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Research Article

Microstructural Explanation of the Mechanical Properties of Al – GNPs Composites with Al_4C_3 Produced by Powder Metallurgy Method and Extrusion

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ABSTRACT

The microstructure of aluminum-based composites with graphene reinforcement in the range of 0.1 to 1.1 wt. %, obtained by powder metallurgy and extrusion, has been characterized. The first series of composites was produced by extrusion at a temperature of 500 °C, at which in situ aluminum nanoscale carbides were formed, and the second by extrusion at 400 °C and subsequent annealing at 610 °C for three hours, at which nano- and microscale carbides were formed. The methods used for investigation are mechanical testing, optical microscopy, SEM and TEM. The mechanical properties and failure mechanisms of composites with in situ obtained aluminum carbides and with carbides obtained after annealing have been explained by means of the microstructural features. The first series of composites has higher strength and plastic properties than the second series. The better complex of mechanical properties of the first composites is due to the in situ formation of nano-sized carbides with a rounded shape, which limits the manifestation of carbide embrittlement and, accordingly, the deterioration of the mechanical properties of the composites. In addition, the rounded nano-carbides form dimples in the fracture surface of the composites, which is a prerequisite for favoring the plastic properties.

Keywords: Aluminum composites, graphene, microstructure, mechanical properties, nano-sized carbide.

INTRODUCTION

Aluminum-based composites reinforced with graphene were thoroughly investigated over the last fifteen years. Graphene has been shown to be a suitable reinforcement for aluminum and aluminum alloys. The good mechanical properties of aluminum-graphene composites are due to the good dispersion of graphene particles, so that a uniform distribution and a homogeneous microstructure are obtained. Powder metallurgy has emerged as the most successful method to achieve uniform dispersion of graphene particulates and ease of fabrication of Al-graphene composites [1]. Accordingly [2], the optimal amount of graphene is 0.3 wt%, while other researchers [3 and 4] reported that the optimum values of graphene are between 0.7–1.0 wt%. It was shown that a small addition (up to 0.5 vol.%) of GNPs can lead to a simultaneous increase in the tensile strength and ductility of the GNPs/Al nanocomposites [5]. According to all investigated studies, the strength of the composite initially increases with increasing graphene content, then begins to decrease. However, the optimal value of the graphene content is different, and it depends on the degree of dispersion of the graphene particles. With the appearance of agglomerates, the deterioration of mechanical properties begins [6, 7].

The chemical bonding between graphene and Al, which occurs through the formation of Al4C3 at the interface between the aluminum matrix and the graphene particle, the amount and size of aluminum carbides are another important factor that affects the strength of the composite [8]. In [9], we have shown that if increased plasticity is

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desired, then the amount of nano-sized and rounded aluminum carbide should be predominant. On the other hand, if higher strengthening properties are desired, carbide formation must be avoided. Our present study is focused on the role clarification of aluminum carbides (size and shape) on the mechanical properties of the aluminum-graphene composites.

MATERIALS AND RESEARCH METHODOLOGY

Materials:

The composite materials studied were produced from aluminum powder with a chemical purity of 99.5% and an average particle size of 37 μm, and GNPs with a thickness of 6–8 nm produced by the io-li-tech Company. The two constituents (Al powder and graphene nano-platelets) were mixed at room temperature in a planetary agate ball mill Pulversette (Fritsch GmbH, Idar-Oberstein, Germany) (seven balls weighing 11.6 g each); speed—700 revolutions per minute; milling time—30 min; in an atmosphere of argon, with the weight of each mixture being 300 g. The graphene content in the powder mixtures varied from 0 wt. % to 1.1 wt. %, namely: 0; 0.1; 0.3; 0.5; 0.7; 0.9 and 1.1 wt.%. The powder-filling mould used to produce the compacts was 45 mm in diameter and 175 mm in height. Seven compacts, in the form of cylinders, were produced by double-sided pressing for 60 s at 381 MPa. The compacts were heated at 370 ˚C for 20 min to equalize the temperature and degas the pre-pressed samples. Two series of specimens were produced by hot extrusion. Extrusion was carried out on a hydraulic press (RUE 250 SS, VEB Wema, Zeulendroda, German Democratic Republic). The pressure applied was 457 MPa, the processing time was 60 s/a piece, the extrusion ratio was 11:1, the diameter of the extruded rods was 12 mm, and the lengths of the rods varied between 500 and 600 mm. A high-temperature lubricant, “Metal Star PA” from Kluber Lubrication (Shanghai, China), was used to reduce friction. The following processing conditions were applied for each of the series: Series #1 extrusion at 500 ± 10 °C, and cooling in the air; and Series #2 extrusion at 400 ± 10 °C, cooling in the air, and annealing at 610 °C for 1800 s.

