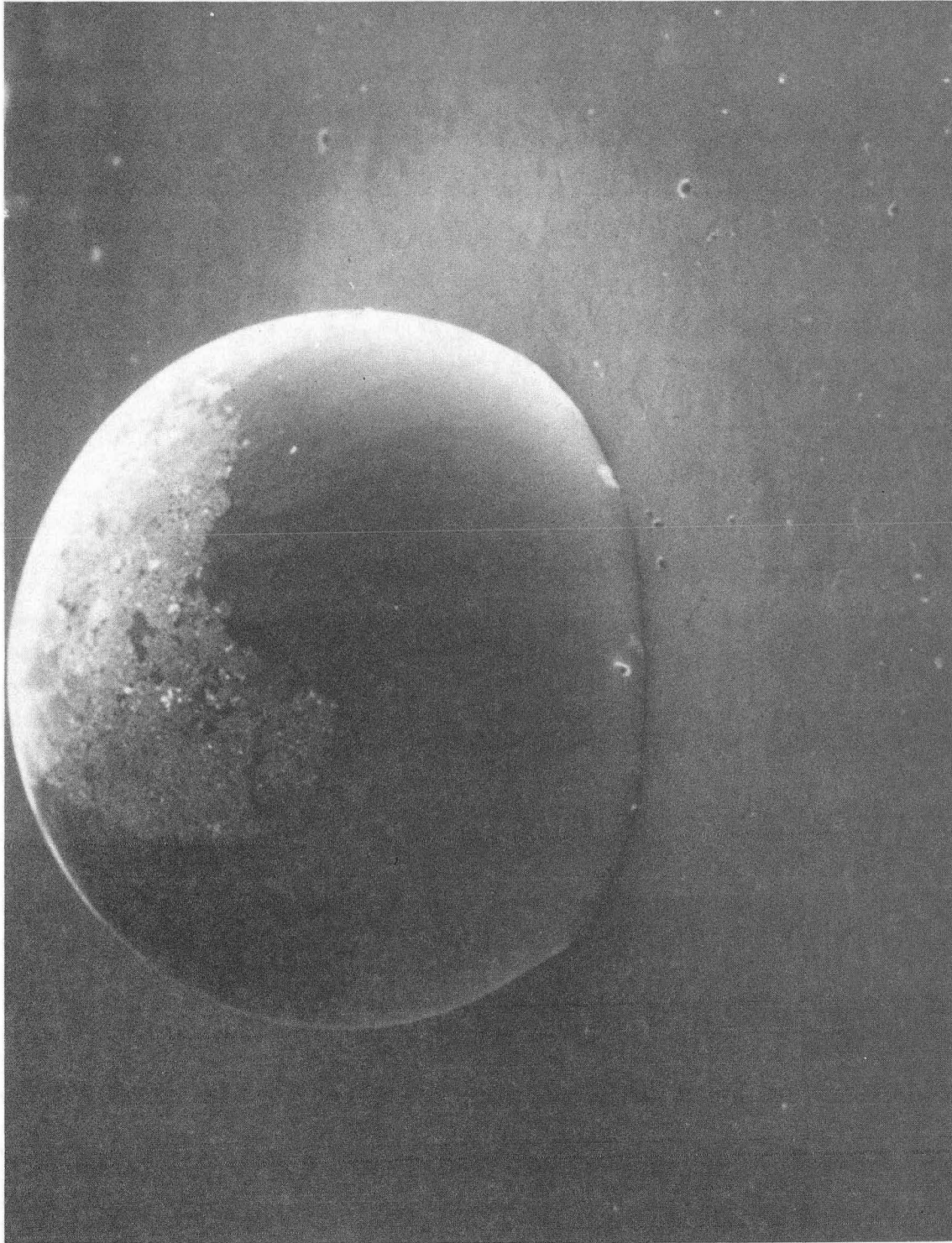
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### Figures

1. Sessile drop with obtuse angle obtained in alumina furnace showing Fe oxide film on surface of Ag and black halo (appearing as whitish area around periphery of drop) of Fe oxide. Also, small Ag droplets visible around the Ag drop.
2. Portion of bottom surface of detached Ag sessile drop of Fig. 1. showing black oxide layer next to periphery and gas voids.
3. Cross-section perpendicular to interface of sessile drop with acute contact angle (Fe on left) showing EDAX line scans for Ag and Fe.

