Solid state diffusion of carbon in the Co-5% Fe-C system at high pressure: metallography and phase equilibrium

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Introduction

Co-Fe-C alloys find applications in many metallurgical processes such as welding and industrial diamond synthesis. In high pressure-high temperature (HPHT) diamond synthesis, it is generally agreed that diffusion is the dominant transport mechanism by which carbon is transported through the molten metal to the growing diamond crystal. In diamond synthesis, the diffusion of carbon through the metal, both in the solid and molten states, is believed to be probably the rate-determining step for the growth of diamonds. The study of pressure effects on rate-limited processes is of great importance and very often unique for directly determining the volume changes associated with these processes. Pressure influences various parameters such as transformation temperatures, phase stability, transport mechanisms and the kinetics of approach to equilibrium, such that the extent and type of transformation in a variety of alloy systems can be altered by altering the pressure.

Very little data exists on the influence of pressure on the diffusion of carbon in the Co-Fe-C system both in the solid and liquid states. Borimskil et al.’s work, at a pressure of 50 kbar, in the temperature range 1100–1400°C and covering Fe-Co alloys containing up to 70% Co was the only work known to the authors on carbon diffusion at high pressure in a cobalt-rich Fe-Co alloy, albeit in the molten state. Their results suggest that the diffusion coefficient of carbon in the molten alloys at high pressure is approximately one order of magnitude lower than that in similar melts at atmospheric pressure. However, they concluded that this reduction was not directly related to high pressure. The effect of pressure on the diffusion coefficient of carbon in Co-Fe-C alloys cannot be fully assessed from these investigations due to differences in experimental technique and pressures employed.

The metallography of Co-Fe alloys treated at high pressures has received very little attention. Metallographic studies can provide much needed information on the stability of phases at different temperatures and pressures.

This study aimed at measuring the solid state diffusion of carbon in the Co-5% Fe-C system at high pressures and at studying the phase diagram of the Co-5% Fe-C system at such high pressures and the resulting microstructures. The microstructures, phase composition and identity of the phases were studied by metallography, X-ray diffraction and X-ray spectral microanalysis of longitudinal sections of diffusion samples.

Experimental procedure

Diffusion experiments at atmospheric pressure

Synopsis

The diffusion of carbon in Co-5%Fe alloy was studied in a belt-type pressure system at temperatures of up to 1330°C and pressures or nominal pressures of 7 020 tons or 42±3 kbar. Under these conditions, this alloy is in the solid state. Discs of graphite and prealloyed Co-5%Fe were used to make up the diffusion couple. The diffusion coefficient increased with increasing pressure due to the tendency of the low density graphite to dissolve in the metallic phase reducing the overall volume and increasing the density of the system. Furthermore, inhomogeneous plastic deformation may have promoted diffusion by creating defects in the alloy. Diffusion couples treated at atmospheric pressure exhibited graphite particles in the metal, while those treated at high pressures exhibited carbide in the form of Widmanstatten laths. Carbon analyses indicated increased carbon solubility with increasing pressure. This was confirmed from calculated high-pressure phase diagrams.

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were carried out in an argon atmosphere using an A DSP 1503P Frisch Sintering Press in the temperature range 1300–1310°C. This press was equipped with a vacuum and inert gas hood and a three-phase temperature control device, comprising three pyroscopes positioned 120° apart. The samples were heated by resistance heating and the temperature was measured by the pyroscopes by converting the infrared radiation emitted by the sample to an electrical signal related to temperature. At the end of the experiments, the temperature was allowed to decrease to room temperature on average, over a period of 300 seconds, by force-cooling with argon gas.

High-pressure experiments were carried out in a belt-type apparatus of the type used for HPHT diamond synthesis. Such a belt-type apparatus comprises a die in the form of a cylindrical bore and two opposed anvils shaped in the form of truncated cones. In use, these cones are supported at the opposed openings of the bore, with an appropriate gasket such as talc, pyrophyllite or mixtures thereof, provided at the openings to allow for high pressures to be achieved.

A 10.6 mm thick layer of high purity graphite discs with a diameter of 59.8 mm and an average individual disc thickness of 0.8 mm, was placed on a 10.6 mm thick layer of pre-alloyed Co-5% Fe metal discs to form the diffusion couple (Figure 1). A 2 mm thick pyrophyllite ceramic pad was placed beneath the metal layer. Another 10.5 mm thick layer of high purity graphite discs was placed under the pyrophyllite ceramic pad. The second layer of graphite discs was used to maintain capsule stiffness and also to minimize metal deformation.

