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THE WETTABILITY OF LIQUID METAL ION SOURCES

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Abstract - Wetting of liquid metal alloys to solid substrates is governed by Young's equation, which relates the degree of wetting to the combined influence of solid-liquid, solid-vapor, and liquid-vapor surface tensions. It is important that a liquid metal alloy source exhibit good wetting with a near-zero contact angle. The wettability of several B-containing alloy systems is considered, with emphasis on the role of surface segregation on contact angle.

I - INTRODUCTION

In order to achieve a successful liquid metal ion source (LMIS) of high melting nonmetals, it is necessary that the LMIS be formed from an alloy that provides both an electrically conductive medium and a low melting eutectic. Once this is accomplished, a suitable substrate material must be selected that allows for good wetting and flow of the alloy to the needle apex (as in the case of the wetted needle type), but not excessive chemical interaction with the solid substrate so that dissolution by the alloy occurs. In this paper we provide evidence from studies of liquid alloy surfaces which shows that wetting of B-containing alloys to nonmetallic substrates is governed by surface segregation of low-level bulk impurities in the alloys. During melting, the impurities segregate to the surface of the alloy and inhibit reaction between alloy and substrate. A poorly wetted droplet with a high contact angle results. Employing surface coatings composed of materials reactive to the impurities acts to suppress segregation and promote wetting.

II - EXPERIMENTAL METHODS

Wetting studies were carried out in an ULTEK TNB-X 250 l/s ultra-high vacuum system containing a Physical Electronics CMA model 10-155 Auger electron spectrometer. The substrate and support mechanism were mounted in a vertical orientation inside the vacuum chamber, and a small fragment of solid alloy was placed in contact with the substrate. Contact was maintained by gravity and no adhesive was used. The system was subsequently evacuated to below 10⁻⁷ torr. Wetting was initiated by resistively heating the substrate with a D.C. power supply until alloy melting and wetting was observed. Temperatures were measured by means of a single wavelength optical pyrometer by comparison to the substrate brightness, whose emissivity characteristics were well-known /1/. Auger surface compositions reported are

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calculated on the basis of sensitivity factors given by Palmberg /2/.

III - WETTING OF NICKEL AND PLATINUM BORIDE ALLOYS

The strong reaction between refractory metals and liquid metal alloys results in severe limitations on the lifetime of high-melting LMIS employing metallic substrates. For example, although Re is well-wetted by B-containing alloys, the susceptibility of Re to attack by the liquid alloy results in lifetimes of the order of a few hours for LMIS using Re needle substrates. Because of this drawback, contact systems using nonmetallic substrates have been examined.

Carbon has been used successfully in many liquid metal environments. It is frequently employed as a crucible material and as an electrode in electric arc melting of metals. Polycrystalline graphite has been successfully used as a substrate for an Al LMIS /3/. Transition metal borides of Ni and Pt are excellent candidates for B source material due to their relatively low melting point (~1000 °C) over a fairly wide range of compositions around 50% atomic B. The expectation that borides of these metals are expected to wet carbon is based upon reported evidence /4/ that metallic Ni by itself wets graphite with a contact angle of 45 degrees. Further, B is often used as an additive to metals to promote wetting on graphite. Pure Cu, for example, has been reported to exhibit a contact angle of 140 degrees on graphite, but Cu with 5% added B has a contact angle of 36 degrees /5/. There is thus good reason to believe that eutectics of NiB and PtB should wet carbon. That experimental observations of wetting behavior prove otherwise will be explained below.

A. Wetting of Nickel and Platinum Boride Alloys to Carbon

Nickel boride alloy prepared by the arc melting technique was applied to a flat ribbon of graphite and heated to melting. Wetting proved to be unsuccessful. The

![Fig. 1 - Wetting of Ni₆₂B₃₈ alloy on graphite. (Top left) View of poorly-wetted droplet at room temperature. (Top right) Cross-sectional slice through droplet. (Bottom) Auger surface elemental composition of 4 positions on the molten droplet. High concentrations of C are evident.](image-url)
melted alloy formed a poorly-wetted droplet with a contact angle greater than 90 degrees. Auger analysis of the molten droplet surface at temperatures near the alloy melting point revealed large surface concentrations of C (and often N). A representative case is given in Figure 1. It was frequently possible to elicit wetting by increases in temperature. When this was done, a wetting front could be observed to expand from a side of the droplet which wet the substrate with a contact angle of near-zero. Auger analysis of this situation showed that the wetting front consisted of material composed solely of alloy components, while the droplet continued to exhibit large concentrations of C and N.

