Removal of Lead from Fe–Pb Mixtures by Evaporation in Stagnant Argon at 1 448 K and the Determination of the Lead Vapor-Argon Interdiffusivity

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Lead, considered as a tramp element in steel, was successfully removed from a 50 % Fe–50 % Pb mixture by evaporation in argon at 1 448 K. The progress of the removal shows that it takes 5 h to completely remove the lead from the mixture, the nonvolatile iron (solid) being left behind in the crucible (alumina). Results point toward a diffusion-controlled evaporation, and the system, which closely simulates Stefan’s tube for studying evaporation of a liquid through a stagnant gas film, allowed the measurement of the interdiffusivity of lead and argon \( D_{\text{Pb–Ar}} \). Since this study dealt with a pseudosteady state diffusion, rather than the steady state one for which the diffusion flux equation is well established, the required pseudosteady state equation was first developed, and, subsequently, utilized with the help of the rate data to find the \( D_{\text{Pb–Ar}} \) at 1 448 K. The measured value, which is \( 1.766(\pm 0.378) \text{ cm}^2/\text{s} \), compares very well with the estimated value of \( 1.774 \text{ cm}^2/\text{s} \).

KEY WORDS: tramp element; lead; iron; evaporation; pseudosteady state diffusion; Stefan’s tube; \( D_{\text{Pb–Ar}} \).

1. Introduction

Lead is often added to steel in manufacturing operations for the special purpose of improving the machinability of steel. However, steel scrap containing this element cannot be recycled to conventional steelmaking processes since it cannot be selectively oxidized from iron. This so-called tramp element causes embrittlement to the steel. The removal of the element from steel scrap is thus an important step toward producing steel with good mechanical properties for general applications. Not many studies of removal of lead from iron have been made so far. Nakamura et al.\(^1\) reported a considerable removal of lead, from an initial value of 152 ppm to the final one of 35 ppm, from a liquid 18Cr–8Ni–Fe alloy by Ca dissolved in CaF\(_2\) melt in an electroslag refining process. It was noticed from some trial experiments, in the present work, carried out at 1 448 K in capped alumina crucibles containing a mixture of iron and lead (forming the metal phase) and calcium and calcium chloride (forming the slag phase) that some lead particles stuck to the inner surface of the crucible lid. This suggested a strong vaporization tendency of lead which could be utilized to remove it from iron by evaporation, without having to use a slag phase. Accordingly, the main objective of the present work was to develop a simple method of removing lead from an iron-lead mixture by evaporation.

The determination of interdiffusivities of different metal vapors and argon is very important. These data may be utilized in the determination of activities of metals in alloys by the transportation technique in which argon is used as a carrier gas. Thus, another objective of the present work was to make a kinetic analysis of the rate data on the removal of lead and to find the interdiffusivity \( D_{\text{Pb–Ar}} \).

2. Experimental Procedure

The experimental arrangement is shown in Fig. 1. Experiments were carried out in uncapped alumina crucibles (12 mm diameter × 25 mm height, 99.8 % Al\(_2\)O\(_3\), Coors Porcelain Co., Golden, CO) using a mixture of iron powder (−325 mesh) and lead powder (−200 mesh), 0.3 g each, of 99.5 % purity, Alpha Products (Chicago, IL), at 1 448 K. The crucible, containing the charge material that had been thoroughly mixed with a steel spatula, was first weighed in

![Fig. 1. Schematic diagram of the experimental set up.](image-url)
a balance (precision, 0.1 mg) and then placed on an alumina pedestal and raised to the 7-cm long uniform temperature zone of a MoSi$_2$ electric resistance furnace (Applied Test Systems, Inc., Butler, PA), which was already set at the desired temperature (1448 K). The furnace, consisting of an alumina furnace tube, was 53-cm long, with a 5-cm inner diameter and 36-cm outer diameter. The temperature of the crucible was measured (accuracy, ±2 K) by a Pt–Pt–10%Rh thermocouple running through the alumina tube of the pedestal and touching the uppermost part of the pedestal on which the crucible was placed. The evaporation was allowed to take place in an argon atmosphere for the desired duration. The argon was freed from the moisture, carbon dioxide, and oxygen before it was passed through the furnace at a flow rate of 365 cc (STP)/min to keep the metal from oxidizing.

