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NANOTWINNED COPPER-GRAPHENE COMPOSITES WITH HIGH HARDNESS

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Abstract. This paper addresses fabrication, structure, and hardness characteristics of nanotwinned (ntw) copper-graphene composites. The composites were fabricated by electrodeposition from 1M $CuSO_4 \cdot 6H_2O$ mixed water-alcohol solution containing graphene-graphite mixture stabilized by non-ionic surfactant. We fabricated two-layer solids each consisting of ntw copper layer and ntw copper-graphene layer. The synthesized two-layer specimens were examined in nanoindentation tests and showed high hardness values up to 3 GPa. The maximum hardness value of 3 GPa is higher than those of pure ntw copper and copper-graphene composites, taken from the literature.

1. INTRODUCTION

Strength and other mechanical characteristics of metallic materials can be significantly enhanced through reinforcement of metallic matrices by second-phase nanoinclusions; see, e.g., [1-3]. For instance, ceramic nanoparticles and nanofibers, metallic nanoparticles and carbon nanotubes are effectively exploited as reinforcing fllers in metal-matrix composites. In recent years, a rapidly growing interest has been devoted to metal–graphene composites in which nanoinclusions of graphene (Gr) – a carbon material with the exceptional mechanical properties [4-6] – are utilized as reinforcing structural elements [7-18]. This approach has shown very promising results.

For instance, Pavithra and co-workers [13], with pulse reverse electrodeposition method, synthesized copper-Gr nanocomposite foils having an average grain size of 1.2 mm. Hardness of the copper-Gr nanocomposite foils were measured in nanoindentation test and compared with that of pure copper foils (with an average grain size of 1.3 mm) fabricated by the same pulse reverse electrodeposition method. It was experimentally revealed that the hardness of the copper-graphene composite has value of ≈ 2.5 GPa, whereas pure electrodeposited copper specimens are specified by the hardness of ≈1.2 GPa [13]. Besides, in the experiment [11], bulk specimens of copper-Gr composite were fabricated and mechanically tested under tensile deformation. The composite specimens showed ≈ 80% increase

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Table 1. Suspensions compositions and specimen numbers.

Number of specimen	*Graphene concentration, g/l*	*Surfactant concentration, ppm*
1	0.05	25
2	0.1	25
3	0.1	50
4	0.25	50
5	0.25	100
6	0.5	50
7	0.5	100

in the yield strength (from 160 to 284 MPa) and ≈ 30% increase in the ultimate tensile strength (from 255 to 335 MPa), as compared to pure copper [11]. copper-matrix composites containing graphene and graphite inclusions are specified by 39% and 10% improvements in strength, respectively (Fig. 3).

Another general approach allowing one to drastically enhance strength and other mechanical characteristics of metallic materials is modification of their structure. In particular, superior strength and good ductility are exhibited by nanotwinned (ntw) metals due to their specific structural features, namely ultrafine grains and extremely high densities of nanoscale twins; see, reviews [19 – 21]. With these unique mechanical characteristics that are of utmost significance for a broad range of applications, ntw metals represent the subject of intensive research efforts; see, e.g., [19 – 39].

In the context discussed, it is very interesting to combine the two aforementioned approaches in order to achieve good mechanical properties in a metal-graphene composite having a structurally modified metal matrix. In previous experiments [40, 41], with electrodeposition method, we fabricated ntw copper-graphene composites being first examples of ntw metal-Gr composite solids. These ntw copper-graphene composites have pronounced structural non-homogeneities that manifest themselves through the formation of cone-like surface areas having typical sizes ≈ 250 microns [40,41]. The structurally non-homogeneous composites showed no enhancement in mechanical characteristics, as compared to pure ntw copper. The main aim of this paper is to fabricate structurally homogeneous ntw copper-graphene composites and examine their hardness characteristics in nanoindentation tests.

