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NANOTWINNED COPPER – GRAPHENE COMPOSITE: SYNTHESIS AND MICROSTRUCTURE

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Abstract. "Nanotwinned copper – graphene" composite samples were manufactured by electrochemical deposition using non-ionic surfactants (polyacrilic acid and Pluronic F-127). The results of TEM and EBSD describing materials microstructure along with XRD data on phase composition and SEM data on surface quality provides an opportunity to discuss the effect of synthesis procedure on the composite structure and properties.

1. INTRODUCTION

The advantages of nanotwinned metals as materials with high mechanical properties was discussed in detail in review [1], such characteristics as high strength and hardness along with improved fracture toughness and fatigue resistance were mentioned, see also papers [2-6]. It should be also noted that, in addition to mechanical properties, there exists a possibility to improve electroconductivity of the material [7]. For this reason, the approaches providing the production of nanotwinned metals with required properties are of current interest. These approaches were discussed in our previous paper [8]. This paper reports nanotwinned copper manufacturing by electrochemical deposition technique; material microstructure and its mechanical properties are considered.

On the other hand, graphene introduction in the metal bulk provides an additional opportunity to vary the properties of the designed material. Basing on reference data on the improvement of "metal-graphene" composites mechanical properties, see e.g. [9-15], authors of the present paper synthesized "aluminium-graphite" composite, synthesis procedure and preliminary data on material microstructure are available in [16]. The attempts to improve copper characteristics using oxide and carbide nanoparticles, see e.g. [17-20], as well as carbon nanowires or nanotubes [21-24] were considered in our work [25]. It was concluded that the addition of inorganic nanoparticles gives an opportunity for partial improvement of the mechanical properties, however, electroconductivity of such composites is usually much lower than that for pure copper.

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Table 1. List of the synthesized samples.

Sample	Surfactant type (PAC – polyacrylic acid, PLU – Pluronic F-127)	Graphene content in the solution, g/L	Surfactant content in the solution,ppm
1	PAC	0.05	25
2	PAC	0.1	25
3	PAC	0.1	50
4	PAC	0.1	100
5	PLU	0.1	25
6	PLU	0.1	50

On the contrary, introduction of carbon nanowires or nanotubes does not significantly affect electroconductivity and provides their mechanical properties improvement. At the same time, such problems as nanotubes and nanowires agglomeration during composite manufacturing, their negative impact on materials porosity and its structure were mentioned. So, an attempt to synthesize "nanotwinned copper – graphene" nanocomposite was undertaken in [25], it was shown that such a composite possesses high mechanical properties, however, the quality of the material produced by electrochemical deposition was rather low, since the applied approach did not provide uniform graphite distribution during the electrochemical deposition process.

Paper [26] describes an improved synthesis procedure of "nanotwinned copper – graphene" composites using graphene suspensions stabilized by non-ionic surfactants. XRD patterns detected for the produced composites indicated carbon introduction in the material, SEM study proves the improvement of material quality. Discussing XRD and SEM data in more detail, the present paper combines them with the results obtained by TEM and ESBD. Microstructure of the composites and the effect of synthesis procedure on the material properties are discussed.

2. EXPERIMENTAL: SAMPLE SYNTHESIS AND THEIR INVESTIGATION

The procedure of sample synthesis was described in detail in our paper [25]. Briefly it can be summarized as follows: the same electrochemical deposition cell (see also [8,25]) with copper anode and stainless steel cathode (parallel plates with 30 mm distance between them, anode-to-cathode surface area ratio of 16) was used. Electrochemical deposition was performed at 0.5 A DC for 2 hours. The same $CuSO_4*6H_2O$ crystal hydrates aqueous solution was prepared at room temperature, ethanol was added up to 37.5 mL/L concentration, the solution was acidified up to pH=1 using sulfuric acid.

