

A General Model for Partitioning of Gases between a Metal and Its Plasma Environment

K. MUNDRA and T. DEBROY

When a metal or an alloy is exposed to a pure diatomic gas such as nitrogen, the concentration of the species in the material can be predicted from Sieverts law. However, such calculations cannot be used to understand processes in which the gas phase near the metal contains excited molecules, atoms, ions, and electrons, in addition to the diatomic gases. The presence of plasma leads to species concentrations in the metal that are much higher than the values predicted by the Sieverts law. At present, there is no unified theoretical model to understand the partition of nitrogen, oxygen, and hydrogen between a metal and its plasma environment. In this work, a theoretical model has been developed to understand the enhanced solubility of gases in metals exposed to plasma environment. The model has been applied to explain several different sets of independent experimental results available in the literature. The analysis of the data shows that the enhanced solubilities can be explained on the basis of superequilibrium concentration of atomic species near the metal surface. Both the enhanced solubilities and the maximum species concentrations predicted by the model are in good agreement with the independent experimental data for various systems.

I. INTRODUCTION

IN many important metal processing operations, such as welding and laser, electron beam, and plasma processing, a metal or an alloy is exposed to a plasma. It has become clear in recent years that the physico-chemical behavior of a plasma-metal system is significantly different from that of the corresponding gas-metal system. For example, rates of vaporization of metals are significantly lower in the presence of a plasma than in an environment without a plasma.^[1,2] Similarly, the interfacial tensions of pure metal drops are significantly reduced in the presence of plasma.^[3] Results of recent research at the Pennsylvania State University and elsewhere^[4-8] indicate that the gas solubilities in the metals exposed to plasma are significantly higher than the values predicted by Sieverts law^[9] for corresponding gas-metal systems.

In the presence of a plasma, the transformation of ordinary molecular species to excited neutral atoms and ions in the gas phase leads to enhanced solubility of gaseous species in the metal. Oxygen and nitrogen contents as high as 0.7 and 0.2 wt pct, respectively, have been obtained in low-carbon steel welds.^[10] These concentration levels are significantly higher than the values predicted by Sieverts law. Ohno and Uda^[4] and Uda and Ohno^[5] have demonstrated that the concentrations of nitrogen in liquid nickel and iron during arc melting are significantly higher than the corresponding equilibrium solubilities when the metals are exposed to diatomic nitrogen under nonarc-melting conditions. Katz and King^[6] also observed that in the presence of an arc discharge, the concentration of nitrogen in liquid iron was significantly higher than the value predicted by Sieverts law. Bandopadhyay *et al.*^[7] studied plasma-enhanced nitrogen solubility in pure tantalum and niobium at

2243 K. Their data showed a much greater nitrogen solubility in each metal in the presence of plasma than without the plasma. Ouden and Griebeling^[8] found that the solubility of nitrogen in pure iron in the presence of an arc was much greater than that calculated by Sieverts law.

The plasma-enhanced solubility of gases in metals has been attributed to the presence of one or more species present in the gas phase. Bandopadhyay *et al.*^[7] attributed the enhanced nitrogen solubility in tantalum and niobium to the existence of high-energy electrons that produce neutral atoms (N) and ions (N⁺). They identified excited neutral atoms N*, molecules N₂* and ions, N⁺ and N₂⁺, in the helium-nitrogen plasma by optical emission spectroscopy. Lakomsky and Torkhov^[11] attributed plasma-enhanced solubility of nitrogen in metals to excited nitrogen molecules, N₂*. Katz and King^[6] argued that once an excited diatomic molecule is adsorbed on a surface, its vibration is significantly dampened. Therefore, it does not play a special role in enhancing solubility. They postulated that the increased solubility in the presence of plasma results from the presence of monatomic nitrogen, N. Similarly, Gedeon and Eagar^[12] calculated equilibrium hydrogen concentration in the weld metal considering monatomic and diatomic hydrogen in the gas phase.

Although the enhanced species concentrations in the metal are consistent with the presence of monatomic species in the plasma, a general model is needed to calculate the extent of enhancement for a given condition. At present there is no unified theoretical model to understand the partition of nitrogen, oxygen, and hydrogen between a metal and its plasma environment. In this work, a theoretical model has been developed to understand the enhanced solubility of gases in a metal exposed to a plasma. The model has been applied to explain several sets of independent experimental results of plasma-enhanced solubility reported in the literature. The analysis of the data shows that in each set of independent

K. MUNDRA, Postdoctoral Fellow, and T. DEBROY, Professor, are with the Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802.

Manuscript submitted March 25, 1994.

experiments, the enhanced solubility can be explained on the basis of a higher-than-equilibrium concentration (superequilibrium concentration) of atomic gas, G, near the metal surface. In other words, the available data are consistent with the concentration of the atomic species, G, in the plasma that is higher than its concentration at equilibrium with the diatomic gas, G₂, at the temperature of the metal surface. Consideration of this fact and the thermodynamic limit of gas solubility allows an understanding of both the enhanced solubilities and the maximum attainable gas concentrations consistent with the available independent experimental data for various metal/plasma systems.

II. MODEL FRAMEWORK

The dissolution process can be subdivided into the following events: (a) homogeneous dissociation of the diatomic gas, (b) local transport of the resulting mixture to the metal surface, and (c) the dissolution of the gas at the temperature of the metal surface. A schematic representation of the events involved in the dissolution process is presented in Figure 1. Welding is chosen as an example.

