

METAL-GRAPHENE NANOCOMPOSITES WITH ENHANCED MECHANICAL PROPERTIES: A REVIEW

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Abstract. This paper presents an overview of research efforts focused on both fabrication and mechanical properties of metal-matrix nanocomposites containing graphene inclusions. A particular attention is devoted to experimental data giving evidence for enhancement of strength, microhardness and Young modulus (due to the effects of graphene inclusions) of such nanocomposites, as compared to both unreinforced metals and metal-matrix nanocomposites reinforced by non-graphene inclusions. Key factors are discussed which influence the role of graphene nanosheets and nanoplatelets in remarkable enhancement of the mechanical characteristics of metal-graphene nanocomposites.

1. INTRODUCTION

Graphene is a new two-dimensional carbon material showing unique mechanical, transport and thermal properties; see, e.g., reviews [1-7]. In particular, graphene is specified by both superior tensile strength of ≈ 130 GPa and Young modulus of ≈ 1 TPa [7,8]. These excellent mechanical characteristics cause a great potential in using graphene inclusions as strengthening elements in polymer-, ceramic- and metal-matrix composites for structural and functional applications; see, e.g., [9-28]. In particular, in recent years, several research groups have fabricated metal-matrix nanocomposites reinforced by graphene inclusions [21-28]. Such nanocomposites exhibit enhanced mechanical characteristics (due to the effects of graphene fillers), as compared to both unreinforced metals and metal-matrix nanocomposites reinforced by non-graphene inclusions. The main aim of this paper is to give an overview of research efforts focused on fabrication

and high mechanical properties of new metal-graphene nanocomposites.

2. GENERAL ASPECTS

In general, the idea to enhance strength and other mechanical characteristics of metallic materials through reinforcement of metallic matrices by nanoinclusions of the second phase has been effectively exploited by many research groups in over the world; see, e.g., [29-31]. For instance, within the approach in question, ceramic nanoparticles and nanofibers, metallic nanoparticles, and carbon nanotubes have been effectively exploited as reinforcing nanoinclusions. Although the results in this area are impressive, the development of strong, durable and cost-efficient metal-matrix composite materials for current and future technologies is still an unsolved problem. In this context, search for novel materials as reinforcing fillers in metal-matrix composites is of crucial significance. In search for new

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fillers, one can distinguish the following key factors that crucially influence the role of nanoinclusions as reinforcing structural elements in metal-matrix nanocomposites:

- (i) Reinforcing inclusions should have high mechanical characteristics such as strength and Young modulus.
- (ii) Geometry of reinforcing inclusions should be characterized by high aspect ratio and high surface area.
- (iii) Strong binding between inclusions and metal matrix should exist.
- (iv) Reinforcing inclusions should be homogeneously dispersed, and their agglomeration should be prevented.

In addition, from a practical viewpoint, fabrication of metal-matrix nanocomposites is desired to be a cost-efficient procedure.

It is a formidable challenge to simultaneously meet the conditions (i)-(iv), in parallel with cost efficiency. In these circumstances, fabrication of metal-matrix nanocomposites with enhanced mechanical characteristics and search for novel materials as reinforcing fillers in such composites represent the subjects of intense research efforts in nanoscience and nanotechnology.

Graphene specified by superior values of both tensile strength ≈ 130 GPa [7,8] and Young modulus $Y \approx 1$ TPa [7,8] is a very promising candidate to serve as a reinforcing material in metal-matrix nanocomposites. In addition, production of graphene (at cost of ≈ 5 EUR/kg [32]) is cheap compared to that of carbon nanotubes having similar mechanical characteristics. Besides, 2D geometry of graphene nanosheets and nanoplatelets is responsible for maximum value of their surface-to-volume ratio and can provide very high aspect ratios. These high geometric parameters as well as superior mechanical characteristics of graphene nanoinclusions are favorable for enhancement of mechanical properties of graphene-reinforced nanocomposites.

Thus, the conditions (i) and (ii), along with the cost efficiency condition, are in fact automatically satisfied for graphene fillers utilized in metal-matrix nanocomposites. In these circumstances, it is important to devote a special attention to the conditions/factors (iii) and (iv) in development of metal-graphene nanocomposites with enhanced mechanical characteristics. In next sections, we will discuss examples of such nanocomposites and consider factors responsible for enhancement of their mechanical properties.

3. METAL-GRAPHENE NANOCOMPOSITES WITH ENHANCED MECHANICAL PROPERTIES: FABRICATION AND MECHANICAL TESTS

In general, fabrication of metal-matrix composites reinforced by graphene inclusions (sheets, nanoplatelets) represents a rather difficult technological problem. As a corollary, successful studies in this area are very limited [21-28]. Below we will consider experiments focused on fabrication of metal-graphene nanocomposites with enhanced mechanical properties.