Our previous study reported in [25] showed that the described approach resulted in rather non-uniform nanotwinned copper coating, this fact was considered as being due to insufficient graphene stabilization in the solution. It was also shown that the application of ultrasound treatment did not provide uniform graphene distribution in water-ethanol solution. To overcome this problem, the following procedure was applied. Graphite-graphene mixture produced by low-temperature graphite splitting (Active-Nano Co., Russia) was used as a graphene source. To stabilize graphene distribution in the solutions during the deposition process, graphene-containing suspensions were prepared using commercial non-ionic surfactants: polyacrilic acid (PAC) and Pluronic F-127 (PLU). As mentioned in [26], these surfactants were chosen due to their high molecular mass and good solubility in water.

A number of "nanotwinned copper – graphene" composites (coatings at stainless steel plates) were manufactured by electrochemical deposition from the solutions containing graphene-surfactants suspensions; the details of the procedure are described in Table 1.

Synthesized samples were studied were studied by XRD (SHIMADZU XRD-6000, Cu-K_α with λ = 1.54 Å at room temperature), SEM (Zeiss Supra V-55), and TEM (Jeol JEM-1230). Additional study providing the understanding of microstructure peculiarities was performed using EBSD approach. TESCAN MIRA 3LMH FEG scanning electron microscope equipped with an EBSD analyzer "CHANNEL 5" and a rectangular greed with a scan step of 50 nm was used here. The acquired data were subjected to standard clean-up procedures, see also

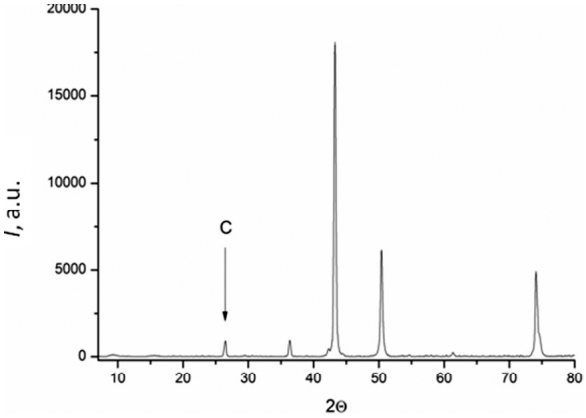

Fig. 1. XRD patterns of Sample 4.

[8]. These procedures involved a grain tolerance angle of 5° and a minimum grain size of three pixels. Similarly to our previous work, the grain sizes were measured using the linear intercept as the distances between high-angle boundaries with misorientations more than 15°.

3. RESULTS AND DISCUSION

XRD and SEM results were discussed in detail in [MPM 2016]. Summarizing the results on XRD patterns (see Fig. 1, XRD patterns for Sample 4), one can see that carbon-containing phase is present in the synthesized composite (reflex at $2\theta = 26°$ is attributed to carbon). Moreover, since the minimal amount of the substance necessary for its XRD identification is conventionally estimated as 5 wt.%, it can be stated that the suggested electrochemical deposition procedure provides the required amounts of carbon-containing phase. Estimates for crystallites size and crystallinity level (crystal-to-amorphous ratio) calculated from XRD data showed that the type of the surfactant (PAC or PLU) along with surfactant concentration significantly affect the samples structure: crystallinity level for Samples 4 and 6 was estimated as 48% and 82%, respectively. At the same time, similar value for pure nanotwinned copper [8] was estimated as 69%. Thus, varying the amount of surfactants during the deposition process, one can intentionally change composite structure.

The analysis of SEM results [26] showed that the surface quality of the growing composite, is affected by the synthesis conditions. It was stated that even a small addition of non-ionic surfactants gives an opportunity to stabilize graphene suspensions and, as a result, to produce uniform coatings with high quality of their surface. To demonstrate these statement, Fig. 2 compares SEM data for the composite surface of Samples 4 (100 ppm PAC) and 5 (25 ppm PLU) deposited at the same graphene concentration of 0.1 g/L.

