Interfacial Tension between Low Pressure Argon Plasma and Molten Copper and Iron

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The interfacial tension between the molten metal and the surrounding plasma environment affects the circulation of molten metal in the weld pool, heat transfer, and the eventual structure and properties of the weld metal. Since the effect of plasma on the interfacial tension of molten metals is not known, interfacial tension values between low pressure argon plasma and pure copper and iron were measured. The variables studied were temperature and the intensity of plasma emission.

I. INTRODUCTION

THE chemical composition, microstructure, and the properties of the weld metal are influenced by the simultaneous occurrence of several important physical processes. These include absorption of heat by the workpiece in the presence of plasma, vigorous circulation of molten metal, the accompanying convective heat transfer in the weld pool, and the solidification of the weld metal. The fluid flow in the weld pool is strongly influenced and in many cases, controlled, by the spatial variation of interfacial tension between the weld pool and the surroundings that contain plasma.

The importance of the role of plasma in the welding processes was recognized in the previous works. However, most of the available literature in this field was addressed to the effect of plasma on the weld properties.[1,2,3] Although the weld penetration is known to be related to plasma intensity[2–5] and the penetration is strongly influenced by the nature and intensity of interfacial tension driven flow,[6,7,8] the effect of plasma on the interfacial tension of liquids was ignored in the previous work. Because of the lack of appropriate interfacial tension data between the plasma and the weld pool, all the previous efforts in the analysis of fluid flow in the weld pool were based, in a rather simplistic way, on the surface tension of gas/metal systems and not on the appropriate interfacial tension between the plasma and the weld pool. In view of the crucial importance of interfacial tension driven flow in the heat transfer, cooling rate and the resulting structure and properties of the weld metal, a rational strategy for the understanding of the welding processes and weld metal properties must include an understanding of the effect of plasma on the interfacial tension of liquid metals.

The work reported in this paper is aimed at partially alleviating the amazing lack of information on plasma/liquid-metal systems. Interfacial tensions of copper and iron were measured in the presence and absence of low pressure argon plasma. The plasma had both ionized and excited neutral atoms — components that are commonly present in the welding environments.[9] Interfacial tension values were determined at various temperatures and plasma intensities.

II. PROCEDURES

A schematic diagram of the experimental setup is shown in Figure 1. A radio frequency (RF) induction furnace capable of supplying up to 10 kW of power at 450 kHz was used as the power source. The sample temperature was measured with a two-color optical pyrometer.

The ultra high purity argon used for the experiments had a maximum impurity content of 10 ppm with no more than 2 ppm oxygen and 3 ppm water vapor. High purity copper and iron (maximum 10 ppm impurities) supplied by Aesar were used in the experiments. The samples weighing about 0.5 g were cleaned, degreased in acetone, and placed on a polished alumina substrate. The substrate was placed horizontally in a graphite susceptor tube which was insulated from the vycor reaction tube by a mullite tube as shown in Figure 1. The RF power was supplied through a 3.4 cm internal diameter coil made up of 0.32 cm diameter copper tube. The coil had seven turns with 0.15 cm spacing between the adjacent turns. Because of the high frequency used for heating, the skin depth of the induced current was very small and the graphite susceptor ensured that the shape of the metal drop was not disturbed by the induced currents. The metal drops were photographed through an optical window fitted at one end of the vycor tube.

The low pressure argon plasma was characterized by emission spectroscopy. The setup consisted of a monochromator with a kinematically mounted diffraction grating to improve resolution, connected to an intensified silicon intensified target detector, which in turn was connected to an optical multi-channel analyzer. The assembly was calibrated using an argon lamp as a standard. A photograph of the low pressure argon plasma is presented in Figure 2.

Interfacial Tension Determination

A recently developed numerical method[10] which is based on the application of the Laplace equation for interfacial tension of a curved surface was used. In this method values of coordinate points of the discretized droplet interface (obtained from an enlarged photograph of the droplet), the

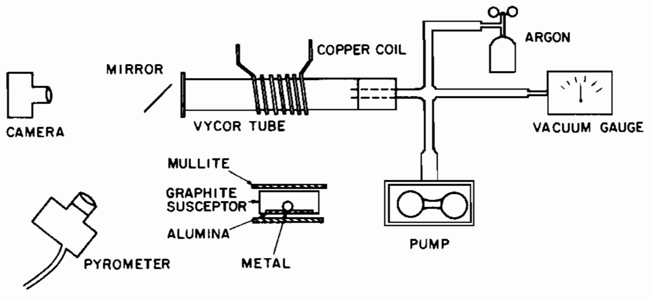

Fig. 1 — A schematic diagram of the experimental setup.