The removal of lead was studied as a function of time only. Five values for the time were considered: 1, 2, 3, 4, and 5 h. As the iron did not evaporate, which was confirmed by analysis with an Atomic Absorption Spectrophotometer, the decrease in the mass of the crucible after the experiment gave a direct measure of the mass of lead removed. The metal was obtained largely as a single whole piece, with no visible separation of the metallic iron and lead on or within it and with no sign of loose iron powder sticking to its top or bottom surface. This indicates that during the run the iron powder was dispersed in the bulk of the liquid lead (it may help to note that, according to the Fe–Pb phase diagram, the coexisting phases are solid iron and liquid lead at 1448 K) and did not accumulate on the liquid surface, causing thereby no hindrance to the evaporation of lead. However, it is to be noted that toward the end of a run of long duration when the lead-content of the mixture was significantly reduced, the consideration of the dispersion of iron powder in liquid lead might have been violated. Since this period constitutes a small fraction of the total evaporation time, its effect on the overall evaporation kinetics should be minimal. Moreover, as will be shown later, the experimental result of the longest run (5 h) has not been considered for kinetic interpretation on the ground of kinetic hindrance to the free evaporation of the liquid lead. A couple of very small globular metal pieces were also found whose mass varied from 0.1 to 2.7% of the total mass of the metal obtained, increasing with the decreasing degree of removal of lead. The metal pieces were all dissolved in 1 : 1 nitric acid by heating and analyzed for lead and iron by an Atomic Absorption Spectrophotometer (PerkinElmer 3030, PerkinElmer, Waltham, MA) using the standard solutions (Fisher Scientific, Pittsburgh, PA), to cross-check the extent of the lead removed as obtained from the decrease in the mass of the crucible. The difference in the two results was confined within 3–3.5%, in the majority of cases.

3. Results and Discussion

The results of the experiments are shown in Table 1, in which the degree of removal of lead, defined as the percent of the initial mass of lead that has been removed by evaporation, is reported on the basis of the change of the mass of the crucible.

Using the results of Table 1, the degree of removal of lead is plotted as a function of time in Fig. 2. Lead was almost completely removed in 5 h. In order to analyze the kinetic data of Table 1, a generalized rate equation for the pseudosteady state diffusion taking place under the experimental conditions is derived next; the moving gas–liquid interface, caused by the continuous descent of the liquid level, resulted in the pseudosteady state diffusion. Notably, the derivation of the steady state diffusion flux of A through a stagnant gas film of B is well documented in text books. The main distinguishing feature between the steady state and the pseudosteady state diffusion is that in the former the gas–liquid interface is kept fixed by maintaining the liquid level at the initial height by a special device and in the latter the interface keeps moving with the descending liquid.

3.1. Derivation of the Pseudosteady State Diffusion Equation

In Fig. 3 is shown a simplified sketch of the pseudosteady state diffusion that takes place during the evaporation.
tion of liquid A, contained in a tube (Stefan’s tube) with the initial level at $Z=Z_i$ and the level continuously going down, through a stagnant film of gas B at constant temperature and pressure. Gas B is nonreactive to liquid A and slowly flows over the tube horizontally at $Z=Z_f$. In the present study, the system A–B is replaced by Pb–Ar and the horizontal flow of B over the tube was, as a necessary part of the experimental design, replaced by the vertical flow of argon along the tube (alumina crucible), which, however, possibly took a horizontal bend around the top of the crucible due to turbulence and mixing, as shown in Fig. 1. Presumably, this had ensured the stagnation of argon within the crucible and established the same composition as the input gas (100 mol% argon, in the present case) at the top of the crucible due to turbulence and mixing, as shown in Fig. 1. Presumably, this had ensured the stagnation of argon within the crucible and established the same composition as the input gas (100 mol% argon, in the present case) at the top of the crucible ($Z=Z_f$) by flushing away the lead vapor coming from the inside of the tube, as in the case of steady state diffusion.3,4)

