DIFFUSION AND ELECTROTRANSPORT OF CARBON IN $\gamma$-PHASE IRON-NICKEL ALLOYS

IFEOMA AGATHA IJOMAH, VICTOR UGOCHUKWU NWOKE AND FRANKLIN AMECHI ANENE, PATRICK SUNDAY AGUH CYNTHIA CHIKODI DANIEL - MKPUME

1 DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING, NNAMDI AZIKIWE UNIVERSITY, P.M.B. 5025, AWKA, ANAMBRA STATE, NIGERIA.
2 DEPARTMENT OF INDUSTRIAL PRODUCTION ENGINEERING NNAMDI AZIKIWE UNIVERSITY, P.M.B. 5025, AWKA, ANAMBRA STATE, NIGERIA.
3 DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING UNIVERSITY OF NIGERIA, NUSKKA.

The diffusivity and electro transport behavior of carbon in an iron-32.5 wt pct nickel alloy was investigated for the temperature range of 1220 to 1415 K for two carbon concentrations. The electrical resistivity was measured as a function of temperature between room temperature and 1625 K for carbon contents of 0.002, 0.10, and 0.21 wt pct. Values for the activation energy for diffusion of 32.0 ± 5.8 and 36.0 ± 5.2 kcal per mole were determined for alloys containing 0.10 and 0.21 wt pct carbon respectively, with slightly smaller values being found for the activation energy for electro transport. The sign of the effective valence indicates that carbon migrates toward the cathode.

OVER the past few years a number of investigations have been carried out on the thermodynamic\textsuperscript{1,2} and mass transport\textsuperscript{3-5} properties of carbon in iron-nickel alloys. Smith\textsuperscript{3} determined the diffusivity of carbon in the Fe-Ni-C system for compositions ranging from 0 to 100 pet Ni and 0.1 wt pct carbon. Bose and Grabke\textsuperscript{4} determined the carbon diffusivity in
iron-nickel alloys as a function of both carbon and nickel concentration. Nakajima and Hirano$^5$ studied the electromigration of carbon in Fe-4 wt pct Ni-0.6 wt pct C.

This interest in the Fe-Ni-C system is attributable, at least in part, to the widespread interest in a group of iron-base alloys identified as Alloy 800 which contain 30 to 40 pct nickel and about 20 pct chromium. These alloys encompass a fairly wide range of compositions and properties but are generally characterized by their good oxidation resistance and creep strength at elevated temperatures. This has led to the consideration or use of Alloy 800 for a number of important applications as diverse as coal gasification containment vessels, breeder reactor fuel element cladding, super heaters and reheater tubes in helium-cooled reactors and steam generator tubes in pressurized water reactors.

This work was undertaken as part of our study of the mass transport behavior of interstitial solutes in the higher melting metals and their alloys. The iron-32.5 wt pct nickel alloy composition was selected for this investigation inasmuch as it lies within the nickel composition of Alloy 800 and the solid solubility of carbon which is somewhat critical to this study is fairly well established.$^6,7$

Of some interest also was the rather large difference between the results of Smith$^3$ and Bose and Grabke$^4$ for the activation energy for diffusion of carbon in iron-nickel alloys of this approximate composition. Results of a companion study of the thermo transport of carbon in the same alloy will be described in a later paper.

**EXPERIMENTAL PROCEDURES**

**Materials and Specimen Preparation**

Iron of 99.95+ pct purity in the form of electrolytic platelets. Analysis showed it to contain <0.001 wt pct Al, 0.002 pct C, <0.05 pct H, 0.001 pct Mn, 0.001 pct Ni, 0.002 pct N, 0.013 pct O, 0.002 pct P, 0.003 pct S and 0.003 pct Si. Nickel rods of 99.99 pct purity containing 0.004 pct carbon, 0.001 pct manganese, 0.0008 pct oxygen and <0.0001 pct hydrogen as the major impurities and the radioactive carbon were all got from Head Bridge Onitsha.
A Fe-32.5 wt pct Ni master alloy containing 0.002 wt pct carbon was prepared by arc melting in an inert gas atmosphere. This was remelted in an electron beam furnace at a pressure of $10^{-7}$ Torr to remove any volatile impurities. Carbon in the form of spectrographic grade graphite was then added in a second arc melting step and in some cases small amounts of amorphous carbon enriched with $^{14}C$ was added at the same time. Following a homogenization treatment at 1273 K for 24h the alloy ingots were swaged into rods 0.64 cm in diameter for resistivity measurements and 0.25 cm in diameter for the electrotransport studies. These were then vacuum annealed at 1273 K for 1h to remove cold work and to coarsen the grain structure.

