Effects of Oxygen and Sulfur on Alloying Element Vaporization Rates during Laser Welding

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Inadequate control of weld metal composition due to vaporization of volatile alloying elements is a serious problem in the welding of many important engineering alloys. Effectiveness of surface active elements such as oxygen or sulfur in blocking vaporization sites on the weld pool surface was investigated. Several iron samples doped with oxygen or sulfur were exposed to a carbon dioxide laser beam in pulsed mode. The time average metal vaporization rates and the emission spectra were compared with those obtained from ultra pure iron samples. Since the weld pool surface area and temperature distribution are affected by oxygen and sulfur, the true effects of these elements on metal vaporization rates cannot be easily evaluated from welding data. Therefore, rates of isothermal vaporization of iron and copper drops doped with oxygen or sulfur were determined both in the presence and the absence of low pressure argon plasma. These rates were compared with the rates of vaporization of ultrapure metal drops. Presence of sulfur or oxygen in metals always resulted in increased metal vaporization rates. The results are analyzed on the basis of interfacial phenomena.

I. INTRODUCTION

ONE of the major problems in the use of a high power density laser beam for the welding of many important engineering alloys is the loss of volatile alloying elements. The inadequate control of weld composition and properties are familiar difficulties in the welding of several aluminum alloys and high manganese stainless steels.[1,2,3] The vaporization of alloying elements from the weld pool is influenced by various factors such as the temperature and concentration distributions at the weld pool surface, the extent of surface coverage by the surface active elements, interfacial turbulence, and the modification of the nature of the interface due to the presence of plasma[4] in close proximity of the vaporizing interface. In a recent paper,[5] we have demonstrated that the rate of alloying element vaporization during conduction mode laser welding of stainless steels is controlled by plasma induced intrinsic vaporization at the weld pool surface.

Surface active elements such as oxygen and sulfur are known to influence the weld pool fluid motion and aspect ratio which, in turn, affect the vaporization rate.[6,7] Heat-to-heat variations in the concentrations of oxygen and sulfur in several commercial alloys are thought to be responsible for the lack of reproducibility of weld geometry and properties. Previous emission spectroscopic investigations by Savitskii and Leskov[8] indicated that during GTA welding of steels, the rates of vaporization of iron and manganese increased with the increase in the sulfur and oxygen concentrations in steel. Similar effects were observed by Dunn, Allemand, and Eagar,[9] who found that the presence of sulfur in the base plate enhanced the intensity of emission of Fe, Cr, and Mn peaks. Although alloying element vaporization is regarded as an important problem during laser processing and the presence of surface active elements is known to affect vaporization, no systematic investigation of the role of oxygen and sulfur on the alloying element vaporization rates has been undertaken so far.

The work reported in this paper was aimed at understanding the roles of oxygen and sulfur on the rates of vaporization of alloying elements during laser welding. Since most commercial alloys contain a large number of elements, ultrapure iron samples, doped with oxygen or sulfur, were welded with a carbon dioxide laser in the pulsed mode to determine the effects of dopants. The time average vaporization rates were compared with the rates determined from the welding of ultrapure samples. The nature of the various species present in the plasma during welding was monitored by emission spectroscopy. The presence of surface active elements such as sulfur or oxygen in the base metal affects the surface area and the temperature distribution in the weld pool — factors that strongly influence vaporization rate. Thus, it is difficult to determine from the welding data if the changes in the vaporization rate due to the presence of surface active elements in the base metal are attributable exclusively to changes in weld pool surface area and temperature distribution or are contributed by additional interfacial effects due to the presence of these elements. In either case, the primary interfacial effect of sulfur cannot be easily separated from the secondary effects of sulfur manifested in changes in surface area and temperature distribution. To determine the true interfacial effect of sulfur on the metal vaporization rate, a series of experiments were designed where iron and copper drops doped with oxygen or sulfur were allowed to vaporize isothermally both in the presence and the absence of a low pressure argon plasma. The rates were compared with the rate of vaporization of ultrapure metal drops under appropriate conditions.

II. EXPERIMENTAL

Pure iron samples of dimensions 0.04 m length, 0.015 m width, and 0.002 m thickness were welded using a carbon dioxide laser at a peak power density of 1.2×10^6 watts/cm^2 at 100 Hz. The maximum impurity content of iron was 10 ppm. Helium was used as the shielding gas. The time

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average vaporization rates were determined from the weight loss of the sample due to welding and the total duration of the experiment. Experimental conditions utilized for doping[10,11] with either sulfur or oxygen are presented in Table I. A few samples were oxidized in a muffle furnace in air at 873 K for two hours.

