Aluminum-based composite reinforced with fullerene soot

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Abstract. Al-based composites with fullerene soot have been successfully prepared using powder metallurgy route. The selected parameters of the powder preparation for extrusion are discussed. The microstructure and phase composition are analyzed by optical microscopy and XRD analysis. It is shown that carbon reacts with Al with very fine carbide particles formation, resulting in micro stress of the aluminum matrix, and providing high strength of the composite. The obtained composites have excellent strength characteristic (660MPa) and satisfactory ductility (4.5%). It was shown that the developed Al-based composites can successfully compete with the best aluminum alloys used for electrical wire production.

1. Introduction

Aluminum alloys used in electrical wire production are subject to a number of requirements for their physical and mechanical properties. Among the main is the requirement for a combination of high strength, satisfactory plasticity, and high electrical conductivity. Pure aluminum possesses high conductivity of about 64% of IACS, but very low strength of about 60MPa [1]. Alloying allows to increase the strength by an order of magnitude of pure aluminum, but leads to a loss of conductivity because of solid solution formation. Nevertheless, development of Al alloys for electro technical application continues rather successfully; to the present the main tendency is addition of low soluble in aluminum elements, such as REM, Zr, Sc. However, such alloying considerably increases the cost of the material, what limits their commercial attractiveness. Another requirement that is imposed on the properties of materials to be used in electro technical application is their thermal stability up to 300ºC. Ordinary aluminum alloys lose their properties at heating either due to recovery of the cold deformed structure or due to coarsening and dissolution of strengthening phases [2, 3].

A new class of materials able to meet the mentioned above targets are composites consisting of pure metal matrix and undissolved in it nanoparticles. This approach allows to combine the high conductivity of pure aluminum with elevated strength caused by nanoparticles. Besides, the ultrafine homogeneously distributed chemically stable particles retain their structure at heating and hinder the self-diffusion of aluminum preventing its recrystallization.

Nano-carbon materials are known to be one of the attractive reinforcing agents due to their excellent physic-mechanical properties [4] and an abundance of carbon in nature. Carbon does not dissolve in aluminum, but reacts with it forming Al₄C₃, which has a high decomposition temperature about 2500ºC. To the present there are rather high level of mechanical properties of the aluminum-nanocarbon composite has been reported in literature [5-15]. According to the different authors the effect of the strengthening was attributed to different phenomena, such as solid solution strengthening [10, 15], grain boundary refinement [7,9], dispersion strengthening [7,9] and good load transfer [5,7-9,12].
As the reinforcing agent carbon nanotubes [6-9], graphene [12-14], and fullerene [10,11,15] have been used. All of these nanocarbon materials are expensive because of complex, high technology production process. In the present paper we would like to consider a possibility to manufacture Al-based composite reinforced with nanoparticle of fullerene soot, estimate strengthening effect and thermal stability.

2. Materials and method
Aluminum matrix composites were produced using an aluminum powder of 98% purity, particle size 80-125 µm, and fullerene soot supplied by Suzhou Dade Carbon Nanotechnology Co. Stearic acid was added to prevent the agglomeration of the fullerene soot, and a mix of NaCl, KCl and CaF2 was added as a flux to improve the contact between the Al particles. The powders were prepared varying fullerene soot concentration up to 3wt.%. Ball milling was performed in 80ml stainless steel chambers with 5mm diameter stainless balls with ball to powder ratio of 10:1 using Fritsch planetary ball mill Pulverisette 7 premium line. The milling was performed in two stages, the first one at 200 rpm for 60 min and the second one at 600 rpm for two hours. To prevent excessive powder heating the milling was performed with 20 min interruptions after each 15 min of milling. All the procedures were conducted in an Ar atmosphere.

For extrusion the ball-milled composite powder was diluted with aluminum powder in a ratio of 2:1, 1:1, and 1:2 correspondingly. The diluted powders were either mix in a tilting drum blender for 2 h or additionally ball milled at 200 rpm for 15 min and at 600 rpm for 15 min in an Ar atmosphere. After that the powder was pre-pressed at 50 MPa in a cylindrical container of 30 mm in diameter, 100 mm in height, and 2 mm thick made of 5056 Al alloy. Then the prepared capsule was heated to 400ºC and hot extruded into 10 mm diameter rods with an extrusion ratio of 9:1. Finally, the rods were hot rolled at 380ºC in calibrated profile rolls. The rolling was conducted three times; as a result, there were samples of a square section with a thickness of 5, 3, and 2 mm. Annealing was performed in resistance furnace in Ar atmosphere at 470ºC.

For optical observation the specimens had been polished and etched with 10% NaOH. The observation was fulfilled on Carl Zeiss Observer D1m microscope.

Vickers microhardness was tested with ZWICK ZHU under a load of 100N and a dwelling time of 10c. The 3-point bend test was carried out on the samples of 60 mm length, with a distance between the supports of 26mm. The test was carried out on the universal testing machine Instron 5965 with a tool for 3-point bending (radius of the supports 10 mm, radius of the loading tip 10 mm) at a strain rate of 10mm/min.

The phase composition was examined with the Bruker D8 Advance diffractometer under Cu Kα radiation. The aluminum solid solution lattice parameter, internal microstresses and size of the coherent scattering region were determined on the base of XRD patterns, which had been collected in the range from 20° to 140° 2Θ with a speed of 2°/min. The definition of the lattice parameter was calculated using Nelson-Riley [16] extrapolation function in order to eliminate the systematic error after the subtraction of K2 doublet. Internal microstresses and size of the coherent scattering region have been determined by line-broadening analysis using Williamson-Hall plot [17].