**Resistivity Measurements**

To obtain values for the electric mobility and effective valence by the nonsteady state method used in this investigation, the electric field, $E$, must be known quite accurately. This required that the resistivity of the alloy be determined for the temperature and composition ranges studied, since this information was not available for the alloys of interest here. The resistivity of the Fe-32.5 pct Ni alloy was determined over the temperature range of 298 to 1623K for three carbon concentrations, 0.002, 0.10 and 0.23 wt pct. The equipment and procedure used for these measurements are described in detail in earlier work by Chiotti.

**Transport, Measurements**

The experimental technique used in this investigation was similar to that previously described by Carlson and coworkers. The apparatus consisted of a stainless steel chamber equipped with water-cooled electrodes, a viewing port and a vacuum system capable of maintaining a pressure of $10^{-7}$ Torr or better during the experiment. A composite specimen consisting of a 2.2-cm long segment of the low carbon alloy butt-welded to a 4.4-cm section of either the 0.10, 0.21 or the 0.23 wt pct carbon alloy was supported between the electrodes by means of copper adapters designed to minimize the temperature gradient.
along the rod. The electric current was supplied by a voltage- and current-stabilized d.c. power source.

Composite rods containing 0.10, 0.21 or in one run 0.23 wt pct C were held at temperatures of approximately 1220, 1310, 1350 and 1415K for periods of time ranging from 110 to 8h. The surface temperature of the rod was measured by an optical pyrometer (with a precision of ± 5 deg) corrected for sight glass absorption and emissivity. An emissivity correction curve was determined for each carbon alloy for the temperature range of interest by comparing the temperature of a series of "black-body" holes drilled into a test specimen with that of the adjacent surface.

The carbon concentration profile of the specimen following the electrotransport experiment was determined in one of two ways. Initially the profiles were determined by cutting the rod into disks approximately 1mm in thickness and counting the β activity of both surfaces by a proportional detector-sealer. Specimens from later runs in which no radioactive tracer was added were sectioned into similar size segments and analyzed by combustion-chromatographic technique.

RESULTS AND DISCUSSION

Resistivity Studies

Variations in the resistivity of the Fe-32.5 pct Ni alloy as a function of temperature are shown by the curves in Fig. 1 for alloys containing 0.002, 0.10 and 0.21 wt pct C. The room temperature resistivity of the low carbon alloy was determined to be 81.9 ± 0.4 μ ohm cm⁻¹ which is in good agreement with Sand's¹⁰ value of 81.7μ ohm cm⁻¹ for an alloy of the same composition. It will be noted that the resistivity increases monotonically over the entire temperature range with a small but constant increase in the resistivity with increasing carbon content. This difference represents the contribution of the carbon to the total resistivity, Δρ. Values of ρ from these curves wore used in the calculation of the electrotransport parameters.
Electrotransport Studies

All of the runs yielded concentration-distance profiles of the form shown in Fig. 2 for the 0.21 wt pct C specimen after 22.5h at 1415 K. The onset of carbon buildup due to electrotransport is seen at the right of the high temperature plateau. The displacement of the midpoint of the curve between the high and low concentration plateaus with respect to the original interface (vertical dashed line) represents the migration distance $\Delta X$. This displacement and the slope were determined analytically for each experiment from a least squares treatment of an inverse error function plot of $(c_x - c_0)/(c_2 - c_0)$ vs distance where $c_0 = (c_1 + c_2)/2$ for those data points between the two plateaus as is shown in Fig. 3. The error in $D$ corresponds to the standard deviation of the slope for each plot.

![Fig. 1 – Plot of resistivity vs temperature for the iron-nickel-carbon alloys used in this study.](image-url)
The analytical expressions used in the calculation of the diffusion and electro transport parameters are derived by Carlson, et al. in earlier papers.\textsuperscript{11, 12}

The results of the transport runs for two carbon concentrations at four different temperatures are summarized in Table I. The 0.10 and 0.23 pct C specimens were analyzed by the radioactive tracer technique whereas the 0.21 pct C run which contained no tracer addition was analyzed by the combustion technique. The electric mobility, $U$, was obtained from the relation $U = \Delta X/Et$ where $\Delta X/t$ is the migration velocity, $V$, and $E$ is the electric field. The electric field was obtained from $E = j\rho$ where $j$ is the current density and $\rho$ is the resistivity of the alloy at the run temperature. The diffusivity $D$ and diffusion constant $D_0$
were determined for each temperature from the slope, \( m \), and intercept respectively using the relation \( m = 1/(4Dt)^{1/2} \). The effective valence, \( Z^* \), was calculated from Nernst-Einstein relation \( Z^* = V_k T/eD \).

![Graph showing inverse error function vs distance for carbon in Fe-32.5 pct Ni-0.21 pct Cat 1415 K for 22.5 h.]