Figure 1 is a schematic diagram of the experimental set-up used for emission spectroscopy during laser welding. As can be seen from the figure, the radiation emitted from the plasma is focused on the slit of a monochromator through a convex lens. A kinematically mounted diffraction grating (600 lines/mm) was used to obtain a high resolution spectrum. An intensified silicon intensified target (ISIT) detector was connected through a controller to an optical multichannel analyzer (Model OMA3). A 2.5 mm high band at the center of the 12.5 mm × 12.5 mm square ISIT detector was monitored in order to avoid peripheral effects due to aberrations to prevent increased line width and reduced resolution.[12] The full width of the ISIT detector was monitored allowing about 600 angstroms wavelength range of the spectrum to be recorded at one time. Information from the detector was transferred to the OMA as plots of intensity vs wavelength. Intensities of the peaks were obtained by subtracting the background noise from the observed intensities.

Figure 2 is a schematic diagram of the experimental set-up employed in the isothermal vaporization experiments. 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 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. The temperature of the droplet was controlled by adjusting the posi-

1. Pyrometer
2. Optical window
3. Inlet
4. RF coil
5. Mullite tube
6. Graphite susceptor
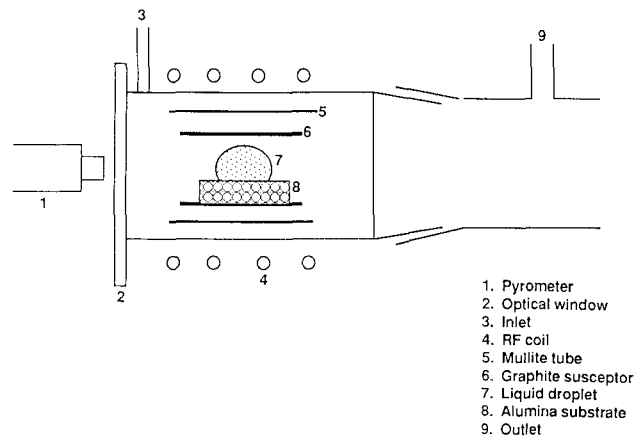7. Liquid droplet
8. Alumina substrate
9. Outlet

Fig. 2—A schematic diagram of the experimental set-up used for isothermal vaporization experiments (shown with a graphite susceptor).

tion of the droplet with respect to the induction coil. A two-color pyrometer was used for the temperature measurement. The chamber pressure was maintained at 80 N/m² or lower. The chamber pressures were selected to ensure a stable and intense plasma. The plasma generated was a mixture of positive ions, electrons, and excited neutral atoms. The coil current was reduced to perform experiments in the absence of plasma. These experiments also required adjustment in the location of the specimen with respect to the coil to attain a target droplet temperature. 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. The gas was cleaned to remove oxygen by passing through a bed of titanium chips at 1073 K. 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. 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 the loss of sulfur was insignificant since the amount of sulfur in the sample was small. In some runs, a

Table I. Experimental Conditions Used for Doping Sulfur and Oxygen in Ultra Pure Iron Samples (Time of Experiment = 3 Hours)

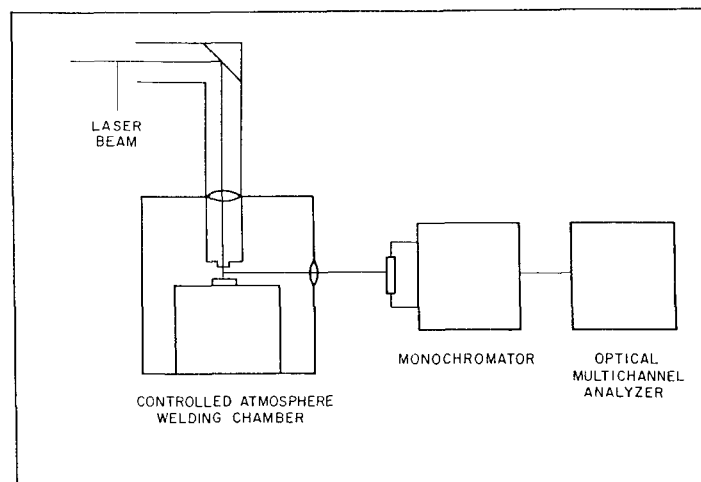| Dopant	Temp. (K)	H_2S/H_2 (Molar Ratio)	CO_2/CO (Molar Ratio)	Wt Pct i
Sulfur	1273	5.45×10^{-3}	—	0.013
Oxygen	1603	—	0.171	0.002

