Rev. Adv. Mater. Tech. vol. 3 no. 3 (2021) 16-20
DOI:10.17586/2687-0568-2021-3-3-16-20

Competition Between Generation of Nanovoids and Nanocracks in Bimodal Metal-Graphene Composites

N.V. Skiba

Institute for Problems in Mechanical Engineering, Russian Academy of Sciences, St. Petersburg 199178, Russia

Received: August 25, 2021

Abstract. A theoretical model which describes micromechanisms of the deformation-induced formation of nanovoids and the competition between the nanovoid formation and the deformation-induced formation of nanocracks in bimodal metal-graphene composites is presented. In the framework of the model, the formation of nanovoids and nanocracks occurs at the grain boundary (GB) disclination dipoles near the graphene inclusions. It is demonstrated that the formation of nanovoids at the GB disclination dipoles is energetically favorable process in deformed bimodal Ni-graphene composite.

1. INTRODUCTION

Bimodal metal-graphene composites (materials consisting of large (micrometer-size) grains embedded into a nanocrystalline/ultrafine-grained (NC/UFG) metal-matrix) demonstrate that combination of bimodal grain size distribution with graphene fillers can provide simultaneously high strength and good ductility of the composite [1-6]. In such materials, the plastically nanocrystalline NC/UFG metal-matrix are responsible for ultrahigh strength, while plastically coarse grains provide good ductility. Fracture processes in bimodal metal-graphene composites (having high strength and good ductility) are the subject of intensive experimental research [5,6], computer simulations [7,8] and theoretical examinations [9]. Metal-graphene composites exhibit either ductile or brittle fracture behavior, depending on their structural characteristics and the conditions of mechanical loading. In particular, in works [5,6], bimodal metal-graphene composites with the Ni [5] and Al–4Cu [6] matrices were produced. The bimodal Al–4Cu-graphene composite exhibited brittle fracture with lamellar structures implying that microcracks formed during plastic deformation of this composite and showed low ductility [6]. At the same time, bimodal Ni–graphene composite exhibited ductile fracture with dimpled structures at fracture surfaces and demonstrated good ductility [5]. In this case, the ductile fracture is viewed to occur through the void nucleation and coalescence mechanism. Thus, it seems important to identify the micromechanisms responsible for micromechanisms of deformation-induced formation of voids as carriers of ductile fracture and the competition between void formation and deformation-induced formation of brittle cracks serving as carriers of brittle fracture in bimodal metal-graphene composites.

The main aim of this paper is to theoretically describe the competition between formation of nanoscale voids and brittle nanocracks at GB disclination dipoles in bimodal metal-graphene composites.

2. MODEL

It is well known that specific plastic deformation mechanisms such as grain boundary sliding, grain boundary migration and deformation twinning can effectively operate in NC/UFG metals. However, the graphene inclusions act as effective obstacles for the implementation of the specific deformation modes. Thus, the suppression of the specific deformation modes often leads to plastic strain instability which causes the formation of GB disclination dipole configurations at the graphene