2. SYNTHESIS

The synthesis of ntw copper-Gr composite was performed by the previously exploited [40,41] electrodeposition method, except for one specific feature. In contrast to the previously exploited [40,41] procedure of electrodeposition of the composite film directly onto stainless steel cathode, here we first deposited pure ntw copper layer (without Gr) onto the steel cathode and then deposited ntw copper-Gr composite film onto the pure copper layer. This approach allowed us to fabricate two-layer solid consisting of structurally homogeneous ntw copper-Gr composite and pure copper layers.

In short, the synthesis procedure was as follows. For use in the electrodeposition process, 1M mixed water-alcohol solution was prepared by dissolving the $CuSO_4 \cdot 6H_2O$ crystal hydrate in water. Then, ethanol was added to the solution up to its 37.5 mL/L concentration, and the solution was acidified up to pH=1, using sulfuric acid. The solution under consideration was exploited for fabrication of pure ntw copper.

Synthesis of ntw copper-Gr composite needs further modification of the solution. In doing so, commercial graphite-graphene mixture produced by low-temperature graphite splitting (Active-NanoCo., Russia) was used as a graphene source. In order to stabilize graphene dispersion in the solution during the electrodeposition process, graphene-containing suspensions were prepared using a commercial non-ionic surfactant Pluronic F-127 (PLU). (The surfactant PLU was chosen due to its high molecular mass and good solubility in water.) List of these suspensions specified by various concentrations of graphene and PLU is presented in Table 1.

For the electrochemical deposition process at DC, we utilized the deposition cell having copper anode and stainless steel cathode – parallel plates