3.1. Al-graphene nanocomposites

Wang with co-workers [21] fabricated Al-graphene nanocomposites showing a dramatic enhancement in strength, as compared to their graphene-free counterpart. In doing so, they utilized the novel approach based on flake powder metallurgy. More precisely, following Ref. [21], there are the following key steps of the fabrication of Al-matrix nanocomposites reinforced by graphene nanosheets:

- (1) Aqueous solution of well dispersed nanosheets of graphene oxide is prepared. The nanosheets are specified by thicknesses being less than 1.5 nm, that is, no more than 5 graphene oxide layers.
- (2) Al flakes are prepared with surfaces being covered by hydrophilic PVA membranes. The flakes typically have a 2D planar morphology with an average thickness of around 2 micrometers.
- (3) Graphene oxide nanosheets are absorbed at surfaces of Al flakes and then reduced (by heating treatment) to graphene nanosheets. As a result, one obtains graphene-Al composite powders, that is, Al flakes with graphene nanosheets homogeneously dispersed at their surfaces.
- (4) Graphene-Al composite powders are compacted and consolidated to fabricate bulk nanocomposite consisting of Al matrix reinforced by homogeneously dispersed graphene nanosheets. The consolidation occurs by sintering of compacted billets of graphene-Al composite powders in Ar atmosphere at 580 °C for 2 hours and consequent hot extrusion at 440 °C with an extrusion ratio of 20:1.

Wang with co-workers performed tensile tests with specimens of 5 mm diameter and 25 mm gauge length machined from extruded rods consisting of Al-matrix reinforced by 0.3 wt.% graphene nanosheets [21]. In the tests, the Al-graphene

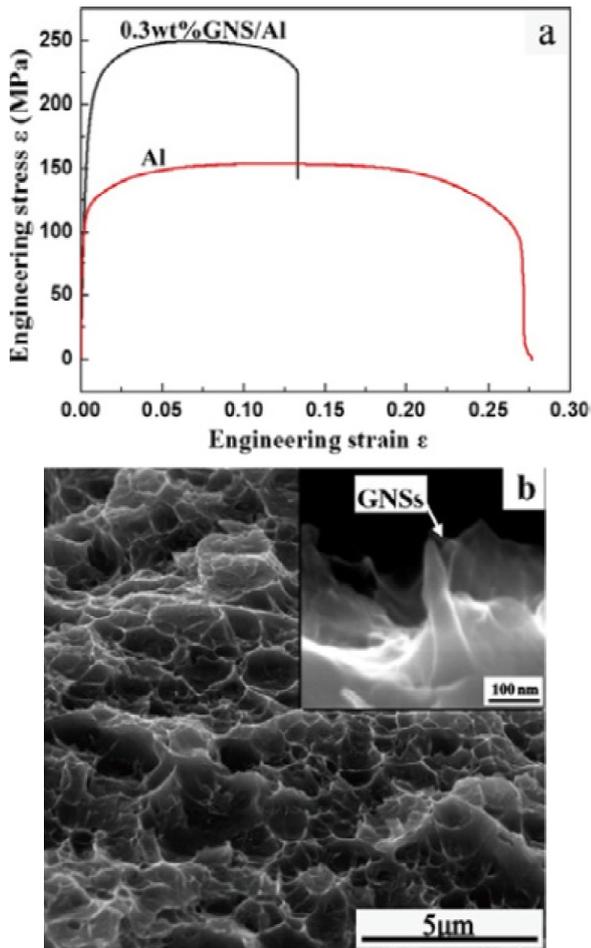


Fig. 1. (color online) (a) Tensile properties of 0.3 wt.% graphene-Al composite and the corresponding flaky Al specimen; (b) fracture surface of 0.3 wt.% graphene-Al composite; the inset shows graphene nanosheets pulled out. Reprinted from *Scripta Materialia*, Vol 66, J. Wang, Z. Li, G. Fan, H. Pan, Z. Chen, D. Zhang, Reinforcement with graphene nanosheets in aluminium matrix composites, pages 594-597, Copyright (2012), with permission from Elsevier.

nanocomposite showed both a tensile strength of 256 MPa and 13% elongation (Fig. 1a) which are by 62% higher and around 2 times lower than the strength (154 MPa) and elongation (27%) of pure (unreinforced) Al matrix, respectively. Thus, the nanocomposite exhibits a very high strength of 256 MPa, along with functional ductility characterized by 13% elongation exceeding the 5% standard for engineering applications. Following Wang *et al.* [21], the reported enhancement in strength due to insertion of 0.3 wt.% graphene nanosheets is most effective, as compared to that of any other reinforcing inclusions in Al. At the same time, the reported enhancement by 62% is much lower than that ex-

pected from theoretical estimates of the potential effects caused by graphene nanosheets on the mechanical properties of Al-graphene nanocomposites. As a corollary, there are reasonable expectations in reaching further large progress in dramatic improvement of strength and other mechanical characteristics exhibited by Al-matrix nanocomposites due to their strengthening by graphene nanosheets [21]. Based on their results, Wang with co-coworkers concluded that reinforcement by graphene nanosheets is most effective for Al-matrix materials and have a huge potential for applications.

The key effects of graphene nanosheets are as follows: grain refinement, dislocation strengthening, and stress transfer. First, since graphene nanosheets hamper grain boundary migration, grain growth is hindered in metal-graphene nanocomposites which thereby tend to have lower grain sizes than their metal counterparts free from graphene. At the same time, following the classical Hall-Petch relationship $\sigma = \sigma_0 + k d^{1/2}$ (where σ is the strength, σ_0 is the dislocation friction stress, k is a material constant, and d is the mean grain size), the strength of materials increases with decreasing the grain size. This factor, however, does not play any significant role in the examined Al-matrix nanocomposites with 0.3% wt. graphene inclusions, because of negligibly low fraction of grain boundaries hampered by so low amount of graphene nanosheets.