Fig. 1—A schematic diagram of the experimental set-up used for the laser welding experiments.

graphite susceptor was used to shield the sample from the eddy currents induced by the RF field. This ensured that the sample surface was not disturbed, unlike the experiments where a susceptor was not used.

III. RESULTS AND DISCUSSION

A. Sessile Drop Experiments

Figure 3 depicts the results of isothermal vaporization experiments. In this figure, the vaporization rate of copper is plotted for Cu, Cu-O, and Cu-S systems, both in the presence and absence of a graphite susceptor. Each data point represents the average of at least two values. It is observed that for each of the three copper systems, the vaporization rate of copper is enhanced by the presence of a surface active element such as oxygen or sulfur, both in the presence and the absence of a graphite susceptor. Furthermore, the presence of a susceptor leads to a lowering of vaporization rates in all cases. Several interesting questions arise from the perusal of the data. How close are the experimental vaporization fluxes to the theoretical promise of the kinetic theory of gases (Langmuir equation)? What role, if any, does the susceptor play, especially in the vaporization of ultra high purity copper? And most important and puzzling, why do the rates increase when sulfur or oxygen is present, even at a low concentration?

1. Experimental and theoretical fluxes

The intrinsic vaporization flux from the surface of pure metal drops under vacuum is represented by the Langmuir equation:

$$J = 4.37 \times 10^{-3} p \sqrt{M/T} \qquad [1]$$

where J is the vaporization flux in kg/m^2 s, p is the pressure in N/m^2, M is the molecular weight, and T is the absolute temperature. The vaporization flux, calculated from Eq. [1], is compared with the experimentally determined flux values both in the presence and the absence of a susceptor in Table II. The calculated and the experimental values all lie within a factor of ten. However, the theoretical value is higher than the corresponding experimentally determined values. Possible reasons for this include the fol-
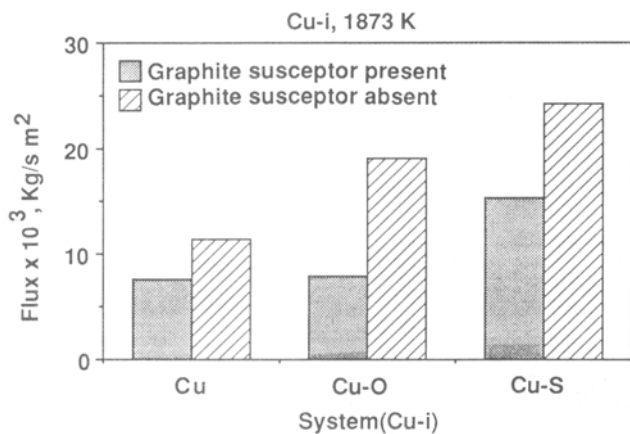
Table II. Rate of Vaporization of Copper Drops

Temperature	1873 K
Equilibrium vapor pressure of Cu	84.2 N/m^2
Vaporization flux according to Langmuir equation	6.8×10^{-2} kg/m^2 s
Experimentally determined flux when susceptor was used	0.76×10^{-2} kg/m^2 s
Experimentally determined flux when susceptor was not used	1.09×10^{-2} kg/m^2 s

lowing: (i) lack of rapid transport in the boundary layer, (ii) surface coverage by impurities that are inevitably present at very low concentrations, even under carefully controlled experimental conditions, (iii) vacuum level in experiments insufficient for application of Eq. [1], and (iv) other factors such as experimental errors in the measurements of surface area and temperature of the drops, and insufficient accuracy in the available value of vapor pressure for use in Eq. [1]. These factors are discussed in the following section.

