PREPARATION AND MICROSTRUCTURE, ELASTICITY AND HARDNESS INVESTIGATION OF AL-ALLOY/NANODIAMOND COMPOSITE

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Abstract: The composite samples of Al-alloy B95 reinforced with nanoparticles of synthetic diamond were prepared by direct-melting the starting B95 at ~700 °C, adding nanodiamond powder in melt and hashing it by Ar-barbotage followed by cooling and quenching. X-ray analysis, TEM, Raman spectroscopy, optical microscopy, scanning probe microscopy, microhardness and nanoindentation measurements were used to study the structural and mechanical properties of bulk specimens. Ultrasonic technique was applied to study linear and nonlinear elastic properties of prepared samples. Relative comparison of the experimental data for of B95 reinforced with nanodiamond composite with the data for the starting B95-alloy is made and discussed.

Keywords: METAL-MATRIX COMPOSITES, ALUMINUM ALLOYS, NANOTECHNOLOGY, NANOCOMPOSITES, MECHANICAL PROPERTIES, SOEC, TOEC

1. Introduction

Existing groundwork of increasing aluminium alloy’s mechanical characteristics with using principles of nanostructuring allows discussing this direction’s availability. Last years many carbon nanosubjects were discovered: fullerites, astralens, onions, nanotubes, ultradispersed diamonds. They allow to find new technology of producing materials, what could name “nanomaterials structural engineering” [1].

Nanostructured materials with essentially new properties and devices with their application promise to solve many technological and design problems. With reduction of a characteristic length such as the grain size or the cluster size, the normal properties of materials are drastically changed. The purpose of these works - to get access to new technologies of nanocarbon-modified Al-based alloys with strength/density ratio of 300 m^2/s. These alloys can be used, for example, in the field of mechanical engineering for development of next generation of components and devices, in fields of compressors and turbochargers blades production (high strength/density ratio of 300 m^2/s) is critical parameter for speed increasing and, as result, efficiency) of turbine; and external layers of superconductive cables - unique strength with high thermal conductivity is critical parameter for the cable envelope.

Al-alloy B95 is one of the highest strength alloys and therefore is rather spread at manufacturing of the profiles which specific durability is the most important factor. This alloy belongs to four-componental system AI – Zn – Mg – Cu. These alloys have the highest durability (to 750 MPa or to 75 kgs/mm²) and high resist from corrosion. They widely use in plane and rocket production. One specific use of B95 is the high-pressure equipment (cells) for study structural and others properties of materials by neutron diffraction method.

In this work the bulk samples of B95 reinforced with nanodiamond (B95/nD) composites were prepared and its structural and mechanical properties were investigated.

X-ray analysis, TEM, Raman spectroscopy, optical microscopy, scanning probe microscopy (SPM), microhardness and nanoindentation measurements were used to study the structural and mechanical properties of bulk specimens.

Linear and nonlinear elastic properties of prepared samples have been investigated by ultrasound method too.

2. Experimental

2.1 Source nanodiamond

Nanodiamonds synthesized by detonation, with a monocrystalline structure type, with particle size around 4 nm, are particularly important for the application of nanotechnology and nanomaterials produced in actual production.

The method of synthesis of nanodiamond, well studied and utilized on an industrial scale by company NANO-SS JSC Bulgaria (and it is only in the European Union) is based on the phase transition of free carbon of explosives with negative oxygen balance in the blast. Pressure and temperature are in the order of 22 GPa and 4500 °K, and time of the process, in order of milliseconds.

Nanodiamond was characterized by means TEM and X-ray measurements. Data of TEM study (Fig.1) showed significant differences between natural diamond and nanodiamond obtained by static and dynamic synthesis. These differences are determined by conditions of synthesis. At the same time, specific properties of detonation nanodiamond, which make it suitable for reinforced composite applications, are determined by these differences.

Fig. 1 Data of TEM study of nanodiamond. Some particles have sizes up to ~20 nm. The rest is less then 5 nm.

Fig. 2 Data of X-ray diffraction study of nanodiamond.