Second, such nanosheets stop lattice dislocations whose slip represents the dominant deformation mode in metals. Suppression of lattice dislocation slip by graphene nanosheets significantly contributes to strengthening of Al-graphene nanocomposites.

The third strengthening mechanism is the stress transfer. In the case under consideration, the third mechanism effectively contributes to the experimentally documented dramatic strengthening of Al-graphene nanocomposites [21]. This statement is supported by experimental observation of pronounced dimples at fracture surfaces (Fig. 1b). Such dimples are elongated along the tensile load direction, with some graphene nanosheets being pulled out at the edges of the dimples (Fig. 1b).

3.2. Mg-graphene nanocomposites

Chen with co-workers [22] fabricated Mg-matrix nanocomposites reinforced by graphene platelets, using a novel nanoprocessing method that involves liquid state ultrasonic processing and solid state

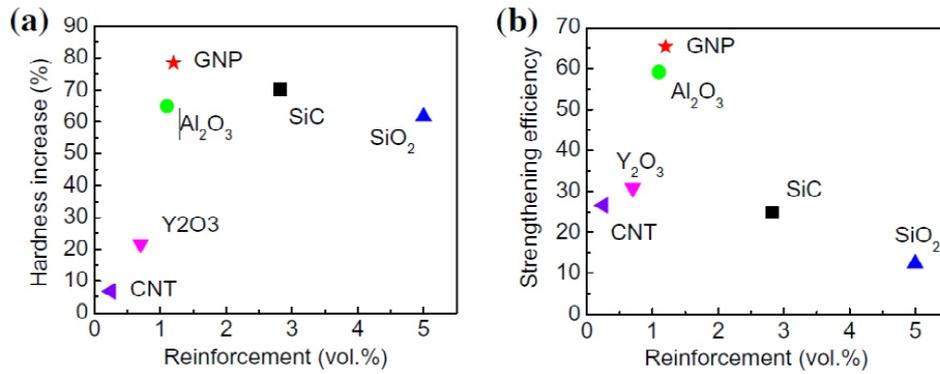


Fig. 2. (color online) (a) Hardness increase and (b) strengthening efficiency of graphene nanoplatelet and other nano-scale reinforcements in Mg-based metal-matrix nanocomposites. Reprinted from Scripta Materialia, Vol 67, L.-Y. Chen, H. Konishi, A. Fehrenbacher, C. Ma, G.-Q. Hu, H. Choi, H.-F. Hu, F.E. Pfefferkorn, X.-C. Li, Novel nanoprocessing route for bulk graphene nanoplatelets reinforced metal matrix nanocomposites, pages 29-32, Copyright (2012), with permission from Elsevier.

stirring. In this study, each platelet typically consists of several graphene layers and has thickness of approximately 10-20 nm, while its length and width are lower than 14 microns. Although in-plane strength of graphene platelets is lower than that of single-layer graphene sheets, chemical stability of platelets and comparatively easy manipulation with them make such platelets to be attractive for use as reinforcing elements in metal-matrix nanocomposites.

At the first stage of the Mg-graphene nanocomposite fabrication [22], graphene platelets are fed into the melt of Mg at 700 °C in parallel with ultrasonic treatment. In doing so, a rather homogeneous dispersion of graphene platelets in the liquid Mg is provided by a high-power ultrasonic probe action; for details, see [22]. Also, the ultrasonic treatment was applied to the melt of Mg for 15 minutes after its feeding by graphene inclusions. The resultant composite system was cast to a plane mold.

Characterization of the Mg-graphene mold structure revealed that, despite of a rather good dispersion of graphene platelets, there are micrometer-sized aggregates of such platelets in the nanocomposite [22]. This aspect motivates the second stage of processing in order to achieve a more homogeneous dispersion of reinforcing nanoinclusions. At the second stage, solid state stirring treatment is applied to the nanocomposite. This treatment serves as an effective method for homogenization of inclusions in composites in their solid state and is realized using a specific, nonconsumable rotating tool [22]. With the solid state stirring, Chen with co-workers [22] fabricated the Mg-matrix nanocomposite containing uniformly distributed and well dispersed graphene platelets. In addition,

as it has been illustrated in a representative example in Ref. [22], bonding between platelets and the Mg matrix is good in the nanocomposite, and platelets are typically located inside Mg grains.

In mechanical test, microhardness was measured [22]. It was found that the microhardness ($= 66 \text{ kg mm}^{-2}$) of the Mg-matrix nanocomposite reinforced by 1.2% graphene platelets is by 78% higher than the microhardness ($= 37 \text{ kg mm}^{-2}$) of pure Mg fabricated at the same conditions. With both these data and analysis of the literature presenting results of other experiments concerning Mg-matrix composites, Chen with co-workers concluded that reinforcement of Mg by graphene platelets is the most effective method for strengthening, as compared to reinforcement by either carbon nanotubes or (ceramic or metallic) nanoparticles. The discussed advantages of graphene platelets as reinforcing structural elements in Mg-matrix nanocomposites are illustrated by comparison in both magnitude and efficiency of the strengthening between the Mg-graphene nanocomposite and Mg-matrix nanocomposites reinforced by carbon nanotubes and nanoparticles (Fig. 2). In doing so, the strengthening efficiency R is given as:

$$R = (H_c - H_m) / VH_m, \quad (1)$$

where H_c is the microhardness of a Mg-matrix composite, H_m is the microhardness of pure Mg, and V is the volume fraction occupied by reinforcing structural elements. With data presented in Fig. 2, Chen with co-workers [22] noted that metal-matrix composites reinforced by graphene represent a new class of nanocomposites with uniquely enhanced mechanical properties.