An Arrhenius plot of In \( D \) vs reciprocal temperature for both carbon levels is shown in Fig. 4. As can be seen from the figure and also from Table I there is a measurable concentration dependence in \( D \) for the temperature range investigated. This is consistent with the results of Bose and Grabke\(^4\) and others\(^{13,14}\) which showed a marked concentration dependence of the diffusivity of carbon in austenitic steel. Different models have been proposed to explain this concentration dependence. With the concept that the driving force in diffusion can be regarded as the gradient of chemical potential of the migrating species. Darken\(^{15}\) derived the following equation for the diffusion of an interstitial solute

\[
D = BKT \left[ 1 + C \frac{d \ln y}{dC} \right]
\]
where $B$ is a composition dependent mobility; $y$ is the activity coefficient of the diffusing species and $C$ the volume concentration. Fisher, et al.\textsuperscript{16} used absolute rate theory to modify Darken's equation to

$$D = Ky' + C \frac{d \ln y}{dC}$$

Table I. Electrotransport Mobilities, Diffusivities and Effective Valences for Carbon in Fe-32.5

<table>
<thead>
<tr>
<th>Pct Ni</th>
<th>Wt Pct C</th>
<th>$E$ (V cm\textsuperscript{-1})</th>
<th>Temperature (K)</th>
<th>$\Delta X \pm 0.005$ (cm)</th>
<th>Time ($10^4$s)</th>
<th>Mobility, $U$ ($10^{-6}$cm\textsuperscript{2}s\textsuperscript{-1}V\textsuperscript{-1})</th>
<th>Diffusivity, $D$ ($10^{-8}$ cm\textsuperscript{2}s\textsuperscript{-1})</th>
<th>$Z^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.0870</td>
<td>1220</td>
<td>0.130</td>
<td>40.1</td>
<td>3.73 ± 0.01</td>
<td>10.0 ± 0.8</td>
<td>3.9 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.1028</td>
<td>1315</td>
<td>0.400</td>
<td>34.6</td>
<td>11.19 ± 0.14</td>
<td>35.4 ± 2.8</td>
<td>3.6 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.0911</td>
<td>1360</td>
<td>0.045</td>
<td>2.9</td>
<td>17.14 ± 1.90</td>
<td>54.3 ± 6.6</td>
<td>3.7 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.2430</td>
<td>1415</td>
<td>0.320</td>
<td>7.9</td>
<td>16.87 ± 0.26</td>
<td>56.2 ± 4.8</td>
<td>3.7 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>0.0865</td>
<td>1220</td>
<td>0.450</td>
<td>34.6</td>
<td>5.76 ± 0.17</td>
<td>15.4 ± 1.0</td>
<td>3.9 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.23</td>
<td>0.0921</td>
<td>1310</td>
<td>0.327</td>
<td>33.5</td>
<td>10.61 ± 0.16</td>
<td>33.2 ± 4.4</td>
<td>3.6 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>0.0527</td>
<td>1335</td>
<td>0.300</td>
<td>25.9</td>
<td>21.96 ± 0.37</td>
<td>65.3 ± 6.5</td>
<td>3.9 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>0.2271</td>
<td>1415</td>
<td>0.600</td>
<td>8.1</td>
<td>32.64 ± 0.27</td>
<td>112.0 ± 5.3</td>
<td>3.6 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4—Arrhenius-type plots for carbon diffusivity in Fe-32.5 pct Ni alloys containing 0.10 and 0.21 pct C respectively.

where $K$ contains at least two undetermined factors namely the activity coefficient of activate complexes and a transmission coefficient, $1/m$, related to the probability of an activated complex undergoing a successful jump in the direction of the next energetically favorable site. In a later work Siller and McLellan$^{17}$ calculated $1/m$ and showed by comparison with experimental data that the absolute rate theory could explain the variation of diffusivity with concentration.
The data of Fig. 4 were fitted to a straight line by a least-squares analysis. Activation energies for diffusion, $Q_D$, of $32.0 \pm 5.8$ and $36.0 \pm 5.2$ kcal/mol were obtained for carbon in the 0.10 and 0.21 pct carbon alloys, respectively where the error limits represent the standard deviations. Wells and Mehl\textsuperscript{14} obtained a value of $32.0 \pm 1$ kcal/mol for carbon in low alloy austenitic steel but found no evidence for any concentration dependence in $Q_D$ over the range of 0.1 to 1.0 pct carbon.

Smith\textsuperscript{3} reported that the nickel concentration also has a measurable effect on the diffusivity and activation energy for diffusion of carbon in iron-nickel alloys. As is seen from Fig. 5 there is a minimum in the activation energy (with an accompanying maximum in the diffusivity) for a fixed carbon concentration of 0.1 wt pct, although the $Q_D$ values of Bose and Grabke are consistently lower than those of Smith. As can be seen from the figure our value of $Q_D$ for the Fe-32.5 pct Ni-0.1 pct C alloy is in better agreement with Smith's data than with those of Bose and Grabke.