A. Dissociation of the Diatomic Gas

The diatomic gas partially dissociates homogeneously to the monatomic gas in the presence of an arc or any other energy source in the gas phase. The extent of dissociation depends primarily on the nature of the power source, the energy dissipated, system geometry, and the nature of the diatomic gas. The calculation of percentage dissociation of diatomic molecules in a plasma with spatially variable properties is complex. Therefore, to quantify the dissociation process, we consider a hypothetical simple equilibrium dissociation reaction at a constant temperature, T_d, which produces the same percentage

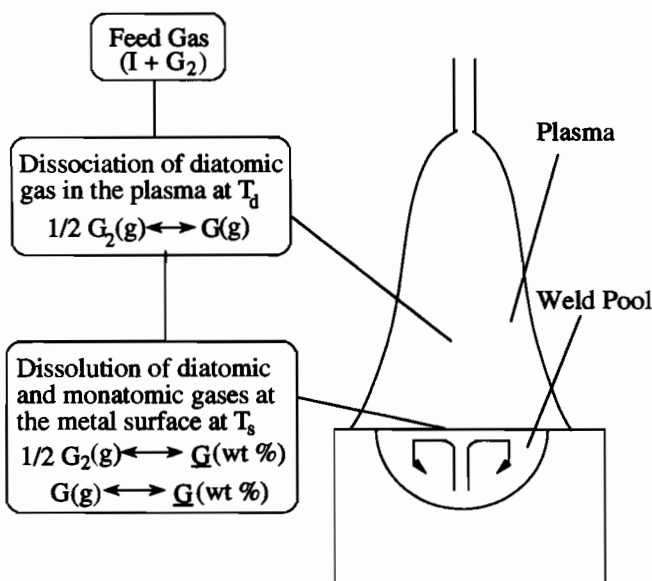


Fig. 1—A schematic diagram showing gas dissolution from plasma in a weld pool.

dissociation as the real process, which may or may not be isothermal. The dissociation of diatomic gas, G₂, can be written as



Since the actual dissociation produces the same extent of dissociation as the equilibrium of Reaction [1] at an effective temperature T_d, we can calculate the extent of dissociation by considering the standard free energy of dissociation, ΔG₁^o|_{T_d}, at this temperature. The relation between the equilibrium partial pressures of gases G₂ and G at T_d is given by

$$p_G = \{p_{G_2}\}^{1/2} e^{-\Delta G_1^\circ|_{T_d}/RT_d} \quad [2]$$

If x pct of the diatomic gas dissociates at an effective temperature T_d, we can write

$$\frac{p_{G_2}}{p_G} = \frac{(100 - x)}{2x} \quad [3]$$

If the inlet gas contains y pct diatomic gas in an inert gas I, and the total pressure in the chamber is P, we have

$$p_I = \frac{(100 - y)P}{(100 + yx/100)} \quad [4]$$

$$p_{G_2} + p_G + p_I = P \quad [5]$$

In Eqs. [2] through [5], we have four unknowns, viz., p_G, p_{G₂}, p_I, and x. Therefore, they can be solved iteratively or graphically to get unique values of these variables for any assumed value of an effective dissociation temperature, T_d.

B. Local Transport of Products

Unlike the dissociation of the diatomic molecules, the recombination of the product atoms in the gas phase is difficult. First, because the extent of dissociation is small, the probability of collision between two atoms of G is much smaller than that between G and G₂ or between G and inert gas I. Second, because the recombination reaction is highly exothermic, it would be necessary to carry the exothermic heat away from the recombined molecule, as in a three-body collision. From a statistical consideration, the probability of a three-body collision is very small. Thus, the homogeneous recombination of the atomic gas G in the gas phase to any significant extent is unlikely. Therefore, it is fair to expect that after the dissociation of the diatomic gas at T_d, no significant change in the partial pressures of diatomic and monatomic gases can occur during the transport of these species toward the metal surface.

C. Surface Reactions

The metal surface temperature, T_s, can be significantly different from the effective dissociation temperature, T_d. Thus, the gases G₂ and G that were at equilibrium at the effective dissociation temperature, T_d, are no longer at equilibrium at T_s. If T_s is significantly lower than T_d, as it is in most cases, the equilibrium partial pressure of G, [p_G]_{T_d}, is significantly higher than the partial pressure of

G at equilibrium with G_2 at temperature T_s . Thus, the actual partial pressure of G in close proximity of the metal surface is at a superequilibrium concentration, *i.e.*, its partial pressure exists at a value that is much higher than the value that would be obtained if G were at equilibrium with G_2 at T_s . The lower limit of the concentration of the dissolved gas, \underline{G}^l , can be obtained by considering the equilibrium between G_2 and the dissolved gas \underline{G} (Sieverts law) as follows:

$$\frac{1}{2} G_2(g) = \underline{G} \text{ (wt pct)} \quad \Delta G_{2|T_s}^0 \quad [6]$$

$$\underline{G}^l \text{ (wt pct)} = [p_{G_2}]^{1/2} e^{-\Delta G_{2|T_s}^0/RT_s} \quad [7]$$

Similarly, the maximum concentration of the dissolved gas in the metal, \underline{G}^m , can be obtained from the consideration of the dissolution of gas, G, in the metal.

$$G(g) = \underline{G} \text{ (wt pct)} \quad \Delta G_{3|T_s}^0 = \Delta G_{2|T_s}^0 - \Delta G_{1|T_s}^0 \quad [8]$$

$$G^m \text{ (wt pct)} = (p_G)_{T_d} e^{-\Delta G_{3|T_s}^0/RT_s} \quad [9]$$

Because the partial pressures of monatomic and diatomic nitrogen, $(p_G)_{T_d}$ and $(p_{G_2})_{T_d}$, respectively, are known from the solutions of Eqs. [2] through [5], the lower and the upper limits of the concentrations, \underline{G}^l and \underline{G}^m , respectively, can be calculated for any value of T_d . The upper limit of the concentration, \underline{G}^m , given by Eq. [9] may not be realized in practice because of either compound formation or gas evolution, as discussed subsequently.

