Neutron diffraction study of metal-matrix composite with fullerite

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Abstract. Interaction of amorphous fullerite C₆₀ with austenitic Fe-33.2 wt. % Ni alloy at pressures 0-8 GPa and temperatures 600-1100 °C was studied by neutron diffraction. The amorphous fullerite was obtained by ball milling and mixed with the powder of the crystalline alloy. The interaction at sintering led to the dissolution of carbon in fcc Fe-Ni solid solution and the formation of carbide (Fe, Ni)₃C, but the Fe-Ni-C alloy did not undergo phase transformations and preserved the original fcc structure. As a result, the alloy hardened, we could also witness a clear barometric effect: at the pressure of 2 GPa the amount of the dissolved carbon and the microhardness turned out to be significantly higher than those at 8 GPa. During sintering amorphous fullerite is undergoing phase transitions and its microhardness is higher than the microhardness of the metal component. At high temperatures of interaction graphite appears. The presence of Fe-Ni alloy in the composite reduces the temperature of graphite formation in comparison with transformations in the pure amorphous fullerene.

Keywords: neutron diffraction; metal matrix composites; fullerenes; sintering; phase transitions; high-pressure; high-temperatures

1. Introduction

It is widely known that metal-matrix composite materials (MMCs) reinforced by ceramic fibers are superior in terms of the properties to monolithic alloys. They combine the best properties of their two components, such as ductility and toughness of the matrix, as well as a high elastic modulus and strength of the reinforcing elements. These composites are widely used as structural materials in aerospace, automotive, chemical, transport and other industries [1]. Replacing ceramic by carbon fibers or graphitic particles holds much promise because of their high thermal conductivity, low density, good self-lubrication, high damping capacity and a low coefficient of thermal expansion. These MMCs have high dimensional stability and suppress vibration [2,3,4].

With the discovery of fullerenes, carbon nanotubes, and graphene, which all possess a unique set of mechanical and physical properties, scientists started to elaborate on metal-matrix composites with fullerene [5-9], carbon nanotubes [10-11], and graphene [10]. The growing production of carbon nanomaterials and reduction of its cost enhances public interest to such studies. Although using composites with carbon nanotubes brings certain advantages [10-11], a high amount of research has been done on composites with fullerene C₆₀ or a mixture of fullerenes as the reinforcing component [5-9].

To develop and produce compositions of such composite materials, one needs to study the interaction of carbon nanomaterials with different metals and alloys under different conditions. In case of fullerenes, most of the performed studies employ crystalline C₆₀. At the same time, it is of interest to investigate the effect of different structural states of fullerenes on such interaction, in particular, the use of amorphous (nanostructured) fullerenes. Previously we have undertaken such studies for the case...
of Al [12] and Fe [13] and received a different behavior of the metallic component in these composites, associated primarily with the presence of polymorphic transformations in iron. It is therefore of interest to study the interaction of amorphous fullerites with an iron alloy, which has no polymorphic transformations.

In this paper, we selected an austenitic (fcc) alloy Fe-33.2 wt. % Ni as a matrix and investigated structural aspects of its interaction with the amorphous C_{60} in a wide range of pressures (up to 8 GPa) and temperatures (up to 1200 °C). The method of neutron diffraction was chosen as the main one. This method is the most suitable for localization of light atoms in the presence of heavy atoms as compared with other structural methods.

2. Experimental methods
Our initial samples of C_{60} fullerenes of 99.5% purity were produced by “NeoTechProduct” by high-temperature treatment of graphite, followed by isolation with organic solvents and subsequent chromatographic separation. The neutron diffraction patterns of our initial crystal fullerenes correspond to the fcc lattice with a period \( a = 1.416 \) nm. Amorphous fullerenes (aC_{60}) were prepared by mechanical grinding of crystal C_{60} (~1–1.5 g) in air in a Fritsch type mill with agate cup and balls at low rates over long periods of time (up to 100 hours) fixing the structural changes by neutron diffraction. As a result, at the site of intense diffraction peaks halos were formed (figure 1) corresponding to the amorphization of fullerite.

For the metal component an alloy Fe-33.2 wt.% Ni was melted, it was then turned into shavings by drilling, and the shavings were further ground into a powder in a Fritsch mill. This powder was mixed with the C_{60} amorphous powder (25 at.%) in the same mill. The Fe-Ni alloy retained fcc crystal structure after milling (figure 2).