Herzig and Heumann have shown\textsuperscript{18} that a plot of $VT/j$ vs $l/T$, gives a straight line relationship from which an activation energy for electrotransport, $Q_E$, can be obtained. As is seen from Fig. 6 there appears to be a concentration dependence in $Q_E$, increasing from $26.2 \pm 4.5$ kcal For carbon in the 0.10 pct C alloy to $35.0 \pm 5.1$ kcal in the 0.21 pct C\textsuperscript{1} alloy. The approximately 20 pct difference between $Q_D$ and $Q_E$ (32.0 - 26.2) for the 0.10 pct C alloy is consistent with what some investigators\textsuperscript{11,19} have observed for other metal systems. On the other hand the immeasurably small difference in these activation energies (36.0 - 35.0) that is observed for the combined 0.21 and 0.23 pct C alloy is more in agreement with what Herzig and Heumann\textsuperscript{18} found for tin and antimony in gold and Nakajima and Hirano\textsuperscript{20} for carbon in $\gamma$ iron. These seemingly contradictory results may merely be a reflection of the rather large errors in the experimental values for $VT/j$ resulting in large errors in $Q_E$. 
Fig. 5—Activation energy for carbon diffusion in Fe-Ni-0.10 pct C alloys obtained by R. P. Smith ∆; S. K. Bose and H. J. Grabke ●; and from this study □.
$10^4/T \ (K^{-1})$

* Fig. 6—Least squares linear plot of $\ln VT/j$ vs reciprocal temperature for carbon in the alloys studied.

![Graph showing least squares linear plot of In VT/j vs reciprocal temperature for carbon in the alloys studied.]

Fig. 7—Least squares linear fit of $Z^*$ vs reciprocal resistivity for the iron-nickel-carbon alloys studied.

As is seen from Table I the values of $Z^*$ full within a narrow range between 3.6 and 3.9 with little indication of any concentration dependence although there appears to be some temperature dependence in $Z^*$. The error in $Z^*$ includes the cumulative errors in $U$ and $D$. Nakajima and Hirano\(^5\) obtained a $Z^*$ value of 3.9 for carbon in a Fe-4 pct Ni-0.6 C alloy at 1233 K, which is in surprisingly good agreement with that obtained for the 0.10 and 0.21 pct alloys at 1220 K. Although this agreement may be fortuitous Nakajima and Hirano observed that $Z^*$ for carbon in iron is not measurably influenced by the nickel content.

According to current theory the driving force for electromigration is the result of a coulombic force $Z_i eE$ and a friction force, $-\delta_i E$ where $Z_i$ is the true or actual valence of the solute ion and $\delta_i$ is the drag coefficient resulting from the interaction between electrons
and the solute. The effective valence \( Z^* \) arises from the sum of these forces such that \( Z^* eE = Z_i eE - \delta_{ei} E \) or \( Z^* = Z_i - \delta_{ei}/e \). From the theories of Fiks\textsuperscript{21} and others\textsuperscript{19, 22} the drag coefficient \( \delta_{ei} \) can be considered to be proportional to \( \Delta \rho / \rho \) where \( \Delta \rho_i \) is the contribution of component \( i \) to the total alloy resistivity \( \rho \). According to Matthiessen's rule as is seen from Fig. 1, \( \Delta \rho_i \) is constant over the temperature range of interest and therefore the above equation can be expressed as a linear expression of the form, \( Z^* = Z_e - B/\rho \). A least squares fit of the data to a straight line for a plot of \( Z^* \) vs \( l/\rho \) is shown in Fig. 7. The constant \( B \) which corresponds to the slope in the above equation contains the residual resistivity, \( \Delta \rho_i \). This suggests that there should be a concentration dependence in the slope of such a plot. Although the slope of the line obtained for the combined 0.21 and 0.23 pct C alloys appears to be slightly greater than for the 0.10 pct C alloy, this difference is not considered to be statistically significant in view of the considerable scatter in the data.

CONCLUSIONS

1) The resistivity of Fe-32.5 pct Ni alloys containing 0.002, 0.10 and 0.21 pct carbon respectively changes monotonically over the temperature range 300 to 1650K.

2) There is a measurable concentration dependence in the diffusivity and electric mobility of carbon in the Fe-32.5 pet Ni alloy.

3) A similar concentration dependence in the activation energies for diffusion and electrotransport was observed.

4) The effective valence of carbon appears to be independent of carbon concentration, but shows a small but measurable temperature dependence.