There are two systems of diffraction reflections are found on the X-ray diagram: 1) very wide, about several degrees in 2 θ, with high intensity and 2) narrower, less intensive reflections. The first system of diffraction reflections belongs to diamond (letter D on the diagram, figures show diffraction indexes of reflections), and the significant width of peaks demonstrates the nanosize of grains of a diamond powder. The intensity rate of reflection peaks corresponds to standards. This and other data characterizes diamond as follows:

- nD content not less then 98 % wt;
- Size 4-6 nm;
- Density not less then 3,48 g/cm³;
- Specific surface up to 400 m²/g;
- Chemical impurity O, N, H. not more then 1%.
2.2 Bulk specimens

The B95/nD composite specimens with 0.1 %wt. nD have been fabricated by direct-melting the starting B95, adding nanodiamond powder in melt followed by cooling and quenching. Pre-coated with copper (Cu-clad) nD with typical sizes of nanoparticles ~ 4 nm were added to the melt at a temperature of B95 about (710-670) °C, which was carefully mixed (hashing by Ar-barbotage). For the experiments, 6 samples with the shape of a cuboid of 10×12×44 mm³ size were cut of the ingots. Presence of diamond at a composite is confirmed by measurements in electron microscopy and Raman spectroscopy. The Raman spectrum measurements (Fig. 3) have confirmed diamond presence in the bulk sample.

The Raman spectrum contains the lines: diamond 1332 cm⁻¹, D-line of graphite at 1350 cm⁻¹, and G-line of graphite at 1580 cm⁻¹. Line D and G are relatively narrow and have the same intensity, indicating the presence of carbon nanoclusters smaller than 5 nm. Raman spectroscopy investigations revealed some diamondlike carbon with sp³ bonds.

HRTEM observation of samples (Fig. 4) show the mean size of nanoparticles ~30 nm in fabricated samples, which, on visible, are nD-filler agglomerates.

Microstructure of samples was confirmed by optical images (Fig.5). They were got with the microscope BX51 «Olympus» gain from 200 to 3000.

3. Results and discussion

3.1 Hardness and Young’s modulus measurements

Hardness of prepared samples was measured using both hardness tester PMT-3 equipped with Vickers indenter and scanning nanoindenter NanoScan.

NanoScan operates on the principles of scanning probe microscopy. The system is designed in TISNCM for surface properties studies and measurements of hardness and elastic modulus. The system based on atomic-force microscope principles and allows to measure at nano-levels of hardness (H) and Young’s modulus (E) materials in width range of physical-mechanical properties. (H~1-150 GPa, E~10-1000 GPa). The elastic modulus was measured by a method of "bring curves" [2,3].

Typical images of a relief of a surface and a map of the modulus of B95/nD composite samples are showed in figure 6.

In the right top corner the impress from indentation by diamond indenter is observed. Young’s modulus for area 1 = 98±3 GPa; for area 2 = 77±2 GPa. On a surface inclusions of more light color for which hardness and the modulus have higher values are observed.

Surface relief profile (Fig. 7) show that the area 1 is raised over a surface. It is caused by higher hardness of a particle, i.e. it gives in to polishing more difficulty.

On a figure 8 the pricks received at record of bring curves and a scratch after sclerometry are visible. In the area 2 sizes of pricks and scratches it is much less, than in the area 1. Nanohardness of the B95/nD sample was in the range 2.7-3.2 GPa, that is only slightly different form the hardness of the B95 aluminum alloy (~2.0 GPa). But there are areas in the B95/nD with hardness more than 7.0 GPa.

It is possible to assume that these regions (inclusions) with the enhanced hardness are the nanodiamond conglomerates. The most part of a surface of samples are characterized concerning high uniformity on values of hardness and the Young’s modulus. Approximately in 10 % on a surface separate inclusions (on a map of the module of elasticity more light sites) with the enhanced mechanical characteristics are fixed.
72 ± 2 GPa. Hardness: for area 1 - 6.8 ± 0.8 GPa; for area 2 - 2.7 ± 0.2 GPa.

The Young's modulus for area 1 - 92 ± 3 GPa; for area 2 - 112 ± 2 GPa.