Wetting of platinum boride eutectics to carbon exhibited behavior similar to that described above for nickel boride alloys. At melting, the alloy formed a poorly-wetted droplet with a contact angle of near 180 degrees. In many cases, the affinity of the alloy for the substrate was so poor that the droplet rolled off the substrate into the vacuum chamber. Auger analysis of the molten surface near the melting point again revealed large concentrations of carbon and nitrogen.

Our conclusions from studies of numerous B-containing alloy systems and stoichiometries are:

1) Pure nickel boride and platinum boride alloys wet and spread over virgin polycrystalline graphite.

2) Nickel boride and platinum boride alloys containing high surface concentrations of carbon and/or nitrogen wet virgin polycrystalline graphite reluctantly or not at all.

B. Wetting of Nickel and Platinum Borides to Other Substrates

In order to isolate the source of the carbon and nitrogen found in the molten alloy surfaces, wetting of eutectic compositions of nickel and platinum borides to non-carbon substrates was studied. This procedure allowed elimination of thermal diffusion between substrate and alloy as the origin of these elements.

Wetting of nickel boride to aluminum oxide is shown in Figure 2. Wetting of NiB to Al2O3 was attempted due to evidence from Lugscheider /6/ indicating that some alloys of nickel and boron were found to wet aluminum oxide. The wetting was poor, consisting of a contact angle of about 130 degrees. More significantly, however, were the large concentrations of C and N at the surface of the poorly-wetted droplet. This material could only originate from the alloy itself, as the experiment was performed under conditions of ultra-high vacuum and the alloy is totally isolated from outside sources of these elements.

Fig. 2 - Auger surface elemental composition vs position for wetting of Ni55B45 on Al2O3. Surface segregation of C and N are evident. The temperature is Tm + 60° = 1355 K.
Similar behavior was found when wetting platinum boride alloy to noncarbon substrates. In particular, when platinum boride was wetted to Re, although the wetting was excellent, the surface was found to possess large concentrations of C and N.

IV - EVIDENCE FOR SURFACE SEGREGATION OF LOW-LEVEL IMPURITIES IN LIQUID METAL ALLOYS

The wettability of solids by liquid metal alloys appears to be governed by surface segregation of low-level impurities inherent to the alloys. Segregation of these impurities has been found in every alloy system we have studied, and allows an integration of a number of diverse results into a coherent picture of wetting behavior. Further, the existence of the surface segregation casts doubt on many previous studies of wetting, as the existence of ppm impurities in the wetting materials can radically affect the contact angle. The evidence for segregation is as follows:

1) Direct experimental observation of large relative concentrations of low-level impurities at molten alloy surfaces. In the case of wetting to nonmetallic substrates such as carbon, the segregated materials act to inhibit wetting. In cases of wetting to metals such as rhenium, wetting is able to occur despite the presence of the surface impurities.

2) Theoretical calculations of surface enrichment. In particular, emission spectroscopic analyses of the alloy materials showed typical levels of carbon impurity near 0.02 w%. Assuming the entire weight percent of C to segregate to the surface of a spherical droplet 0.5 mm in radius, the thickness L of the C layer formed may be calculated to be

$$L = 3.17 \times 10^{-6} \frac{D(NiB)}{D(C)} \text{ cm} = 1140 \text{ Å}$$

where $D(NiB)$ and $D(C)$ are the densities of nickel boride alloy and graphite respectively. We have assumed the density of graphite to be 2.0 gm/cm$^3$, and have calculated the density of NiB (7.2 gm/cm$^3$) from values given in the literature /7,8/.

Such analyses demonstrate that it is feasible for the high concentrations of C observed at the molten surfaces to originate from surface segregated material. Since the alloy fragments used in the wetting studies are fractured from the interior of the melt, the impurities are characteristic of bulk material.

3) Microscopic examinations of poorly-wetted droplets. Figure 1 above shows SEM photos of a nickel boride eutectic wetted above a graphite substrate. Auger analysis of the molten droplet surface showed large percentages of C and N, shown in the accompanying bar charts. The view at room temperature, shown in the left photo of the figure, shows that the droplet surface is covered with recrystallized precipitates of hexagonal material that scanning Auger analysis proved to be graphite. Similar examinations of cross-sectional slices through such droplets showed no evidence of second phase graphite in the interior of the droplet. The interior appears uniform and homogeneous, characteristic of pure alloy material.

4) The composition of alloy material flowing from the interior of poorly-wetted droplets. In several instances it has been possible to fracture poorly-wetted droplets of alloy by heat treatment. The efflux of material originating from the interior of the droplets was found to consist of pure alloy material that exhibited excellent wetting of the graphite substrate. That impurities are found on the surface of the droplet but not in the droplet interior is further evidence for surface segregation of low-level impurities in the alloys which occurs on melting.