Research Methodology:

The tensile tests were conducted on an AMSLER 20SZD599 test machine (Amsler, Switzerland) according to the requirements of the BDS EN ISO 6892-1:2020 standard for testing of Metallic materials [10]. The applied load at its maximum varied from 13 kN to 18 kN, depending on the tested specimen. The load at fracturing of the specimen was 7 kN. The accuracy was 0.5% of the applied load. Three samples from each series with the same weight fraction of graphene were tested. The means of the ultimate tensile strength (UTS), yield strength (YS), and relative elongation under tension (RET) were determined.

The specimens from the extruded rods were investigated using tensile testing, LM, SEM (EDS), and TEM. Samples from the as-produced bars were wet-ground in longitudinal sections on grinding paper from 320 to 3000 # and mechanically polished in two steps using Oxide Polishing Suspension (OPS–Struers, Copenhagen, Denmark) to be prepared for examination using light microscopy. The microstructure was revealed with a 0.5% water solution of HF. The observations were performed using a metallographic microscope MIT 500 (Cnoptec, Chongqing, China), at magnifications up to 1000×. SEM and EDS analysis were performed on an SEM–HIROXSH-5500P (Bruker, Billerica, MA, USA) with an integrated EDS system “QUANTAX 100 Advanced” under the following conditions: (a) accelerating voltage: 20 kV; (b) scanning distance: 3 to 7 mm; and (c) secondary electron detector. The HRTEM analysis was performed on JEM 2100 (JEOL, Tokio, Japan) at an accelerating voltage of 100 kV. The specimens were prepared by Leica EM UC7 Ultramicrotome (Danaher Corporation, USA).

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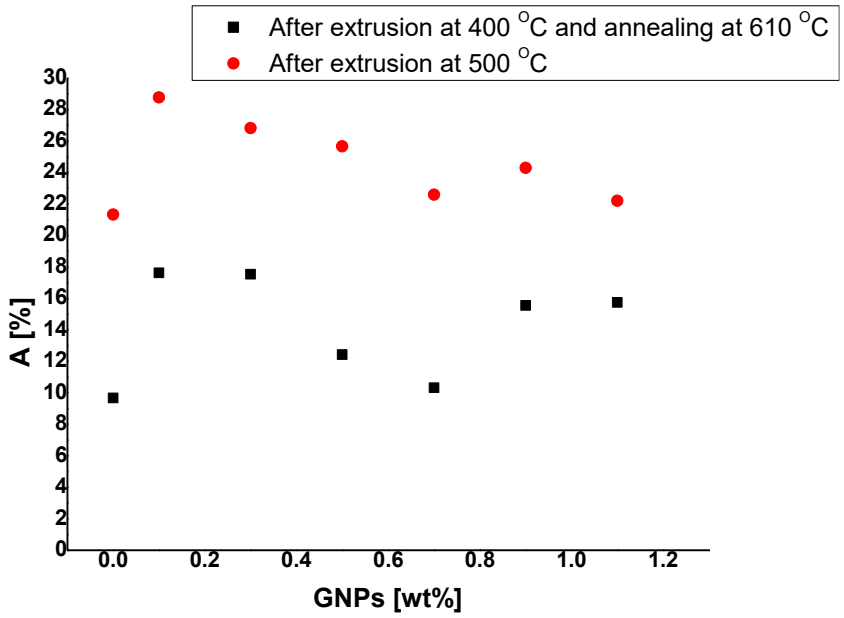
RESULTS AND DISCUSSION