III. THERMODYNAMIC LIMIT OF GAS DISSOLUTION

The thermodynamic limits for the maximum concentration of oxygen or nitrogen in the liquid metal in the presence or absence of plasma are established either by the formation of compounds, such as nitrides in nitrogen-metal systems and oxides in oxygen-metal systems, or by the nucleation of gas bubbles at heterogeneous nucleation sites. In some systems, the formation of compounds may be more favorable than the nucleation of gas bubbles. For example, in the Fe-O system at 1900 K, the maximum amount of dissolved oxygen is about 0.25 wt pct and FeO (l) forms when this limit is exceeded. However, in Fe-N system at 1873 K and 1 atm pressure of N_2 , the maximum solubility of nitrogen is limited to 0.045 wt pct. If the concentration of dissolved nitrogen were to exceed this limit, nitrogen gas would desorb from the melt. Thus, independent of the mechanism of dissolution and the concentration of the monatomic species in the gas phase, the thermodynamic limit of the dissolution would be reached at a certain concentration of the species in the liquid metal. However, in the presence of plasma, this limiting concentration can be reached at a much lower partial pressure of dissolving gas in the feed gas mixture because of the partial dissociation of the dissolving gas.

IV. RESULTS AND DISCUSSION

A. Plasma Species

A schematic diagram of the plasma near the metal surface is presented in Figure 2. The plasma consists of

excited neutral atoms, molecules, and ions. In the plasma, the flux of the highly mobile electrons to the liquid surface is far greater than the flux of the heavier species. As a result, an electrically insulated metal surface becomes negatively charged when exposed to plasma. The adsorption of negatively charged species such as N^- is highly improbable, and they would not contribute to enhanced solubility. Furthermore, positively charged species such as N^+ and N_2^+ will be attracted towards the surface, where they will absorb electrons near the surface and will be converted to N and N_2 . Excited molecules cannot contribute to enhanced solubility because they will lose the excess vibrational energy when adsorbed on metal surfaces.^[6] Thus, the increased solubility likely results from the presence of the monatomic nitrogen in the gas phase.

B. System I: Niobium and Tantalum in Nitrogen-Helium Plasma

Bandopadhyay *et al.*^[7] conducted nitrogen-dissolution experiments with two different metals under identical conditions. In these experiments, high-purity tantalum and niobium samples maintained at 2243 K were separately exposed to a well-characterized helium and nitrogen containing glow-discharge plasma, and the amounts of nitrogen in the metals were determined as a function of time.

To analyze their data, we combine Eqs. [2] through

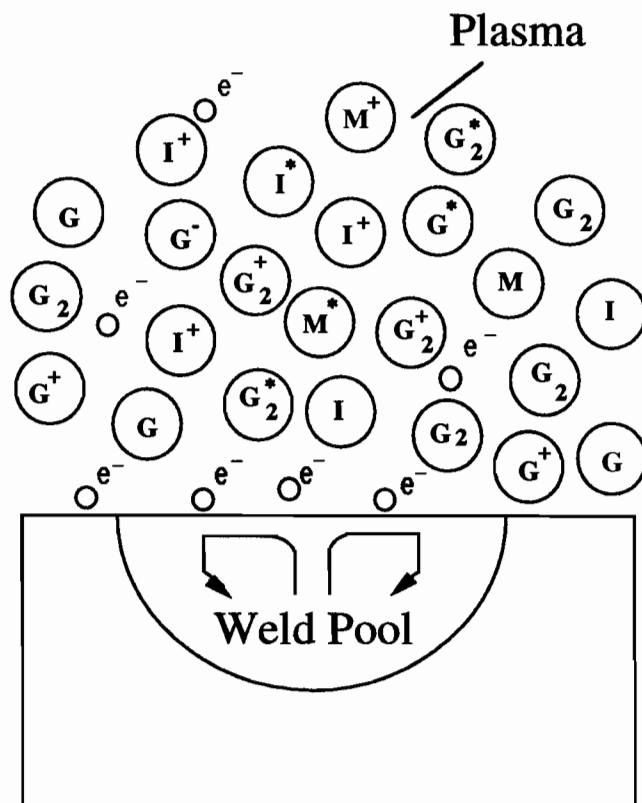


Fig. 2—A schematic diagram of the gaseous species near a metal surface exposed to plasma. The plasma consists of electrons (e^-), neutral atoms (G, I, M) and molecules (G_2), excited atoms (I^* , G^* , M^*) and molecules (G_2^*), and ions (G^- , G^+ , G_2^+ , I^+).

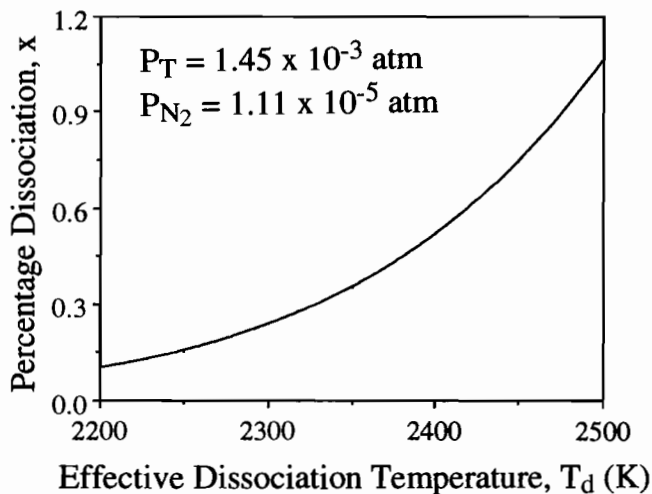


Fig. 3—Plot of effective dissociation temperature vs percent nitrogen dissociated for the experimental conditions of Bandopadhyay *et al.*^[7]

[5] to have a relationship between the percentage dissociation, x , and an effective dissociation temperature, T_d .

$$\left\{ \frac{z(100-x)}{2x} \right\}^2 + z^2 \frac{(100-x)}{2x} + \frac{(100-y)P}{(100+yx/100)} = P \quad [10]$$

where $z = e^{(\Delta G_1^\circ|_{T_d}/RT_d)}$, y is the percent of diatomic gas in the inert gas, x is the percentage of the diatomic gas that dissociates at T_d , P is the total pressure in the reaction chamber, and $\Delta G_1^\circ|_{T_d}$ is the standard free energy for the dissociation of the diatomic gas at T_d .