The pyrophyllite ceramic pad served as a diffusion barrier between the metal and the bottom graphite layer. The graphite-metal-graphite stack was inserted into a pyrophyllite ceramic tube having an inner diameter of 60 mm. The pyrophyllite ceramic tube was sealed with 2 mm thick pyrophyllite ceramic pads. Tantalum cups were placed on both ends of the pyrophyllite ceramic tube and a tantalum sheet wrapped round the pyrophyllite ceramic tube. This was inserted into a hollow KBr salt tube, which acted as a pressure transmitting medium. The tantalum cups and the tantalum sheet together provided an encapsulating medium for the ‘reaction volume’ due to tantalum’s high melting point and its electrical conductivity.

The reaction volume as described above was inserted into a pyrophyllite ceramic outer tube of outside diameter equal to the press die bore diameter. The ends of this outer tube were sealed with thin mild steel discs. The reaction volume was then annealed for 18000s in a belt-type press for the HPHT experiments using a resistance heater sleeve. Several diffusion anneals were carried out at different temperatures and loads/pressures. At the end of each anneal, the current was turned off, thereby initiating a temperature drop, while maintaining high load/pressure. The load was then reduced to zero in about twenty minutes.

Cylinders 22 mm in diameter were cut longitudinally by electro-diamond machining of the annealed diffusion couples. These were used for various analytical procedures including carbon analyses and metallographic examination. Carbon content and hence diffusion depth, the extent to which the carbon had diffused from an interface into the metal, was determined by a glow discharge optical emission spectroscope using the following parameters: 1200 V regulated voltage, 120 mA current, preburn time of 6 seconds and a sputtering rate of 0.036 mg s⁻¹. The carbon content analysis method used had a spatial resolution of 2 µm. Three carbon diffusion profiles were obtained for each sample to ensure reproducibility, and the carbon solubility was determined as the maximum carbon content measured. Longitudinal sections through the couples were prepared for metallographic examination and studied using optical and scanning electron microscopes.

Figure 1—Arrangement of a diffusion couple used in the determination of carbon diffusion in the Co-5%Fe alloy at high pressure
Results

Carbon diffusion in Co-5% Fe alloy

Carbon diffusion coefficients were determined from concentration-penetration depth profiles (Figure 2) by solving Fick’s second law:

\[
\frac{\partial^2 c}{\partial t^2} = D \frac{\partial^2 c}{\partial x^2} \tag{1}
\]

for the following conditions:

\[
\begin{align*}
\dot{c} &= c_o \quad (x > 0, \ t = 0) \\
c &= c_s \quad (x > 0, \ t > 0) \\
c &= c_o \quad (x = \infty, \ t > 0) \\
\text{and} \quad \frac{\partial c}{\partial x} &= 0 \quad (x > 0, \ t = 0)
\end{align*}
\]

where \(t\) is the time in seconds, \(D\) is the diffusion coefficient (\(\text{cm}^2 \text{s}^{-1}\)), \(x\) is the depth in cm and \(c_s\) and \(c_o\) are the carbon concentrations at the metal surface and initial carbon content of the metal, respectively. Since the carbon concentration at the far end of the metal layer remained unchanged throughout the experiments, the diffusion couple was assumed to be semi-infinite. For the above initial and boundary conditions, Fick’s second law has the following solution for a semi-infinite couple

\[
c - c_o = A \exp \left( -\frac{x^2}{4Dt} \right) \tag{2}
\]

where \(A\) is a constant and \(c\) is the measured carbon concentration. The diffusion coefficients were determined from the slope of linear plots of \(\ln (c-c_0)\) vs \(x^2\), (Figure 3). The linearity of these plots indicates that the chosen solution to Fick’s second law adequately describes the experimental carbon distribution in the Co-5% Fe alloy studied. The diffusion coefficient values at atmospheric pressure and 1290, 1310 and 1330°C and different press loads are summarized in Table I. These results show that, in the Co-5% Fe alloy investigated, the diffusion coefficient of carbon increased with increasing press load and temperature.

