ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 21, No. 3. 2015

Hybrid Composite Materials Aluminum – Carbon Nanostructures

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crossref http://dx.doi.org/10.5755/j01.ms.21.3.7355

Received 16 June 2014; accepted 08 November 2014

We investigated formation of carbon nanofibers grown by chemical deposition (CVD) method using an acetylene-hydrogen mixture on the surface of micron-sized aluminum powder particles. To obtain uniform distribution of the carbon nanostructures on the particles we deposited nickel catalyst on the surface by spraying from the aqueous solution of nickel nitrate. It was found that increasing the time of the synthesis lowers the rate of growth of carbon nanostructures due to the deactivation of the catalyst. The Raman spectroscopy measurements confirm the presence of disordered carbon corresponding to CNFs in the specimen. X-ray photoelectron spectroscopy showed the presence of aluminum carbide in the hot pressed samples. An aluminum composite material prepared using 1 wt.% CNFs obtained by uniaxial cold pressing and sintering showed 30 % increase in the hardness compared to pure aluminum, whereas the composites prepared by hot pressing showed 80 % increase in the hardness. Composite materials have satisfactory ductility. Thus, the aluminum based material reinforced with carbon nanostructures should be appropriate for creating high-strength and light compacts for aerospace and automotive applications and power engineering.
Keywords: aluminium, carbon nanofibers, hot pressing, hardness, thermal conductivity.

1. INTRODUCTION

Aluminum and its alloys are one of the most commonly used construction materials. Therefore, the improvement of the mechanical and physical properties of aluminum alloys is a very important task for many applications.

Carbon nanostructures have high strength characteristics, which makes them promising components for hybrid metal matrix composite materials, including aluminum matrix composites. Numerous works have been devoted to studying the structure and properties of such materials, and their number continues to grow [1]. One of the main technological problems in the synthesis of hybrid composite metal matrix materials containing carbon nanotubes or carbon nanofibers (CNF) are the distribution of the hardening phase in the volume of the composite, the strength of its bonding with the matrix, and the chemical and structural stability of the carbon ordered structures in the composite. These problems are solved by the authors of [2 – 6] by various methods and, in the first turn, in the stage of preparation of the composite powder.

Recently we tried a new process to produce uniform distribution of the carbon nanostructures on the surface of Al powder particles [7]. Good distribution of carbon structures is provided by synthesizing nanofibers from a gas phase directly on the surface of Al matrix particles with nickel catalyst additions. Also the formation of CNFs on the surface of micron-sized aluminum powder particles by chemical vapor deposition method using an acetylene-hydrogen mixture [7] had been studied. It has been shown that a good dispersion of CNFs on the surface of Al particles was achieved by adding 0.02 wt.% of Ni catalyst.

In this paper we study structure, thermal and mechanical properties of Al/CNF compact materials made by hot pressing of aluminum composite powders at different temperatures and compare it with composites of the same chemical composition, made by traditional powder metallurgy route: cold pressing and sintering.

2. EXPERIMENTAL

For our investigations we utilized sprayed aluminum powder with the particle size below 63 μm and purity 99.5 wt.%. The main admixtures were silicon, iron and copper, the content of which did not exceed 0.4, 0.35 and 0.02 wt.%, respectively. The powder particles had a spherical shape and a rough surface. To grow carbon nanostructures, a nickel catalyst was deposited on the surface of the powder. Uniform distribution of catalytic particles and subsequently CNFs were obtained at the concentration of the nickel of 0.02 wt.%. The nickel source was a $Ni(NO_3)_2$ $6H_2O$ salt that has a high solubility in water and decomposes to NiO at a temperature of 300 – 350 °C in air atmosphere. Then the powder was heat treated additionally in a hydrogen atmosphere for complete decomposition of the salt and reduction of nickel.

The temperature of the CNF synthesis was varied from 500 to 700 °C. We use acetylene gas as a carbon source. Synthesis runs in the H_2/C_2H_2 mixture for 5 – 15 min. The hydrogen-to-acetylene ratio in the gas mixture during the synthesis H_2/C_2H_2 was maintained to be 8.3/1.

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At the first step the composite powders were compacted by uniaxial cold pressing at the pressure of 500 – 600 MPa in order to make cylindrical samples of 10 mm in diameter and a height of 4 mm. Then the specimens were compacted to full density by the two methods: (i) hot pressing and (ii) sintering at 600 °C in an argon environment.

Hot pressing was carried out on a hydraulic press DA0040 of 1000 ton-force in the pressure chamber of the "truncated hemisphere" at 5 ± 0.5 GPa at variable temperatures. The pellet was placed in a high pressure vessel between two graphite tablets. Heating the high pressure container was performed by passing the alternating electrical current (0.3 – 0.8 kA) at a voltage of 3 – 6 V in the mode of stabilization of electric power. The accurasy of stabilization of electric power is not less than 5 %. The temperature inside the container was determined from the calibration "power - temperature" curve with the accuracy of ± 50 °C.

