

EFFECT OF LOW-PRESSURE ARGON PLASMA ON METAL VAPORIZATION RATES

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Rates of vaporization of liquid iron and copper drops were determined both in the presence and the absence of a low-pressure argon plasma. The vaporization rates of pure metal drops and metal drops that were doped with small amounts of oxygen or sulfur were found to decrease when plasma was present. The results are consistent with the presence of a charge distribution field in close proximity of the interface.

In numerous emerging and established materials processing operations the surface of a metal is exposed to a plasma environment consisting of electrons, ions, and neutral atoms in both excited and ground energy states. Familiar examples include the low-pressure plasma materials synthesis, high-energy beam processing, and the plasma deposition and sputtering phenomena. Since the presence of plasma can have a significant effect on the physico-chemical processes at the metallic interface, and since metal vaporization occurs in many advanced materials processing operations, the role of plasma on the rates of vaporization of iron and copper drops was investigated. Experiments were conducted both in the presence and the absence of a plasma environment in each system so that the results from the metal-neutral gas environment can serve as controls for comparison with the data from the metal-plasma systems.

The low-pressure argon plasma was generated by inductively coupling argon with a radiofrequency induction furnace capable of providing up to 10 kW of power at 450 kHz. The rf power was supplied through a 3.4 cm internal diameter coil made up of 0.32 cm diameter copper tube wound on a vycor reaction tube. The coil had seven turns with 0.15 cm spacing between the adjacent turns. During a typical run, the sample temperature and coil current were maintained constant. The chamber pressure was maintained constant for all experiments. The temperature of the droplet was controlled by adjusting the posi-

tion of the droplet with respect to the induction coil. A two-color pyrometer was used for the temperature measurement. The ultrahigh-purity argon used for the experiments had a maximum impurity content of 10 ppm with no more than 2 ppm oxygen and 3

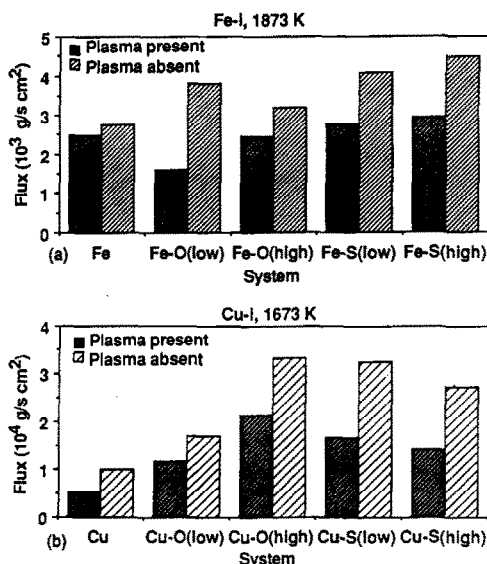


Fig. 1. Vaporization flux both in the presence and the absence of plasma for (a) iron-solute systems where (low) and (high) denote solute concentrations of 0.03 and 0.25 weight percent respectively and (b) copper-solute systems where (low) and (high) denote solute concentrations of 0.1 and 0.5 weight percent respectively. Chamber pressure was 0.3 and 1.0 mm Hg for iron and copper systems respectively.

ppm water vapor. High-purity iron and copper (maximum 10 ppm impurities) supplied by Aesar were used in the experiments. The samples weighing between 0.5 and 1.0 g were cleaned, degreased in acetone and were placed on an alumina substrate inside a vycor reaction tube. Since most commercial materials contain impurities, some of the samples were doped with small quantities of oxygen or sulfur. The rate of vaporization was determined from the weight change of the sample and the exposure time. In samples containing sulfur, approximately half of the initial sulfur content was lost during the experiments. However, the error in the determination of the vaporization rate due to loss of sulfur was insignificant since the quantity of sulfur in the sample was small. The low-pressure argon plasma was characterized by emission spectroscopy.

The results of the vaporization experiments are presented in fig. 1. It is observed from fig. 1a that for each of the three iron systems, the vaporization rate of iron in a neutral gas environment was higher than

that in the plasma environment. A similar effect was observed for the vaporization rate of copper in copper systems (fig. 1b). In the plasma both the excited neutral and the ionized iron and argon species were present as can be observed from the spectra presented in fig. 2. In view of the high mobility of the electrons among the various charged species in the system, the flux of the electrons to the liquid metal surface is far higher than the flux of the heavier species in the plasma. As a result, the liquid metal surface acquires negative charge and the region in close proximity of the surface becomes densely populated with positively charged argon and metal ions as shown in fig. 3. The attraction between the positively charged metal ions and the negatively charged vaporizing surface leads to enhanced condensation of metallic species. The reduction in the vaporization rate due to the presence of plasma is compatible with the enhanced condensation of iron due to a space-charge effect shown schematically in fig. 3.