The results from tensile testing are show graphically in *Fig. 1*



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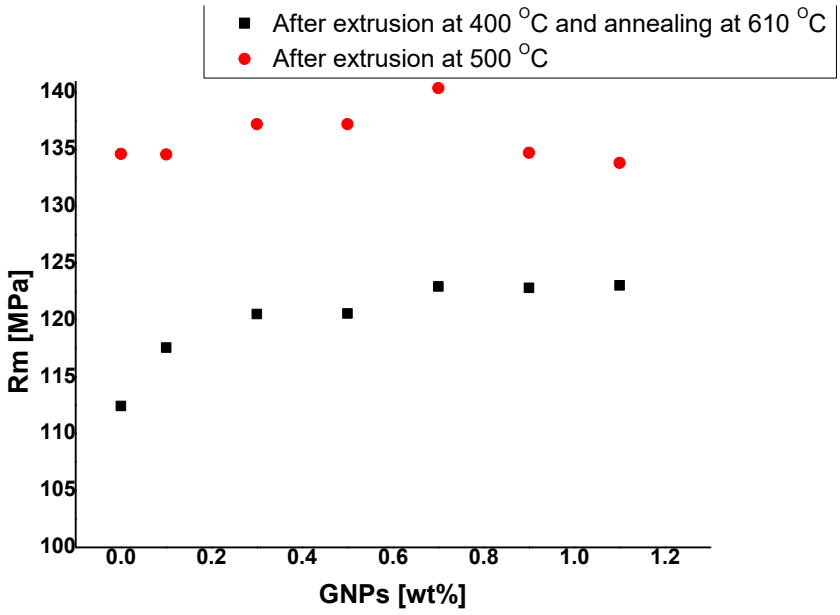

b

Fig. 1. Dependence of tensile strength – a) and relative elongation – b) of two series Al-GNPs composites on graphene content

It is noteworthy that in both series of composites the tensile strength increases with increasing graphene content. This trend occurs up to 0.7% GNPs, after which the tensile strength decreases in series #1, and remains practically the same in series #2. A similar initial increase in strength properties and subsequent decrease is also observed in composites that do not contain aluminum carbides. The explanation for the decrease in strength properties after a

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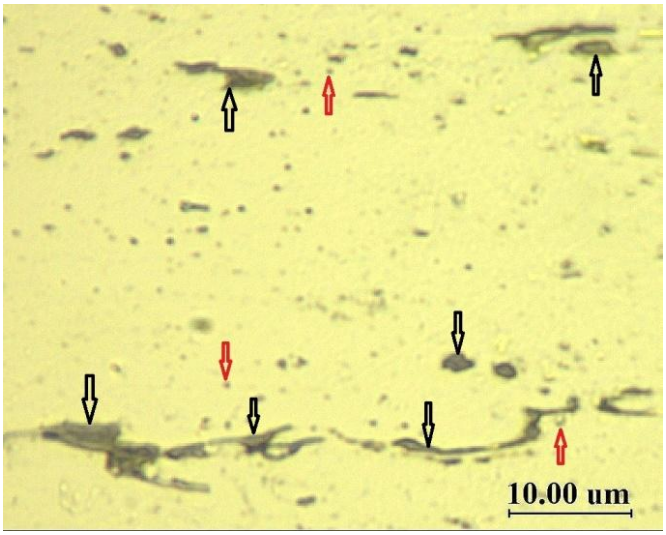
certain value of graphene content lies in the formation of agglomerates of graphene nanoplatelets, i.e., uneven, inhomogeneous distribution of graphene in the volume of the composite. Regarding composites containing aluminum carbides, it could be assumed that this decrease is also due to an increase in the content and/or size of aluminum carbides, since Al_4C_3 is very brittle. In our two series of composites, there is a presence of aluminum carbides, as can be seen from *Fig. 2*. Therefore, the change in tensile strength of series 2 composites with increasing graphene content is similar to that of series 1 composites, but at much lower values. These lower values are due to the larger size of the carbides and their different shape from the rounded one in the composites extruded at 400 °C and annealed at 610 °C for 3 hours, when large and elongated carbides are formed. Proof of this statement is the presence of micron-sized carbides in *Fig. 3 a* and *b*. The elongated carbide shown in *Fig. 3b* suggests that an entire graphene particle was transformed to carbide during the annealing of a sample with 0.1 wt.% GNPs, extruded at 400 °C and annealed at 610 ± 10 °C during 3h. These long and brittle carbides, naturally, cause low strength and ductility properties and a brittle nature of fracture.



