Redox conditions of metal-carbon melts and natural diamond genesis

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Participation of metallic iron in the processes of natural diamond formation has recently been suggested based on experimental studies, as well as the observation of native iron inclusions in natural diamond. The redox conditions of diamond-producing metal-carbon melts in the Earth’s mantle are therefore of interest. We calculated the values of oxygen fugacity, corresponding to the equilibrium of Fe-C and Fe-Ni-C melts with wüstite and diamond at a pressure of 60 kbar. Diamond crystallization from Fe-Ni-C-O melts at usual P-T conditions of the catalytic diamond synthesis was shown experimentally. It was also shown that iron-carbon melts are stable at the values ranging from the stability field of iron to that of wüstite. From metal-carbon melts either iron (iron-nickel) or wüstite can crystallize along with diamond, depending on the redox conditions. The stability of the metal-carbon melts is not limited to such reducing conditions as solid metals, and such conditions could have existed in the ancient Earth’s mantle.
The oxidation of solid iron and iron dissolved in Fe-C-O or Fe-Ni-C-O melt is described by the equations:

\[
\text{Fe} + \frac{1}{2} \text{O}_2 = \text{FeO}_{\text{IW}} \\
[\text{Fe}] + \frac{1}{2} \text{O}_2 = \text{FeO}_{[\text{Fe}]W}
\]

where [Fe] is the Fe-component of Fe-C-O or Fe-Ni-C-O melt.

Thermodynamic relations for the evaluation of oxygen fugacity in the buffered equilibrium are

\[
\ell n f_W^{\text{FeO}} \{T, P\} - 2G_{\gamma} \{T, P\} - G_{O_2} \{T, P_0\} = \frac{RT}{T} \left[ X_{\text{Fe}} \gamma_{\text{Fe}} \right]
\]

where \( G_{\text{FeO}}, G_{O_2}, G_{\gamma} \) are the molar free energies for wüstite, oxygen, solid iron (\( \gamma \)-phase) and molten (pure) iron, respectively; \( X_{\text{Fe}} \) is the molar fraction of Fe in Fe-C-O or Fe-Ni-C-O melt in equilibrium with wüstite and diamond; \( \gamma_{\text{Fe}} \) - activity coefficient of iron in the melts.

Comparing the equation, we receive the formula for the calculation of the oxygen fugacity in the equilibrium [Fe]W as compared to the IW buffer:

\[
\Delta \ell n f_{O_2} = \ell n f_{W}^{[\text{Fe}]W} - \ell n f_{O_2}^{\text{IW}} = \frac{2}{RT} \left[ G_{\gamma} - G_{\ell} - T \ell n (X_{\text{Fe}} \gamma_{\text{Fe}}) \right]
\]

In the calculation of \( G_{\gamma} - G_{\ell} \), the iron melting curve (Ohtani et al., 1984) was used, since melting temperatures at high pressures are determined in the experiments with high accuracy. At the melting temperature \( G_{\gamma} = G_{\ell} \) for other temperatures \( G_{\gamma} \) were calculated from the equation:

\[
G_{\gamma} - G_{\ell} = \left( T - T_f \right) \Delta S_f + \int_{T_f}^{T} \left( C_p^\gamma - C_p^\ell \right) dT
\]

where \( T_f \) and \( \Delta S_f = 7.641 \text{ J/(K·mole)} \) (Kato and Ringwood, 1989) are the melting temperature and entropy; \( C_p^\gamma \) and \( C_p^\ell \) are the molar heat capacities for solid and molten iron (Barin and Knacke, 1973).