As seen from the figure, both coatings demonstrate the features typical for epitaxial growth. However, rather high amount of PAC surfactant, see Fig. 2a, results in more uniform surface; while less content of PLU surfactant, Fig. 2b, leads to the formation of more sharp edges, crystal structure is evident here. Note that linear dimensions of the objects on Sample 4 surface are higher than those typical for Sample 5 surface. These data are in good agreement with the above discussed results on the crystallinity level calculations from XRD data. Indeed, PAC addition gives rise for some amorphization of the produced coatings, on the contrary, PLU surfactant increases sample crystallinity. Note that in spite of the different surface character, both samples demonstrated good surface uniformity and the absence of macrodefects in them, film integrity is quite acceptable. An interesting feature of the coating deposited using high PAC concentrations is a presence of some pores with typical linear dimensions of 1 μm, usually they are seen as dark circles (Fig 2a), however, sometimes these structures are reproducing crystal shapes. Since this effect is observed for the samples with high graphene contents, we consider them as being due to some growth microdefects due to graphene inclusions on the growth surface.

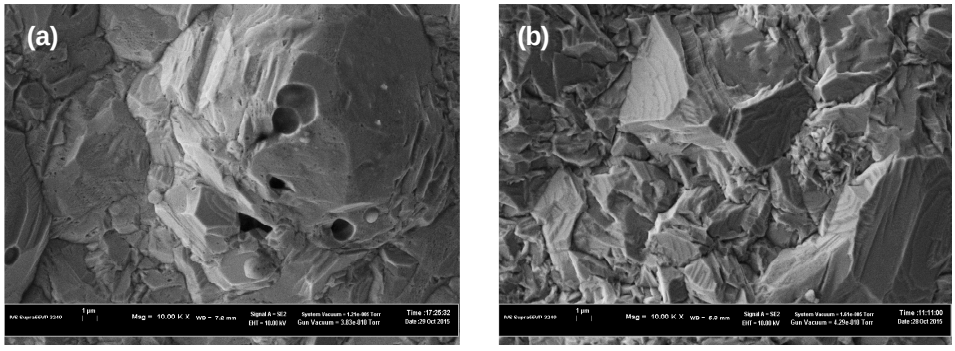

Fig. 2. SEM data for the surface of Sample 4 (a) and Sample 5 (b).

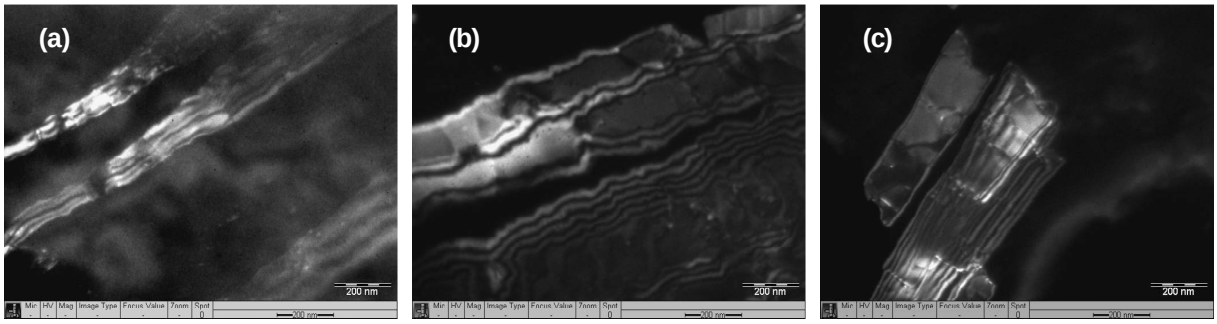

Fig. 3. TEM images demonstrating structures typical for nanotwinned copper: (a) Sample 3, (b) Sample 4, (c) Sample 5.