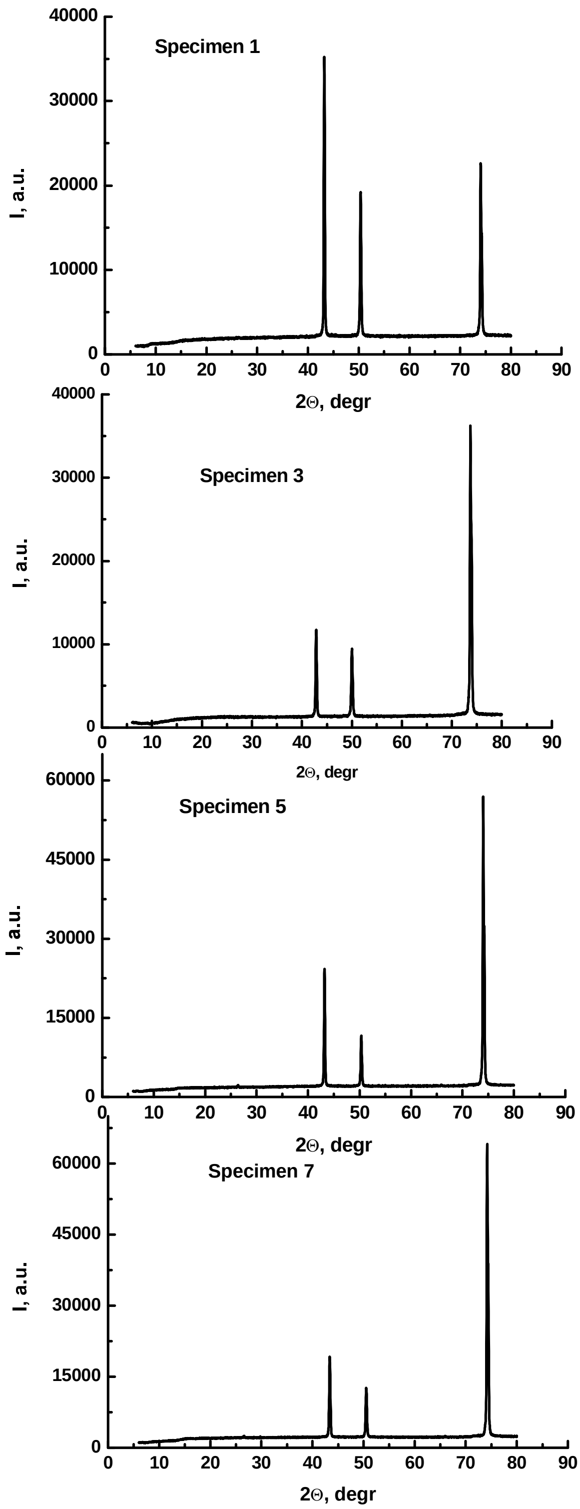

Fig. 1. X-ray diffraction data from Cu-Gr composite specimens.

distant by 30 mm from each other – with anode-to-cathode surface area ratio being 16 (for more details, see [40-42]). The deposition process was conducted in two steps. First, using the solution without Gr and PLU, the electrochemical deposition of pure copper was performed in the cell at 0.25 A DC during 30 min. As a result, the copper layer was synthesized on the stainless steel cathode. At the second stage, with the solutions specified by seven (7) various combinations of Gr and PLU concentrations (Table 1), ntw copper-Gr composite layers were deposited on the pure copper layers. The deposition of a composite layer on a copper layer was performed in the cell at 0.25 A DC for 2 h. The procedure under discussion resulted in seven two-layer platelets each consisting of ntw copper-Gr composite and pure copper layers.