The experiments allowed to determine SOEC wave propagation time and its change while an external force is applied to a sample. The experiments allowed to determine SOEC wave propagation time and its change while an external force is applied to a sample.

Installation allowed to measure the acoustic velocities on external stress using an automated ultrasonic unit. The setup function is based on acoustic waves on the magnitude of uniaxial stress imposed to it have been measured experimentally.

Direction of propagation of an elastic wave in the sample and direction of uniaxial compressive stress were orthogonal. Polarization of transverse waves was or parallel or orthogonal to a direction of uniaxial stress. The stress were orthogonal.

The velocities of elastic waves in the samples were measured using an automated ultrasonic unit. The setup function is based on pulse-echo method. Installation allowed to measure the acoustic wave propagation time and its change while an external force is applied to a sample. The experiments allowed to defined SOEC wave propagation time and its change while an external force is applied to a sample. The experiments allowed to defined SOEC wave propagation time and its change while an external force is applied to a sample. The experiments allowed to defined SOEC wave propagation time and its change while an external force is applied to a sample. The experiments allowed to defined SOEC wave propagation time and its change while an external force is applied to a sample.

For quantitative characterization of nonlinear elastic properties of a material we measured the TOEC of composite samples by using a proved dynamometer. These measurements allowed us to calculate TOEC’s values.

To improve the accuracy of the three third-order elastic coefficients, we carried out 4 measurements for each of the samples. Using the data for SOEC, presented in table 1, and known formulas for calculation TOEC from experimental dependences of sound velocities on external stress [6], system of four linear equations for the three TOEC for each of the materials were obtained. These overdetermined systems have been solved on a computer using the least-squares method. The solution of these equations allowed us to determine the TOES in the B95 alloy and B95/nD composite. The results of TOES calculations shown in table 2.

### Table 1: Elastic properties of B95 alloy and B95/nD composite

<table>
<thead>
<tr>
<th>MATER.</th>
<th>(\rho_0) g/cm(^3)</th>
<th>(C_y\times10^{11}) N/m(^2)</th>
<th>(S_y\times10^{12}) N/m(^2)</th>
<th>(V_L), (V_T) km/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11</td>
<td>C14</td>
<td>S11</td>
<td>S12</td>
<td>V_L</td>
</tr>
<tr>
<td>B95</td>
<td>2,700</td>
<td>10,4</td>
<td>2,47</td>
<td>14,9</td>
</tr>
<tr>
<td></td>
<td>± 0,06</td>
<td>± 0,03</td>
<td>± 0,03</td>
<td>± 0,06</td>
</tr>
<tr>
<td>B95/nD</td>
<td>2,850</td>
<td>10,2</td>
<td>2,65</td>
<td>14,3</td>
</tr>
<tr>
<td></td>
<td>± 0,06</td>
<td>± 0,06</td>
<td>± 0,06</td>
<td>± 0,06</td>
</tr>
</tbody>
</table>

### Table 2: TOEC for B95 and B95/nD in 10\(^{11}\) N/m\(^2\)

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>(C_{111})</th>
<th>(C_{112})</th>
<th>(C_{113})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B95</td>
<td>-2.96 ± 01</td>
<td>-0.92± 0.3</td>
<td>2.38 ± 0.3</td>
</tr>
<tr>
<td>B95/nD</td>
<td>-7.8 ± 2.13</td>
<td>-0.74 ± 2.12</td>
<td>4.55 ± 1.22</td>
</tr>
</tbody>
</table>

### 4. Conclusion

Nanostructured and nD modified Al alloy have higher (by factor of 2-3) mechanical properties than starting material.

Analysis of experimentally determined values shows that the addition of nanodiamond in the B95 alloy results in a change of both SOEC and TOEC. However, TOEC is the most sensitive to the addition of nanodiamond.

Next steps: Optimization according to target applications. Estimation of capability of others metals nanostructured and modified by nD/nC.

### 5. References


### 6. Acknowledgements

The authors acknowledge L.F. Solov’eva, G.I. Pivovarov and E.V. Tatyabin for many assistance and useful discussions. The present work was supported through a research grant from Russian Ministry of Education and Science (Contract Nos.16.552.11.7014, 16.523.11.3002).