We studied the structure of the samples by the methods of scanning (SEM, Leo DSM 982 Gemini and JEOL JSM-7500F) and transmission (TEM, Philips CM200 FEG) electron microscopy. The Raman spectra were recorded at room temperature in monochromatic radiation of a YAG laser (532.25 nm, 30 mW). The density of the sintered specimens was determined by hydrostatic weighing.

The measurements of thermal diffusivity (cm^2/s) were carried out on the DXF-200 equipment by TA-Instruments. To create a momentum of temperature on the front side of the sample using the flash of xenon lamp, and the change in temperature on the back side of the sample is fixed by contact thermocouple. For mea surements, the flash duration was set to 500 ms. Heat conductivity was calculated by using of measured values of thermal conductivity by equation:

$$\lambda = \alpha \cdot \rho \cdot c_p, \quad (1)$$

where, c_p (J/(g*K)) is heat capacity and ρ (g/cm^3) is density of sample. Declared by the manufacturer the accuracy of thermal diffusivity, heat capacity, and thermal conductivity measurements is ± 2.3 %, ± 4.0 % ± 5. 0% respectively.

3. RESULTS AND DISCUSSIONS

The preliminary tests on treating the aluminum powder in an acetylene-hydrogen mixture showed that the decomposition of the acetylene on the surface of the aluminum powder which yielded carbon, started from 550 °C; the growth in the mass was up to 0.1 % in 10 min of the synthesis and increased linearly upon increase in the temperature. The powder particles were coated with a layer of carbon containing individual beams of nanofibers, which seems to be a consequence of the presence of an iron impurity in the initial powder.

To obtain good distribution of carbon nanostructures in the matrix we deposited a nickel catalyst onto the surface of the aluminum particles. After Ni catalyst deposition carbon nanostructures were synthesized at a temperature of 550 °C for 5 – 15 min. It was found that increasing the time of the synthesis lowers the rate of growth of carbon nanostructures due to the deactivation of the catalyst because of disappearance of the places of dominant nucleation of carbon nanostructures on the surface of the powder [8]. Carbon fibers cover the matrix particles virtually fully and the diameter of the fibers is 20 – 40 nm as shown in the Fig. 1 a. The mass grows primarily due to the increase in the length of the fibers. The maximum weight increase is about 20 wt.%.

The Raman spectra (Fig. 1 b) show the presence of a peak at 1320 cm^{-1} (a *D*-peak) and tangential fluctuations (a *G*-peak) at 1590 cm^{-1}; the high parameter I_D/I_G confirms formation of multilayer graphene structures that correspond to the structure of carbon fibers. Transmission electron microscopy studies have shown that the carbon product is represented by carbon nanofibers with a structure of a “pile of coins” type.

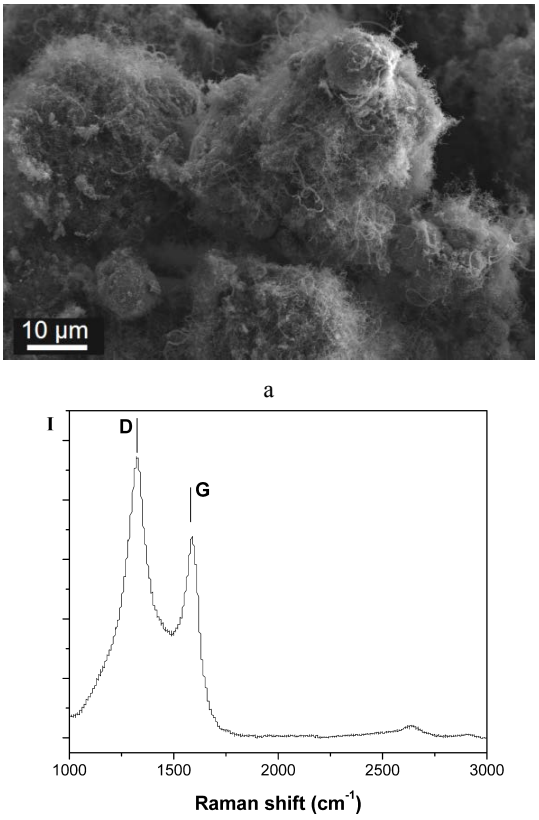

Fig. 1. SEM image (a) and Raman spectrum (b) of CNFs synthesized during 15 min at 550 °C at the Ni concentration of 0.035 %

Preliminary experiments on fabrication of compact materials containing 1 wt.% carbon nanostructures by cold pressing and sintering shows that the density of the sintered specimens exceeds 98 % of the theoretical value. As compared to the control specimens from aluminum powder with catalyst, the hardness increases by 20 % at satisfactory ductility. When the specimens obtained are deformed by rolling with reduction of up to 40 % at room temperature, visible defects are absent.