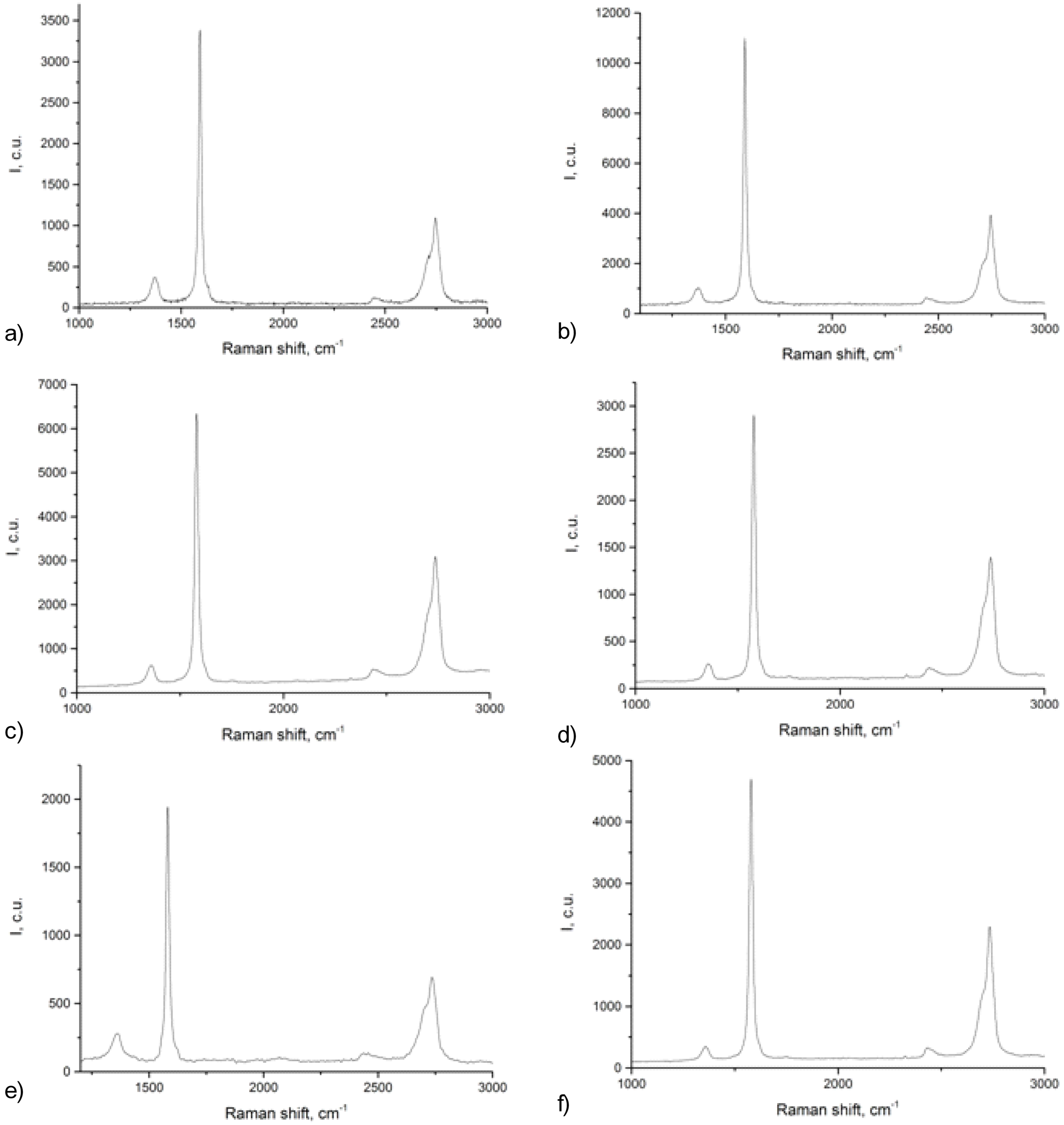

Fig. 2. Raman spectra of Cu-Gr composite specimens 1 (a), 2 (b), 4 (c), 5 (d), 6 (e) and 7 (f).

3. STRUCTURE

We examined structural features of the ntw copper-Gr composites. Fig. 1 presents results of X-ray diffraction analysis (SHIMADZU XRD-6000, Cu-Kα at λ = 1.54 Å) of the specimens 1 to 7. As it follows from Fig. 1, the metallic phase is the pure copper having preferred crystallographic orientations corresponding to peaks in the X-ray diagram at 2θ = 51 and 74°.

The conditions and method for synthesis of the composites are by practice the same as with those used in Refs. [40,42] for fabrication of ntw coper and ntw copper-Gr composites. In the experiments [40,42], the presence of large amounts of twins was identified by electron microscopy characterization. In the context discussed, it is logically to assume that large amounts of twins are present in the composites examined in this paper. Also, this statement will be verified by a detailed structural analysis addressing twins in the fabricated composites in our further research.

Examination of carbon allotropes in the ntw copper-Gr composites was carried out exploiting Raman