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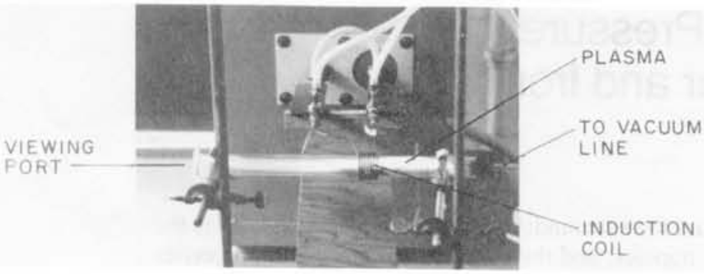

Fig. 2—A photograph of argon plasma.

value of the density difference across the interface, and the value of the local acceleration due to gravity are required for the calculations. Although this procedure does not require precise measurements of the horizontal and vertical distances along the meridional section of the droplet which is necessary for the conventional interfacial tension calculation procedure using the tables of Bashforth and Adams,[11,12] the procedure was found to be fairly expensive in computer time. Furthermore, for several experiments, no significant difference was found between the interfacial tension values obtained by these two techniques. For the subsequent determinations, the interfacial tension data were calculated from photographically magnified droplet images using the tables of Bashforth and Adams.[11]

III. RESULTS AND DISCUSSION

A. *Plasma Characterization*

Figure 3 shows a typical plot of intensity in arbitrary units as a function of wavelength for the argon plasma utilized in this work. It is observed from the wavelengths that both ionized and excited neutral argon atoms are present in the plasma. The plasma produced during the arc and laser welding processes is known to contain both ionized and excited neutral atoms of the inert shielding gas.

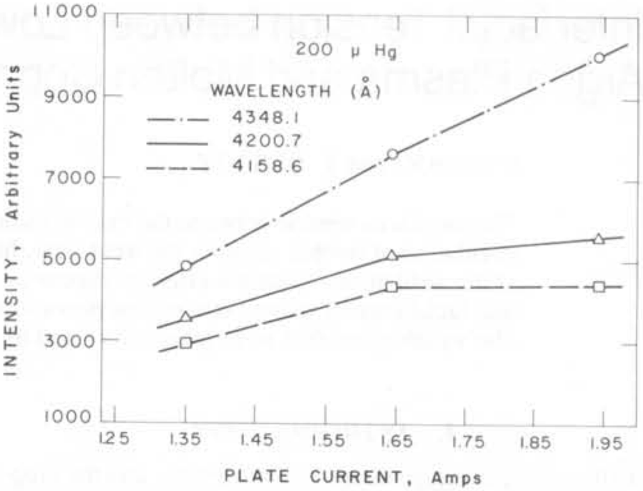

Fig. 4—Intensity of emission of argon plasma *vs* power (plate current) for various wavelengths at a pressure of 200 μm Hg.

The intensity of the various peaks in the plasma could be controlled by varying the input power (current) and the chamber pressure. The increase in the intensity of three major argon peaks with the increase in the power (plate current) is shown in Figure 4. In Figure 5 the influence of the chamber pressure on the intensity is observed in the pressure range 0.20 to 0.45 torr. The intensity of emission is a function of both the kinetic energy of the colliding molecules and the total number of collisions. In this pressure range, the population density is fairly high and the kinetic energy of the molecules increases as the pressure is reduced. At pressures lower than a critical value (about 0.2 torr) the reduction in the population density was found to lower the intensity of the plasma emission.

