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$Fe+C_{60}$ NANOSTRUCTURED MATERIAL WITH ADVANCED MECHANICAL PROPERTIES

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Abstract. *Discovery of the fullerenes and rapid development of the synthesis techniques for various forms of nanocarbons (such as nanotubes) stimulates development of a new family of so called nanomaterials. There is general idea to use different forms of nanocarbons or nanocarbon compounds to produce nanostructured composites with metals. Different approaches are being developed today but most of them have some limitations. High-pressure-high-temperature technique is probably the only universal that allows producing a large variety of bulk, 100% dense nanostructured materials.*

In the work presented we report on results of creation and investigation of a new Fe-C nanocomposite material with high values of elastic modulii and hardness that has been created by means of high-energy (ball milling) pre-treatment of iron+10 %wt. fullerene C_{60} followed by high-pressure-high-temperature treatment. The highest values achieved for a series of samples are the following: 210 GPa for bulk modulus; 100 GPa for shear modulus; 260 GPa for Young's modulus; 13.5 GPa for microhardness.

Ultrasonic pulse (microacoustic) technique at frequency 25 MHz was applied to study elastic properties of the samples. Optical microscopy, TEM, X-ray and microhardness investigations were carried out to study the structure and the properties of the obtained samples.

It was found that high-pressure treatment at 7.7 GPa and temperatures higher than $800^{o}C$ make structural changes accompanied with sharp increase of mechanical properties.

1. Introduction

Iron-carbon system is widely used today. It is basic for quite big number of modern materials like steels and alloys. Ferrous metals are used in diamond synthesis. Catalytic activity of iron and ferrous metals is now used in synthesis of nanomaterials like nanotubes and other "nanocarbons". The catalytic mechanism is not absolutely clear.

Fe-C system is under investigation for a long time already, but till now many effects and phenomena related to nano-size structural features need closer observation. It was found recently that so-called time-to-rupture of martensitic steel that contains 9% chromium may be increased (at 923 K) by factor of 100 over the strongest creep-resistant steel currently available (which contains about 0.08% wt. carbon) [1]. This effect is due to presence of large number of fine particles, between 5 and 10 nanometres in size. The small particles consist of metal alloyed with either carbon or nitrogen. Another way of steel design is based on development of fine bainite structure by means of alloying steel with Al or/and Co and special treatment. The aim is to create uniform structure of 20-40 nm bainite plates free from allotriomorphic ferrite and almost free from athermal martensite [2,3]. General idea of key role of nano-size structure elements is widely acknowledged as fruitful for new materials development. Attempts to incorporate different nano-carbons such fullerens and nanotubes into metal materials are under way. It was found [4] that Fe+8%C_{60} powder composition heated at 640-710°C may produce a new phase. This result is interesting from the following point of view. A nano-structured material that consist of one-sort atoms (for example pure iron after severe plastic deformation) often have low stability and tend to grain-grow at mild temperatures. To stabilize the nano-structure "second" constituent should be present and it should be very stable itself. C_{60} molecule satisfies these criteria.

There are several general ways to produce bulk nano-structured materials: severe plastic deformation; crystallization from amorphous; layer deposition, etc. High-pressure-high-temperature technique has the following advantages: it has lower "chemical composition limitation", "produces" about zero residual porosity materials, and prevents grain growth.

In the work presented we report on results of investigation of a composite produced from iron and fullerene C_{60} by means of high-pressure-high-temperature technique. A series of samples was produced by means of high-energy ball milling of iron-fullerene mixture followed by treatment under high pressure (7.7 GPa) and different temperatures. Ultrasonic technique was applied to study elastic properties and their bulk irregularities of the samples. Optical microscopy, TEM, X-ray and microhardness investigations were carried out.

2. Experimental details

Iron powder (99.98% purity) has been mixed with C_{60} powder (99.98% purity), the composition was Fe+10 wt.% fullerite C_{60}. It was ball-milled with carbon steel balls in stainless-steel container in protective environment (argon atmosphere). Profiled anvils (toroid-type) apparatus was use for high-pressure-high-temperature treatment of the ball-milled material. Pressure calibration of the apparatus has been made using bismuth polymorph transitions as pressure marks. Chromel-alumel thermocouple was used to measure temperature. A series of experiments has been made at 7.7 GPa pressure and different temperatures (400, 600, 800, 1000, 1200 and 1350^{o}C) and 60 second exposure. The dimensions of the as treated samples were the following, diameter about 5 mm, and height about 3 mm.

The density of the samples was measured with weight-in-liquid technique (accuracy 1%). Results of the measurements are presented in Table 1.