Annealing of (Fe-Ni)-aC_{60} powder was performed in a high-temperature vacuum furnace at 900 and 1200 °C for 5 min in each cycle, followed by cooling down to room temperature. Sintering under high pressure occurred in the following way: raw material was pressed to pellets of dimensions 3 mm in height and 5 mm in diameter. Thermobaric treatment of these pellets was carried out by using high pressure toroid-type chambers [14]. The pressure was generated in a cell from lithographic stone placed between hard alloy anvils with a special profile. The pressure accuracy was ±0.2 GPa, and the temperature gradient along the sample height was less than 20 K. The high-pressure treatment was carried out at 2.0, 4.5 and 8.0 GPa in the temperature range 600-1100 °C. After stabilization of the applied pressure, the samples were heated to the desired temperature at heating rate \( \approx 100 \) K/min and held for 60 seconds. Then the cells were cooled down rapidly to room temperature (\( \approx 100 \) K/s), before the pressure was released. These sintered samples were in the tablet form, having a diameter of 5
mm and a height of ~ 1 mm. Thus, the samples were studied ex-situ.

The structure of the samples was examined using the neutron diffraction method on the neutron multidetector (224 scintillation detectors) diffractometer DISC [15] with the stationary nuclear reactor capacity of 4-5.5 MW, the wavelength $\lambda$ of monochromatic heat neutron waves of 0.1664 nm (the part of $\lambda/2$ is less than 1%), and neutron flux $\sim 10^{10}$ m$^{-2}$·s$^{-1}$. The diffraction pattern processing was performed using a full profile Rietveld refinement with the help of “Fullprof” software. We also determined the microhardness by the device DuraScan20.

3. Experimental results
The investigation of the diffraction patterns (figure 2) showed that at all studied temperatures and pressures the interaction of the Fe-Ni alloy with amorphous $C_{60}$ does not change its crystal structure and, after cooling to room temperature, fcc crystal lattice is preserved. However, with temperature increase the lattice period of the fcc lattice increases significantly (figure 3) and additional lines appear in the diffraction spectrum (curves 2-4 in figure 2). Analysis of the diffraction spectra by the Rietveld method using the package “FullProf” shows the formation of the cementite (Fe, Ni)$_3$C alloyed by nickel [16,17].

Increase in the lattice spacing $\Delta a$ (figure 3) at pressures from 2 to 8 GPa is 0.01-0.048 Å (~ 0.3-1.3% of the lattice spacing of the initial Fe-Ni powder) and grows with the temperature. The value of $\Delta a$ decreases with pressure, i.e. there is a clear barometric effect.

However, after furnace annealing of the powder (consisting of a mixture of Fe-Ni alloy with amorphous fullerite) at high temperatures of 900 and 1200 $^\circ$C the change in the lattice spacing is much smaller: 0.004 and 0.01 Å respectively.

The change in the amount of cementite was determined from the relative intensity of overlapping lines (311) and (132) (marked with w in figure 2). This maximum was used because it does not overlap with the peaks of the fcc phase. Its relative intensity increases with sintering temperature and is practically independent of the applied pressure (figure 4).

In the samples annealed in a furnace without application of a high pressure, the maximum height was significantly less, but also increased with temperature.

The presence of the carbon phase, clearly visible in the microstructure cannot always be traced on the diffraction spectra. In the spectrum of the original mixture $aC_{60}$ (Fe-Ni) there are two weak halos at $2\theta=10^\circ$ and $2\theta=20^\circ$, which are characteristic for amorphous fullerite (figure 1), but in the annealed or sintered samples the halos cannot be detected on the background of the metal phase spectrum. In sintering at 750 $^\circ$C and above the most intense graphite peak (002) appears (figure 2). The relative intensity of this peak (amount of graphite) (figure 5) increases with temperature and decreases with pressure. Graphite is not observed when the powder anneals at 900 and 1200 $^\circ$C in a vacuum furnace.

The properties of the carbon phase do not show such a clear dependence on temperature and pressure, as is the case for the metal component. Microhardness amounts to 0.54-0.73 GPa, and in the majority of the investigated composites it exceeds the microhardness of a metal component by 2-3 times.

4. Discussion
The results demonstrate that at high temperatures and high pressures there is a strong interaction between amorphous $C_{60}$ and the iron-nickel austenitic alloy, which leads to the dissolution of carbon in a fcc metal lattice (a lattice parameter increases) and the formation of carbide (Fe, Ni)$_3$C while
retaining the original crystal structure of the metal component. Dissolution of carbon and carbide formation led naturally to the increase of the hardness of the metal component.

The observed increase of the lattice spacing in the iron-nickel austenite indicates the dissolution of carbon in austenite. We evaluated the concentration of carbon in solid solution by the known dependence of the austenite lattice parameter on a nickel concentration $C_{\text{Ni}}$ and carbon concentration $C_{\text{C}}$:

$$
\Delta a = 0.001* C_{\text{Ni}} + 0.0316* C_{\text{C}}
$$

where $\Delta a$ in Å and the concentration in wt.%. The maximum concentration (after sintering at 2 GPa and 1100 °C) is ≈1.5 wt.% C and only half of that (≈0.7 wt.% C) at 8 GPa and 1100 °C. The same reduction of $C_{\text{C}}$ is observed with pressure increase at other temperatures. For example, at 600 °C $C_{\text{C}} \approx 0.5$ wt.% at 2GPa and ≈0.35 at 8 GPa. The observed decrease in the concentration of dissolved carbon with pressure increase can be explained by the fact that carbon is dissolved by the interstitial type and thus increases the volume of the alloy, which impedes excess pressure. At the same time independence of the amount of cementite of the pressure can be explained by the fact that the cementite density (~ 7.9 g/cm³ [19]) is close to the density of the Fe-Ni alloy (~ 8.1 g/cm³).