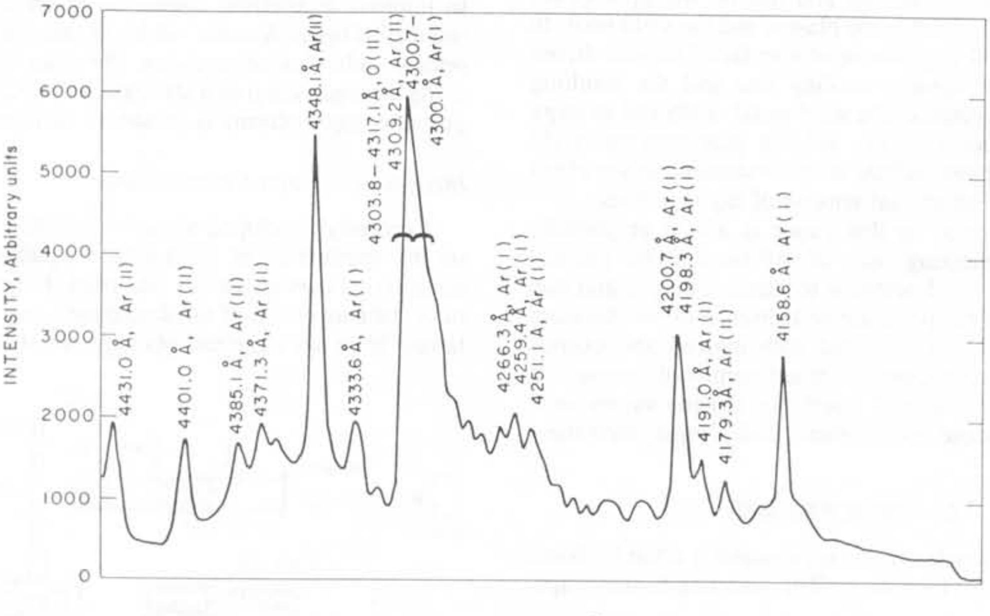

Fig. 3—Intensity of emission of argon plasma *vs* wavelength at a chamber pressure of 450 μm Hg and plate current at 1.65 amps.

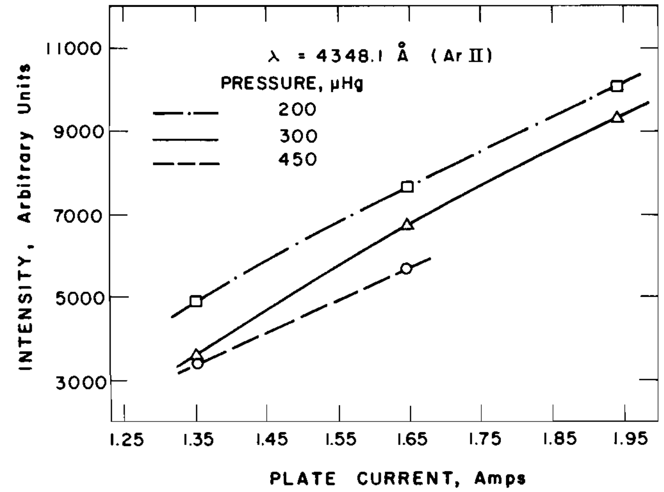

Fig. 5—Intensity of emission of argon plasma at a particular wavelength *vs* power (plate current) for various chamber pressures.

B. *Interfacial Tension*

Interfacial tensions of pure copper and iron in argon were measured in the presence and absence of plasma. The chamber pressure selected for the experiments was such that a fairly intense plasma could be obtained. The intensity of the plasma as a function of chamber pressure was determined prior to conducting the experiments. In the absence of plasma, the measured values of interfacial tension, γ, between liquid copper and argon are represented by

$$\gamma = 1.39 - 3.9 \times 10^{-4}(T - 1356) \quad \text{N/m} \quad [1]$$

in the temperature range 1300 to 1573 K. The data are presented in Figure 6. The values compare reasonably well with the recent measurements of Kasama *et al.*,[13] and the agreement indicates the appropriateness of the procedures used for the determinations. When argon plasma was present, the interfacial tension in the copper system was significantly lower than that in the absence of plasma as can be observed from the data in Figure 6. A similar effect was also observed when experiments were conducted with pure iron droplets. The interfacial tension data with and without the presence of argon plasma are presented in Figure 7. Comparison of the measured values of the interfacial tension of iron in the absence of plasma with the corresponding results of Kasama *et al.*[14] show a small discrepancy between the two sets of values. Kasama *et al.*[14] measured the interfacial tension of iron by the levitation technique. They indicated that since the problem of container contamination is eliminated in the levitation technique, the interfacial tension values determined by this technique represent values for extraordinarily clean metal surfaces and the values are normally higher than the values determined by other techniques. The lowering of interfacial tension in both iron and copper systems is consistent with a plasma induced surface segregation of surface active elements as will be explained in the subsequent discussions.