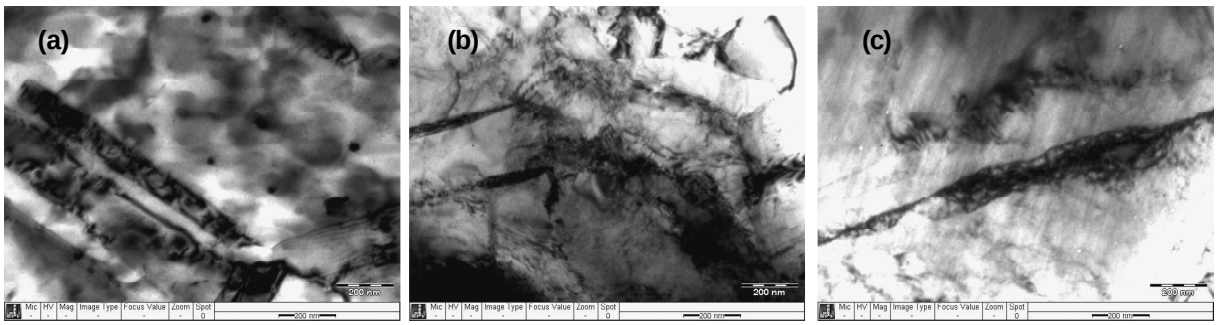

Fig. 4. TEM images demonstrating structures typical for graphene inclusions: (a) Sample 2, (b) Sample 3, (c) Sample 5.

Fig. 3 demonstrates TEM images for Samples 3, 4, and 5 (Figs. 3a, 3b, and 3c, respectively). The presence of structures typical for nanotwinned copper can be seen here. This fact indicates that graphene introduction did not change general characteristics of the electrochemical deposition procedure developed in [RAMS Nano-Cu] and nanotwinned copper coatings still can be produced using it. It should be also noted that nanotwinned structures manifested themselves for samples produced using both types of surfactants. Note that the conclusion on the nanotwinned copper structure that follows from TEM data is in a good agreement with EBSD data, see below.

Fig. 4 (TEM images for samples 2, 3, and 5) demonstrate graphene introduction in the composite bulk. Basing on the data reported in [10] and our previous work on "aluminium-graphene" composites [16], we consider the extended dark objects on TEM images as an indicator of graphene inclusions, note that these inclusions are seen on the images of the samples produced using both surfactant types. This fact is quite important since XRD data (see [MPM2016] for more details) proved the fact of graphene introduction to the composite bulk only for the samples with rather high graphene content, for a number of samples these values were lower than the detection limit of the method. In particular, the result demonstrated in Fig. 4c for Sample 5 is very significant since it demonstrates that graphene is included in the composite bulk even at most critical deposition conditions: low graphene content in the solution and PLU surfactant that retards graphene introduction in the composite (see [26]). Thus, TEM data indicated that copper is nanotwinned in the composite; the introduction of graphene in all samples was proved.

Fig. 5 demonstrates the distribution of the misorientation angles (MA) calculated from EBSD data for "nanotwinned copper-graphene" composites (Samples NN 1-6) in comparison with the same data obtained for pure nanotwinned copper, see [8]. Let us discuss it in some details. Fig. 5a presents the MA distributions for nanotwinned copper sample, it can be seen from the image that the fraction of 60° angle, corresponding to nanotwinning is a dominant one, it is ~ 50%. This type of distribution is also typical for composites produced using PLU surfactant suspensions (Samples 5 and 6, Figs. 5f and 5g, respectively). As was mentioned above, the use of PLU suspensions results in highly crystalline structures with low graphene content. Indeed, distribution depicted in Fig. 5f is quite similar to that typical for pure nanotwinned copper (Fig. 5a). The fraction of 60° angle decreases with the increase in the suspension content (Fig. 5g), in spite of the fact that graphene content in the solution was the same. This fact supports our conclusion that the increase