A few words may be said here, for the purpose of clarification, about pseudosteady-state diffusion, which is somewhere between the steady-state and the unsteady-state diffusion. Pseudosteady-state diffusion shows commonness with the steady-state diffusion with respect to the concentration accumulation term $(\partial C/\partial t)$ being zero in the shell mass balance equation for the species $i$, while both it and the unsteady-state diffusion result in an unsteady concentration profile $(\partial C/\partial Z$ being a function of time $t)$. In an unsteady-state process a nonzero accumulation term leads to the unsteady profile, while in a pseudosteady-state process the interfacial reaction (vaporization, chemical reactions, etc.) causes the movement of the interface, resulting in a continuously changing concentration profile.

A mass balance over an incremental column height $\Delta Z$ states that at pseudosteady state

$$(SN_{Az})_Z{(SN_{Az})}_Z = (\partial C_i/\partial t)S\Delta Z = 0 ............(1)$$

in which $N_{Az}$ is the flux of A in the Z-direction relative to stationary coordinates and $S$ is the cross-sectional area of the column. Division by $\Delta Z$ and taking the limit as $\Delta Z$ approaches zero gives

$$-\frac{dN_{Az}}{dZ} = 0 ..................(2)$$

Now, the relation between the two fluxes $N_{Az}$ (relative to stationary coordinates) and $J_{Az}^*$ (relative to molar average velocity $V^*_A$ of the mixture), in terms of the mole fraction $X_A$ and the flux $N_{Bz}$ is

$$N_{Az} = J_{Az}^* + X_A(N_{Az} + N_{Bz}) ..................(3)$$

Inserting into Eq. (3), the expressions for $J_{Az}^*$, obtained from Fick’s first law of diffusion as $-CD_{AB}dX_A/dZ$ (where $D_{AB}$ is the interdiffusion coefficient of A–B), and $N_{Bz}$, which is given by $N_{Bz} = C_B V_{Bz} = 0$, because of stagnant B (i.e., $V_{Bz} = 0$), we have

$$N_{Az} = -\frac{CD_{AB}dX_A/dZ}{1 - X_A} ..................(4)$$

On rearrangement,

$$N_{Az}dZ = -\frac{CD_{AB}dX_A}{1 - X_A} ..................(5)$$

Integration of Eq. (5) between the limits $Z_1$ (a variable, typical of pseudosteady state diffusion) and $Z_2$ on the left-hand side and the corresponding limits $X_{A1}(=1-X_{B1})$, the equilibrium concentration (mole fraction) of A at the liquid–gas interface (where chemical equilibrium is assumed to prevail since the evaporation is considered diffusion controlled), and $X_{A2}(=1-X_{B2})$, the arbitrarily fixed concentration (mole fraction) of A in the flowing gas at the top of the tube, on the right-hand side, along with the considerations that $N_{Az}$ is independent of $Z$ (from Eq. (2)), that the total concentration $C$ is a constant at constant temperature and pressure, and that the interdiffusivity $D_{AB}$ is very nearly independent of concentration (for a low density of the gas mixture A–B), gives

$$N_{Az} = \frac{CD_{AB}}{Z_2 - Z_1} \ln \frac{X_{B2}}{X_{B1}} ..................(6)$$