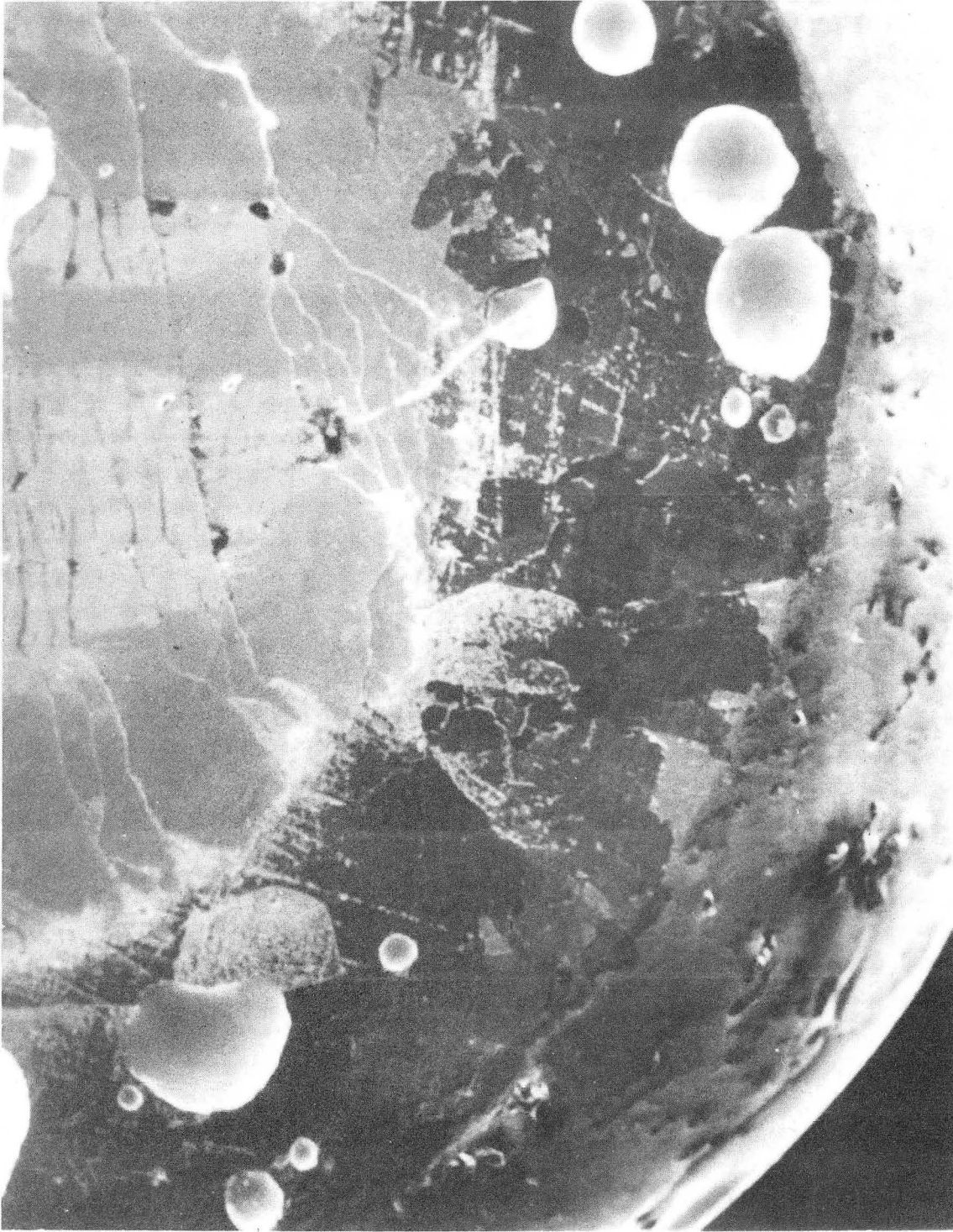
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Figure 1