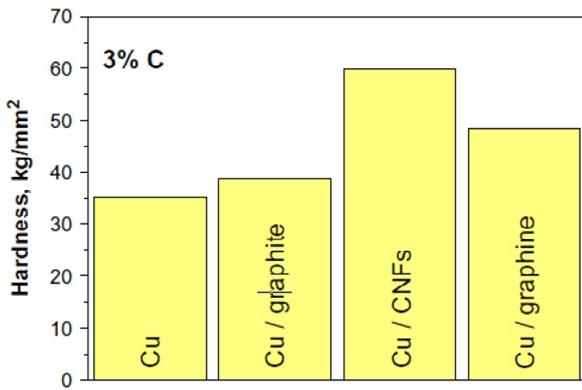


Fig. 3. (color online) Strength characteristics of copper-based composites. Reprinted from *Acta Materialia*, Vol 61, A.G. Nasibulin, T.S. Koltsova, L.I. Nasibulina, I.V. Anoshkin, A. Semencha, O.V. Tolochko, E.I. Kauppinen, A novel approach to composite preparation by direct synthesis of carbon nanomaterial on matrix or filler particles, pages 1862-1871, Copyright (2013), with permission from Elsevier.

The basic micromechanisms responsible for a remarkable strengthening effect in graphene-Mg nanocomposites are identified as effective load bearing and a pronounced role of graphene platelets as obstacles for lattice dislocation slip [22]. The effective load bearing is related to good bonding between graphene and Mg matrix. The second factor comes into play due to both plane-like geometry of graphene platelets and their superior strength characteristics, in which case free dislocation path is dramatically reduced by strong platelets in graphene-metal nanocomposites.

3.3. Cu-graphene nanocomposites fabricated by two-stage procedure involving synthesis of copper powders covered by graphene coatings and mechanical compaction

Papers [23,24] presented results of research focused on mechanical behavior of new Cu-graphene nanocomposites fabricated in a two-stage procedure. At the first stage, Nasibulin with co-workers [23,24] exploited chemical vapor deposition technique in order to synthesize n -layered graphene coatings on micron-sized powders of copper. Transmission electron microscopy analysis of copper-graphene composite powders showed the number n of graphene layers synthesized at optimum con-

ditions (in particular, at temperature $T = 940$ °C) to be in the range from 8 to 12. At the second stage of the fabrication procedure, copper-graphene composite powders were compacted by cold rolling in a laboratory double cold rolling mill in two steps. After the first-step rolling, compacted specimens were annealed at $T = 900$ °C in a hydrogen atmosphere during one hour. Then the second-step rolling was performed. Finally, the copper-graphene composite specimens were annealed at $T = 420$ °C in a hydrogen atmosphere during one hour.

The resultant specimens of the copper-graphene composite were mechanically tested to measure their elongation-to-fracture (in three-point bending test) and microhardness. The experimentally documented mechanical characteristics of the copper-graphene composite were compared with those of pure copper specimens and the previously [33] revealed mechanical characteristics of copper-matrix composite with graphite inclusions and copper-matrix composites containing carbon nanofibers (CNFs), in the case of Cu-3%C composition for all the three composites (Fig. 3). First of all, the experiments [23,24] show a pronounced (39%) increase in the microhardness (characterizing strength) of the copper-graphene composite, as compared to its pure copper counterpart. This increase in the microhardness occurs at expenses of a dramatic decrease in elongation-to-failure (characterizing ductility) from value of 55%, for pure copper, down to value of 17%, for the copper-graphene composite.

Also, comparison of the mechanical characteristics of copper-matrix composites fabricated by the same methods [23,24,33] and reinforced by various carbon inclusions (graphene, graphite, CNFs) revealed advantage of copper-matrix composites containing CNFs. In particular, these composites exhibit 70% increase in the microhardness, as compared to pure copper (Fig. 3), whereas copper-matrix composites containing graphene and graphite inclusions are specified by 39% and 10% improvements in strength, respectively (Fig. 3). Also, for copper-CNF composites, elongation-to-failure has value of around 47%. This value significantly exceeds elongation-to-failure values of 18% and 17%, for copper-graphite and copper-graphene composites, respectively.