At any instant, the molar rate of evaporation of liquid A, $-dn_A/dt$, equals the molar rate of diffusion, $W_{Az}$, at the liquid–gas interface:

$$-\frac{dn_A}{dt} = -\frac{d(S \cdot Z_i \cdot \rho_{mA})}{dt} = W_{Az} = N_{Az} \cdot S = \left(\frac{CD_{AB}}{Z_2 - Z_1} \ln \frac{X_{B2}}{X_{B1}} \right) S ....(7)$$

where $\rho_{mA}$ is the molar density of A. By separation of variables and using the integration limits of $i=0$ and $i=t$, and the corresponding limits of $Z_i = Z_i^0$ and $Z_i = Z_i^t$, we obtain, after cancellation and rearrangement of terms,

$$-\int_{Z_i^0}^{Z_i^t} (Z_2 - Z_i) dZ_i = \frac{CD_{AB}}{\rho_{mA}} \ln \frac{X_{B2}}{X_{B1}} \int_0^t dt .......(8)$$

which, after the integrations, gives

$$Z_2(Z_i^0 - Z_i^t) - \frac{1}{2}(Z_i^t)^2 - (Z_i^0)^2 = \frac{CD_{AB}}{\rho_{mA}} \left( \ln \frac{X_{B2}}{X_{B1}} \right) t$$

$$.............(9)$$

i.e.,

$$\left(\frac{Z_i^0 - Z_i^t}{Z_2 - \frac{1}{2}Z_i^0 - \frac{1}{2}Z_i^t}\right) = \frac{CD_{AB}}{\rho_{mA}} \left( \ln \frac{X_{B2}}{X_{B1}} \right) t$$

$$.............(10)$$

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Equation (10) is the required pseudosteady state diffusion equation, which gives the progress of the descent of the liquid level. This equation will next be used to confirm the diffusion-controlled mechanism of the evaporation of liquid lead and to find the diffusivity $D_{\text{Pb–Ar}}$ accurately.

It may be noted that the traditional steady state equation (which is actually Eq. (6), with $Z_1$ being a time-independent constant) cannot be utilized to determine the diffusivity $D_{\text{AB}}$ without a loss of accuracy as it requires either the maintenance of the liquid level at $Z=Z_1$ by some external device, which is difficult to achieve, or the ignoring of the descent of the liquid level.

It may be further noted in passing that Eq. (10), in addition, solves one interesting practical question, which is: how long does it take to empty a given amount of liquid, by diffusion-controlled evaporation, from within a tube over which a nonreactive gas flows? The expression for the required time $t_c$ is obtained by evaluating the expression: (volume of 0.3 g which is actually Eq. (6), with $Z_1$ being a time-independent constant) cannot be utilized to determine the diffusivity $D_{\text{AB}}$ without a loss of accuracy as it requires either the maintenance of the liquid level at $Z=Z_1$ by some external device, which is difficult to achieve, or the ignoring of the descent of the liquid level.

It may be further noted in passing that Eq. (10), in addition, solves one interesting practical question, which is: how long does it take to empty a given amount of liquid, by diffusion-controlled evaporation, from within a tube over which a nonreactive gas flows? The expression for the required time $t_c$ is obtained by setting $Z_1=0$:

$$t_c = \frac{Z_1^0 \left( Z_2 - \frac{1}{2} Z_1^0 \right) \rho_{\text{Pb},A}}{CD_{\text{AB}} \ln \frac{X_{B_2}}{X_{B_1}}}$$

(11)