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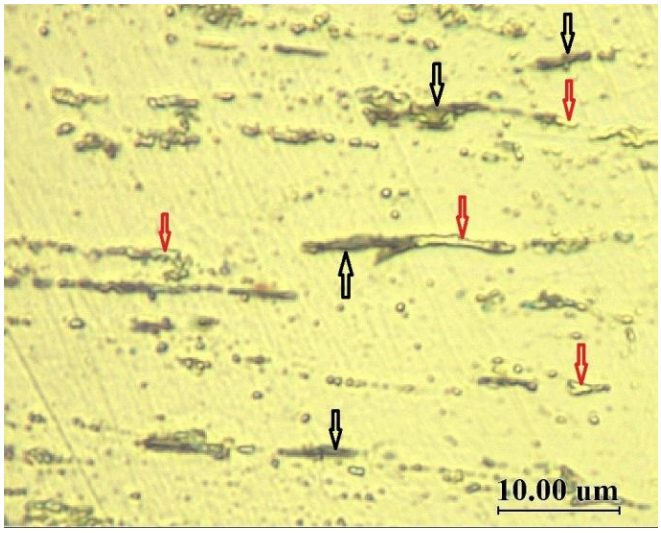

b

Fig. 2. Microstructure of aluminum composites reinforced with 0.7 wt.% GNPs: a) - extruded at 500 ± 10 °C and b) extruded at 400 °C and annealed at 610 ± 10 °C during 3h. Black arrows indicate GNPs, red arrows indicate carbides.

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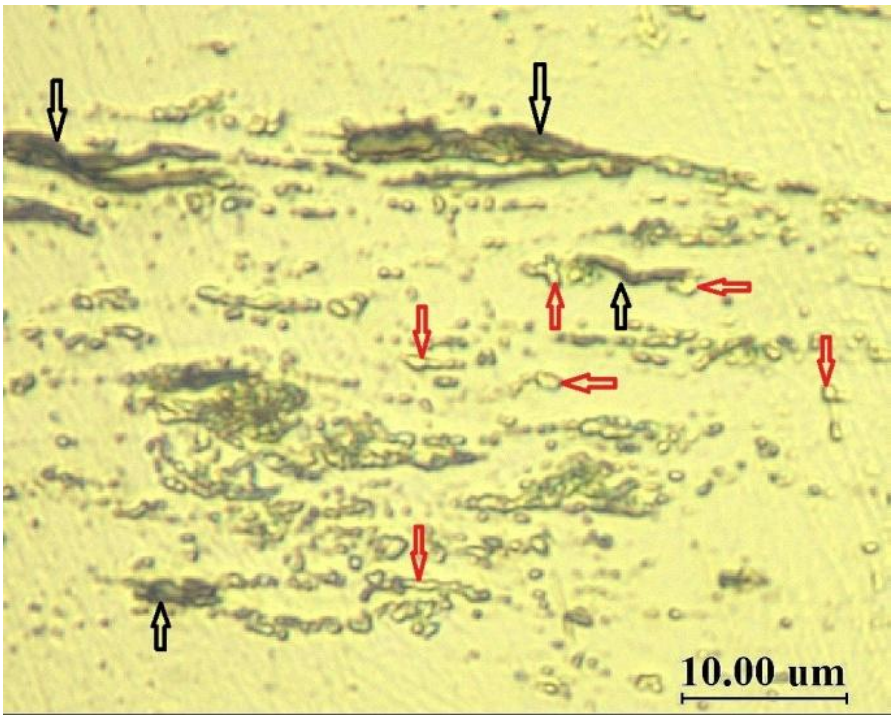