The molar fractions \( X_{\text{Fe}} \) in the Fe-C-O and Fe-Ni-C-O melts were estimated from isobaric sections of the systems Fe-C, Fe-O, Fe-Ni-C, Ni-C, Ni-O, reported by Strong and Hanneman (1967), Bundy et al. (1973), Kamenetskaya and Korsunskaya (1980), Ershova et al. (1981), Ohtani et al. (1984), Kato and Ringwood (1989), Ringwood and Hibberson (1990, 1991), Kocherzhinskii et al. (1993), Chepurov et al. (1997). Comparing the phase diagrams of systems, we derived empirical equations for the solubility of iron and carbon in the melts at 60 kbar:

\[
X_{\text{Fe}} = 0.8 - 2 \times 10^{-4} \left( t - 1200 \right),
\]

where \( t \) is the temperature (°C) (Fe-C-O melt)

\[
X_{\text{Fe}} = 0.57 - 1.75 \times 10^{-4} \left( t - 1100 \right)
\]

(Fe\(_{0.7}\)Ni\(_{0.3}\)-C-O melt)

\[
X_{\text{Fe}} = 0.25 - 7.5 \times 10^{-5} \left( t - 1300 \right)
\]

(Fe\(_{0.3}\)Ni\(_{0.7}\)-C-O melt)

\[
X_{\text{C}} = 0.18 + 2.5 \times 10^{-4} \left( t - 1100 \right)
\]

(Fe\(_{0.7}\)Ni\(_{0.3}\)-C-O melt)

\[
X_{\text{C}} = 0.16 + 2.5 \times 10^{-4} \left( t - 1300 \right)
\]

(Fe\(_{0.3}\)Ni\(_{0.7}\)-C-O melt).

The Fe-C and Ni-C melts are described (Korsunskaya et al., 1973; Kamenetskaya and Korsunskaya, 1980; Ershova et al., 1981) by a regular-solution model with an extra term for the volume of mixing. Kato and Ringwood (1989) regarded Fe-O melts as ideal, while the activity
coefficient of iron is accepted to be equal to one. Considering that the solubility of oxygen in these liquid metals is an order of magnitude smaller than that of carbon, it is reasonable to assume that Fe-C-O and Fe-Ni-C-O melts have similar properties as Fe-C and Fe-Ni-C melts and therefore the activity coefficient of iron was calculated using an equation proposed for metal-carbon melts (Kamenetskaya and Korsunskaya, 1980; Ershova et al., 1981):

$$RT\ln\gamma_{Fe} = (E_m + PV_m)X_{C}^{2}$$

where $V_m = -5 \text{ cm}^3/\text{mol (Fe-C)}$ or $-4 \text{ cm}^3/\text{mol (Ni-C)}$ and $E_m \text{ (cal/mol)} = -26730 + 8.8T \text{ (Fe-C)}$ or $-19142.4 + 7.0T \text{ (Ni-C)}$ are the volume and energy of mixing, respectively.

There are three main reasons for the uncertainty in the calculated values of $\Delta\lg$. First, this is the uncertainty in the carbon solubility in an iron melt at high pressure. Second, incorrect calculation of iron activity coefficient in iron-carbon melt is rather less important reason. Third, uncertainty in the melting temperature of iron is insignificant reason. The three reason yield total uncertainty in the oxygen fugacity of $\pm 0.3 \text{ lg units}$.

**Experimental procedures**

The experiments were performed using a multi-anvil high-pressure apparatus of the “split sphere” type (Chepurov et al., 1997) at 55–60 kbar and 1450–1500°C. Experiments lasted from 5 to 40 hrs. The high-pressure unit was made of infusible oxides having no phase transitions at the experimental conditions (tetragonal ZrO$_2$ with addition 5 wt.% CaO for stabilization the tetragonal phase). A tubular graphite heater was used. During experiments the pressure was determined from changes in the electric resistance of Bi and PbSe before heating of the high-pressure unit. The temperature was measured with a PtRh thermocouple. The thermocouple and the pressure reading pickup were calibrated using the graphite-diamond (Kennedy and Kennedy, 1976) and the quartz-coesite (Mirmrwal and Massonne, 1980) phase transitions and the melting temperatures of metals in the high-pressure unit (DTA). Samples were quenched at a rate of 100–150°C/s without pressure release.

Starting materials were chemically pure graphite, Ni, Fe, NiO. The design of the run capsules is shown in Fig. 1. The source of carbon (graphite) was placed in the hottest (central) zone. Then the pressed Fe-Ni mixture (weight Fe:Ni = 3:7) + graphite (3% from metal weight) with the adding of NiO (10–30 wt.% from Fe + Ni + C composition) was inserted. Diamond seed crystals were put into the coldest zone. The mixture of metallic Fe and Ni (instead of pure iron or nickel) was used to reduce the melting temperature of the metallic charge.