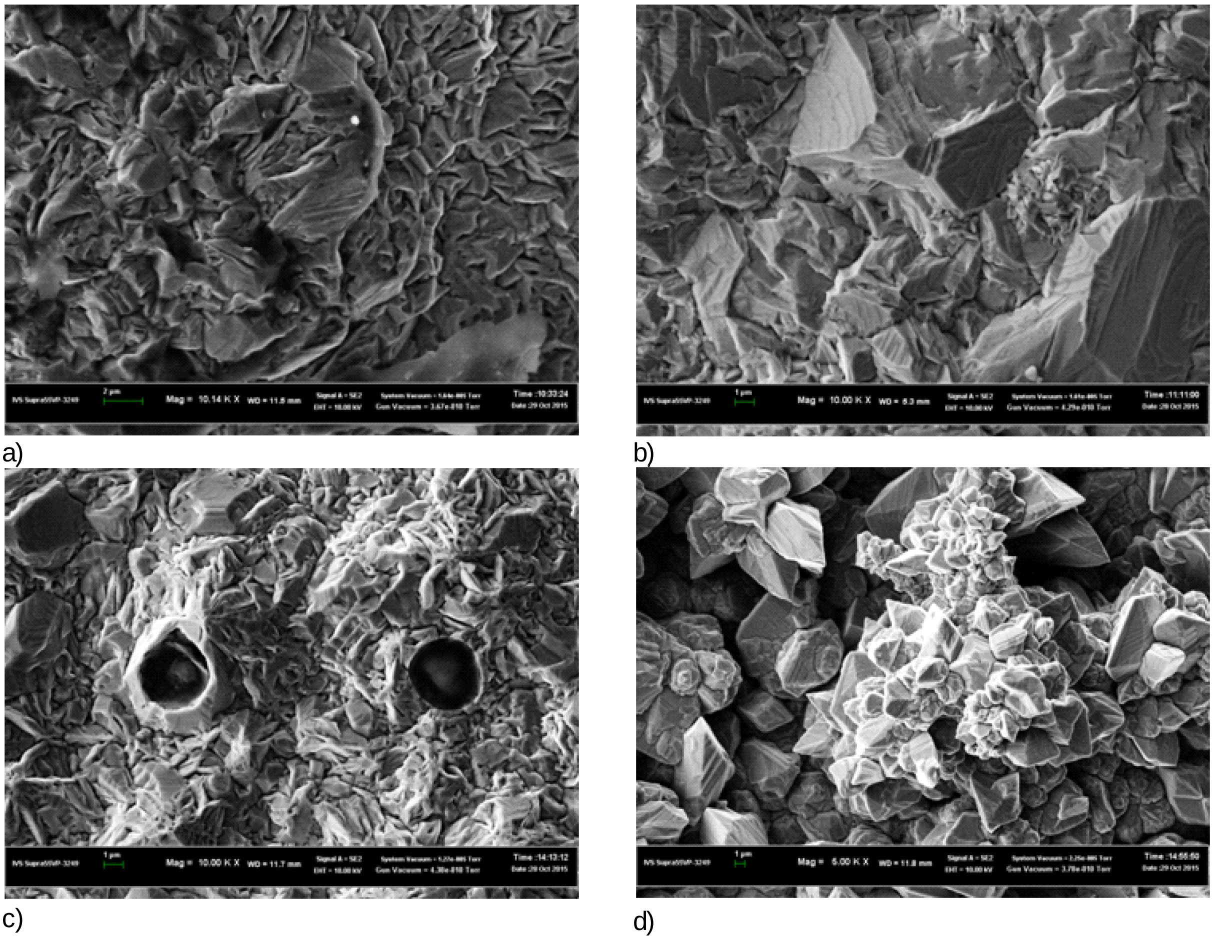

Fig. 3. Scanning electron micrographs from Cu-Gr composite specimens 1 (a), 2 (b), 3 (c) and 6 (d).

spectroscopy (SENTERRA, T64000, excitation wave length 488 nm, gate voltage 40 V). Its results are presented in Fig. 2 showing Raman spectra of the synthesized specimens (except for the specimen 3 demonstrating too high luminescence which makes impossible analysis of separate peaks). For all the spectra from the composites, intensity of the G peak at 1550 cm^{-1} is higher than that of the 2D peak at 2880 cm^{-1} (Fig. 2). This feature is indicative of the fact that large amounts of few-layer Gr nanoplatelets are present in these composites. Besides, with comparison of peak intensities at X-ray diagrams specifying the composite specimens, one finds that largest amount of Gr is present in the specimen 2.

Surface microstructures of the ntw copper-Gr composites were characterized with scanning electron microscopy (Zeiss Supra V-55). Figure 3 presents typical micrographs of surface areas of the composites under consideration. As it follows from Fig. 3, the composite specimens are structurally homogeneous. In particular, cone-like surface areas are absent in these specimens, in contrast to the previously fabricated [40, 41] ntw copper – Gr composites.

4. HARDNESS

The hardness characteristics of the synthesized ntw copper – Gr composites were examined in nanoindentation tests (NanoTest 600; MicroMaterials) exploiting Berkovich-type diamond tip. Details of nanoindentation tests were considered in Ref. [42]. Here we will present the most interesting results of these tests (in which hardness values were estimated according to the Oliver-Pharr method [43]).