(i) *Role of gas phase mass transfer:* The flux for the transport of copper vapor from the surface of the drop to the bulk gas phase through the mass-transfer boundary layer surrounding the drop, J_m, is given by:

$$J_m = (p - p^b) k_g / RT \qquad [2]$$

where p and p^b are the vapor pressures of copper at the interface and in the bulk gas phase, respectively, at a temperature T, R is the gas constant, and k_g is the mass transfer coefficient. Calculation of p^b from the experimental data of vaporization rate and the flow rate of argon indicated that p^b was negligible compared to p. The calculated value of J_m and the data used for the calculations are presented in Table III. It is to be noted that the value of flux computed from mass transport considerations is higher than that predicted by the Langmuir equation (see Table II). Thus, if copper vapor is generated in close proximity of the droplet surface at a rate given by the Langmuir equation, the vapor can be readily transported across the boundary layer at the rate at which it is generated without any accumulation of

Table III. Estimation of Vaporization Flux under Gas Phase Mass Transfer Control

Temperature, T	1873 K
Tube diameter	2.54×10^{-2} m
Argon flow rate at room temperature and pressure	0.83×10^{-6} m^3/s
Chamber pressure	80 N/m^2
Vapor pressure of copper at the surface, p	84.2 N/m^2
Diffusivity of copper vapor in argon, D	0.52 m^2 s
Sherwood number,* Sh	2.37
Diameter of the copper drop, d_p	2.66×10^{-3} m
Mass transfer coefficient,** Kg	2.32×10^2 m/s
Vaporization flux under gas phase mass transport control	8.0×10^{-2} kg/m^2 s

*Sh $= 2 + 0.6$ Re$^{1/2}$ Sc$^{1/3}$
**$Kg = D$ Sh/d_p

Cu-i, 1873 K

Fig. 3 — Vaporization flux at 1873 K both in the presence and absence of a graphite susceptor for copper-solute systems. The solute concentration was 0.1 wt pct, and the chamber pressure was maintained at 80 N/m^2.

the vapor in close proximity of the vaporizing interface. Thus, the fact that experimental values of the vaporization flux is lower than the theoretical Langmuir rate cannot be attributed to sluggish transport of the vapor through the gas boundary layer.

(ii) *Surface coverage effects:* If certain surface sites are occupied by surface active elements, the experimental vaporization rate can be lower than the theoretical rate. Small amounts of surface active elements such as oxygen are inevitably present even in high purity copper. Furthermore, minor amounts of impurities can be introduced in the sample from the solid ceramic substrate on which the drop rests during experiments. Calculation of surface coverage on the basis of adsorption considerations indicates that 10 ppm of oxygen in the copper drop can occupy about 50 pct of the surface sites at 1875 K. When the oxygen content is 0.1 wt pct, more than 95 pct of the surface sites can be covered by oxygen. Thus, it appears that the low experimental flux can be conveniently attributed to the presence of small amounts of surface active impurities — at least in principle. However, when the rates of vaporization of copper from samples that were doped with oxygen or sulfur were measured, the rates were found to be higher than those observed from pure copper drops. Thus, low values of vaporization flux cannot be attributed to only the surface coverage effects. When surface active elements are present in copper, the effect of surface coverage is outweighed by other effects that increase the vaporization rate. A more complete discussion of the role of oxygen and sulfur is deferred to a subsequent section.

(iii) *Insufficient vacuum:* Equation [1] is applicable only under perfect vacuum conditions, and it does not take into account recondensation of vapors at inadequate vacuum levels. Therefore, it is possible that the difference between the experimentally observed rate and the calculated rate results, at least in part, from this effect.

(iv) *Other factors:* The discrepancy between the experimentally determined flux and the theoretical rate computed from Eq. [1] can be contributed by errors in the estimation of surface area, measurement and control of temperature, and inaccuracies in the available vapor pressure data. The surface area of the droplet was determined from photographic measurements and appropriate relations of solid geometry and it is unlikely that the error in the estimation of surface area was significant. Small fluctuations of temperature about a mean value might have resulted in a somewhat higher experimental rate than the true rate corresponding to a constant temperature. This is because the vapor pressure is a strong function of temperature and, consequently, a slight increase in temperature results in a larger increase in rate than the lowering of the rate resulting from an equivalent decrease in temperature. Thus, the temperature fluctuation would result in the enhancement of rate, and the low value of experimental rate cannot be attributed to errors in temperature control. In the calculation of theoretical vaporization flux we used the most recent vapor pressure data that were available. Indeed, some of the other commonly referred sources of vapor pressure compilations report values as high as 20 pct higher than the values used in the present study. Thus, the differences between the theoretically calculated and the experimental values of flux cannot be attributed to the error in the vapor pressure data.