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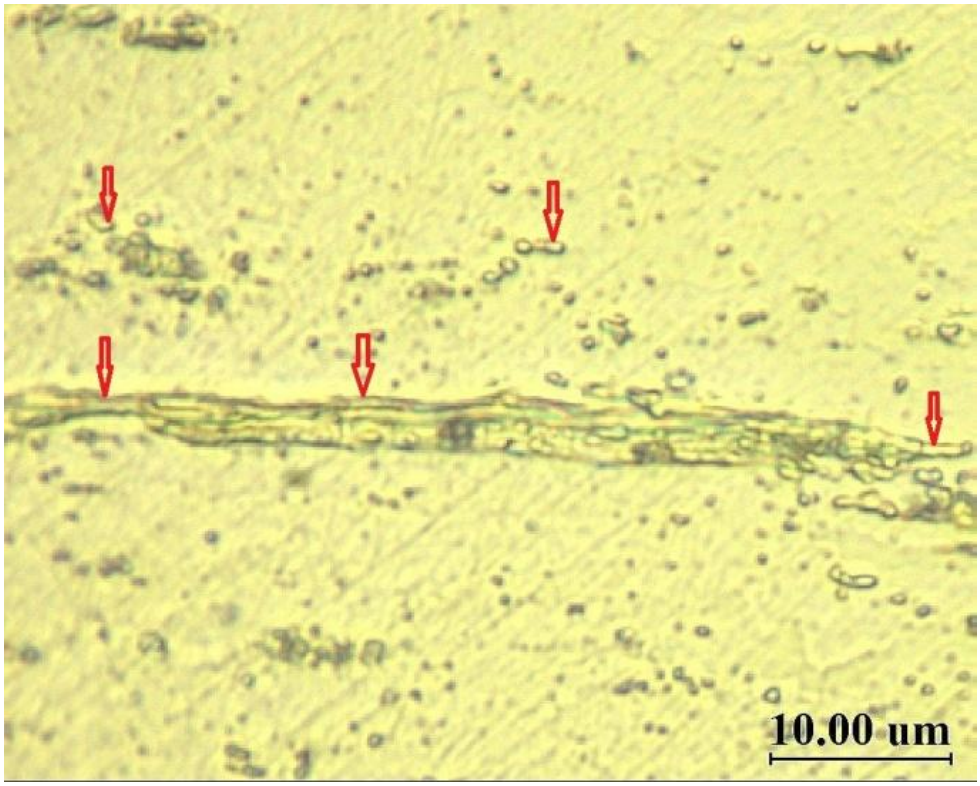

b

Fig. 3. Microstructure of aluminum composites reinforced with GNPs extruded at 400 °C and annealed at 610 ± 10 °C during 3h. Black arrows indicate GNPs, red arrows indicate carbides

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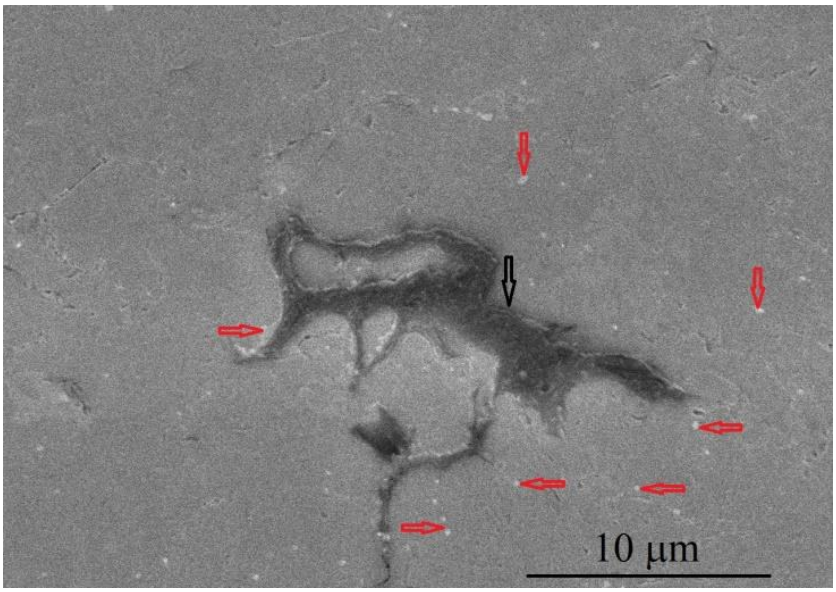

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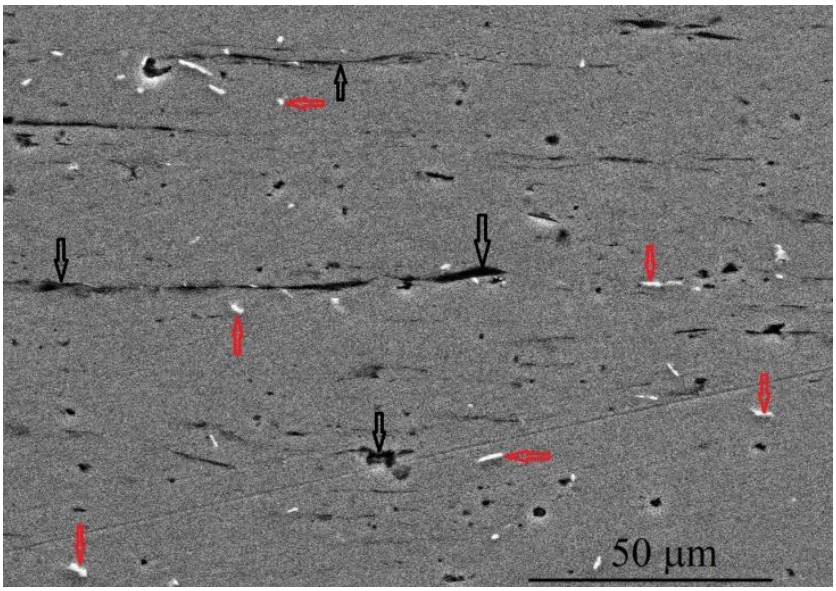