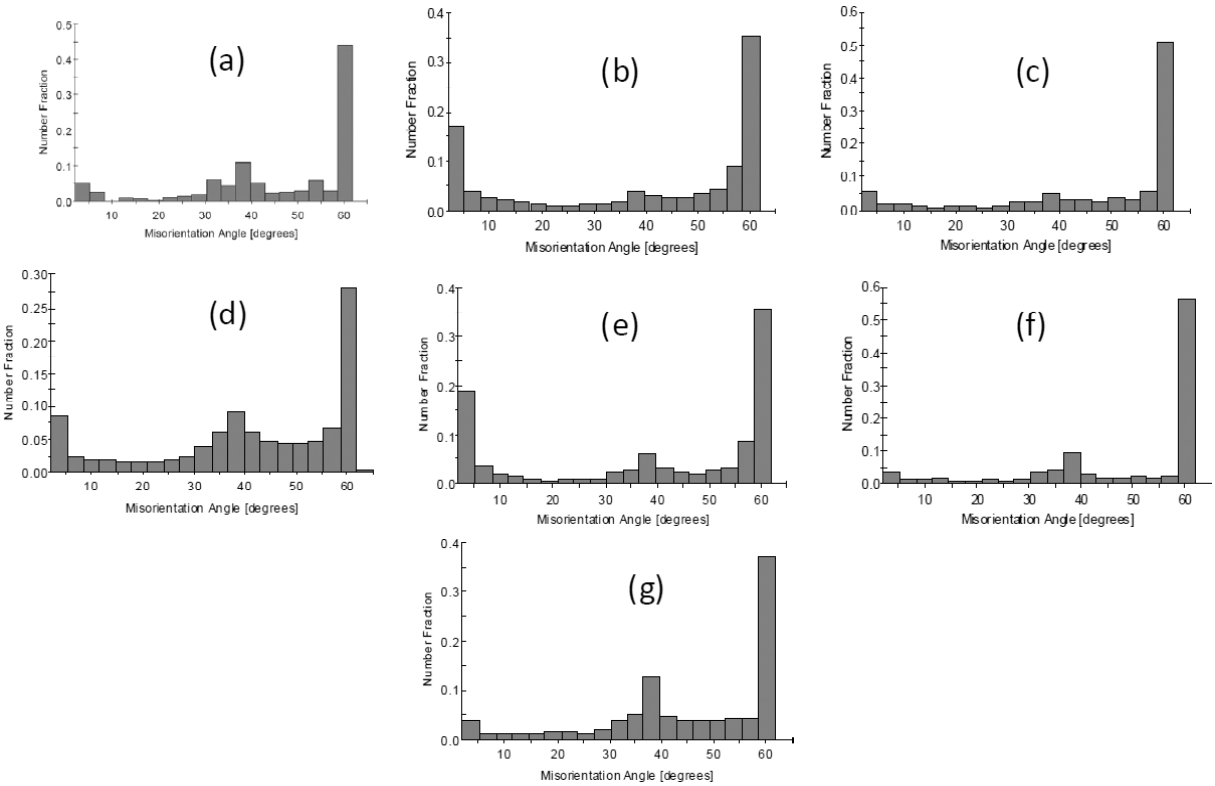

Fig. 5. Misorientation angle distributions from EBSD data: (a) – nanotwinned copper [8], (b)-(g) – Samples 1-6, respectively.

in the surfactant suspension content affects the graphene introduction into the composite bulk.

In contrast to PLU surfactant, the effect of PAC surfactant is not so simple. Comparing Figs. 5b-5e with the results obtained for nanotwinned copper without graphene (Fig. 5a), one can conclude that amorphization and high levels of graphene contents that can exceed 5 wt.% (according to XRD data) results in the decrease in the 60° MA angle fraction, generally, it is less than 40% for these composites. However, this value calculated for Sample 2 (Fig. 5c) is quite comparable with the value for pure nanotwinned copper. So, one can conclude that there is some optimal regime for the use of PAC surfactant suspensions that combines high crystallinity and high amount of 60° MA angles with the preference of intensive graphene introduction in the composite bulk typical for the synthesis procedure using PAC suspensions. Fig. 6 presenting SEM data for Sample 2 can be considered as an indirect support for the above statement. Indeed, comparing this figure with data presented in Fig. 2, one can see that the surface structure in this case combines small linear sizes of the objects typical for Samples synthesized using PLU suspensions with their smooth shapes typical for the amorphization in case of PAC suspensions application.