It is to be noted that the experimental vaporization flux was lower than the vaporization flux calculated on the basis of kinetic theory of gases under perfect vacuum. However, the difference can neither be attributed to sluggish mass transport in the boundary layer nor can it be explained as a direct consequence of the presence of surface active impurities. At the pressure level maintained in the reaction chamber, 40 to 80 N/m^2, to sustain a stable plasma, the theoretical promise of Eq. [1] cannot be met in practice, apparently due to recondensation of metal vapors.

2. *Interfacial turbulence — Effects of susceptor and surface active elements*

Since a high frequency power source was used for the experiments, the skin depth of the induced current was very small. Thus, the presence of a graphite susceptor ensured that there was no significant electromagnetically driven flow in the droplet. The data in Figure 3 indicate that the presence of a susceptor decreased the vaporization rate in all the systems studied, namely Cu, Cu-O, and Cu-S systems. This effect can be explained by considering the fact even high purity copper contains very small (<10 ppm) amounts of surface active impurity and that there is a significant difference in the intensity of electromagnetically driven fluid motion in the presence and the absence of a graphite susceptor. This effect is consistent with interfacial turbulence phenomena which occur when a surface active element is present.[13]

Experiments performed by Langmuir on the evaporation of ether from water illustrate this phenomenon.[13] 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 raising the surface tension, as shown in Figure 4. 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 increase surface area and the rate of vaporization. The oxygen and sulfur present in the copper samples result in interfacial turbulences and lead to enhanced vaporization rates of copper.

Figure 5 shows the results of isothermal vaporization rate of iron and copper systems both in the presence and absence of a plasma. It is observed from the data that the presence of plasma lowers the vaporization rate. The reduction
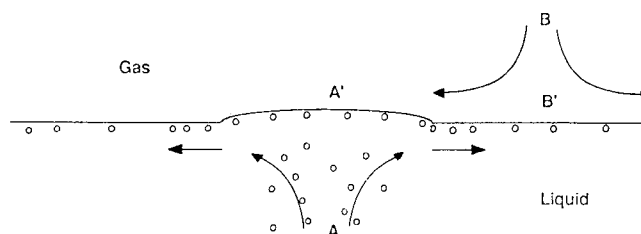

Fig. 4 — A schematic representation of interfacial turbulence phenomenon. An eddy, A, brings a small volume of solution of a surface active agent to the surface, while an eddy, B, in the gas depletes the surface active solute. The surface at A' spreads toward B' and carries some underlying liquid with it.[13]
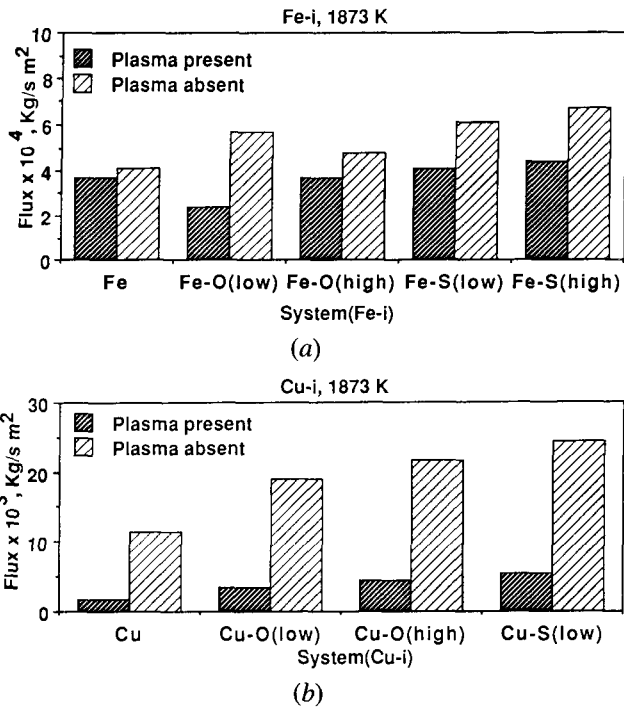
Fig. 5—Vaporization flux at 1873 K both in the presence and the absence of plasma for (a) iron-solute systems where (low) and (high) denote solute concentrations of 0.03 and 0.25 wt pct, respectively, and (b) copper-solute systems where (low) and (high) denote solute concentrations of 0.1 and 0.5 wt pct, respectively. Chamber pressures were 40 N/m^2 and 80 N/m^2 for iron and copper systems, respectively.