For the experimental conditions of Bandopadhyay *et al.*^[7] the computed values of percentage dissociation,

x , obtained from Eq. [10] is plotted as a function of an effective dissociation temperature, T_d , in Figure 3. The free energy data required for the calculations are given in Table I. It can be observed from the figure that as an effective dissociation temperature in the plasma increases, the percentage dissociation also increases. The computed nitrogen solubilities in the tantalum sample due to diatomic and monatomic nitrogen obtained from Eqs. [7] and [9] are plotted in Figure 4(a) for various effective dissociation temperatures. The experimental result of Bandopadhyay *et al.*^[7] for tantalum is also superimposed on the graph. From the perusal of the data, we can make two important conclusions. First, the solubility resulting from diatomic species is significantly lower than the experimentally observed solubility. Second, an effective dissociation temperature of approximately 2390 K can explain the observed nitrogen concentration in tantalum. The conditions in the experiments of Bandopadhyay *et al.*^[7] were such that the metal samples did not affect the properties of the plasma. Because both niobium and tantalum do not vaporize to any appreciable extent at the reaction temperature, the plasma properties did not change with the change in the nature of the metal samples. Because the effective dissociation temperature represents an important character of the plasma, it should not change when the tantalum sample is changed to niobium in the chamber containing plasma. Thus, for the hypothesis that the enhanced solubility results from the presence of monatomic nitrogen to be correct, the experimental solubility data for niobium should be consistent with an effective dissociation temperature of 2390 K. The solubility vs effective dissociation temperature for niobium sample is given in Figure 4(b). Also superimposed on the graph is the result of Bandopadhyay *et al.*^[7] The effective dissociation temperature for the tantalum-nitrogen sample was also found to be 2390 K. Thus, the concentration of nitrogen in both tantalum and niobium exposed to helium-nitrogen

Table I. Free Energy Temperature Relationships Used for the Calculations*

Metal/Gas	Reaction	Free Energy Temperature Relationship	Reference Number
	$\frac{1}{2} \text{N}_2 (\text{g}) = \text{N} (\text{g})$	$86,596.0 - 15.659 T$	17
	$\frac{1}{2} \text{O}_2 (\text{g}) = \text{O} (\text{g})$	$60,064 - 15.735 T$	17
Tantalum/Nitrogen	$\frac{1}{2} \text{N}_2 (\text{g}) = \underline{\text{N}} (\text{wt pct})$	$-43,483.5 + 10.394 T$	18
	$\text{N} (\text{g}) = \underline{\text{N}} (\text{wt pct})$	$-130,079.5 + 26.053 T$	
Niobium/Nitrogen	$\frac{1}{2} \text{N}_2 (\text{g}) = \underline{\text{N}} (\text{wt pct})$	$-42,512.6 + 11.357 T$	18
	$\text{N} (\text{g}) = \underline{\text{N}} (\text{wt pct})$	$-129,108.6 + 27.016 T$	
Liquid Iron/Nitrogen	$\frac{1}{2} \text{N}_2 (\text{g}) = \underline{\text{N}} (\text{wt pct})$	$860.0 + 5.71 T$	19
	$\text{N} (\text{g}) = \underline{\text{N}} (\text{wt pct})$	$-85,736.0 + 21.405 T$	
Silver/Oxygen	$\frac{1}{2} \text{O}_2 (\text{g}) = \underline{\text{O}} (\text{wt pct})$	$11,850.8 + 5.339 T$	20
	$\text{O} (\text{g}) = \underline{\text{O}} (\text{wt pct})$	$-48,213.1 + 21.074 T$	

*Free energy data are in cal/g mole.

plasma is consistent with an effective dissociation temperature of 2390 K. Furthermore, a unique effective dissociation temperature which represents the extent of dissociation of diatomic nitrogen can explain the plasma-enhanced solubility in the experiments of Bandopadhyay *et al.*^[7] for experiments with both niobium and tantalum.

C. System 2: Iron in Nitrogen-Argon Plasma at Different Nitrogen Pressures

The model was also tested against the experimental observations of Ouden and Griebing.^[8] They exposed high-purity iron drops to mixtures of nitrogen and argon in the presence of an arc. The nitrogen content in the

gas mixture was varied from 0 to 25 pct. The total pressure in the chamber was maintained at 1 atm and the samples were kept at 1873 K. The experimental results are presented in Figure 5. It is observed that for a nitrogen partial pressure of 0.01 atm, the solubility of nitrogen in the iron drop is 0.021 wt pct. It can be observed from the equilibrium solubility vs effective dissociation temperature curve, presented in Figure 6, that an effective dissociation temperature close to 2010 K is required

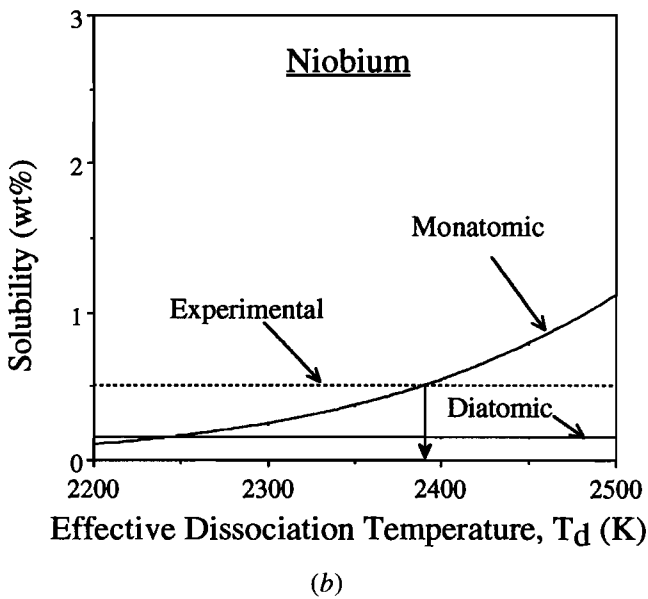
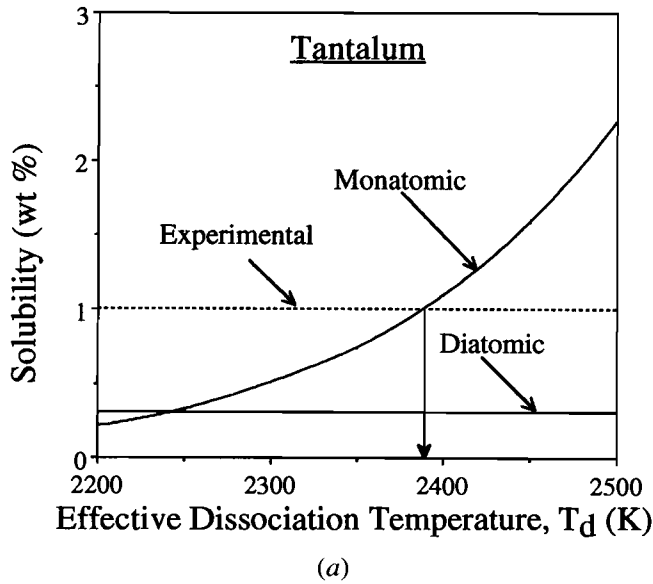