Following Nasibulin with co-workers [23,24,33], in addition to the “pure” effects of CNFs, the matrix microstructure of copper-CNF composites is also responsible for their higher mechanical characteristics, as compared to those exhibited by copper-

graphite and copper-graphene composites. The fact is that the matrix microstructure of copper-CNF composites is specified by an average grain size $d = 4 \mu\text{m}$, whereas copper-graphite and copper-graphene composites are characterized by $d = 10 \mu\text{m}$ and $7 \mu\text{m}$, respectively [23,24,33]. Metals with smaller grain size typically show higher strength and hardness, as compared to its counterparts with comparatively large grains; see, e.g., [34]. (This trend is violated in the only case of nanomaterials having ultrasmall grain sizes $< 15\text{-}30 \text{ nm}$; see, e.g., [34-36].) Besides, since graphene inclusions are typically located at grain boundaries, they tend to be homogeneously dispersed in metals with small and ultrasmall grains (because they have a lot of potential sites) and are effective in grain growth inhibition in such metals.

3.4. Cu- and Ni-graphene nanolayered composites

Kim with co-workers [25] fabricated Cu- and Ni-graphene nanolayered composites showing superior strength characteristics. So, nanolayered composites consisting of alternating layers of metal (Cu or Ni) and monolayer graphene were synthesized by chemical vapor deposition method. Cu-graphene composites with repeat layer thickness $\lambda = 70 \text{ nm}$ and Ni-graphene composites with $\lambda = 100 \text{ nm}$ exhibit strengths of 1.5 and 4.0 GPa, respectively [25]. These values are highest for ever fabricated metal-graphene composites.

Cu-graphene nanolayered composites with $\lambda = 70, 125$ and 200 nm as well as Ni-graphene nanolayered composites with $\lambda = 100, 150,$ and 300 nm were synthesized by chemical vapor deposition method described in detail in Ref. [37]. This method allows one to fabricate metallic nanolayers with graphene interfaces having mostly a single (85%) atomic layer structure and, in some part, a bi-layer structure (Fig. 4a). For examination of mechanical characteristics, Kim with co-workers utilized nanopillar compression tests (developed and effectively exploited in mechanics of metallic nanopillars; see, e.g., [38,39]). In doing so, nanolayered metal-graphene nanopillars with a diameter of 200 nm and height of $400 - 600 \text{ nm}$ were fabricated by focused ion milling method and then mechanically compressed (Figs. 4 (b and c) and 5 (a and b)). Typical stress-strain curves for Ni- and Cu-graphene nanolayered nanopillars with various values of the repeat layer spacing λ are shown in Figs. 5c and 5d. The flow stress at 5% plastic strain as a function of λ , for Ni- and Cu-graphene nanolayered

nanopillars, is presented in Figs. 5e and 5f, respectively. These figures show the trend that the flow stress increases in an approximately linear way with diminishing the metal layer thickness λ . In particular, the flow stress has its maximum values of 1.5 and 4.0 GPa, for Cu-graphene composite with $\lambda = 70 \text{ nm}$ and Ni-graphene composites with $\lambda = 100 \text{ nm}$, respectively [25]. The latter value is around 52% of the theoretical strength for Ni.

Note that, in parallel with graphene interfaces, both the nanolayered structure and the nanopillar geometry can significantly increase the flow stress of the composite materials under examination. Kim with co-workers [25] estimated the strengthening effects of the nanolayered structure and the nanopillar geometry in the case of metal-graphene nanolayered composites on the basis of the corresponding experimental data reported in the literature. With this consideration, it was concluded that the strengthening effect of graphene interfaces in the metal-graphene composites is much more significant than the combined effects of the nanolayered structure and the nanopillar geometry.

The key factor responsible for superior strength of metal-graphene nanolayered composites represents the role of graphene interfaces as highly effective obstacles for lattice dislocation slip [25]. This statement was illustrated by experimental evidence for large amounts of dislocations that are present in a plastically deformed layer and do not penetrate across a graphene interface between this layer and its neighboring layer free from dislocations in a Cu-graphene nanolayered nanopillar (Fig. 4c).

3.5. Cu-graphene nanocomposites synthesized by molecular-level mixing and spark plasma sintering

Hwang with co-workers [26] suggested a new method for fabrication of metal-graphene nanocomposites, the namely two-step procedure involving both a molecular-level mixing process and spark plasma sintering. The molecular-level mixing process consists of attaching functional groups onto graphene flakes and making chemical bonding between graphene and metal powders. The spark plasma sintering consolidates metal powders into a polycrystalline solid through local joule heating and spark plasma generated between neighboring powders. This method allows one to provide good dispersion of reduced graphene oxide (RGO) flakes within a metal matrix and high adhesion energy between graphene and metal [26].