in the vaporization rate due to the presence of plasma is compatible with the enhanced condensation of iron vapors due to a space charge effect shown schematically in Figure 6. The ionized and excited iron and argon atoms shown in this figure were detected in the plasma by emission spectroscopy. In view of the high mobility of the electrons among the various charged species in the system, the region in close proximity of the iron surface is densely populated with positively charged iron and argon ions. Furthermore, the surface of the metal drop becomes negatively charged since the electrons strike the metal surface at a higher flux compared to that of ions.[14] The attraction between the positively charged ions and the negatively charged droplets
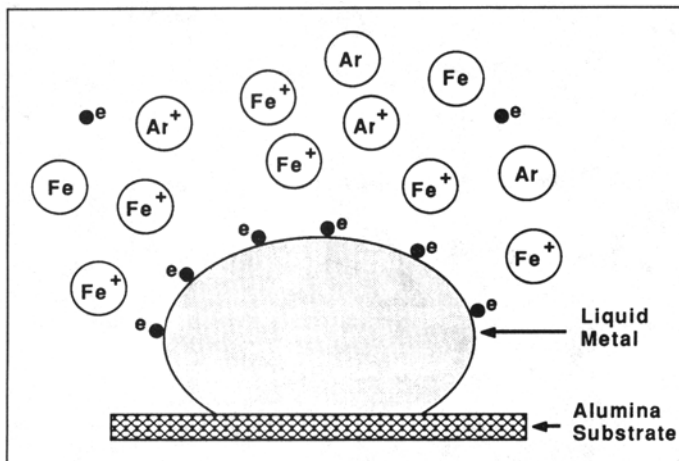

Fig. 6—A schematic representation of the space charge effect.

leads to higher condensation rates. The comparatively high condensation rate, in turn, results in the reduction of the vaporization rate when plasma is present. This phenomenon is important in understanding the fundamentals of weld pool composition control, since during welding, metals vaporize from the weld pool surface which is surrounded by a plasma plume.[5]

B. Assessment of Laser Welding Data

Figure 7 shows a typical plot of intensity in arbitrary units as a function of wavelength from the plasma produced during laser welding of ultrapure iron. It is observed from the wavelengths[15] that iron in the plasma is primarily present in its excited neutral state. The intensity of each of these peaks is related to the vaporization rate of iron.[16] The intensities of three of the major peaks of iron, viz., 4045.8, 4202.0, and 4271.8 Å, are plotted in Figure 8 for pure iron, iron doped with oxygen, iron doped with sulfur, and for an iron sample which was oxidized. It is observed from the figure that presence of oxygen or sulfur increases the intensity of emission from iron atoms in the plasma. This finding is consistent with the increase in the vaporization rates
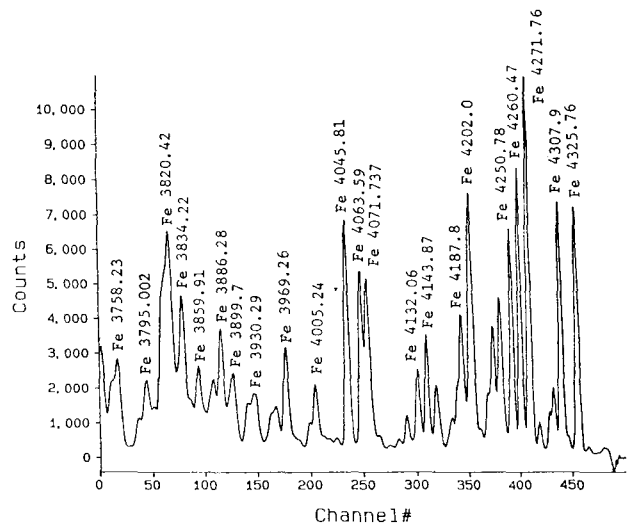