Fig. 4—Computed solubility of nitrogen exposed to diatomic and monatomic nitrogen as a function of effective dissociation temperature in (a) tantalum and (b) niobium for the experimental conditions of Bandopadhyay *et al.*^[7] The observed experimental solubilities are also presented. Total pressure: 1.45×10^{-3} ; partial pressure of nitrogen (N_2): 1.11×10^{-3} ; sample temperature: 2243 K.

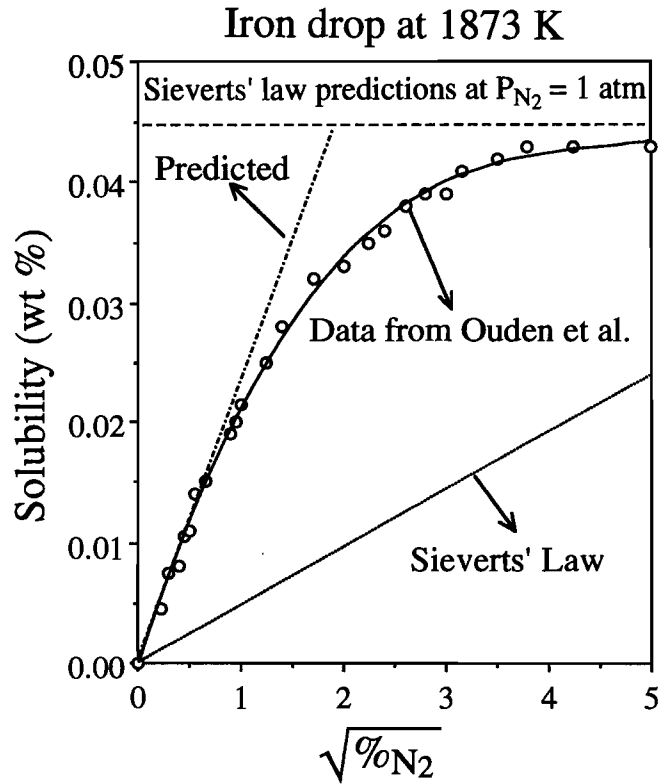


Fig. 5—Experimental results of nitrogen solubility in iron for the experimental conditions of Ouden and Griebing.^[8] Nitrogen solubility predictions based on Sieverts law are also presented. The solubility predicted at low partial pressures of nitrogen assuming an effective dissociation temperature of 2010 K is superimposed.

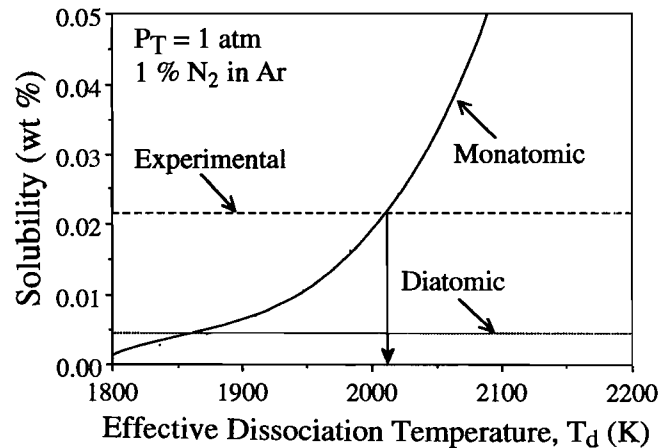


Fig. 6—Plot of solubility vs effective dissociation temperature for the experimental conditions of Ouden and Griebing.^[8]

to attain a solubility of 0.021 wt pct under the conditions of the experiments. If we assume that the effective dissociation temperature does not change significantly with the change in the composition of the gas, we can plot the solubility vs percentage nitrogen for an effective dissociation temperature of 2010 K. The results are superimposed on the experimental observations in Figure 5. It is observed that at a low partial pressure of nitrogen, the predictions are in good agreement with the experimental observations. The deviations at higher nitrogen pressures can be attributed to the fact that the assumed effective dissociation temperature of 2010 K may not be valid in the entire pressure range. Also, as the nitrogen content in the melt increases, there is a possibility of off-gassing in the vapor phase at the surface of the metal. As a consequence, some nitrogen will diffuse away from the metal into the plasma. Furthermore, Ouden and Griebing^[8] observed gas-bubble formation beyond a nitrogen content of 16 pct in the nitrogen-argon feed gas mixture, and no further increase in solubility was noticed. It will be explained subsequently that the concentration of nitrogen in iron can be limited by bubble formation resulting from the desorption of the dissolved nitrogen. In the experiments of Ouden and Griebing,^[8] the equilibrium partial pressure of diatomic nitrogen exceeds the total pressure when the nitrogen concentration in iron reaches about 0.045 wt pct as shown in Figure 5.