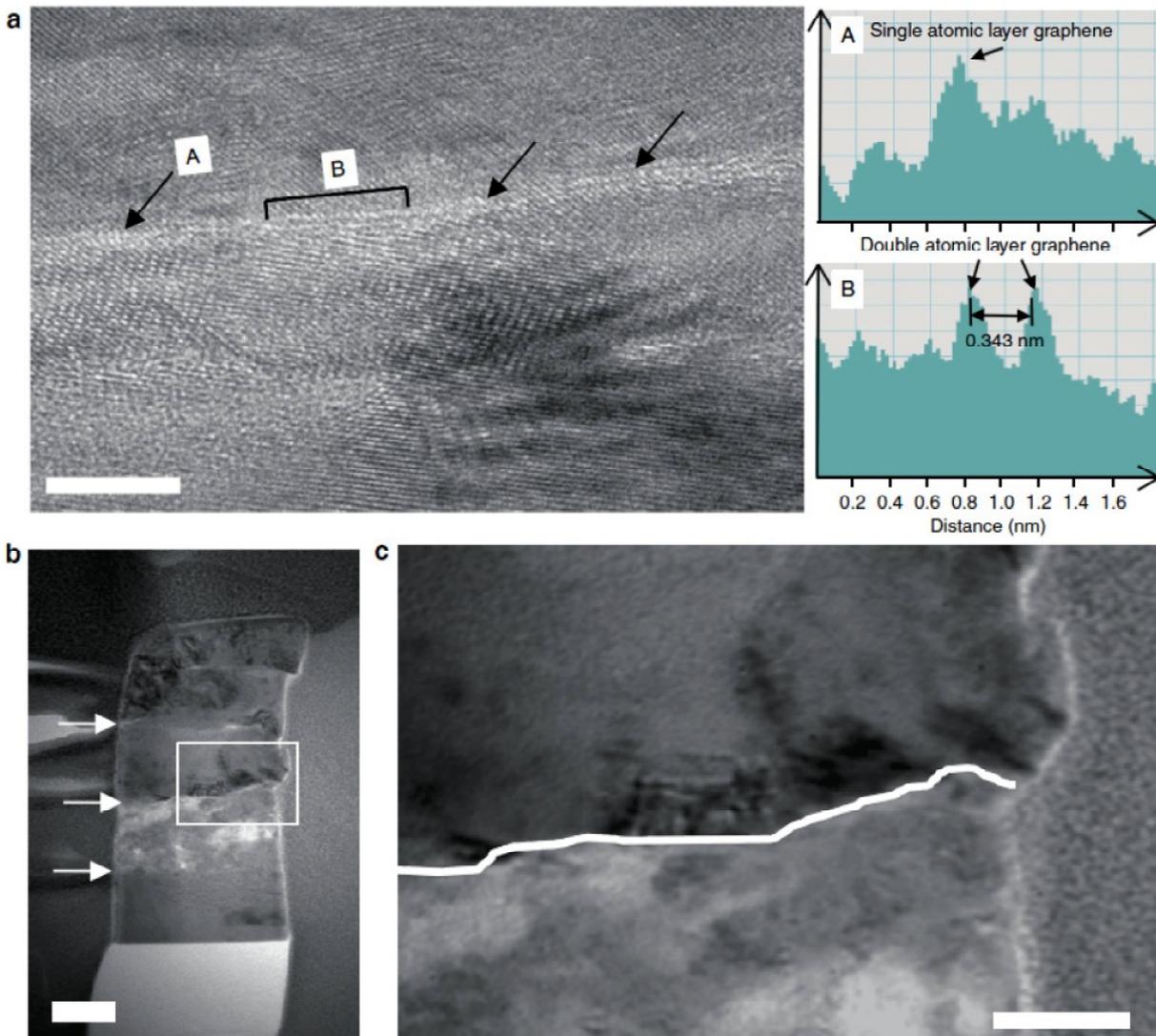


Fig. 4. (color online) Transmission electron microscopy (TEM) analysis of the Cu-graphene nanolayered composite. (a) TEM image of a metal-graphene interface that shows mostly single layers with some double layers. Scale bar, 5 nm. (b) TEM image of a Cu-graphene nanopillar with 125-nm repeat layer spacing at a low magnification after deformation. Scale bar, 100 nm. (c) TEM image of a Cu-graphene nanopillar after deformation that shows a higher density of dislocations above the graphene interface. Scale bar, 50 nm. Reprinted by permission from Macmillan Publishers Ltd: Nature Communications, Vol 4, Y. Kim, J. Lee, M.S. Yeom, J.W. Shin, H. Kim, Y. Cui, J.W. Kysar, J. Hone, Y. Jung, S. Jeon and S.M. Yan, Strengthening effect of single-atomic-layer graphene in metal-graphene nanolayered composites, article 2114, copyright (2013).

In the experiment [26], specimens of Cu-matrix nanocomposite containing RGO flakes were synthesized by the two-step procedure under discussion. These specimens were mechanically tested under tensile deformation, and the characteristic adhesion energy between copper and graphene was measured. In particular, following Hwang with co-workers [26], specimens of Cu-matrix nanocomposite containing 2.5 vol.% RGO flakes showed $\approx 80\%$ increase in the yield strength (from 160 to 284 MPa) and $\approx 30\%$ increase in the ultimate

tensile strength (from 255 to 335 MPa), as compared to pure copper. The strengthening effect of RGO flakes is attributed to the two key factors: the role of RGO flakes as effective obstacles for dislocation slip and high values of adhesion energy between copper matrix and graphene. For instance, in the case under examination, Cu-graphene nanocomposite is specified by the adhesion energy of $\approx 165 \text{ J m}^{-2}$, being much higher than that ($\approx 0.72 \text{ J m}^{-2}$) for as-grown graphene on Cu substrate [26].