b

Fig. 4. GNPs and Al_4C_3 in Aluminum composites reinforced with: a) - 0.5 wt.% GNPs extruded at 500 ± 10 °C and b) 0.7 wt.% GNPs extruded at 400 °C and annealed at 610 ± 10 °C during 3h. Black arrows indicate GNPs, red arrows indicate carbides.

In *Figures 2 and 3*, it is clearly seen that the sizes of the carbides in the composite extruded at 400 °C and annealed at 610 °C for three hours are larger. In addition to the spherical shape of the carbides in the composites of series 2, rod-shaped and angular shapes are also found – *Fig. 3 a* and *b*. The presence of these facts gives reason to believe that the decrease in tensile strength is favored not only by increasing the graphene content, which forms agglomerates, but also by increasing the size of the carbides and changing their shape from spherical to elongated or angular. SEM observation also fond nano-sized spherical carbides in the composites of series #1 – *Fig. 4 a*. A part of the carbides in the composites of series #2 are nano-sized with spherical form while the rest are micron-sized with elongated form – *Fig. 4b*. The size and the shape of carbides in the composite of series #1 do not depend on the graphene content in the composite. This is demonstrated in *Fig. 5 a* and *b* where carbides are shown in a composite

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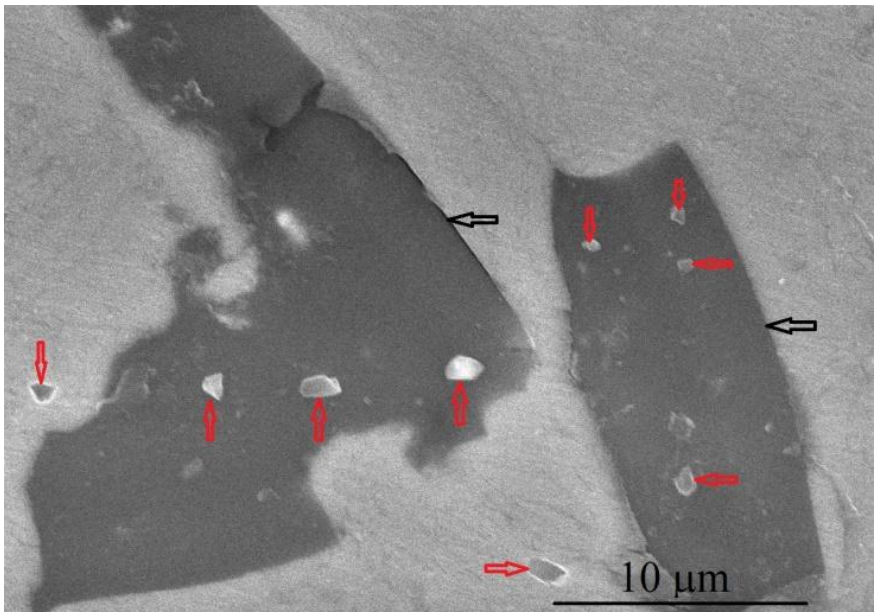
with 0.3 wt.% GNPs and 1.1 wt.% GNPs. It is evident that the extrusion conditions are favourable for the formation of nano-carbides with a rounded form. They provide both better strength and plastic properties of composites, as can be seen from *Fig. 1 a* and *b*.