Fig. 4 demonstrates dependences of hardness on indentation depth. As it follows from Fig. 4, values of hardness are very high. In particular, highest values of hardness for the specimens 2 and 7 are around 3 and 2.9 GPa, respectively. These values are larger than those ($\approx$ 2.7 GPa or lower) specifying pure ntw copper [42,44-46].

It is worth noting that the high hardness values ($\approx$ 2.9 and 3 GPa) were measured during nanoin-

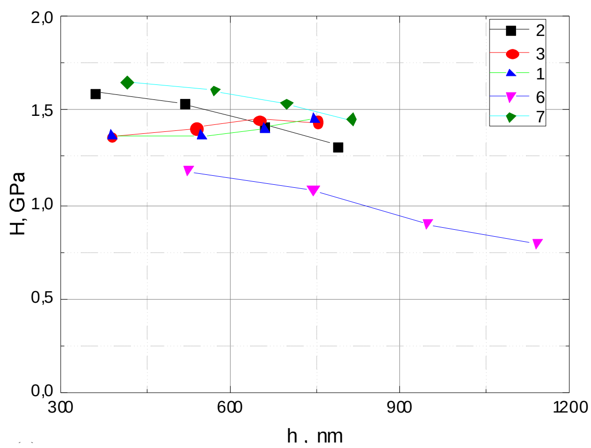

Fig. 4. Dependences of hardness on indentation depth for specimens 1, 2, 3, 5 and 7.

dentation of ntw copper layers belonging to the two-layer composites fabricated in our experiment. In contrast, hardness values of ntw copper-Gr composite layers belonging to the two-layer composites are comparatively low. In the most cases, they are in the range from 1.3 to 1.7 GPa. Hardness enhancement inherent to the ntw copper layer of the fabricated composites is a very interesting aspect that needs further examination and understanding.

In a first approximation, one may assume that free surface effects dramatically decrease hardness of ntw copper-Gr composite layers belonging to the two-layer composites in nanoindentation tests. This assumption is logical, because, generally speaking, free surface effects can significantly modify plastic deformation processes in nanostructured materials (like ntw metals); see, e.g., [47,48]. At the same time, internal regions of the ntw copper-Gr composite are specified by high flow stresses that enhance hardness measured in nanoindentation of ntw copper layers belonging to the two-layer composites, as compared to the situation with pure ntw copper. Thickness of a ntw copper layer is around 2 microns, while nanoindentation depth ranges from 250 to 700 nm. In these circumstances, plastic deformation induced nanoindentation definitely occurs in the ntw copper-Gr layer, and its flow stress thereby influences/enhances hardness value measured in the ntw copper layer belonging to the two-layer composite.

5. CONCLUDING REMARKS

Thus, ntw copper-Gr composites were synthesized by electrochemical deposition from 1M $CuSO_4 \cdot 6H_2O$ mixed water-alcohol solution containing graphene-graphite mixture stabilized by non-ionic surfactant PLU. More precisely, we fabricated two-layer solid platelets each consisting of ntw copper layer and ntw copper-graphene layer. This approach allowed us to avoid the undesired formation [40,41] of cone-like surface areas having typical sizes ~250 microns. The synthesized two-layer specimens were examined in nanoindentation tests and showed high hardness values up to 3 GPa. The maximum hardness value of 3 GPa is higher than those (≈ 2.7 GPa or lower) specifying pure ntw copper [42,44-46] and hardness (≈ 2.5 GPa) of copper-Gr composites without the ntw structure [13]. They were measured during nanoindentation of ntw copper layers belonging to the two-layer composites. In contrast, hardness values of ntw copper-Gr composite layers belonging to the two-layer composites are comparatively low. Hardness enhancement inherent to the ntw copper layer of the fabricated composites represents a very interesting fact that needs further examination.

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