3. Results and Discussion
SEM image of the composite powder produced by high energy ball milling are presented in Figure 1. As it is seen, the milled particles are equiaxial dense agglomerates of size about 20- 40µm. Figure 2 shows photographs of the as-extruded and rolled samples, as well as the samples after bending test.
For extrusion the ball milled powder were diluted with pure aluminum powder. The dilution was undertaken with an aim to stimulate plastic deformation of the composite during extrusion and prevent an excessive equipment wear. The parameters of the dilution and mechanical properties of the samples are presented in Table 1. The corresponding stress-strain curves are shown in Figure 3. All the samples had been compacted by the same way: through extrusion and rolling to 3 mm of thickness.

The samples cut from the extruded rode prepared from powder diluted in the blender are very different from each other, it may be explained by the fact that mixing in a blender does not allow to achieve homogeneous mixture of aluminum and composite particles because of their different morphology.

Table 1. Parameters of the dilution and mechanical properties of the samples.

| No | Mode of dilution | Initial concentration of the ball milled composite powder, wt.% C | Dilution ratio X/Y, X-composite powder, Y – pure aluminum | Resultant concentration, wt.% C | HV | σb, MPa | ε, % |
|----|------------------|---------------------------------------------------------------|----------------------------------------------------------|--------------------------------|----|---------|------|

Figure 1. SEM microphotographs of the composite powder after milling.

Figure 2. Photographs of as-extruded (a) and rolled (b) samples, (c) – the rolled samples after bending test.
Figure 3. Bending deformation curves at for the samples prepared with equal content of carbon, but according to various dilution parameters. Microstructure of the extruded and rolled samples in depending on the dilution parameters are presented in Figure 4.
Figure 4. Optical images of the samples microstructures in depending on the dilution parameters (Table 1): a) 1; b) 2; c) 3; d) – 4.

All the microstructures contain light and dark constituents; the first one corresponds to the soft pure aluminum matrix and the second - to the hard composite particles distributed in the latter. Ball milling leads to the more homogeneous and fine structure compared to that obtained after mixing in a drum blender. During ball milling soft aluminum particles envelope the harder composite ones leading to a disintegration of the composite agglomerates and promoting the homogeneous distribution. The microstructure of the sample obtained by the dilution of Al-2%C in a ball mill to Al-1%C (sample number 4 in Table 1 and Figure 4,d) has the best appearance, it is very dense, fine, and homogeneous. Owing to the achieved microstructure this sample has the best combination of strength and ductility. Annealing at 470ºC does not lead to notable structural change.

XRD patterns of the powders, as well as extruded and annealed samples are presented in Figure 5. Lattice parameter, crystallite size and microstress evaluated from XRD data are summarized in Table 2.

Ball milling leads to a strong broadening of the Al XRD peaks compared to the initial powder. The XRD peaks broadening means a decrease of the crystallite size and microstress growth caused by the high concentration of the introduced defects and crystallite disintegration. After compacting and annealing the crystallite size increases due to recrystallization, however, the microstress does not relax nor during compacting neither annealing.

In the insertion of Figure 6 is the region of the XRD pattern where peaks of Al₄C₃ may be observed. It is seen that the carbide appears on a stage of compacting obviously because of heating. The peaks belonging to Al₄C₃ are very wide, what is caused by a very low size of this precipitates. Annealing does not change the form and location of the Al₄C₃ peak.

Table 2. Aluminum lattice parameter, microstress and crystallite size (size of coherent scattering region) determined by XRD.

| Composition         | Microstress | Crystallite size, nm | Lattice parameter, nm |
|---------------------|-------------|----------------------|-----------------------|
| Al initial powder   | -           | -                    | 4.0478±0.0004         |
| Composite powder    | 0.20        | 48                   | 4.0474±0.0005         |
| Compact sample      | 0.12        | 79                   | 4.0500±0.0005         |
| Annealed sample     | 0.11        | 137                  | 4.0507±0.0005         |
According to Al-C equilibrium phase diagram [18] carbon does not dissolve in Al crystal lattice. However, high energy mechanical milling is believed [19] to be possible to significantly expand solid solution composition limits. Taking into account a radius of Al atom equaled to 143 pm, for interstitial solid solution formation a size of octahedral interstitial site should be no less than the radius of a C atom equaled to 70 pm, it should lead to an increase of Al lattice parameter for more than 20%. As found by XRD Al lattice parameter has not grown after milling, i.e. aluminum lattice did not comprise carbon atoms [21-27]. An increase of the Al lattice parameter after heating along with simultaneously growing microstress (Table 2) may be explained by an elastic stress caused by a formation of ultrafine carbide phase coherently bound to aluminum matrix. Change of microhardness measured for the compacted and annealed at 470 ºC for 4, 8, 12 h samples does not exceed 10%, what confirms the stability of the obtained structure.

Figure 6 compares the mechanical properties obtained for the selective samples in the present work with those for traditional and new Al-based materials. The obtained composites have excellent strength characteristic and satisfactory ductility. Figure 7. shows location of the composites in the strength – resistivity diagram among the advanced alloys containing REM, Zr, Sc. It is seen that the Al-based composite reinforced with carbon nanoparticles can successfully compete with the best aluminum alloys.

![Figure 6. Comparison of the mechanical properties (tensile) of the obtained materials with existing ones.](image_url)
Figure 7. Comparison of the properties for the developed material with Al alloys used for electrical wire production.

4. Conclusion

Al-based composites with fullerene soot have been successfully prepared using powder metallurgy route. The microstructure and phase composition had been analyzed. It was shown that carbon does not dissolve in aluminum, but at compacting forms very fine carbide particles, resulting in micro stress of the aluminum matrix, and providing high strength of the composite. The obtained composites have excellent strength characteristic and satisfactory ductility. It was shown that the developed Al-based composites can successfully compete with the best aluminum alloys used for electrical wire production.

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