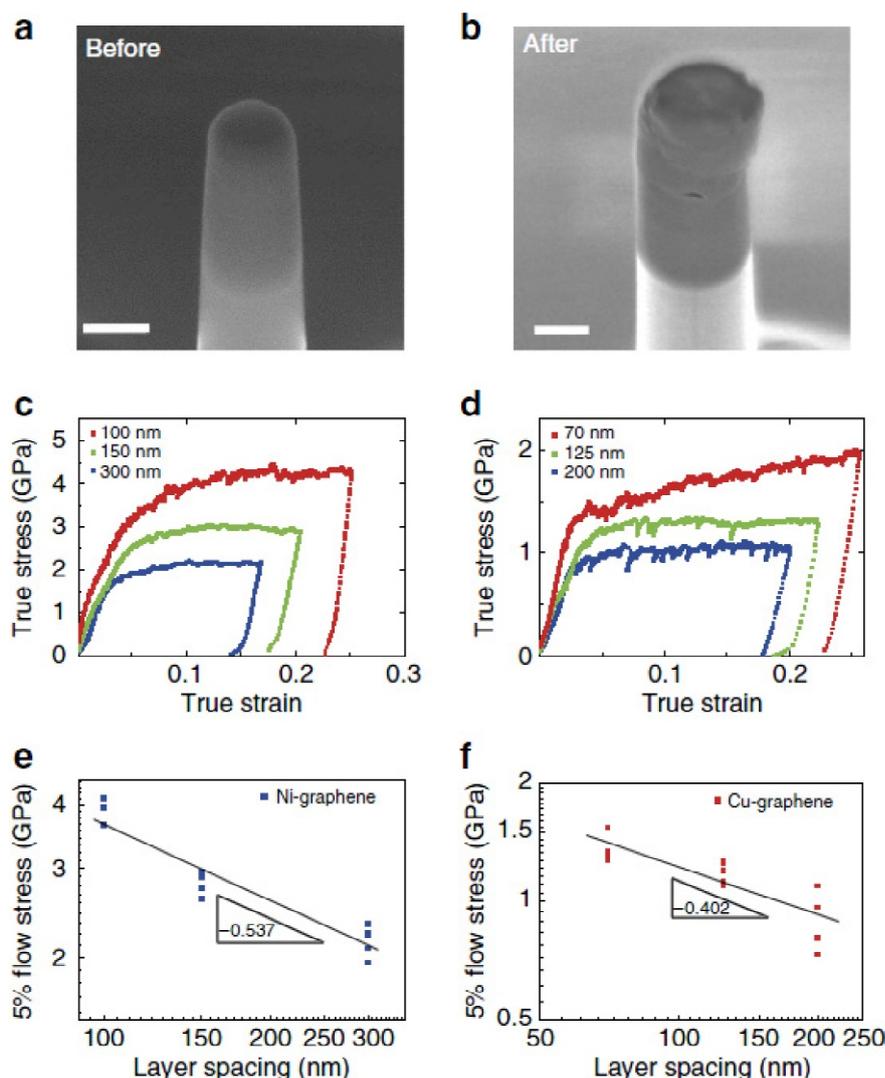


Fig. 5. (color online) Results of nanopillar compression test. Scanning electron microscopy image of a Cu-graphene nanopillar with 125-nm repeat layer spacing (a) before and (b) after compression testing. Scale bar, 200 nm. Stress versus strain curves for (c) Ni-graphene and (d) Cu-graphene of various repeat metal layer spacings. The flow stresses at 5% plastic strain versus repeat metal layer spacing plots for (e) Ni-graphene and (f) Cu-graphene nanolayered composites. Reprinted by permission from Macmillan Publishers Ltd: Nature Communications, Vol 4, Y. Kim, J. Lee, M.S. Yeom, J.W. Shin, H. Kim, Y. Cui, J.W. Kysar, J. Hone, Y. Jung, S. Jeon and S.M. Yan, Strengthening effect of single-atomic-layer graphene in metal-graphene nanolayered composites, article 2114, copyright (2013).

3.6. Cu-graphene nanocomposite foils synthesized by electrodeposition

Pavithra with co-workers [28] focused their research on fabrication and mechanical testing of Cu-graphene nanocomposite foils. The Cu-graphene nanocomposites with Cu-matrix having an average grain size of $1.2 \pm 0.4 \mu\text{m}$ were fabricated by pulse reverse electrodeposition method. Graphene and/or GO sheets with 1-5 atomic layers are located at grain boundaries and serve as effective inhibitors of grain growth in the Cu-graphene nanocomposites.

Hardness and an elastic modulus of the Cu-graphene nanocomposites were measured in nanoindentation test and compared with the corresponding mechanical characteristics of pure Cu foils (with an average grain size of $1.3 \pm 0.3 \mu\text{m}$) fabricated by pulse reverse electrodeposition method. In doing so, it was experimentally revealed that the hardness and the elastic modulus of the Cu-graphene composite have values of $\approx 2.5 \text{ GPa}$ and $\approx 137 \text{ GPa}$, respectively, whereas pure electrodeposited Cu specimens are specified by the hardness of $\approx 1.2 \text{ GPa}$ and the elastic modulus of $\approx 116 \text{ GPa}$ [28].

Also, Pavithra with co-workers [28] examined grain growth processes in the pure Cu and Cu-graphene nanocomposite specimens under 30 min annealing in argon atmosphere at 300 °C. They found that grain size in the Cu-graphene composite in practice does not change after the annealing treatment, whereas grain size of pure Cu exhibits increase from 1.3 up to around 10 μm . These experimental data are indicative of the drastic hampering effect of graphene on grain growth in metal-matrix nanocomposites. In these circumstances, it is logical to conclude that metal matrices in metal-graphene nanocomposites typically have lower grain size and thereby higher strength, as compared to corresponding characteristics of pure metals.