**RESULTS AND DISCUSSION**

**Calculated data**

Figure 2 shows the calculated curves for the (Fe,C,O)-melt + diamond + wüstite and (Fe,Ni,C,O)-melts + diamond + wüstite equilibrium buffers at 60 kbar, along with the curves of C-CO-CO$_2$ (CCO), Fe(30 wt.%):Ni(70 wt.%)-
wüstit (INW) (Chepurov et al., 1997, 1999) and iron-wüstite (IW), iron-quartz-fayalite (IQF) and wüstite-magnetite (WM) (Kadik and Lukanin, 1986). The buffer curves 1, 2, 3 represent higher conditions than equilibrium buffers involving solid components above 1000–1200°C, i.e. the metal-carbon melts are stable under more oxidizing conditions than native metals. At values corresponding to the field between IW and curves 1, 2 or 3, wüstite, and under more reducing conditions, metallic iron or iron-nickel crystallizes from metal-carbon melts. Along with metal and wüstite, according to the P-T parameters, diamond or graphite may occur.

**Experimental data**

The experimental runs are summarized in Table 1. In the experiments with the addition of 5–30 wt.% of NiO to the charge, graphite was completely transformed into diamond, and the growth of diamond seed crystals was observed. In the type of experimental setup used here (Fig. 1), the complete transition of graphite into diamond in metal (Fe, Ni, Co, Mn)-carbon systems occurs during the first minutes by carbon recrystallization through a thin film of a melt (Chepurov et al., 1997), i.e. several minutes after the run starts, carbon in the pellet (N3, Fig. 1) transformed completely into diamond. Growth of seed diamond crystals during the runs occurred by the transfer of carbon from its source through the volume of the melt and resulted in crystals up to 3 mm in size. The diamonds are green with a light yellow tint, some of them were twinned (Fig. 3). The diamond crystals contain black inclusions of the metallic solvent and crystal faces are frequently step-like and blocked. In the experiment 7-26-99, in which the charge contained 50 wt.% of NiO,

![Graph](image.png)

**Fig. 2.** $\log f CO_2$ values of various buffers at 60 kbar. Buffers: IQF - iron + quartz + fayalite, IW - iron + wüstite, INW - Fe(30 wt.%)Ni(70 wt.%) + wüstite, WM - wüstite + magnetite, NNO - nickel + NiO, CCO - C + CO + CO$_2$, 1 - (Fe,C,O)-melt + diamond + wüstite, 2 - (Fe$_{0.7}$Ni$_{0.3}$,C,O)-melt + diamond + wüstite, 3 - (Fe$_{0.3}$Ni$_{0.7}$,C,O)-melt + diamond + wüstite.

**Table 1.** Conditions and results of experiments on diamond synthesis and growth in the system (Fe,Ni) - NiO - graphite

<table>
<thead>
<tr>
<th>N of exp.</th>
<th>NiO content in the charge (wt.%)</th>
<th>Relative content (mol.%)</th>
<th>Experimental parameters</th>
<th>Experimental results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Ni</td>
<td>O</td>
<td>P (kbar) ($\pm 2$)</td>
</tr>
<tr>
<td>1-31-97</td>
<td>5</td>
<td>29</td>
<td>67</td>
<td>4</td>
</tr>
<tr>
<td>3-44-97</td>
<td>13</td>
<td>25</td>
<td>65</td>
<td>10</td>
</tr>
<tr>
<td>2-25-98</td>
<td>13</td>
<td>25</td>
<td>65</td>
<td>10</td>
</tr>
<tr>
<td>8-6-98</td>
<td>30</td>
<td>18</td>
<td>62</td>
<td>20</td>
</tr>
<tr>
<td>7-26-99</td>
<td>50</td>
<td>12</td>
<td>57</td>
<td>31</td>
</tr>
</tbody>
</table>
diamond synthesis and growth of the seed crystals did not occur.