For further studies the front and back faces of the specimens were polished. Ultrasonic pulse (microacoustic) technique at frequency 25 MHz was applied to study elastic properties of samples. Ultrashort (40 ns pulses) probing ultrasonic technique was used for measurements. Elastic modulii were calculated on the basis of the measured sound velocities and densities of the samples. The sound velocity V_L and V_T measurement accuracy was ~3%. Experimental procedure has been described in details previously [5].

Vickers hardness measurements were made with diamond 136^0 pyramidal indenter, 1 N load and 30 seconds dwell time.

3. Results

For all the samples (of Fe+10wt.%C_{60} composition) first treated in ball mill and than under high-pressure and temperature mean measured values of density ρ, longitudinal V_L and shear V_T ultrasonic wave velocities and microhardness H_μ , calculated values for bulk modulus K, shear modulus G, Young's modulus E Poisson's ratio σ are presented in Table 1. It was found that shear modulus G and Young modulus E increase with synthesis temperature at 7.7 GPa. Quite good correlation was found for elastic modulus *K* and microhardness H. Bulk modulus K, as well as microhardness H_{μ} curves have maximum value at 800-1000^{O}C.

Elastic moduli *K*, *G* and microhardness H_{μ} dependencies on the synthesis temperature are presented in figure 1. The samples, synthesized at the temperatures 400^{o}C and 600^{o}C have values of the acoustical velocities typical for construction steels. The samples, synthesized at the temperature T = 800^{o}C and above have velocities values (V_L and V_T) exceeding previous by ~20%. The samples, synthesized at the temperature 800^{o}C and above have mean value of bulk and shear modulii higher than construction steel's does (see Table 1).

Table 1.

Measured mean values of density ρ, longitudinal V_L, shear V_T, ultrasonic wave velocities and microhardness H_{μ}, calculated values for bulk modulus *K*, shear modulus *G*, Young's modulus *E* Poisson's ratio σ as a function of temperature T of treatment under high pressure 7.7 GPa.

T ^{0}C	ρ g/cm^{3}	V_L km/s	V_T km/s	*K*, GPa	*E*, GPa	*G*, GPa	σ	H_{μ} GPa
400	7.52	6.03	3.25	170	200	80	0.30	9.13
600	7.65	6.10	3.10	187	195	74	0.33	9.45
800	7.63	6.30	3.17	200	205	77	0.33	13.35
1000	7.67	6.50	3.30	210	220	85	0.33	12.40
1200	7.61	6.17	3.39	170	225	90	0.29	9.35
1350	7.56	6.37	3.72	160	260	100	0.23	7.80
Steel	7.60	6.20	3.24	185	210	80	0.31	~11

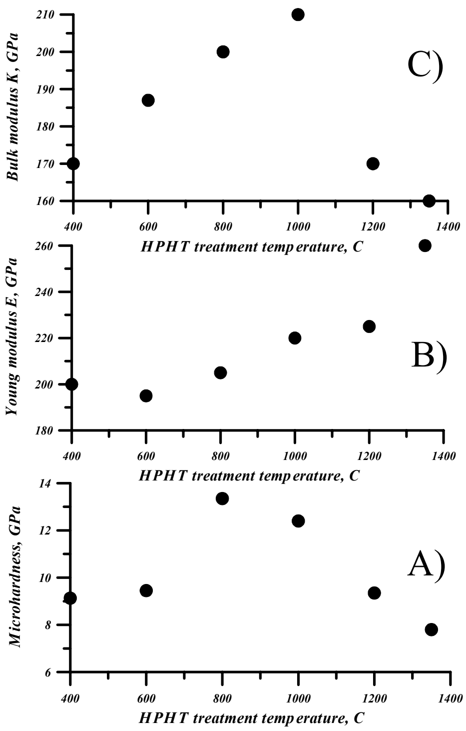

Fig. 1. Dependence of A) microhardness; B) Young modulus; C) bulk modulus on the temperature of treatment under pressure 7.7 GPa

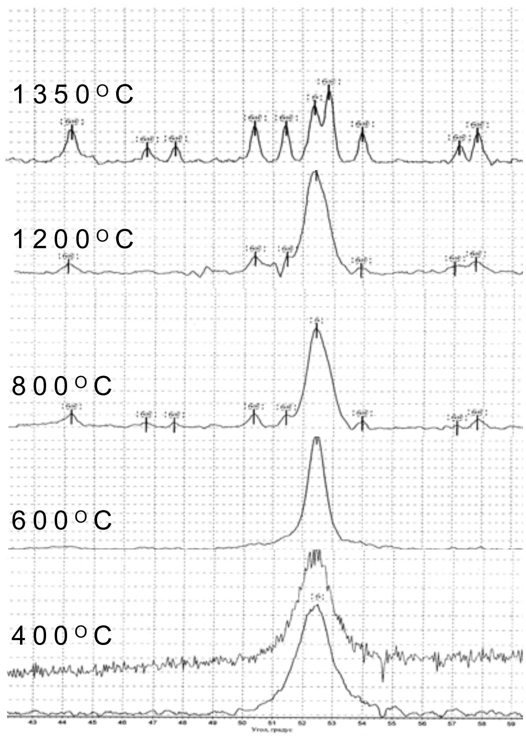

Fig. 2. X-ray patterns of the samples treated under pressure 7.7 GPa and different temperatures.