Hot pressing of samples was run at the temperatures of 480, 720, and 980 °C and the pressure of 5 GPa. The pressure dependence of aluminum melting point is described by equation [9]:

$T_{melt}(p) = T_{melt}(p_0) + dT/dp$, (2)

where $T_{melt}(p_0)$ = 660 °C, and dT/dp = 64.1 K/GPa, $dT/dP = 6.41*10^{-2}$ [K/MPa], i.e. at the 5 GPa pressure the melting point of aluminum is about ~ 980 °C.

Fig. 2 a shows micrographs of a typical microstructure of the samples after compaction. Study of the structure in all cases showed absence of porosity, all the samples had a density close to theoretical value. The microstructure forms equiaxed, close to hexagonal grains of aluminum, separated by carbon layers with thickness less than 1 μm. Energy-dispersive analysis showed the absence of carbon as well as copper and iron inside the grains.

Photoelectron spectroscopy shows (Fig. 2 b) the presence of oxygen, aluminum and carbon. Elements chemical states evaluated by using XPS spectra had been studied in details in [10]. Al is in the form of metallic state and aluminum oxide Al_2O_3. Average oxygen content vary from 2.7 to 3.5 wt.% and increases with the increasing of carbon content. Such increase in oxygen content may be explained by oxygen chemically bonded and absorbed on the CNF surfaces. In the composites oxygen preferably presence in the form of alumina and also there are exist C – O groups, which may characterize the surface layers of CNF [11]. Atomic ratio Al/O is usually about 2.0/3.2.

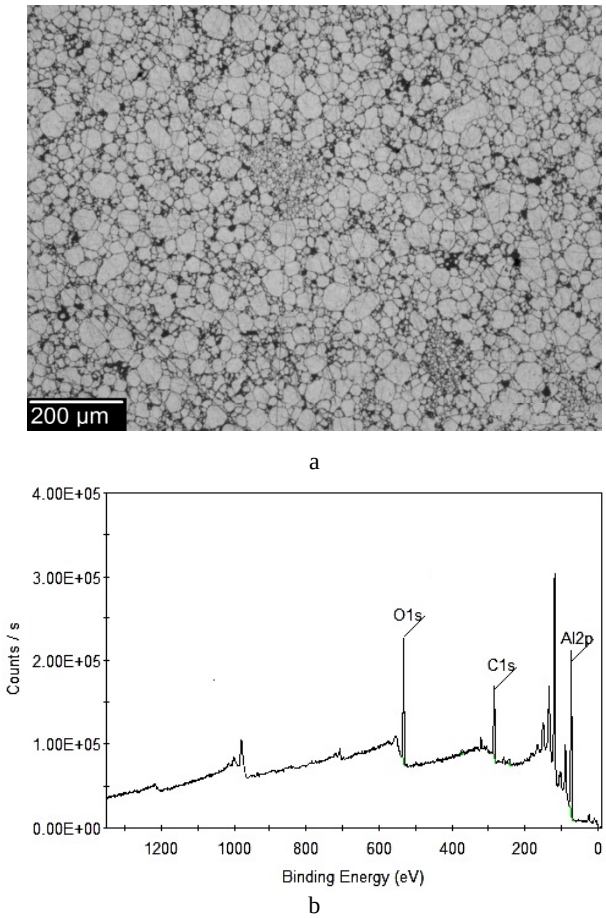

Fig. 2. SEM image of microstructure (a) and XPS survey spectra (b) of Al/1% CNF composite hot pressed at 720°C

XRD analysis shows only peaks belong to aluminum in the initial powder and samples compacted at 480 and 720 °C (Fig. 3). The crystalline alpha alumina appears at the 980 °C, 5 GPa. No any other crystalline phases such as carbides or oxides were found.

We have also carried out a comparative analysis with Al/CNF composites prepared by cold pressing and sintering and Al/CNF composites prepared by hot pressing (Fig. 4). As expected, any CNF additions to aluminum led to hardening of the composite. However, Al/CNF composite prepared by hot pressing showed about 80 % increase in the hardness compared with samples prepared by cold pressing and sintering.

There is significant increase in hardness at the CNF content up to 1 %, which continuously increases up to 1.5 %. The hardness of samples contained 2 % CNF haven't any changes and even shows the tendency to decrease. Insignificant decrease of hardness can be observed with the increase of hot pressing temperature from 480 to 720 and 980 °C. Such a reduction is not observed for aluminum samples without additives of carbon nanostructures.