Metallography

The atmospheric and high pressure Co-5% Fe samples were examined using optical and scanning electron microscopy. The sections were etched in 3% nital. An intimate bond was found to have formed at the graphite-metal interface. The alloy exhibited a carbon depleted zone about 0.2 mm thick at its interface with the graphite layer in all HPHT samples, Figure 4. An explanation for the existence of this zone is provided below. The diffusion depth increased with increasing press load for a given temperature, as can be seen from Figure 2. In all HPHT samples, the diffusion zone was comprised of two distinct areas: (i) a primary zone of varying

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**Figure 2**—Carbon concentration-depth profiles in Co-5%Fe at (a) 1290 °C and (b) 1330°C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Diffusion coefficient (\times 10^{-6}) ((\text{cm}^2 \text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6020 tonne</td>
</tr>
<tr>
<td>1290</td>
<td>0.800</td>
</tr>
<tr>
<td>1310</td>
<td>-</td>
</tr>
<tr>
<td>1330</td>
<td>0.899</td>
</tr>
</tbody>
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**Table I**

Carbon diffusion coefficient in the Co-5%Fe alloy
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Figure 3—Plots of ln(c) vs x² (where c is the carbon concentration and x is the depth) for carbon diffusion in Co-5\% Fe at (a) 1290°C and (b) 1330°C and various press loads

Figure 4—Micrograph of diffusion zone showing a carbon depleted band (top). Etched, 3\% Nital, 50X

depth located adjacent to the carbon depleted zone and characterized by a Widmanstatten pattern, Figure 5, and (ii) a secondary zone further from the interface, showing grain boundary carbide and graphite precipitates in the metal matrix.

Samples treated at ambient pressure exhibited graphite particles in the metal matrix, Figure 6. There was no evidence of carbide precipitation.

The increase in the width of the diffusion zone with increasing press load supports the experimentally determined diffusion coefficient values. The extent of the primary zone increased with increasing pressure, also indicating more rapid diffusion at higher pressures. This was further confirmed by its absence in samples treated at atmospheric pressure.

EDS analyses, Figure 7, showed that the Widmanstatten pattern is a carbide, probably of the type (Fe₁ₓCo₍₀·₂₎)_₃C₇. This carbide structure was well defined, starting at the grain boundaries and penetrating the grains on selected crystallographic planes. EDS spectra of different phases in the alloy are shown in Figure 7. These indicate a higher carbon content in the carbide laths compared to the grain boundary. Microhardness tests on longitudinal sections showed that the primary zone was much harder than the secondary zone. This can be attributed to the presence of the Widmanstatten carbide laths in the primary zone.

Scanning electron microscopy showed that the carbide laths had a fairly regular spacing and that they were interrupted along their length by fine particles of graphite, Figures 8 and 9. There was a reduced amount of Widmanstatten carbide in the vicinity of the graphite particles.
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Phase equilibrium in the Co-5%Fe-C system

The Co-Fe-C phase diagram for a 5%Fe alloy was calculated at atmospheric pressure and pressures up to 45 kbar, Figure 10, using Thermo-Calc®, a software system developed at the Royal Institute of Technology (Stockholm), for thermochemical equilibrium calculations, comprising modules for equilibrium calculations, phase diagram calculations and tabulations of thermochemical quantities. Thermo-Calc® uses a data bank of assessed thermochemical data and models for the phases in the system. In this case, the calculations were done using a proprietary high pressure high temperature transition metals-carbon database. This phase diagram is very similar to that of the binary Co-C system. Increases in pressure lead to (i) an increase in carbon solubility in the austenitic or face centred cubic (fcc) phase, (ii) a shift of the liquidus and solidus lines upwards, (iii) an increase in the eutectic temperature and eutectic carbon content from 1315°C and 0.99wt-% at ambient pressure to 1420°C and 1.8wt-% at 45 kbar. The combined effect of factors (i), (ii) and (iii) is to expand the austenitic or face centred cubic (fcc) phase region.

The eutectic temperature of the Co-5% Fe-C system at ambient pressure was experimentally determined, by melting the Co-5% Fe alloy in the presence of graphite, and found to be between 1315 and 1320°C. The measured and calculated carbon solubilities in the austenitic or face centred cubic (fcc) phase at ambient pressure and 1310°C were 0.73 and 0.88%C, respectively. The corresponding values at 45 kbar and 1330°C were 1.28 and 1.58%C. The relationship between the calculated carbon solubility in the austenitic or face centred cubic (fcc) phase and pressure was linear, Figure 11. The carbon solubilities were determined from the measured maximum carbon contents at the graphite-metal interface or ‘zero’ diffusion depth from the carbon concentration-depth profiles similar to those shown in Figure 2.
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Figure 7—Semi-quantitative EDS spectra showing carbon concentrations in (a) the carbide laths, (b) the matrix and (c) the grain boundary carbide.