The solubility data of Ouden and Griebing^[8] at low pressures indicates that nitrogen dissolution is proportional to the square root of partial pressure of nitrogen. This behavior is similar to that predicted by Sieverts law. Based on the solubility relationship, it was concluded in previous works^[13,14] that nitrogen dissolution in plasma obeys Sieverts law. However, in some cases, the presence of monatomic nitrogen in the plasma can also exhibit a concentration vs partial pressure relationship similar to Sieverts law. Substituting for p_G from equation (2) in equation (9), we have

$$\underline{G}^m(\text{wt pct}) = [p_{G_2}]^{1/2} e^{-(\Delta G_{1/2}^0/RT_s + \Delta G_{3/2}^0/RT_s)} \quad [11]$$

$$\text{or } \underline{G}^m(\text{wt pct}) = K_{en} [p_{G_2}]^{1/2} \quad [12]$$

where K_{en} is the enhanced equilibrium constant and is given by

$$K_{en} = e^{-(\Delta G_{1/2}^0/RT_s + \Delta G_{3/2}^0/RT_s)} \quad [13]$$

When an effective dissociation temperature is unaffected by the changes in the partial pressure of the diatomic gas. Eq. [12] shows that the solubility resulting from monatomic nitrogen is proportional to the square root of partial pressure of molecular nitrogen. However, the proportionality constant is enhanced because of the presence of monatomic nitrogen.

D. System 3: Large Scale Experiments with Iron Exposed to Nitrogen-Argon Plasma

Katz and King^[6] exposed large quantities of liquid iron to nitrogen-argon plasma. Although spatial variation in the plasma properties is expected in large scale system, an interesting observation can be made from the results. The data of Katz and King^[6] are presented in Figure 7. The results show that the nitrogen concentration in iron

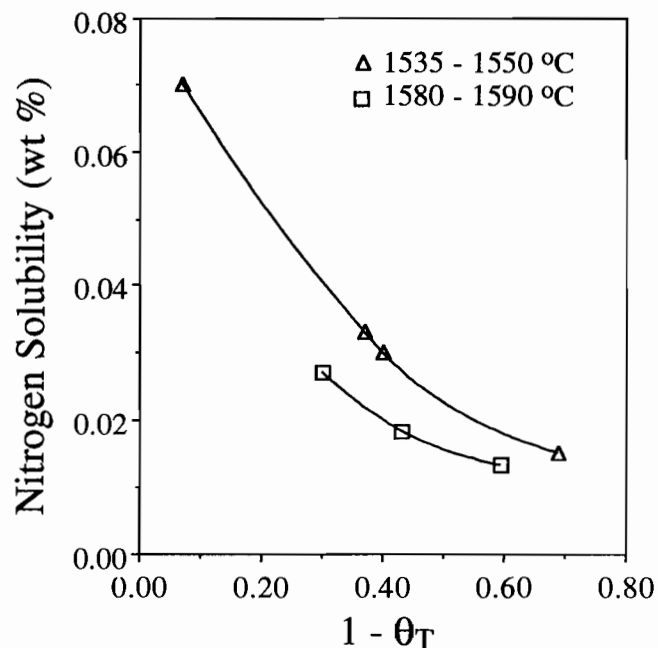


Fig. 7—Steady-state nitrogen content vs surface availability at two different temperatures for ARMCO iron.^[6] Experiments were conducted with argon-5 pct N₂ plasma. The symbol θ_s is the measure of the fraction of total sites occupied by surface active elements such as oxygen and sulfur.

increased with a decrease in the temperature of the liquid iron for the same fraction of total sites occupied by the surface active elements. This is in contrast to the behavior predicted by Sieverts law, which predicts an increase in the solubility of nitrogen with temperature for iron. The calculated equilibrium solubility of nitrogen as a function of partial pressure and temperature for diatomic and monatomic species are presented in Figures 8 and 9, respectively. The free energy data used for the calculations are given in Table I. It can be observed from Figure 8 that at a given partial pressure of diatomic nitrogen in the gas phase, the equilibrium nitrogen concentration increases slightly with temperature. Thus, the variation of nitrogen concentration with substrate temperature observed by Katz and King^[6] cannot be explained by the equilibrium calculations involving diatomic nitrogen in the gas phase. In the experiments of Katz and King,^[6] the effective dissociation temperature, and therefore the partial pressure of monatomic nitrogen in the plasma, would be constant for different experiments because the plasma is generated under identical conditions. The results in Figure 9 shows that for the same partial pressure of the monatomic nitrogen in the gas, the solubility increases with a decrease in temperature for a given fraction of surface sites occupied by the surface active elements. This trend is consistent with the variation of equilibrium concentration of nitrogen with temperature in the presence of monatomic nitrogen, presented in Figure 9. If the data are extrapolated to nitrogen absorption on clean surfaces, *i.e.*, at $\theta_T = 0$, the nitrogen concentration in the experiments of Katz and King^[6] can be explained by effective dissociation temperatures of approximately 2000 and 1990 K for the experiments conducted at 1813 and 1853 K, respectively.