### 3.2. Application of the Pseudosteady State Diffusion Equation to Find $D_{\text{Pb–Ar}}$ at 1448 K

The diffusivity $D_{\text{AB}}$ can be determined by plotting the left-hand side expression of Eq. (10) against $t$ and inserting the known values of $C$, $\rho_{\text{Pb},A}$, $X_{B_2}$, and $X_{B_1}$ into the slope of the straight line generated. Referring back to the present study for which A–B represents Pb–Ar, $Z_1^0$ (in cm) can be obtained by evaluating the expression: (volume of 0.3 g of liquid lead, in cc + volume of 0.3 g of solid iron, in cc)/(π·0.6 cm; the radius of the crucible is 0.6 cm). The value is found to be ((0.3/10.11) + (0.3/7.87))/(1.13) = 0.06 cm, the densities of liquid lead and solid iron being 10.11 and 7.87 g/cc, respectively. The value of $Z_1^0$ can be similarly obtained by replacing 0.3 g of liquid lead (retained at $t=0$) by the mass of liquid lead retained at $t=t_c$, as obtained from Table 1, in the preceding expression. Table 2 lists the values of $Z_1^0$ as well as $(Z_1^0 - Z_1^0)(Z_2 - (1/2)Z_1^0 - (1/2)Z_2^0)$ for different $t$, noting that $Z_1^0$ = height of the crucible = 2.5 cm; the values corresponding to $t=5$ h (run 91) are excluded intentionally to avoid the possibility of a shift in the rate controlling mechanism that makes the governing rate equation (Eq. (10)) invalid toward the completion of the removal of lead. The shift might be due to an overwhelming abundance of iron powder when 92.9% lead has already been removed, causing some hindrance to the free evaporation of the liquid lead.

In Fig. 4, the plot of $(Z_1^0 - Z_1^0)(Z_2 - (1/2)Z_1^0 - (1/2)Z_2^0)$ vs. $t$ is linear, confirming the diffusion-controlled mechanism proposed, and yields a slope of 0.0154 (±0.0033) cm²/h, with the confidence interval of 0.95 shown in parenthesis, which means

$$\frac{C D_{\text{Pb–Ar}}}{\rho_{\text{Pb}} P_{\text{Ar}}} \ln \frac{X_{\text{Ar}=2}}{X_{\text{Ar}=1}} = 0.0154 (± 0.0033)$$

(12)

Putting into Eq. (12) the values: $C$ = $P/RT$ = 1/(82×1448) = 8.42 × 10⁻⁸ mol/cc; $P_{\text{Ar}}$ = 10.11/207.2 = 0.049 mol/cc; $X_{\text{Ar}=1}$ = 1 (pure argon, as mentioned previously); and $X_{\text{Ar}=2} = P_{\text{Ar}}/(1-P_{\text{Ar}})/P_{\text{Ar}} = (1-P_{\text{Ar}})/P_{\text{Ar}} = 0.986$ (solid iron being nonvolatile and the solubility of iron in liquid lead at 1448 K being 0.04 wt%). A negligibly small value, the total pressure $P$ of 1 atm is shared by the partial pressure $P_{\text{Ar}}$ of Ar, $P_{\text{Ar}}$ being 0.049 atm, and the saturated vapor pressure of liquid lead, $P_{\text{Pb}}$, at the liquid–vapor interface $Z_1^0$; the evaluation of $P_{\text{Pb}}$ is shown subsequently), $D_{\text{Pb–Ar}}$ is found to be 1.766 (±0.378) cm²/s.

The preceding saturated vapor pressure $P_{\text{Pb}}$ of 0.014 atm at $T=1448$ K was found out by considering the equilibrium

$$\text{Pb (liquid)} = \text{Pb (vapor)}$$

$$\Delta G^0 = 181960 - 90.127 T \text{ J/mol}^0$$

(13)

and using the relation

$$\Delta G^0 = -RT \ln P_{\text{Pb}}$$

(14)

Now, a comparison of the experimentally determined value (1.766±0.378 cm²/s) of $D_{\text{Pb–Ar}}$ with the theoretically predicted one may be made, as shown subsequently.
3.3. Estimation of the Interdiffusion Coefficient \( D_{\text{Pb–Ar}} \) at 1 448 K

The Chapman–Enskog formula\(^6\) for the interdiffusion coefficient of a binary gas A–B obeying the ideal-gas law is

\[
D_{\text{AB}} = \frac{1}{P} \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \left( \rho_{\text{AB}} \Omega_{\text{D,AB}} \right) \tag{15}
\]

in which the units are: the interdiffusion coefficient \( D_{\text{AB}} \), cm\(^2\)/s; temperature \( T \), K; the molecular weight \( M \) of the species indicated by the subscript, g/mol; the total pressure \( P \), atm; the collision diameter \( \sigma_{\text{AB}} \), \( \AA \); and \( \Omega_{\text{D,AB}} \) (which is the collision integral for A–B mixture at dimensionless temperature, \( \kappa T/\epsilon_{\text{AB}} \), for the Lennard–Jones 6–12 potential, \( \kappa \) being the Boltzmann constant and \( \epsilon_{\text{AB}} \) the Lennard–Jones parameter), dimensionless.