Corresponding author: N.V. Skiba, e-mail: nikolay.skiba@gmail.com

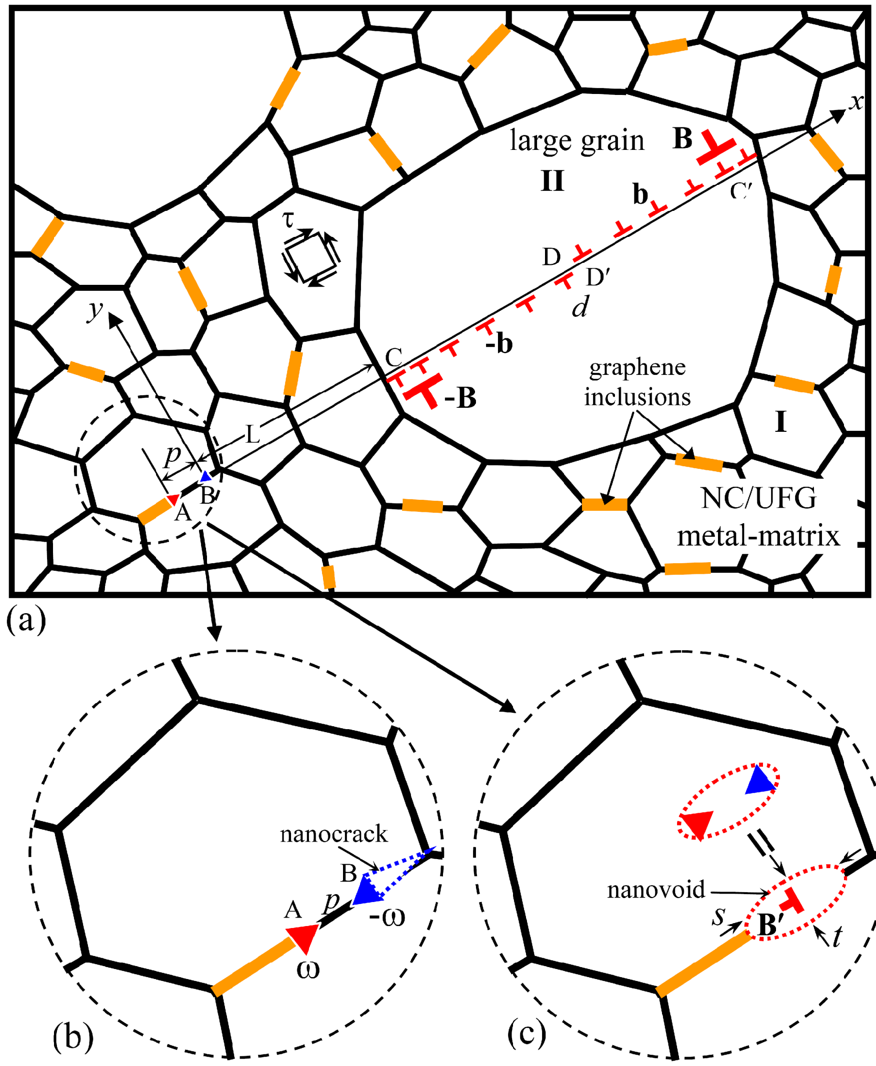

Fig. 1. Model of the formation of a nanocrack and a nanovoid at a GB dislocation dipole near a GB graphene inclusion in bimodal metal-graphene composite. (a) General view. (b) Formation of a nanocrack at the disclination with the strength -ω of the disclination dipole AB. (c) Formation of a nanovoid with the axes *s* and *t* around the disclination dipole AB. In this case, the disclination dipole AB becomes equivalent to an edge dislocation with Burgers vector *B´*.

inclusions (Fig. 1a). The GB disclination dipoles serve as stress sources capable of initiating the formation of nanocracks, carriers of brittle fracture and also can initiate the diffusion-controlled formation of nanovoids, carriers of ductile fracture. Besides, the lattice dislocations slip which realizes in large grains usually leads to the formation of pile-ups of the lattice dislocations (Fig. 1a). The pile-ups of the lattice dislocations create long-range stress fields that can stimulate the formation of nanocracks at the GB disclination dipoles.

Consider a two-dimensional model of bimodal metal-graphene nanocomposite under mechanical load (Fig. 1a). In the model, the bimodal metal-graphene nanocomposite consists of NC/UFG metal-matrix I reinforced by graphene inclusions and large (micrometer-size) grains II with an average grain size *d* embedded into a NC/UFG metal-matrix (Fig. 1a). The chemical compositions of the NC/UFG metal-matrix I and large grains II are identical. In the framework of the model, the NC/UFG metal-matrix contains the GB disclinations dipoles at the GB graphene inclusions while the large grains contain the pile-ups of the lattice dislocations (Fig. 1a).

Consider a GB dislocation dipole AB having strengths ±ω (hereinafter called ±ω-disclination dipole) and arm (distance between the disclinations A and B of the dipole) *p* located in NC/UFG metal-matrix and pile-ups of the lattice dislocations CD and C´D with length (Fig. 1a). Further, analyze the energy characteristics of the generation of a nanocrack at a graphene inclusion in the combine stress field of the dipole AB, the pile-ups CD and C´D´, and the external shear stress ω (Fig. 1b), and nanovoid around the disclination dipole AB (Fig. 1c).

