Thermomigration of Carbon in Metals

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An investigation of thermomigration in interstitial solid solutions of carbon in \( \beta \)-Ti, V, \( \alpha \)-Fe, Co, Ni, and Pd has been carried out using a radioactive tracer technique. A substantial solute redistribution occurred towards the hotter regions in \( \alpha \)-iron and vanadium and towards the colder regions in palladium whilst for Co, Ni and \( \beta \)-Ti very little segregation was observed. The measured heats of transport were (in kcal per g-atom): \( \alpha \)-Fe, \(-14.1 \pm 1.5\); V, \(-4.9 \pm 1.0\); Pd, \(+8.4 \pm 1.5\); Co, \(+1.5 \pm 1.5\); Ni, \(-1.6 \pm 1.4\); \( \beta \)-Ti, \(-1.0 \pm 1.0\). An examination of the results obtained together with all of the published data for interstitial solute thermomigration suggests that electronic effects could be of major importance in determining the redistributions observed.

When an initially homogeneous multicomponent material is placed in a temperature gradient a concentration gradient is frequently established. This is called "thermomigration." Despite both the technological and theoretical importance of thermomigration, very few reliable quantitative investigations have been carried out in solid metallic systems and there is barely a rudimentary understanding of the driving forces for the phenomenon. This is reflected in the current theoretical approaches to the subject and at the present time there does not exist a model capable of predicting, even qualitatively, the effect of thermomigration in solids. It was to provide additional quantitative data with which to compare the consequences of subsequent theoretical models that the work embodied in this communication was undertaken.

The simplest metallic system for the purposes of theoretical comparison is the interstitial solid solution. Solute mobility is high at quite moderate temperatures and effectively only the solute moves, the solvent lattice serving as a fixed frame of reference. Thus complications which arise when both species in a binary system move are avoided. The basic macroscopic equations governing thermomigration in such systems are obtained from irreversible thermodynamics and have been discussed by several authors. The theoretical comparison is the interstitial solid solubility of solute movement. \( Q^* \) is defined by irreversible thermodynamics as the flux of heat, \( \cdot \) accompanying the quantity characteristic of the phenomenon; its sign and magnitude determine the direction and magnitude of solute movement. \( Q^* \) is defined by irreversible thermodynamics as the flux of heat, \( \cdot \) accompanying the unit flux of matter, \( J_u \), in an isothermal system

\[
\ln C_i = \left( \frac{Q^*_i}{k} \right) \nabla (1/T)
\]

where \( C_i \) is the solute concentration, \( k \) is Boltzmann's constant and \( T \) the absolute temperature. The parameter \( Q^*_i \) is called the "heat of transport" and is the quantity characteristic of the phenomenon; its sign and magnitude determine the direction and magnitude of solute movement. \( Q^*_i \) is defined by irreversible thermodynamics as the flux of heat, \( J_u \), accompanying the unit flux of matter, \( J_i \), in an isothermal system

\[
Q^*_i = \left( \frac{J_u}{J_i} \right) \nabla T = 0
\]

Herein, then, lies the theoretical significance of thermomigration. Measurements of \( Q^*_i \) can, in principle, provide information on the energy transfer processes associated with elementary diffusive atomic jumps. In other words, they can contribute to the understanding of activated processes.

In the present study, \( Q^*_i \) has been measured in a number of metal-interstitial systems. The interstitial species in all cases was carbon and the solvent metals were selected with a view to investigating the possible effects of solvent lattice structure on thermomigration. Specifically, the bcc metals Fe (\( \alpha \) phase), Ti (\( \beta \) phase) and V, and the fcc metals Co, Ni, and Pd were studied. Of these, only carbon thermomigration in iron appears to have been investigated previously.

Experimental

A steady state radiotracer technique was used to measure \( Q^*_i \) in all experiments. The time to establish the steady state is proportional to \( \exp (-t/\Theta) \), (Ref. 5), where \( "t" \) is the time of the run and

\[
\Theta = \frac{a^2}{\pi^2 D}
\]

is called the relaxation time. \( "a" \) is the specimen thickness in the direction of the temperature gradient and \( D \) is the solute diffusivity at the mean run temperature. Ideally, infinite time is required to attain ultimate steady state conditions. However, for \( t = 50 \), the final state is approached to within \( \exp (-5) \approx 0.0063 \), or 99.3 pct which is adequate for the purpose of determining \( Q^* \). In this research, all specimens were annealed for at least 50. The diffusion coefficients used in calculating \( \Theta \) for the systems investigated are those reported in Refs. 6 through 11.*

A) Sample Preparation

Detailed chemical analyses of the solvent metals used in the thermomigration investigations are listed in Table I. All specimens were in the form of thin circular discs between 0.375 and 0.425 in. in diam and 0.040 to 0.080 in. thick. Carbon was introduced into the specimens by sealing them off with a source of carbon 14 in a silica capsule containing a partial

*Diffusion coefficient for carbon in palladium assumed to be of the same order as that for carbon in nickel and cobalt.
Table I. Chemical Analyses of Metals Used in Thermomigration Studies

<table>
<thead>
<tr>
<th>Metal</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Sn</th>
<th>W</th>
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<tbody>
<tr>
<td>Titanium 99.9 pct Pure</td>
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<td>3</td>
<td>112</td>
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<td></td>
<td>50</td>
<td>80</td>
<td>30</td>
<td>Rem.</td>
<td>30</td>
<td>Rem.</td>
<td>500</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Vanadium</td>
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<td>20</td>
<td>65</td>
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<tr>
<td>Iron</td>
<td>70</td>
<td>250</td>
<td>500</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
<td>100</td>
<td>Rem.</td>
<td>500</td>
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<td>Cobalt</td>
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<td>Trace</td>
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<td>Nickel</td>
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<tr>
<td>Palladium 99.99 pct Pure</td>
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Fig. 1—Schematic diagram of temperature gradient apparatus.

Fig. 2—Schematic diagram of thermocouple arrangement used for measuring specimen temperatures.

The temperature gradient apparatus used for the investigations is shown schematically in Fig. 1. Basically, it consisted of a cylindrical iron heating block, which transferred heat to the top face of the specimen, and a cylindrical austenitic stainless steel cooling block, which dissipated heat from the bottom face of the specimen. The cooling block was soldered to a water-cooled support and the temperature gradient in the specimen could be adjusted by varying the length and diameter of this bottom block. Heat was supplied to the upper heating block by a small molybdenum furnace winding.

The temperature of each face of the specimen was measured using the arrangement shown in Fig. 2. Each thermocouple wire was individually spot-welded to the specimen in the plane of the specimen face. Before welding, the end of each wire was flattened on an anvil to a thickness of approximately 0.001 in. so as to constitute as small an irregularity as possible on the specimen face. The advantage in using this type of arrangement as against a conventional sheathed thermocouple lies in the fact that access to the specimen is possible directly, without the necessity for holes or recesses in the heating and cooling blocks. If the interface between the specimen and the adjoining block is at a uniform temperature the electromotive force produced by the thermocouple should be a true indication of the actual temperature.

Prior to positioning on the water-cooled support, the heating block, specimen with attached thermocouples, and cooling block were brazed together. This served the double purpose of securing the different parts of the arrangement and ensuring good thermal contact between the specimen and the two blocks. Brazing was effected by interposing thin copper foils approximately 0.0015 in. thick between the specimen and the heating and cooling blocks, and heating the assembly under high vacuum until the copper melted and flowed about the thermocouple leads. High frequency heating permitted rapid cooling of the assembly once the copper...