Literature data on the solubility of oxygen in Fe-Ni-C or Fe-Ni melts under high pressures are not available and the solubility of oxygen in Ni melts was studied only for pressures up to 30 kbar (Kato and Ringwood, 1989). According to these data, the oxygen solubility in the nickel melt is a several times higher than in the iron melt. Thus, at a pressure of 30 kbar and a temperature of 1650°C the nickel melt dissolves about 4 mol.% of oxygen while the iron melt dissolves only about 1 mol.% (Kato and Ringwood, 1989).

In our experiments with NiO content in the charge ≥13 wt.% (Table 1), the oxygen content in the system was sufficient for the saturation of the system. Due to higher oxygen solubility in the nickel melt relative to the iron melt, the increase in NiO content leads to an increase in the oxygen content of the melt. It is known that the addition of impurities (Cu, Pb, S etc.) into the systems consisting of 3d transition metals and carbon rises the P-T conditions, required for the conversion of graphite into diamond (Chepurov et al., 1997). This is due to a lowering of the catalytic activity of the metal-carbon melts in the course of dilution with other elements. Our experiments showed the highest oxygen content in the melt for run 7-26-99. Diamond crystallization from such a melt probably requires higher temperatures and pressures. In the oxygen-saturated metal-carbon melts containing high proportion of iron, diamond formation takes place at the usual P-T conditions for catalytic diamond synthesis.

**Implication**

In natural diamonds inclusions of native iron, wüstite and, more rarely, magnetite are observed. Their mutual occurrence in the form of monophase or polyphase inclusions in one diamond is typical (Sobolev et al., 1981; Gorshkov et al., 1997; Stachel et al., 1998; Bulanova et al., 1998). Based on the observation of an inclusion paragenesis consisting of iron + wüstite Bulanova (1995) and Bulanova et al. (1998) concluded that diamond formation takes place under conditions corresponding to the IW buffer.

The data presented here show that from metal-carbon melts either metals or their oxides can crystallize, depending on the redox conditions. In the case of equilibrium crystallization of the metal-carbon melt in an open system, where the oxygen fugacity in the melt is fixed by the instant mass exchange with the surroundings, one phase crystallizes from the melt-iron or wüstite. In a closed system or in the case of rapid crystallization of the melt, the oxygen concentration varies. In the course of metal crystallization the oxygen concentration increases and after reaching a certain value, two phases—iron and wüstite—begin to crystallize from the melt. If the oxygen fugacity in the system lies in the stability field of wüstite, wüstite is the first phase to crystallize from the melt causing the oxygen concentration in the melt to decrease, eventually leading to simultaneous crystallization of metallic iron or iron-nickel and wüstite. Such a mechanism is experimentally confirmed by the simultaneous observation of wüstite and metal inclusions in diamonds synthesized in the Fe-Ni-C system (Pal’yanyov et al., 1997). Wüstite inclusions are trapped in the diamonds during the initial and final stages of their growth, thereby reflecting the direction of the evolution of in the melt.

![Fig. 3. A part of synthetic diamond crystal with octahedral habit with twin lamella.](image-url)
The age of the oldest diamonds in peridotites is 3.2 billion years (Richardson et al., 1984). The age of young diamonds is about 360 million years (Shimizu and Sobolev, 1995). There were extremely reducing conditions in the ancient mantle with oxygen fugacity ( ) near that for equilibrium between minerals and Fe-Ni metallic phase. It changed in time getting more and more oxidizing (Kadik, 1999; Kadik et al., 2000). The values of at the equilibrium involving metal-carbon melts are close to those of the INW buffer (Fig. 2). Thus, one may suppose that the metal-carbon melts were stable in the ancient Earth’s mantle.

The composition of natural mantle melts is heterogeneous. The melts contain silicates, sulfides, carbon, and other components. Under the reducing conditions of the ancient mantle, the melts contained also Fe and Ni an a pure form. These 3d transition elements provided diamond formation during reduction of oxide- and silicate-carbon systems at high P-T conditions. More young diamonds formed under more oxidizing conditions, for instance in carbonate melts.

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REFERENCES


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