Considering the binary system Pb–Ar of the present study, for which \( T=1 448 \) K; \( M_{\text{Pb}}=207.2 \) and \( M_{\text{Ar}}=39.94; \) \( P=1 \) atm; \( \sigma_{\text{Pb–Ar}}=(1/2)(\sigma_{\text{Pb}}+\sigma_{\text{Ar}})=3.34 \AA \), the Lennard–Jones parameters \( \sigma_{\text{Pb}} \) and \( \sigma_{\text{Ar}} \) being 3.26 Å\(^7\) and 3.418 Å\(^8\) respectively; and \( \Omega_{\text{D,AB}}=0.894,9\) corresponding to \( \kappa T/\epsilon_{\text{Pb–Ar}}=3.83 \), obtained by using the relation, valid for nonpolar, nonreacting molecule pairs, \( (\epsilon/\kappa)_{\text{Pb–Ar}}=[(\epsilon/\kappa)_{\text{Pb}} \cdot (\epsilon/\kappa)_{\text{Ar}}]^{1/2} \), where \( (\epsilon/\kappa)_{\text{Pb}}=1.92T_{\text{m,Pb}} \) \( \gamma=1154 \) K (the melting point of lead, \( T_{\text{m,Pb}} \), being 601 K), and \( (\epsilon/\kappa)_{\text{Ar}}=124 \) K.\(^8\) Putting these values in Eq. (15), \( D_{\text{Pb–Ar}} \) is found to be 1.774 cm\(^2\)/s, which is in very good agreement with the experimental value of 1.766 cm\(^2\)/s.

Even when the alternative relation \( (\epsilon/\kappa)_{\text{Pb}}=1.15T_{\text{m,Pb}} \gamma=2322 \) K (the boiling point of lead, \( T_{\text{b,Pb}} \) being 2 019 K, from Eq. (13)) is considered, the estimated value, repeating the previous calculation, becomes 1.623 cm\(^2\)/s, which shows a deviation of about 8% only from the measured value.

Considering the agreement of the measured and estimated values, the interdiffusion coefficient \( D_{\text{Pb–Ar}} \) is reported from the present work as 1.766 (±0.378) cm\(^2\)/s at 1 448 K.

4. Conclusions

Lead, considered as a tramp element in steel, was successfully removed from a 50% Fe–50% Pb mixture by evaporation in argon at 1 448 K. It took 5 h to completely remove the lead from the mixture, the nonvolatile iron (solid) being left behind in the crucible (alumina). Results point toward a diffusion-controlled evaporation, and the system allowed the measurement of the interdiffusivity of lead and argon (\( D_{\text{Pb–Ar}} \)). Since this study dealt with a pseudosteady state diffusion, the required pseudosteady state equation was first developed, which was obtained in the following general form

\[
(Z^1_1 - Z^1_i) \left( Z^2_1 - \frac{1}{2} Z^1_i - \frac{1}{2} Z^2_i \right) = \frac{C D_{\text{AB}}}{\rho_m} \left( \ln \frac{X^2_i}{X^1_i} \right) t
\]

This equation was subsequently utilized with the help of the rate data to find the \( D_{\text{Pb–Ar}} \) at 1 448 K. The measured value, which is 1.766 (±0.378) cm\(^2\)/s, compares very well with the estimated value of 1.774 cm\(^2\)/s. The estimation was made using the Chapman–Enskog formula for the interdiffusion coefficient of a binary gas A–B obeying the ideal-gas law.

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