V - THE EFFECT OF SURFACE COATINGS ON WETTING

Thermodynamic considerations are key to understanding the wettability of solids by liquid metal alloys. Wetting is governed by rapid surface segregation of low-level bulk impurities which arise during alloy manufacture. The segregated
material forms a reaction barrier which inhibits contact between alloy and substrate and results in poor contact angles. There are three possible solutions to this problem. The first is to eliminate the alloy impurities by employing ultra-pure starting materials and strict control of the arc melting process. The second is to skim away the alloy impurities after the impurities have segregated. The third is to introduce materials into the contact system which possess high chemical affinity to the major segregating impurities, either as a surface coating or by incorporation into the alloy during the arc melting process. The material acts to suppress segregation by tying up the alloy impurities during compound formation. Due to the favorable Gibbs free energies of formation of SiC and B4C, coatings of B and Si are expected to combine with C and promote wetting.

The effect of a B surface coating on the wetting of nickel boride alloy to a graphite substrate whose front surface was coated with 325 mesh red boron is shown in Figure 3. The boron layer was applied as a slurry with acetone with a paintbrush. The wetting is excellent, and flow is observed to occur beyond the boron underlayer and onto the nonboron coated backside of the ribbon. Auger analysis of the molten surface show radically depressed percentages of C relative to the case for wetting on a virgin graphite substrate. Further, the surface is enriched with boron, and has a much different stoichiometry than the bulk. This is due to surface segregation of B, which arises because (nonmetallic) B possesses a lower surface tension than (metallic) Ni.

Fig. 3 - Wetting of Ni55B45 alloy to boron-coated graphite. (Left) View of the front side wetting. (Right) Auger surface elemental composition of the substrate and alloy at its melting point.

Fig. 4 - Wetting of Pd72Bi28 to a silicon-coated graphite emitter structure after 100 hours of heating at 1200 K.

Surface coatings of Si affect wetting similarly. Figure 4 shows the wetting of a
palladium boride alloy to a carbon tip with an underlayer of silicon. The photos were taken after 100 hours of heating at a temperature of 30 degrees above the melting point. The wetting procedure consisted of coating a graphite emitter with a slurry of powdered Si and propanol, which was then heated to the melting point of Si. At melting, the Si wets and spreads superbly over the graphite. The interfacial compound which forms is SiC, which was verified by Auger spectroscopy after flashing away the free Si. The wetting layer therefore consists of an interfacial compound of SiC covered by a thick layer of free Si. At this point, the PdB alloy was added in powdered form with propanol, and then electron bombarded until the alloy melted.

VI - THE INFLUENCE OF SURFACE SEGREGATION ON WETTING

Surface segregation of low-level, low surface tension carbon and nitrogen impurity in the form of C, B,C, and BN is the primary cause for wetting failure in contact systems of graphite and B-containing binary alloys. We say that nitrogen in the form of BN segregates because it is unlikely that N exists in the alloys in elemental form. Further, BN has been directly identified in the alloy surfaces by evaluation of Auger chemical shifts. At melting, carbon and nitrogen present as alloy impurities segregate to the surface. The resulting layer of carbon, boron nitride, and boron carbide inhibits interaction between the alloy components and the substrate and results in an unfavorable combination of surface tensions. Boron nitride and boron carbide possess favorable Gibbs free energies of formation and may be expected to form during the arc melting process and at temperatures near the melting points of the eutectic compositions of the boron alloys we have studied.

Boron and silicon surface coatings facilitate wetting by tying up the carbon that would ordinarily segregate by formation of interfacial boron carbide and silicon carbide. In effect, the surface coating acts as a getter for segregated material. The resultant chemical reaction is precisely what is necessary for wetting. The coatings work because of what the alloy sees at the melting point. A C-C nonreaction is replaced by a C-B or C-Si reaction. When the alloy is purified in this way, the alloy may then wet virgin material because there is no more segregated material blocking the interaction of alloy and substrate. This explains why liquid alloy material initially needs a surface coating, but then can wet and spread over virgin graphite.

The fullest impact of surface coatings on wetting is realized when the coating consists of a thick (i.e., > 5 micron) layer of free B or Si. That is, surfaces where these elements are largely flashed away, or surfaces consisting of carbides of B and Si result in poor wetting. This may be explained by consideration of the relative magnitudes of cohesion and adhesion in the contact system. Good wetting results when the adhesion between the substrate and alloy is large compared to the cohesion of either material. For wetting of carbide surfaces, additional energy is necessary to overcome the chemical bonding of Si to B and C. For wetting to free Si and B, no additional energy is necessary. In other words, free Si and B are required to tie up the segregated carbon in the system, and this is facilitated if these elements are not already tied up to begin with.

REFERENCES

/5/ Ibid., p. 421.