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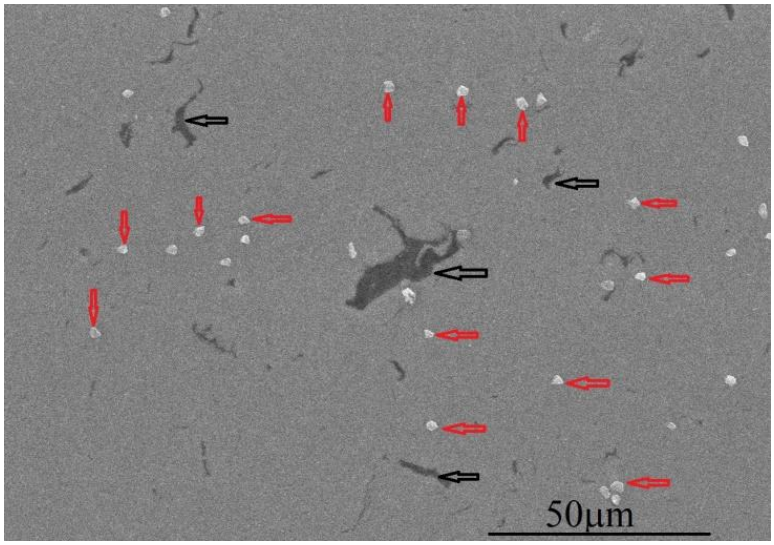

b

Fig. 5. GNPs and rounded nano-sized carbides in composites of series #1 with: a) 0.3 wt.% GNPs and b) 1.1wt.% GNPs. Red arrows indicate carbides.

Another microstructural reason for the good mechanical and fractographic properties of the composites is revealed by TEM analysis.

The specimen was taken from the cross-section of the extruded rods, so the plane of observation coincides with the direction of extrusion. In *Fig. 6 a,* is given the bright field image of the studied composite. The enlarged images of two separate areas are given in *Fig. 6 b* and *c*.

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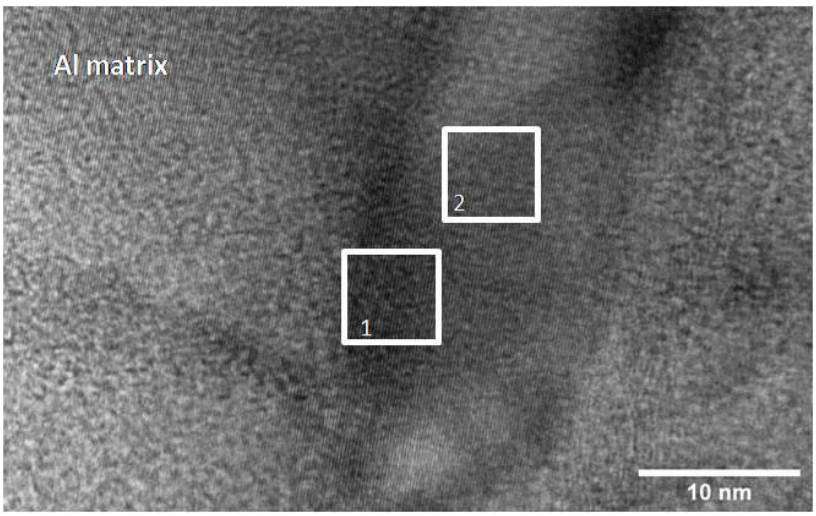
The first area is marked with a square and number 1 in *Fig. 6 a*. After FFT (Fast Fourier Transformation), it is clear that the darkest phase in the image corresponds to aluminum carbide Al_4C_3. The d-spacing is calculated to be 1.66 nm, which indicates the (110) plane of the carbide (Al_4C_3 COD #96-154-0875, a= 3.32900 Å; c= 24.98000 Å, R -3 m, trigonal). The carbide in the image is 3nm in diameter and more than 25 nm long. The enlarged image of it is given in *Fig. 6 b*.

The second area is also marked with a square, but with number 2 in *Fig. 6a*. After FFT analysis, it is determined as GNP (Graphite COD # 96-901-2706, a= 2.45600 Å; b= 4.25400; Å c= 6.69600 Å, Fmmm, orthorhombic). Based on the different contrast, the visible sizes of the GNP is >10nm in width and ~22 nm long. The enlarged image of GNP's fringe is given in *Fig. 6c*.

The carbide was produced by interfacial reaction between the two phases, Al and GNPs. The interfaces of GNP and Al_4C_3 are in contact intimately, and the carbide in turn is tightly locked in the Al matrix, thus ensuring an anchor effect between GNPs and the Al matrix. Thanks to the carbide formed this way, not just a mechanical bond is established between the two phases of the composite, but a chemical one, which would have a beneficial effect on the mechanical characteristics of the composite [11]. No sharply different orientation of the fringes of GNP and Al_4C_3 is noticeable, and this gives us reason to believe that the orientation is either Al_4C_3 (0003)//Al (002) or Al_4C_3 (0003)//Al (2-20) [12].