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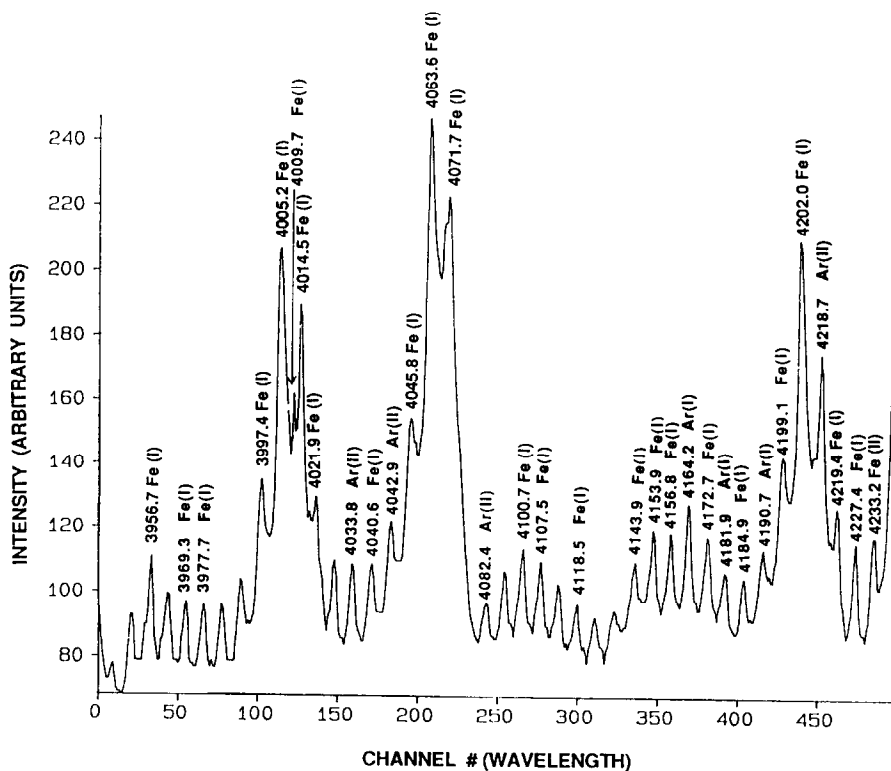


Fig. 2. Intensity versus wavelength at a chamber pressure of 300 $\mu\text{m Hg}$ and plate current at 1.6 A.

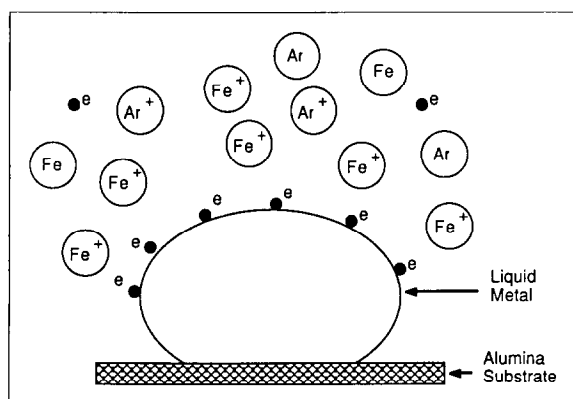


Fig. 3. Schematic representation of the plasma near the interface.

of surface active impurities such as oxygen or sulfur. Since these materials are preferentially adsorbed at the surface, their presence can influence the nature of the interfacial phenomena. Based on conventional thermodynamic treatment, one would expect that the presence of surface active elements such as sulfur or oxygen would lead to a reduction of the number of available surface sites for vaporization. As a result, based on adsorption considerations, a reduction in the vaporization rate would be expected when these elements are present. However, it is observed from fig. 1 that for both iron and copper systems, the vaporization rates of the metals are enhanced by the presence of a surface active element such as oxygen or sulfur. It is to be noted that these findings are consistent with the independent results of metal vaporization during welding of various iron base alloys. Emission spectroscopic data have indicated the increase in the intensity of iron peaks resulting from the presence of sulfur in the alloy [1-3]. The role of surface active elements, such as sulfur and oxygen,

can be explained by the interfacial turbulence which occurs when surface active elements are present at the interface [4]. Experiments performed by Langmuir on the evaporation of ether from water illustrate this phenomenon [4]. When talc was scattered on the surface of water, the particles exhibited abrupt local movements. This is because the eddies in the water facilitate segregation of ether to the surface where it gives rise to a local surface tension decrease. At the same time the eddies from the ambient atmosphere remove the ether thereby rising the surface tension. At any given instant, the interface consists of areas of relatively low and relatively high surface tensions. The spatial variation of interfacial tension causes local flow and surface fluctuations exhibited by the motion of the talc particles. These local movements of the interface increases the surface area and the rate of vaporization. When experiments are conducted with copper or iron drops that were doped with oxygen or sulfur, the presence of the dopants leads to interfacial turbulence and increased metal vaporization rates. Again, the metal vaporization rates in the presence of plasma are lower than the rates in the absence of plasma due to the space-charge effect.

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