3.7. Ni-graphene nanocomposites synthesized by electrodeposition

Kuang with co-workers [27] exploited electrodeposition method to fabricate Ni-graphene nanocomposite films. The nanocomposite films are characterized by 0.12 wt.% graphene fraction with graphene nanoinclusions well dispersed in the form of multilayered sheets in Ni-matrix. Also, transmission electron microscopy studies revealed that graphene sheets in Ni-matrix tend to be curled and entangled together [27].

The hardness and Young modulus of the Ni-graphene composite specimens were measured in nanoindentation tests. These mechanical characteristics of Ni-graphene composites were found to be dramatically enhanced as compared to those of pure electrodeposited Ni. So, the hardness and Young modulus of the Ni-graphene composite have values of 6.85 GPa and 252.76 GPa, respectively, whereas pure electrodeposited Ni is specified by the hardness of 1.81 GPa and Young modulus of 166.70 GPa. Following Kuang with co-workers [27], the experimentally revealed remarkable (≈ 4 -fold) increase in the hardness is mostly related to the role of graphene inclusions as effective stoppers of lattice dislocation slip.

4. Concluding remarks

Thus, the newest and very effective approach to create metallic materials with high strength, hardness and Young modulus is to implant graphene platelets and few-layers sheets in metallic matrices. In particular, metal-graphene nanocomposites with low volume/weight fractions of graphene inclusions exhibit dramatically enhanced strength and hardness. For instance, in the experiment [21], the Al-graphene

nanocomposite (consisting of Al-matrix reinforced by 0.3 wt.% graphene nanosheets) showed both a tensile strength of 256 MPa which is by 62% higher than the strength (154 MPa) of pure Al. The reported enhancement in strength due to insertion of 0.3 wt.% graphene nanosheets is most effective, as compared to that of any other reinforcing inclusions specified by 0.3 wt.% fraction in Al.

Kim with co-workers [25] fabricated Cu- and Ni-graphene nanolayered composites showing superior strength characteristics. So, Cu-graphene composites with repeat layer thickness $\lambda = 70$ nm and Ni-graphene composites with $\lambda = 100$ nm exhibit strengths of 1.5 and 4.0 GPa, respectively [25]. These values are highest for ever fabricated metal-graphene composites.

Kuang with co-workers [27] fabricated Ni-graphene nanocomposite films characterized by 0.12 wt.% graphene fraction with graphene nanoinclusions well dispersed in the form of multilayered sheets in Ni-matrix. The hardness of the Ni-graphene composite has value of 6.85 GPa. This value is by ≈ 4 times larger than the hardness (1.81 GPa) of pure electrodeposited Ni [27].

The key effects of graphene nanosheets and nanoplatelets on mechanical characteristics of metal-graphene nanocomposites are as follows: dislocation strengthening, stress transfer and grain refinement in metallic matrices. First, graphene nanoinclusions effectively hinder lattice dislocation slip being the dominant deformation mode in metals. This effect comes into play in all the metal-graphene nanocomposites under consideration [21-28] and most probably causes the dominant contribution to their strengthening. Suppression of lattice dislocation slip by graphene nanosheets is confirmed by computer simulations of deformation behavior exhibited by Al-graphene nanocomposites [40].

The second strengthening mechanism in metal-graphene nanocomposites is the stress transfer. In general, effect of this mechanism on both strength and elastic properties of a nanocomposite is sensitive to chemical binding between graphene and a metallic matrix. In addition, there are geometric factors that enhance the stress transfer in metal-graphene nanocomposites. The fact is that, with curved shape, large values of aspect ratio, large width and length of graphene platelets/sheets, these graphene nanoinclusions are bent, anchored and often wrapped around metallic grains at grain boundaries in metal-graphene nanocomposites. As a corollary, graphene nanoinclusions have large contact area with a metallic matrix and thus provide effec-

tive load transfer. Besides, their geometry highly prevents their pull-out, leading to pronounced toughening effects in pre-cracked nanocomposites.

Third, since graphene nanosheets hamper grain boundary migration, grain growth is hindered in metal-graphene nanocomposites at the stage of their fabrication and in the course of their plastic deformation. As a result, metal-graphene nanocomposites tend to have lower grain sizes, as compared to their pure metal counterparts. At the same time, following the classical Hall-Petch relationship $\sigma = \sigma_0 + k d^{1/2}$ (where σ is the strength, σ_0 is the dislocation friction stress, k is a material constant, and d is the mean grain size), the strength of materials increases with decreasing the grain size. This factor – suppression of grain growth in metal matrices by graphene nano-inclusions – can significantly contribute to strengthening of metal-graphene nanocomposites.

Finally, note that fabrication of metal-graphene nanocomposites for high strength, hardness and elastic properties is in its infancy. In the near future, it is logical to expect explosive progress in fundamental science, fabrication and applications of such nanocomposites whose potential to transform so many technologies is tremendous.

ACKNOWLEDGEMENTS

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