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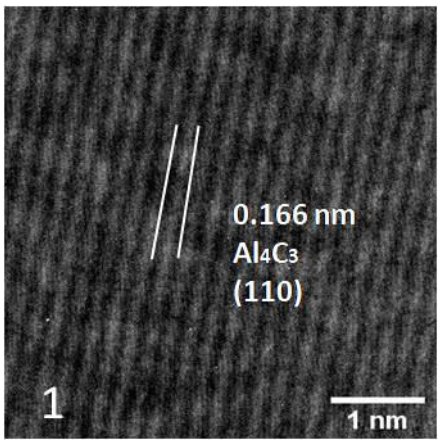

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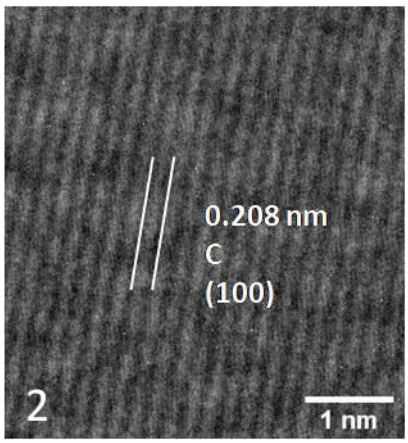

c

Fig. 6. HRTEM image of sample containing 1.1 wt. % GNPs - a); area of square 1 - b) and area of square 2 - c)

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The nano-sized carbides with a rounded shape, which provide a good set of mechanical properties, form numerous rounded dimples in the fracture of the composite specimen and thus determine the ductile mode of the fracture – *Fig. 7.*

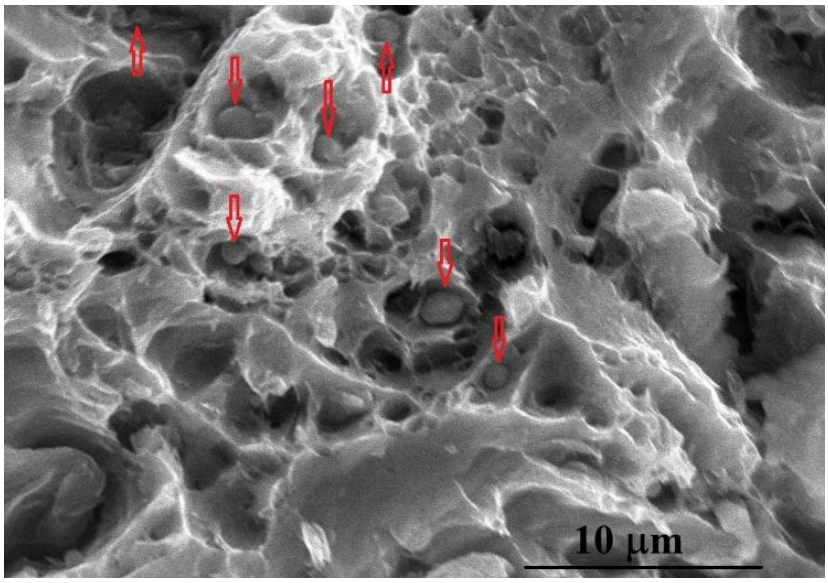

Fig. 7. Fracture surface of aluminum composite with 0.7 wt.% GNPs extruded at 500 ± 10 °C. Red arrows indicate carbides.

CONCLUSION

The higher strength and plastic properties of aluminum composites strengthened with GNPs and extruded at 500 °C (series 1) compared to those of aluminum composites strengthened with GNPs and extruded at 400 °C and subsequently annealed at 610 °C for 3 h (series 2) are due to the presence of 100% nano-sized carbides with a rounded shape. The carbide is tightly locked in the Al matrix, thus ensuring a chemical bond between GNPs and the matrix. This has a beneficial effect on the mechanical characteristics of the composite. The nano-sized carbides are also prerequisites for ductile fracture of the composite, forming dimples in the composite's structure.

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Declaration of Competing Interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability:

Data will be made available on request.

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