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Figure 2

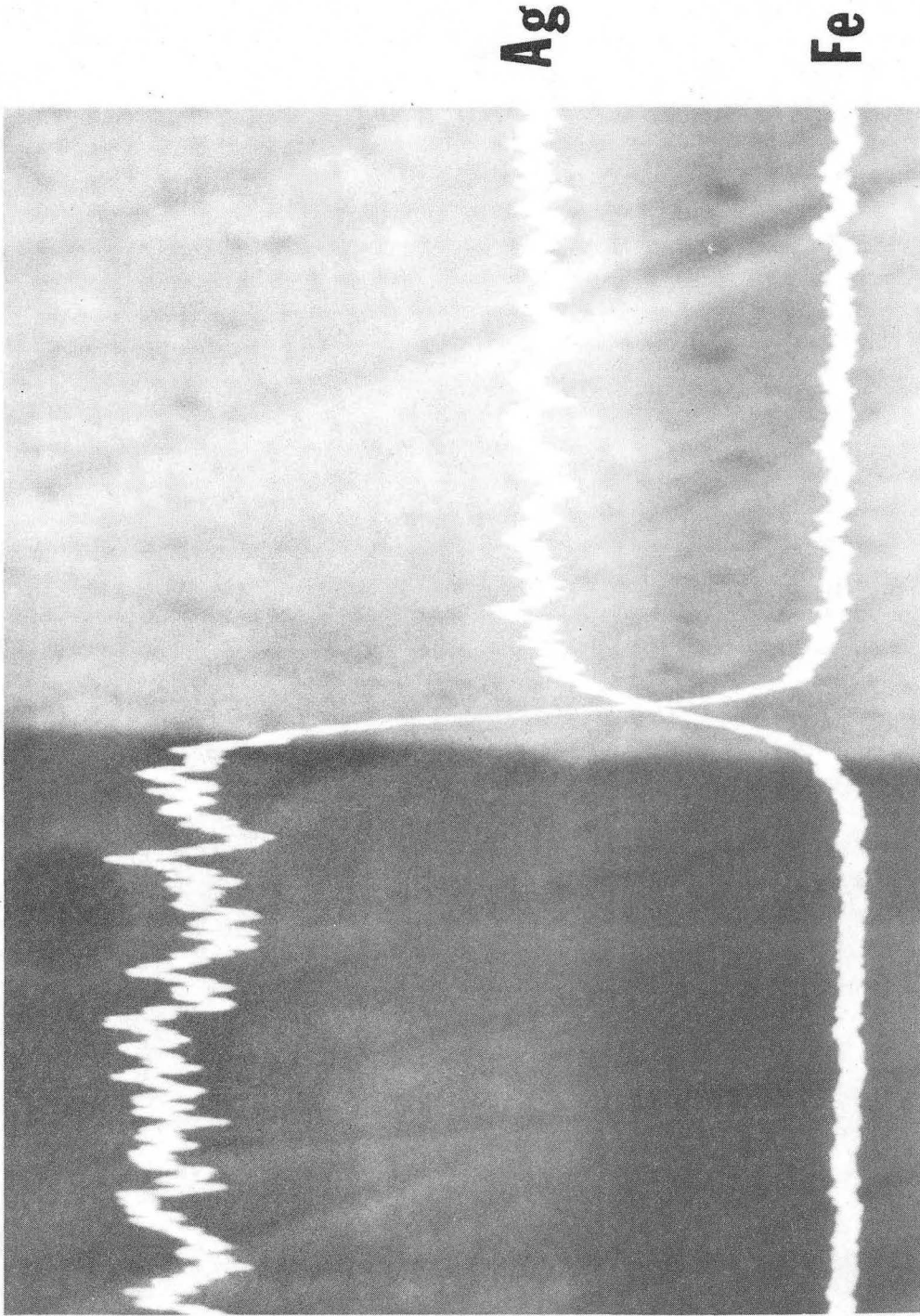


Figure 3  
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