Fig. 7—A typical spectrum of the plasma produced during laser welding of ultrapure iron sample using helium as the shielding atmosphere (gas flow rate = 3.33 × 10^{-5} m^3/s, welding speed = 0.005 m/s, current = 35 mA, pulse length = 0.003 s, frequency = 100 Hz).
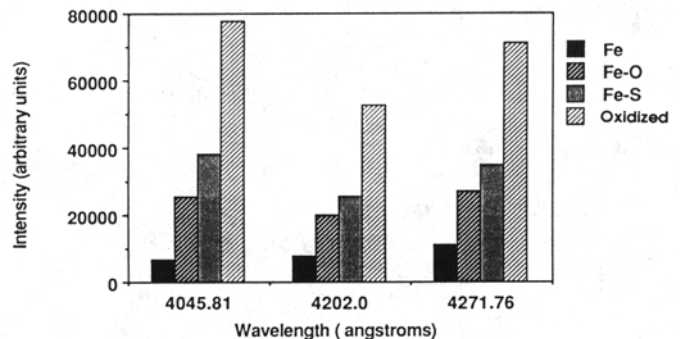

Fig. 8—Bar graph depicting the increase in the intensity of the major peaks of iron for the doped and the oxidized iron samples (gas flow rate = 3.33 × 10^{-5} m^3/s, welding speed = 0.005 m/s, current = 35 mA, pulse length = 0.003 s, frequency = 100 Hz).

for the doped and oxidized samples, as shown in Figure 9. Previous investigations by Dunn, Allemand, and Eagar[9] and by Savitskii and Leskov[8] have also shown that during welding the presence of surface active elements such as sulfur enhances the rates of vaporization of alloying elements. They[8,9] proposed that the enhancement in the vaporization rate of iron in the presence of sulfur is due to the formation of sulfides which have low thermal reaction and sublimation heat effects. However, with the low concentration of sulfur present in the samples used in the present study, sulfide formation is not expected to play a significant role in the vaporization kinetics. The presence of sulfur and oxygen in the weld pool may result in an increase in the absorption of the laser beam and, consequently, may contribute to enhanced vaporization rates and high intensity of emission of the iron peaks. However, factors other than increased absorptivity also influence the vaporization rate. For example, the presence of surface active elements enhances the unevenness of the weld pool surface topography. This leads to an increase in the surface area from which vaporization can occur. The enhancement of vaporization rate can also be attributed, at least in part, to interfacial turbulence, an effect which was discussed in the preceding section.

IV. SUMMARY AND CONCLUSIONS

When iron samples doped with oxygen or sulfur were exposed to a carbon dioxide laser beam in pulsed mode, the time average vaporization rate of iron was found to be higher than that observed from an ultrapure iron sample. The intensity of emission of iron lines in the plasma was enhanced when oxygen or sulfur was present. The increase is consistent with both the possible increase in the absorptivity of the laser beam due to the presence of sulfur or oxygen and due to the interfacial turbulence effect.

Rates of isothermal vaporization of metal drops were enhanced when oxygen or sulfur was present in iron and copper drops. The increase in the rate is consistent with the interfacial turbulence caused by the surface active elements. The vaporization rates were diminished when a graphite susceptor was used to prevent electromagnetically driven flow on the droplet surface. The presence of low pressure argon plasma led to reduction of metal vaporization rates from the drops due to a space charge effect.

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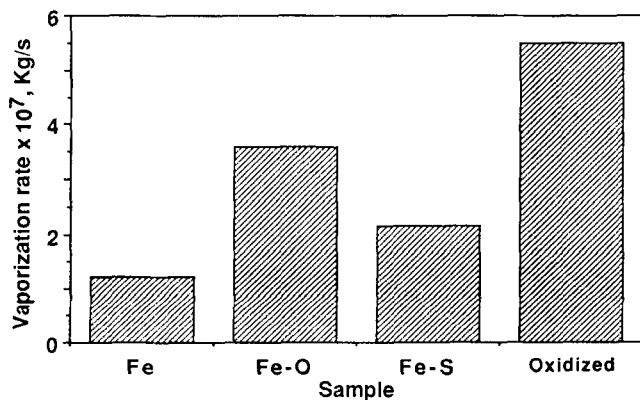16. M. M. Collur and T. DebRoy: Metall. Trans. B, in press.

Fig. 9—Comparison of the time average rate of vaporization of iron from ultrapure iron sample with that from sulfur doped iron sample (Fe-S), oxygen doped iron sample (Fe-O), and oxidized iron sample (FeO) (gas flow rate = 3.33×10^{-5} m^3/s, welding speed = 0.005 m/s, current = 35 mA, pulse length = 0.003 s, frequency = 100 Hz).