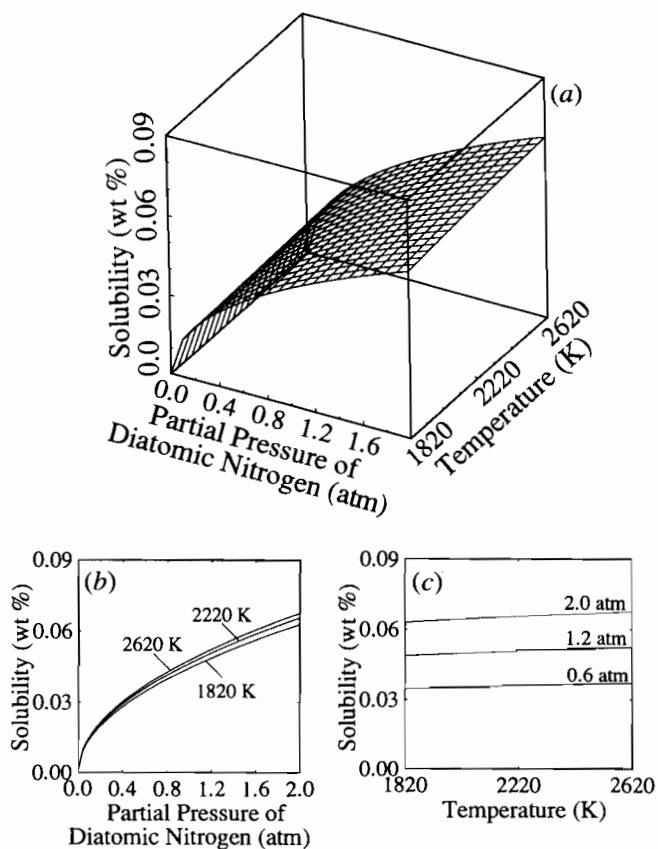


Fig. 8—Equilibrium solubility of nitrogen in iron exposed to diatomic nitrogen. The computed values are shown (a) as a function of temperature and partial pressure of diatomic nitrogen, (b) as a function of partial pressure of diatomic nitrogen for three different temperatures, and (c) as a function of temperature for three different partial pressures of diatomic nitrogen. Figures (b) and (c) are presented for improved clarity.

E. System 4: Silver in Oxygen Plasma

Madey and DebRoy^[15] conducted oxygen dissolution experiments in silver. They exposed high-purity silver samples to an oxygen plasma generated using a microwave power source. The silver samples were heated to 923 K and the total pressure in the chamber was maintained close to 0.004 atm. The experimental solubility was observed to be close to 4.5×10^{-3} wt pct. For the experimental conditions of Madey and DebRoy,^[15] Sieverts law predicts a solubility of 6.7×10^{-6} wt pct based on the free energy data presented in Table I. Thus, the solubility predicted by Sieverts law is significantly less than the experimental solubility. However, the enhanced solubility can be explained using an effective dissociation temperature of 1153 K in the model.

F. Significance of Dissociation Temperature

The experimental observations of Bandopadhyay *et al.*^[7] of enhanced solubility in tantalum and niobium maintained at 2243 K could be explained on the basis of an effective dissociation temperature of 2390 K. Likewise, the experimental observations of Ouden and Griebing^[8] of enhanced solubility in iron maintained at 1873 K could be explained on the basis of an effective

dissociation temperature of 2010 K. The enhanced solubility in silver at 923 K in oxygen plasma in the experiments of Madey and DebRoy^[15] can be explained using an effective dissociation temperature of 1153 K. In the experiments of Katz and King,^[6] there is variation in the surface coverage of iron by the surface active elements, spatial variation of plasma properties, and substrate temperature. Therefore, a unique effective dissociation temperature cannot explain the enhanced solubility. However, the data can be explained by taking an effective dissociation temperature 100 to 200 K higher than the substrate temperature. Thus, in all these experiments, the enhanced dissolution could be explained on the basis of an effective dissociation temperature that was higher than the substrate temperature by 100 to 300 K.

Geddon and Eagar^[12] postulated that in arc welding, hydrogen will dissociate at a reaction temperature governed by the temperature of the cathode boundary layer. Thus, the percentage dissociation of the diatomic gas in the cathode boundary layer will depend on many factors, such as the diatomic gas present in the system, partial pressures of the individual gases, total pressure, the arc voltage, and the arc current. Furthermore, the residence time of the gaseous species in the plasma, determined by the gas flow rate, would also be important. Determination of the effect of an individual parameter on the percentage dissociation is difficult. However, the analysis of the various results show that the enhanced solubility can be explained in many cases by choosing an effective dissociation temperature 100 to 300 K higher than the substrate temperature.

G. Gas Bubble Formation

During weld solidification, the formation of gas bubbles and pin holes is a common occurrence. Ouden and Griebing^[8] observed the formation of gas bubbles in their experiments with iron drops exposed to nitrogen-argon plasma when the solubility of nitrogen in iron was close to 0.043 wt pct. Similarly, Ohno and Uda^[4] observed the formation of bubbles in nickel during their arc-welding experiments. Similar observations were made by Uda and Ohno^[5] in their arc-melting experiments with iron. In all these experiments carried out at 1 atm total pressure, the solubility of nitrogen did not increase with increasing nitrogen partial pressure in the gas mixture once the bubble formation began. The bubble formation was observed when the species concentration was close to the concentration predicted by Sieverts law for a hypothetical diatomic nitrogen pressure of 1 atm. However, the equilibrium concentrations of nitrogen in the metal predicted by Sieverts law utilizing the actual partial pressures of diatomic nitrogen were much below the experimentally observed concentrations. The presence of monatomic nitrogen in the plasma enhances the dissolution, and concentrations close to Sieverts law predictions for 1 atm pressure of nitrogen are reached at partial pressures of nitrogen much lower than 1 atm. Once the Sieverts law solubility for a nitrogen pressure of 1 atm is reached, the following reaction in the liquid metal becomes important:



V. SUMMARY AND CONCLUSIONS

A theoretical model was developed to gain a better understanding of the principles of enhanced dissolution of oxygen and nitrogen in the weld metal from its plasma environment. In the presence of plasma, the concentration of the dissolved gaseous species in liquid metal can be higher than the value predicted by the Sieverts law. The model coupled with data from several independent experimental investigations showed that the enhanced solubility of gases in the weld metal results from higher-than-equilibrium (superequilibrium) concentration of atomic species near the weld surface. The super-equilibrium concentration was calculated on the basis of an effective dissociation temperature, which is determined by the factors that affect the percentage dissociation of the diatomic gas in the plasma. The effective dissociation temperature was calculated to be 100 to 300 K higher than the substrate temperature for each of the plasma-metal systems analyzed here. The nucleation of gas bubbles or the formation of compounds (oxides or nitrides) limits the concentration of the dissolved gas in the metal in contact with a plasma.