When we anneal the powder mixture in a vacuum furnace, much less carbon dissolves in the alloy and a smaller amount of cementite is formed. This is apparently due to a less close contact of carbon and metallic phases in the absence of high pressure.

It is difficult to compare our data on the solubility of carbon with the data of other studies. Although there are many publications on the alloys Fe-C and Fe-Ni-C at high pressures [e.g., 16, 17,20-22], most of them are devoted to modeling the structure of the Earth’s core, and the studies were conducted at high temperatures close to the melting point. A comparison is also complicated by the fact that different studies have a high variation in the times of the sample exposure at carbon dissolution temperatures, and even sometimes fail to reach equilibrium concentrations, as was the case in the present work. However, some comparisons can still be made. For instance, in the alloy Fe-6 wt.% Ni approximate solubility of carbon is 0.85 wt.% at 2000 °C and 9 GPa and it decreases with pressure increase up to 20 GPa [17]. The Fe-C system has also demonstrated that the maximum solubility of C in austenite decreases from ≈2 wt.% at 5 GPa to ≈0.5 wt.% at 130 GPa [21]. This maximum solubility was observed at the eutectic temperature, which increases with increasing pressure from 1293 up to 2979 °C. As can be seen, our results do not contradict the data available in the literature.
Preserving the fcc crystal lattice of the iron-nickel alloy with 33.2 wt.% Ni at cooling after sintering is consistent with literature data. In the alloy Fe-31 wt.% Ni-0.02 wt.% C, which is close to our alloy composition, the martensite point is below room temperature (≈205 K) [22], and even in the alloy Fe-25.3 % Ni-0.73% C (wt.%) with a lower Ni content at room temperature a stable fcc structure was observed [24]. Mechanical activation of the mixture of iron-nickel alloy (50 wt.% Ni) with powder of carbon phase (carbon nanotubes) causes no change in the crystal structure [25]. This is consistent with the existence of the fcc structure of our original powder after mechanical activation and after annealing at 900 and 1200 ºC.

The formation of carbide (Fe, Ni)3C, observed in the present work, is consistent with the available data on the Fe-Ni-C alloys at high temperatures and pressures. Thus, according to the cross section of the ternary Fe-Ni-C diagram at 1050 ºC and 10 GPa [16] our composite should contain a metal solid solution and the carbide (Fe,Ni)3C. Although Fe-Ni-C alloys in [16] were sintered from powders of metals and graphite with longer exposures (several hours), while we sintered metal and amorphous fullerite powders over a short time (1 minute) the same structure was registered in our alloy at 1100 ºC and 8 GPa.

During sintering not only the metal component of the composite changes, but also the carbon phase alters. These changes comprise the transformation of amorphous fullerene in amorphous and crystalline graphite [27]. The resulting transformation products of amorphous fullerite have increased microhardness that substantially exceeds microhardness of the metal component. Increased microhardness of the carbon phase enables it as a potential hardening phase in the metal matrix composites.

At high pressures with increasing temperature crystalline C60 is known to transform into several polymerized phases, which at higher temperatures are transformed into amorphous and crystalline graphite [26]. In an amorphous fullerite, the stage of formation of polymerized phases is absent and graphite is formed at lower temperatures [27]. In our composite, the line (002) of graphite appears at pressures of 2-8 GPa at 750 ºC or higher, while in the pure amorphous fullerite these temperatures are significantly higher, reaching 1050-1300 ºC [27]. It turns out that the presence of Fe-Ni alloy promotes the conversion of amorphous fullerene to crystalline graphite.

While furnace annealing the powder mixture of amorphous fullerite and the Fe-Ni alloy, we observed no graphite after annealing at 1200 ºC, which agrees well with the data of [28], in which under the same annealing conditions of pure amorphous C60 crystalline graphite did not appear even at 1500 ºC. The effect of the Fe-Ni alloy on this process is not observed, apparently due to a poor contact of fullerene and metal powders, and it is consistent with the relatively small change in the alloy lattice spacing (weak carbon saturation).

5. Conclusions

It is shown that between amorphous C60 and the austenitic Fe-33.2 wt.% Ni alloy at high temperatures and pressures there is a strong interaction that leads to saturation of the alloy by carbon and formation of carbides (Fe, Ni)3C, while retaining the fcc crystal structure of the alloy. The interaction is weakened with increasing pressure from 2 to 8 GPa. The interaction also reduces the stability of amorphous fullerite against transformation into a stable modification -crystal graphite.

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