X–ray investigation result for all samples (of Fe+10wt.%C_{60} composition) first treated in ball mill and than under high-pressure 7,7 GPa and different temperatures are presented in Fig. 2. It was found that below 800^{o}C temperature of treatment only broad iron peaks are present. The peaks become sharper when temperature increases. At 800^{o}C additional peaks appear that were identified as carbide peaks. It should be noted that 10wt.% of C_{60} in composition equals 34 atomic % of carbon. That means that concentration of carbon is high, for example Fe_3C carbide contains 25 atomic % of carbon. It is quite interesting that we did not find expected evidences for high content of carbides in the samples till the samples were treated by temperatures as high as 1350^{O}C approximately (see Figure 2). That means that below 1350^{O}C carbon (or carbon-reach) phase does not produce “strong” x-ray peaks.

4. Discussion

The following three mechanisms play key role if the mechanical properties of the samples are considered: initial dispersion of the constituents (and its growth with the increase of the treatment temperature); precipitation of fine carbides (and other phases); initial presence and formation of new superhard phases of fullerene.

Possible explanation of the temperature dependence of the mechanical properties of samples may be as follows. Quite high values of hardness of the 400-600^{O}C samples may be due to nano-structure formed during ball-mill pretreatment followed by high-pressure and temperature treatment. Direct TEM investigations (Fig. 3) and estimation of the block-size based on the analysis of X-ray peak profiles gives evidences that the structure of the material below 800^{O}C comprise nano-size grains (smaller than 30 nm). Temperatures above 800^{O}C make grains grow bigger than 100 nm.

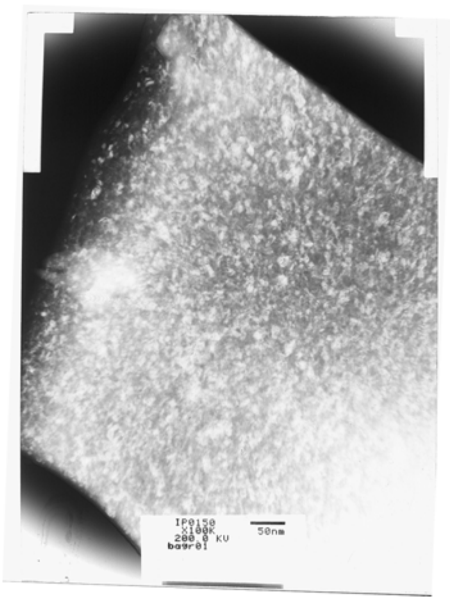

Fig. 3. TEM image of the Fe+10wt.%C_{60} sample ball-mill and than treated at 7.7 GPa + 400^{O}C.

At temperature above 800^{O}C hardness becomes even higher and than decrease if treatment temperature is higher than 1000^{O}C. Analysis of the x-ray results reveal that at temperature 800^{O}C carbides start to precipitate but amount of the carbides is much less than might be expected from Fe-C composition. That means that some part of the carbon remains in state "invisible" for X-rays. It is known that at temperatures 800-1000^{O}C new hard phases of fullerene [7,8,9] may form. This carbon phases may be disordered and very hard [7,8]. They may greatly influence the mechanical properties. The fact that amount of carbides is much less than possible says for possible role of hard phases of fullerene.

At temperatures higher than 1000^{O}C amount of the carbide precipitates and size of carbide grains increase. All these coincide with decrease of the hardness of the samples and probably with "degradation" of the hard phases of fullerene.

At temperatures about 1300^{O}C most of the carbon is in a form of carbides.

Conclusion

New nanomaterial with advanced mechanical properties has been created with high energy (ball milling) pre-treatment of iron+10 wt.% fullerite C_{60} followed by high-pressure/high-temperature treatment. The highest values achieved for a series of samples are the following, 210 GPa for bulk modulus; 100 GPa for shear modulus; 260 GPa for Young's modulus. Dispersion strengthening with nano particles and zero porosity are the reasons for high elastic properties and hardness values from structural point of view. Carbon reach, C_{60}-originated highly disperse or amorphous structure constituents makes mechanical properties of the material high. Its comprise iron carbides and hard fullerene phase probably.

It was found that temperatures above 800^{o}C during high-pressure treatment at 7.7 GPa produce structural changes accompanied by increase of mechanical properties.

High-energy mechanical pretreatment (ball milling) followed by high-pressure-high-temperature treatment was found to be "good technological chain" to produce materials with excellent properties.

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