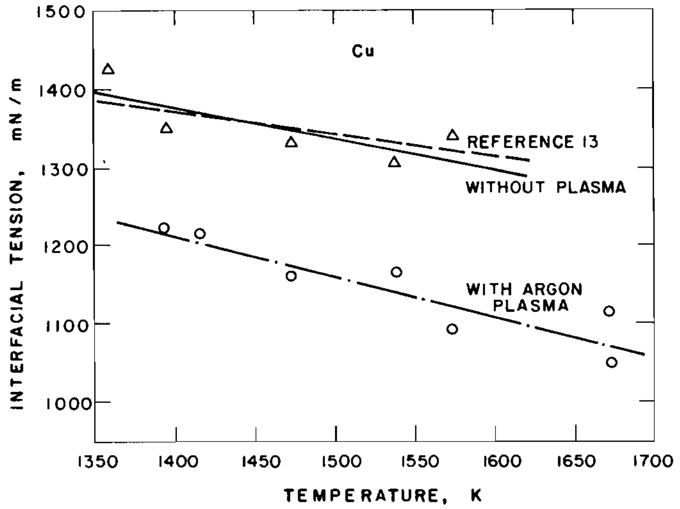

Fig. 6—Interfacial tension between liquid copper and argon with and without the presence of plasma. Plate current and chamber pressure were in the ranges of 1.4 to 1.65 amps and 170 to 200 μm Hg, respectively.

In the absence of plasma environment the interfacial tension, γ, in Fe-O system can be expressed by the following equation:[15]

$$\gamma = 1.943 - 4.3 \times 10^{-4}(T - 1809) - RT\Gamma_s \ln[1 + k_1 a_0 e^{(-\Delta H^\circ/RT)}] \quad \text{N/m} \quad [2]$$

where Γ_s is the surface excess at saturation which has a value of 2.03×10^{-8} Kg mole/m^2. The symbols k_1 and ΔH° represent entropy and enthalpy factors in the oxygen adsorption reaction and their values are 0.0138 and -1.463×10^5 KJ/Kg mole, respectively. The gas constant, R, has a value of 8.314×10^3 J/K Kg mole. The interfacial tension of iron in argon plasma was found to be 1.745 N/m at 1825 K and 1.7 N/m at 1905 K. On the basis of Eq. [2] it can be shown that the reduction in the interfacial tension of iron due to plasma is equivalent to the depression in the interfacial tension caused by bulk oxygen concentrations of 13 and 23 ppm of oxygen dissolved in iron at 1825 K and 1905 K, respectively, in the absence of plasma. Similarly, for the copper system, the depression in surface tension caused by the argon plasma is similar in effect to that produced by 41 ppm oxygen at 1473 K and 94 ppm oxygen at 1673 K. Thus, in both copper and iron systems, the depression in surface tension due to plasma is equivalent to that caused by the surface segregation of oxygen that results from low concentrations of oxygen in metal in the absence

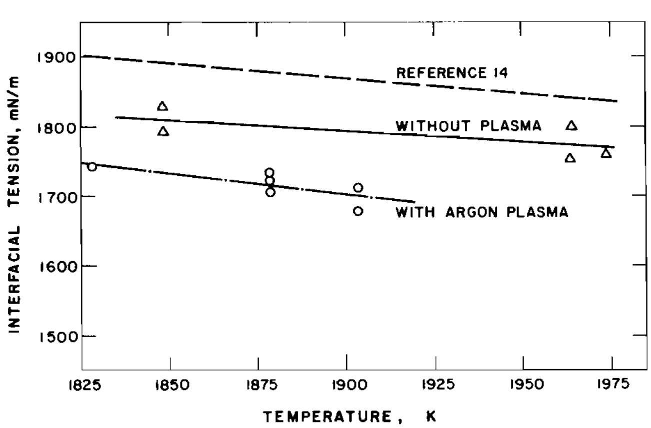

Fig. 7—Interfacial tension between liquid iron and argon with and without the presence of plasma. Plate current and chamber pressure were in the ranges of 1.2 to 1.4 amps and 150 to 200 μm Hg, respectively.

of plasma. It will be argued in the following paragraphs that the presence of low pressure argon plasma is conducive to enhanced surface segregation of oxygen; *i.e.*, when plasma is present, a given depression in interfacial tension can be attained at a much lower oxygen concentration than normally required in the absence of plasma.

Since the ionization potentials of both copper and iron are about almost half that of argon,[16] ionized metal vapors are present in close proximity of the metal droplets. The concentration of cations in the plasma near the interface is high because of the high concentration of the metal vapor. The cations in turn facilitate the adsorption of anions on the surface of the liquid metal drop. Because of this effect, the amount of bulk oxygen concentration necessary to lower the interfacial tension of metals in argon plasma would be much lower than the bulk oxygen concentration necessary in the absence of plasma environment.

The lowering of surface tension by plasma induced enhanced surface segregation is consistent with results of vaporization rate measurements in our laboratory. Results of Collur *et al.*[17] indicate that the rate of vaporization of copper decreases in the presence of low pressure argon plasma in the temperature range 1400 to 1600 °C. The reduction in the vaporization rate is consistent with the plasma induced enhanced surface coverage.