Fig. 7 presents the summary on the grain size distributions for Samples 1-6 calculated from EBSD data. As follows from the figures, grain sizes in the synthesized "nanotwinned copper – graphene" composites generally lie in the range 0.5-10 μm. However, it is evident that this parameter also may be intentionally affected by synthesis procedure: indeed, grain size distributions with the maximum ~1-1.5 μm were obtained for Samples 3 and 5, higher sizes with the maximum of ~5-7 μm are typical for Samples 1,4, and 6. Above discussed Sample 2 (see Figs. 5 and 6) that was suggested to be the optimal composite has the highest average grain sizes, it is the only one with the maximum shifted

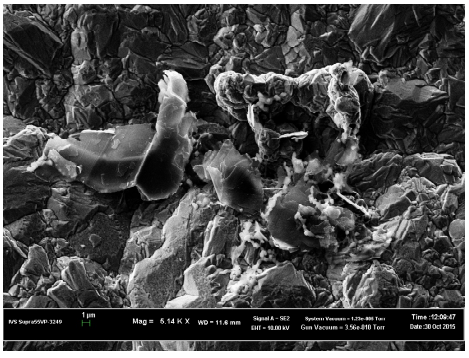

Fig. 6. SEM data for Sample 2.

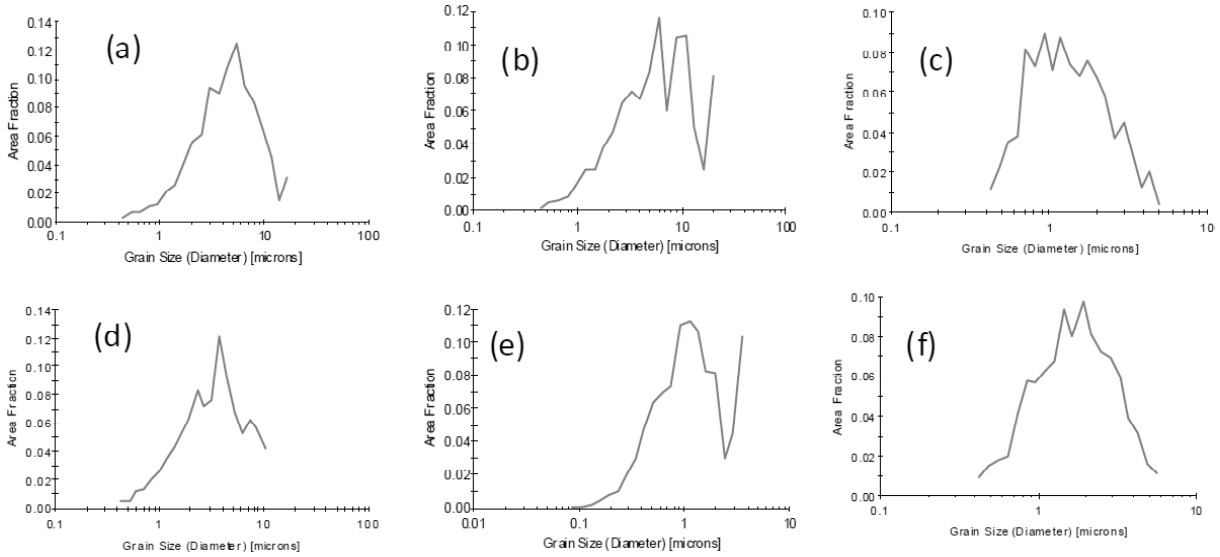

Fig. 7. Grain size distributions for Samples NN 1-6, images (a)-(f), respectively.

to 8-10 μm and a high part of grains with sizes exceeding 10 μm. So, it can be concluded that the choice of the proper electrochemical deposition procedure provides an opportunity to manufacture "nanotwinned copper graphene" composite with the required grain size distributions.

4. CONCLUSIONS

"Nanotwinned copper – graphene" composite coatings were grown by electrochemical deposition from solutions containing graphene suspensions with non-ionic surfactants (polyacrilic acid and Pluronic F-127). XRD study indicated the presence of carbon-containing phase in the deposited coatings; the results of TEM investigation proved that the manufactured samples are nanotwinned copper with graphene inclusions. SEM and ESBD results on samples microstructure showed that the choice of the electrochemical deposition procedure provides an opportunity to vary the microstructure characteristics in a wide range changing the crystallinity level from 50 to 80% and the average grain size values from 0.5-1 to 10 μm.

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