PRODUCTION OF COMPACT NANOSTRUCTURED IRON+C60 MATERIAL BY MEANS OF HIGH PRESSURE AND TEMPERATURE

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Abstract: *New nanocomposite material with advanced mechanical properties was created by high energy (ball milling) pre-treatment of iron+3 wt.% fullerene C_{60} powder 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, which are ~20% higher than the values of cast iron of the same composition.*

The samples were investigated using the following techniques: metallography, acoustic spectroscopy, scanning probe microscopy and microhardness.

1. Introduction

A new branch of nanomaterials is under development today. There is an idea to use different forms of nanocarbon or nanocarbon compounds to produce nanostructured composites [1]. Iron and carbon nanocomposites are of particular interest.

Solid metal-carbon matrix of metallofullerenes and method of forming the same was patented [2]. The method is based on heating of high carbon component (fullerene reach) with low carbon component up to melting point (of carbon reach component).

Optical microscopy, X-Ray diffraction (XRD) analysis and magnetic properties measurements were carried out to characterize Fe-85 vol.% Fe_3C [3] prepared by mechanosynthesis of elemental Fe and graphite powder. It was found that mechanical properties (i.e. hardness) correlate well with fine grain size.

Dry sliding wear tests were carried out on nanophase Fe-Fe_3C white iron produced by mechanosynthesis and hipping [4] which was obtained by Fe and graphite milling and cold isostatic pressing at 300 MPa.

Raman spectroscopy, microhardness and wear resistance measurements were used to study the transformation of fullerites C_{60}+C_{70} in a mixture with iron powder upon changing temperature (800-1200^{o}C) and pressure (1-5 GPa) of compacting treatment [5], the treatment providing the fullerite transformation to particles (up to 700 μm in diameter). The formation of superhard amorphous carbon phase from fullerenes in carbon matrix was found and investigated.

Martensitic steel dispersed with nanometre-scale carbonitride particles was produced using conventional processing techniques [6]. Time-to-rapture at 923 K was increased to record value.

In the work presented we report on high mechanical properties found for iron+fullerene C_{60} composite. High-energy ball milling of iron-fullerene mixture was followed by treatment under high pressure (7.7 GPa) and different temperatures. A series of samples was produced. Ultrasonic technique was applied to study elastic properties and their bulk irregularities of the samples. Optical microscopy, scanning probe microscopy and microhardness investigations was fulfilled.

2. Samples preparation

Fe+3 wt.% fullerite C_{60} composition was chosen taking into account the following. It seemed very probable that iron and carbon would form carbides, most probably Fe_3C. There are 6.7 wt.% of carbon in Fe_3C. For the composition Fe+3 wt.% C_{60} we are supposed to have free iron in any case and amount of carbides is supposed to be considerable.

Iron powder of high purity was mixed with C_{60} powder and than ball-milled with steel balls in stainless-steel container in protective environment. It was found that 6 hours milling reduced the average size of the iron grains from 50 μm to less than 1 μm. Glove box precautions were applied to reduce contamination. High-pressure/high-temperature treatment of the composition was made with profiled anvils (toroid-type) apparatus. Pressure calibration of the apparatus was made using bismuth polymorph transitions as pressure marks. Chromel-alumel thermocouple was used to measure temperature. A series of experiments was made at 7.7 GPa pressure and 60 second exposure to different temperatures (400, 600, 800, 1000, 1200 and 1350 ^{0}C). The dimensions of the samples were about 5 mm diameter and 3 mm height.

Density of the samples was measured with weight-in-liquid method. Results of the measurements are presented in Table 1.

For further studies the front and back faces of specimens were polished and treated for metallographic study. The height of the samples with plane-parallel surfaces was 2.3 mm.

Ultrasonic pulse (microacoustic) technique at frequency 25 MHz was applied to study elastic properties of composite samples. Ultrashort probing ultrasonic 30-40 ns pulses were used for measurements. Experimental procedure was described in details previously [7]. Elastic module were calculated on the basis of the measured sound velocities and densities of the samples. The data on sound velocities V_L and V_T were obtained with an accuracy of ~3%.

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

Optical microscopy investigations were fulfilled to track out visual peculiarities of surface.

Probe microscopy investigations of polished surfaces were made to map profile and to measure microhardness of the surface. Peculiarities of the measurement techniques with scanning probe microscope NanoScan which were used it this work were described previously [8].

3. Results and discussion

3.1. Investigation of structure

Optical microscopy investigations add to scanning acoustic microscopy and scanning probe microscopy of the surface of the samples and revealed the following. Samples treated below 800^{o}C consist of different size (~5–40 μm) grains with irregular shape (figure 1a). But these grains are not "true" ones. Closely packed small iron particles covered with fullerene originated carbon make bigger aggregates or grains. 800^{o}C temperature of high-pressure treatment is the temperature when the structure of the samples changes considerably. At this temperature the "optical structure", "scanning probe microscopy structure" and "scanning acoustic microscopy structure" consists of small grains about 1 μm in size or smaller (figure 1b). Above this temperature the grains "start to grow slightly" and achieve ~3 μm size at 1350^{o}C (figure 1c).