Figure 8—Back scattered scanning electron microscope image showing graphite nodules, Widmanstatten carbide, grain boundary carbide, and dark platelets on the grain boundary and in the carbide laths. Etched, 3% Nital, 8000X.
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Discussion

The observed increase in diffusion coefficient of carbon with increasing pressure is interesting. Cox and Homan\textsuperscript{2} found that the diffusion coefficient of carbon in \(\alpha\)-iron decreased under conditions of hydrostatic pressure. This was attributed to a volume decrease due to reduced interatomic distances and elimination of microvoids.

In the present experiments, the pressure conditions were probably not purely hydrostatic. Such conditions can be expected to generate defects in the lattice\textsuperscript{9,10}, due to plastic deformation. Defects could very well provide sites and paths for diffusing solute atoms, thereby potentially enhancing the diffusion process. Thus, at high pressures, diffusion will tend to decrease due to lattice contraction and increase due to increased lattice defects. The tendency of the system to reduce its volume and thereby increase its density would tend to enhance carbon solubility and diffusivity in the metal. A higher density would be obtained at high pressure and temperature by reducing the volume of graphite, i.e., by diffusion of carbon into the alloy. Maintaining a high pressure and reducing the temperature would favour the exsolution of carbon as carbide. Reducing the pressure and the temperature, would favour the exsolution of carbon as graphite. These effects can be expected from a consideration of the Le Chatelier principle.

Figure 9—Back scattered scanning electron microscope image showing graphite particles in the matrix and in association with Widmanstatten and grain boundary carbide. Etched, 3% Nital, 1000X

Figure 10—The Co-5% Fe-C phase diagram at different pressures

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The increased width of the diffusion zone with increasing pressure shows clearly that diffusion was enhanced at high pressures. The Widmanstätten carbide laths formed during cooling under high pressure are also a clear indication of the stabilizing effect of pressure on the denser phase. In contrast, in experiments conducted under ambient pressure, only graphite was obtained despite the high quenching rates.

The formation of graphite particles on the carbide laths and in the matrix, during cooling, suggests a strong tendency of the system to form the equilibrium phases. These graphite particles appear to have been the result of the decomposition of the mixed carbide. Their mode of occurrence suggests that small cracks formed in the carbide laths providing suitable sites for the nucleation of the graphite. Such cracks may also enhance decomposition of the carbide due to void formation, and a balance between carbide and graphite is therefore obtained.

The Widmanstätten carbide formed due to a reduction in carbon solubility during cooling. The carbide laths nucleate at grain boundaries and grow rapidly along preferred crystallographic planes in order to reduce supercooling of the solid solution and bring it closer to equilibrium.

The carbon depleted zone described in this study has been observed before in diffusion experiments but has not been explained. This zone is related to the cooling of the couple and super saturation of the diffusion zone in carbon. The carbon in the zone adjacent to the graphite diffuses back to, and re-deposits on the graphite leaving the zone depleted in carbon. Material further away becomes supercooled and precipitates carbide laths. These phenomena are analogous to the precipitation of ferrite adjacent to graphite in graphitic cast irons and pearlite further away from the graphite due to supercooling of the austenite. The Widmanstätten pattern formed in the diffusion zone is characteristic of supercooled material.

There are appreciable deviations between the measured and calculated carbon contents of the austenite at 1310 and 1330°C and pressures of one atmosphere and 45 kbar. These may be due to inaccuracies in the experimental results or to possible inadequacies of the model used in the calculations.

The exact values of carbon solubility at different temperatures and pressures will probably not be known until further experimental results on the Co-5% Fe-C system become available.

Conclusions

The diffusivity and solubility of carbon in a Co-5% Fe alloy increased with increasing press load or pressure and temperature as a result of volume reduction at high press load and due to plastic deformation of the alloy.

Cooling of diffusion couples under high pressure stabilized the denser carbide phase in the alloy. Cooling under ambient pressure stabilized the graphite phase.

Calculations showed that pressure expands the austenitic or face centred cubic (fcc) phase region in the Co-5% Fe-C system and increases carbon solubility in the alloy.

The measured solubilities of carbon in the austenite at pressures of one atmosphere and 45 kbar and temperatures of 1310 and 1330°C differed appreciably from the calculated values.

References