It is observed from Figures 6 and 7 that the reduction of interfacial tension due to the presence of the argon plasma was more pronounced in the copper system than in the iron system. In view of the limited amount of oxygen available ($O_2 < 2$ ppm, $H_2O < 3$ ppm) in the ultra high purity argon and from the solid surfaces present in the experimental system, the lowering of interfacial tension is related to the surface excess of oxygen at a given oxygen concentration. Lupis[18] related the tendency of surface segregation to an adsorption coefficient at infinite dilution of the surface active species. His data for the adsorption coefficient at infinite dilution for oxygen are 2500 for Fe-O system and 10,000 for the Cu-O system. Thus, qualitatively, the larger decrease in the interfacial tension of the Cu-O system than the Fe-O system is consistent with the greater propensity of oxygen to segregate at the surface of the Cu-O system.

To understand the role of plasma intensity on the surface tension of pure copper, experiments were conducted at a constant pressure level at 1473 K. The plasma intensity was adjusted by changing the input power (plate current). The interfacial tension values are presented as a function of plasma intensity in Figure 8. A statistical analysis of the data gave a mean value of 1170 mN/m with a standard deviation of 46 mN/m. The two dotted lines on this figure indicate the precision of these determinations (± 50 mN/m) and cover most of the measured values. It appears that the interfacial tension is not significantly influenced by the intensity of the plasma.

The interfacial tensions of iron and copper in the presence of argon plasma were lower than the corresponding values in the absence of plasma. However, the temperature coefficient of surface tension did not change significantly when the plasma was present. In the welding literature the importance of both the absolute value of the interfacial tension,[19] γ, and the temperature coefficient,[6,7] $d\gamma/dT$, in influencing the weld penetration is well documented.[20,21] The value of $d\gamma/dT$ is related to the intensity and direction of the recirculating flow of molten metal in the weld pool and affects weld penetration through the heat transfer process. The importance of the absolute value of interfacial tension stems from the fact that the depression of the liquid pool surface due to the arc pressure is resisted by the force due to interfacial tension. It is thought that the lowering of interfacial tension of iron due to the presence of argon plasma during arc welding would be useful in explaining the depression of the weld pool surface and the resulting weld penetration. Furthermore, there is a need to obtain interfacial tension data in the presence of plasma over an extended high temperature range for the simulation of transport processes in the weld pool. Such efforts are currently underway at Penn State.

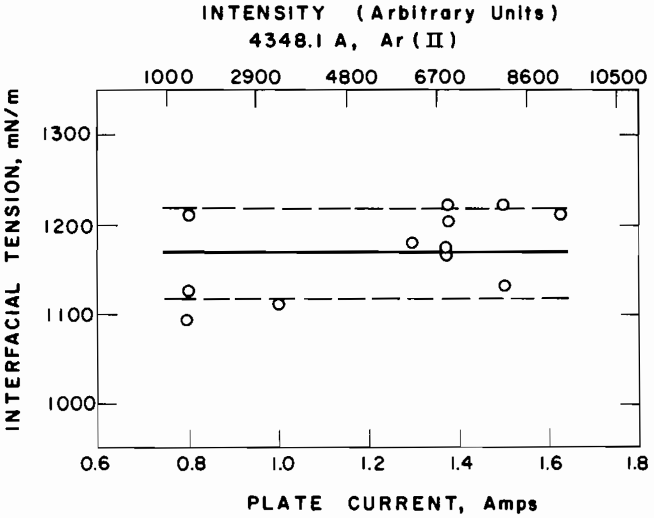

Fig. 8 — Interfacial tension between copper and argon plasma at 1473 K as a function of intensity of emission of plasma (plate current) at 200 ± 10 μm Hg.

IV. SUMMARY AND CONCLUSIONS

Interfacial tension of pure copper and iron were measured both in the presence and absence of low pressure argon plasma generated by the application of radio frequency induction current. The emission spectroscopic studies of the argon plasma indicated the presence of both ionized and excited neutral argon atoms.

The presence of argon plasma lowered the interfacial tension of both iron and copper systems. The reduction was more pronounced in the copper system than the iron system and is consistent with the plasma induced surface segregation of oxygen. This enhanced surface segregation mechanism is also consistent with the reduction of the vaporization rate of copper droplets in the presence of low pressure argon plasma observed in our laboratory. In the range of plasma intensity studied, the interfacial tension did not change appreciably with the plasma intensity.

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