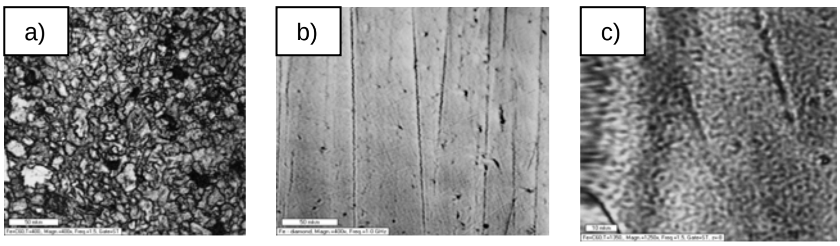

Figure 1. Structure of the high-pressure treated samples. Acoustic microscopy images. a) 300x300 μm, T=400 ^{0}C; b) 300x300 μm, T=1000 ^{0}C; c) 100x100 μm, T=1350 ^{0}C.

3.2. XRD investigations

X–ray investigations revealed that temperature region about 800^{o}C is the region of considerable structural changes. X-ray patterns for the samples below 800^{o}C contain broad Fe lines only. Since 800^{O}C lines of Fe_3C start to develop and at ~1000^{O}C Fe_3C lines are "very strong" though "small" Fe lines are also present. X-ray patterns above 1000^{O}C consist of Fe_3C and Fe lines.

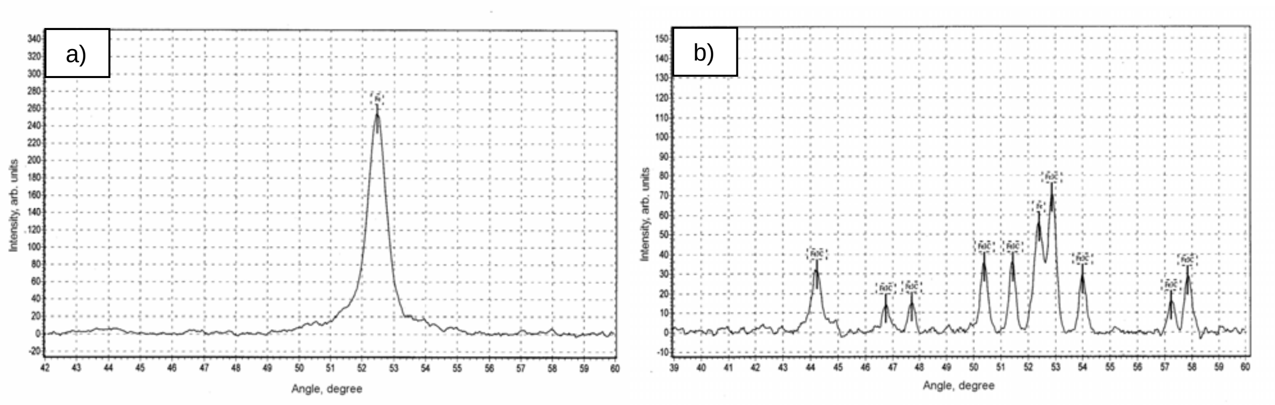

Figure 2. X-ray investigation results for the samples treated under high pressure at **a**) 600^{O}C; **b**) 1000^{O}C.

3.3. Elastic moduli and hardness

Mean values of ultrasonic velocities and corresponding values of elastic constants and hardness for all obtained samples are presented in Table 1. It should be noted that shear modulus and Young's modulus grow steadily with the synthesis temperature increase. There is quite good correlation between elastic modulus *K* and microhardness. Bulk modulus as well as microhardness reach maximum values for the samples synthesized at 800 and 1000^{O}C. It should be said that attempts to make microhardness measurements device were also made with NanoScan. The NanoScan microhardness temperature dependence is similar, but the values are 20-30% higher.

Table 1. Fe+3 wt.%C_{60} synthesized at P=7.7 GPa. Average values of density ρ, longitudinal V_L and shear V_T ultrasonic wave velocities, bulk modulus *K*, shear modulus *G*, Young's modulus *E* Poisson's ratio σ and microhardness H_μ as a function of synthesis temperature T.

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	280	80	0.31	~3

High values of elastic module of the samples treated above 800^{O}C under high pressure may be discussed from two adjacent points of view. The first of the points considers structure. The second considers the properties of the sample constituents. Grain refinement after high-energy treatment, dispersion strengthening with sub-micron fullerite originated carbon or carbonaceous particles, zero porosity are general reasons for high hardness and elastic properties values from structural point of view. The structure of all the samples in general consists of small Fe particles, about 1 μm in size or smaller and some carbon reach constituent gluing the particles.

As it can be read from x-ray data "carbon reach" constituent of the samples treated with high pressure above 800^{o}C is Fe_3C mostly. But there are some doubts that the Fe_3C is the only carbon-originated constituent. Bulk modulus *K* value for Fe_3C is about 174 GPa [9]. There are evidences that C_{60} subjected to high-pressure/high-temperature transforms into state with extremely high moduli [10], bulk modulus *K* may have value above 450 GPa, Young's modulus E above 600 GPa, shear modulus *G* above 300 GPa. It is known [11] that fullerene C_{60} treated under high-pressure/high-temperature transforms into very hard and extremely hard phases, most of the phases being disordered or long range lattice disordered, X-ray patterns for the phases contain broad and few lines.

Conclusion

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.

New nanomaterial with advanced mechanical properties was created with high energy (ball milling) pre-treatment of iron+3 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, which are ~15-25% higher than the values of the cast iron of the same composition. Grain size reduction after high-energy treatment (down to 1 μm), dispersion strengthening with nanoparticles, zero porosity are the reasons for high elastic properties and hardness values from structural point of view. Mechanical properties of the structure constituents are very high.

Temperatures above 800^{O}C during high pressure treatment at 7.7 GPa make radical structural changes accompanied with sharp increase of mechanical properties.

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