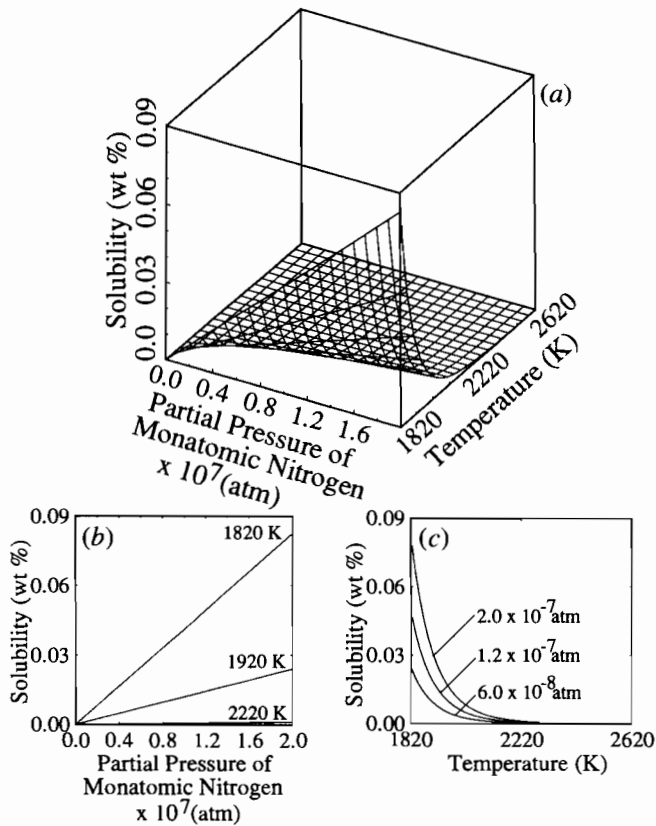


Fig. 9—Equilibrium solubility of nitrogen in iron exposed to monatomic nitrogen. The computed values are shown (a) as a function of temperature and partial pressure of monatomic nitrogen, (b) as a function of partial pressure of monatomic nitrogen for three different temperatures, and (c) as a function of temperature for three different partial pressures of monatomic nitrogen. Figures (b) and (c) are presented for improved clarity.

Desorption of nitrogen can occur by heterogeneous nucleation of nitrogen bubbles at various sites. Once the pressure in the bubbles exceeds the ambient pressure, they can be expelled out. This behavior limits the nitrogen solubility in metals exposed to plasmas when nitride formation is not favored.

H. Compound Formation

The extent of dissolution can also be limited by the formation of compounds such as oxides in some cases. For example, in the iron-oxygen system the maximum solubility is governed by the formation of FeO (l). Kuwana and Sato^[16] conducted welding experiments with pure iron in a controlled argon-oxygen atmosphere. They observed that oxygen dissolution increases with the increase in the partial pressure of oxygen in the feed gas. However, once the oxygen concentration reached close to 0.26 wt pct oxygen, there was no further increase in the dissolved oxygen concentration because of the formation of FeO (l). The temperature of the molten pool was measured to be about 1910 K. Thus, the presence of plasma may promote the kinetics of oxygen dissolution, but the amount of dissolved oxygen into liquid iron is limited by the formation of FeO (l).

ACKNOWLEDGMENT

This work was supported by the United States Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, under Grant No. DE-FG02-84ER45158.

REFERENCES

1. P. Sahoo, M.M. Collur, and T. DebRoy: *Metall. Trans. B*, 1988, vol. 19B, pp. 967-72.
2. P. Sahoo and T. DebRoy: *Mater. Lett.*, 1988, vol. 6, pp. 406-08.
3. P. Sahoo and T. DebRoy: *Metall. Trans. B*, 1987, vol. 18B, pp. 597-601.
4. S. Ohno and M. Uda: *Trans. Nat. Res. Inst. Met.*, 1981, vol. 23 (4), pp. 243-48.
5. M. Uda and S. Ohno: *Trans. Nat. Res. Inst. Met.*, 1978, vol. 20 (6), pp. 358-65.
6. J.D. Katz and T.B. King: *Metall. Trans. B*, 1989, vol. 20B, pp. 175-85.
7. A. Bandopadhyay, A. Banerjee, and T. DebRoy: *Metall. Trans. B*, 1992, vol. 23B, pp. 207-14.
8. G. Den Ouden and O. Griebeling: *Recent Trends in Welding Science and Technology*, S.A. David and J.M. Vitek, eds., ASM INTERNATIONAL, Metals Park, OH, 1990, pp. 431-35.
9. R.D. Pehlke: *Unit Processes in Extractive Metallurgy*, Elsevier, New York, NY, 1979, p. 141.
10. S. Kou: *Welding Metallurgy*, John Wiley and Sons, New York, NY, 1987, p. 61.
11. V.I. Lakomsky and G.F. Torkhov: *Sov. Phys.*, 1969, vol. 13, p. 1159.
12. S.A. Gedeon and T.W. Eagar: *Weld. J.*, 1990, vol. 69, pp. 264s-271s.
13. *The Physics of Welding*, International Institute of Welding, J.F. Lancaster, ed., Pergamon Press, Oxford, United Kingdom, 1986, p. 181.
14. IIW Doc. No. II-1051085, AWS A.4.4-86, 1986.
15. D. Madey and T. DebRoy: Pennsylvania State University, University Park, PA, unpublished research, 1994.
16. T. Kuwana and Y. Sato: *Trans. Jpn. Weld. Soc.*, 1988, vol. 19 (2), pp. 135-42.

17. J.F. Elliott and M. Gleiser: *Thermochemistry for Steelmaking I*, Addison-Wesley Publishing Co., Reading, MA, 1963, p. 75.
18. E. Fromm and H. Jehn: *Metall. Trans.*, 1972, vol. 3, pp. 1685-92.
19. R. Pehlke and J.F. Elliott: *TMS-AIME*, 1960, vol. 218, p. 1088.
20. E. Fromm, H. Speck, W. Hehn, H. Jehn, and G. Hörz: *Physics Data: Gases and Carbon in Metals, Part XXII: Group IB Metals(2)*. Max-Planck Insitut für Metallforschung, Institut für Werkstoffwissenschaften, Stuttgart, Germany, 1982, p. 8.