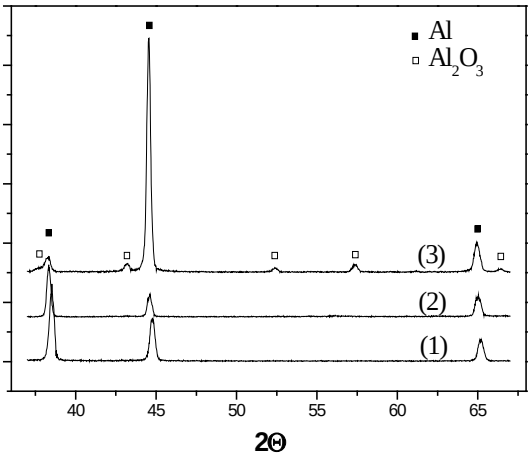

Fig. 3. XRD patterns of Al/1%CNF composites powder (1) and compacts pressed at 720°C (2), 980°C (3)

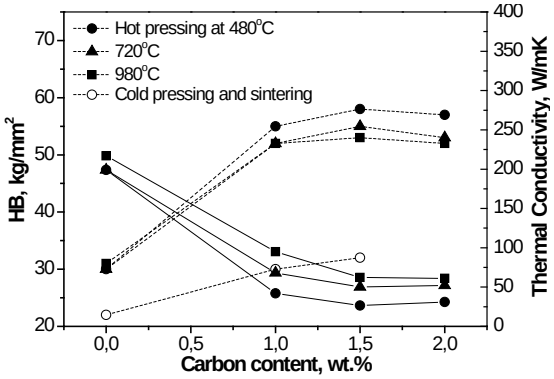

Fig. 4. Hardness (dashed lines) and thermal conductivity (solid lines) versus carbon content in hot pressed samples

As compared with the samples prepared by cold pressing and sintering the hot pressed samples have comparatively low plasticity. All samples, pressed at the 480 °C, have no any visible elongation at the bending tests that may be explained by the absence of interconnections between the carbon layers and aluminum grains. Also those samples have the minimal value of the thermal conductivity, probably because of significant heat resistance in the grain boundaries.

The specific elongation of the samples with 1 % CNF

compacted at the temperature of 720 °C is about 5 % at the hardness of 54 HB. At the same conditions the samples of pure aluminum have elongation of 12 %. The plasticity of samples decreased with the increase of compacting temperature and carbon content.

The values of thermal conductivity of pure aluminum samples are in the interval 200 – 217 W/(m·K). That is close to conductivity of compact Al of high purity, which is 237 W/(m·K) at 300 K [9]. The thermal conductivity of Al/CNF composites has growth up with the increase of compacting temperature independently of the chemical composition, however much smaller as compare with the samples prepared by cold pressing and sintering (150 – 190 W/(m·K)). Low thermal conductivity of aluminum/CNF composites is 25 – 100 W/(m·K), associated with the presence of thermal barrier at the filler – matrix interface that is also noted in [12, 13]. Increasing the thermal resistance provided by boundaries forming carbide and/or oxide as the thermal conductivity of such compounds significantly lower the conductivity of pure metal and is in the range of 10 to 40 W/(m·K) [14] for carbides, and is about 30 W/(m·K) for alumina [9].

In general, it should be noted that the hardness of the samples, depending on the carbon content in the range from 0 to 1.5 wt.% increases from 30 to 57 HB. The highest ductility aluminum-carbon material nanostructure observed in 1 wt.% of the CNF and pressing temperature of 720 °C.

The properties of aluminum alloys reinforced with carbon nanomaterials, usually carbon nanotubes, are overvieved in [15]. Generally hardness increase is in the interval of 20 – 85 %. Our results allow us to expect that the properties of a powder material can be raised considerably by using equichannel angular pressing, extrusion and other advanced methods of compaction. Comparison with literature data for aluminum alloys shows that the hardness values is correspond duralumin hardness after heat treatment, suggesting the possibility of their use as a high-strength structural materials.

4. CONCLUSIONS

An aluminum composite material prepared using 1 wt.% CNFs obtained by uniaxial cold pressing and sintering showed 30 % increase in the hardness compared to pure aluminum, whereas the composites prepared by hot pressing showed 80 % increase in the hardness. Composite materials have satisfactory ductility of about 5 % at the compacting temperature of 720 °C. Thus, the aluminum based material reinforced with carbon nanostructures should be appropriate for creating high-strength and light compacts for aerospace and automotive applications and power engineering.

Acknowledgments

The research has been performed at Peter the Great St. Petersburg Polytechnic University under the contract № 14.Z50.31.0018 with the Ministry of Education and Science of the Russian Federation

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