3. FORMATION OF NANOCRACKS AT GB DISCLINATION DIPOLE

Following the work [10], the GB nanocrack of length l can be generated at the disclination with the strength -ω of the disclination dipole AB (Fig. 1b). The condition $q(\tilde{l}) > q_c$ for the nanocrack generation is given by the following expressions [10]:

$$q(\tilde{l}) = \tilde{l}\left[\left(\frac{2(\sqrt{1+\tilde{l}}-1)}{\tilde{l}} - \ln\frac{\sqrt{1+\tilde{l}}+1}{\sqrt{1+\tilde{l}}-1}\right)^2 + \left(\frac{\tau_c}{D\omega}\right)^2\right], \qquad (1)$$

$$q_c = 16\pi(1-\nu)(2\gamma_s - \gamma_{gb})/(Gp\omega^2),$$

where G is the shear modulus, and ν is Poisson's ratio, $\tilde{l} = l/p$, γ_s is the specific (per unit area) free surface energy, and γ_{gb} is the specific (per unit area) grain boundary energy, $\tau_c = \tau + \tau_p$, τ_p is shear stress caused by the dislocation pile-ups CD and C˘D˘ in the neighboring large grain.

According approach [10], the function $q(\tilde{l})$ has one maximum value q_m and the formation of a nanocrack occurs if $q_c<q_m$. Condition $q_c<q_m$ can be rewritten as $p>p_c$, where $p_c = 16p(1-\nu)(2\gamma-\gamma_b)/(Gq_m\omega^2)$ is the minimum value of the dipole arm p at a given value of ω at which nanocrack formation at -ω-disclination of the disclination dipole AB is energetically favorable.

Estimate the value τ_p of the shear stress from the pile-ups CD and C′D′ in large grain II acting along GB with the disclination dipole AB. The simplest estimate of the shear stress τ_p can be obtained by modeling the pile-ups CD and C′D′ as dipole of superdislocations [11] with Burgers vectors $\pm B = \pm Nb$, where $N = (1-\nu)d\tau/Gb$ [11] (Fig. 1a). Using the well-known formula [11] for the stress $\sigma^B_{xy}(x,y)$ of an edge dislocation in an infinite medium and formula for N the expression of the value τ_p is given by the following formula:

$$\tau_p = \sigma^{\pm B}_{xy}(0,0) = \frac{2\tau d^2}{\pi L(d+L)}, \qquad (2)$$

where L is a distance between large grain and -ω-disclination of the disclination dipole AB.

4. FORMATION OF NANOVOIDS AT GB DISCLINATION DIPOLES

Calculate the energy change ΔW that characterizes the nucleation of an elliptic nanovoid with axes s and t (Fig. 1c) around the disclination dipole AB. The energy change $\Delta W = W_2 - W_1$ a can be represented as the sum:

$$\Delta W = \Delta W_\Delta + W^e_s - W_{gb}, \qquad (3)$$

where ΔW_Δ is the change of the disclination dipole AB energy due to the nanovoid formation, W^e_s is the free surface energy of the elliptic nanovoid, and W_{gb} is the energy of the GB fragments that disappear due to the nanovoid formation.

It is known that a disclination dipole is identical to a wall of edge dislocations and their total Burgers vector magnitude is related to the dipole arm p and disclination strength ω by the equality [12] $B'\approx\omega p$ (Fig. 1a). Thus, the proper energy of the disclination dipole after the nanovoid formation is given by the known expression [13] for the proper energy W_{sd} of the corresponding superdislocation (with the Burgers vector $B'=\omega p$) located within the nanovoid. Then, the energy change ΔW_Δ of the disclination dipole due to the nanovoid formation can be represented as the difference [13]:

$$\Delta W_\Delta = W_{sd} - W^\infty_\Delta = -\frac{D\omega^2 p^2}{2} \times\left(\ln\frac{s+t}{4s} + \frac{s-t}{2(s+t)} + \frac{7-6\nu}{4(1-\nu)}\right), \qquad (4)$$

where W^∞_Δ is the energy of the disclination dipole in an infinite medium, $D = G/[2\pi(1-\nu)]$.

The free surface energy W_s of the nanovoid per its unit length can be written as follows:

$$W^e_s = 2s\gamma_s \,\mathrm{E}\left(1-\frac{t^2}{s^2}\right), \qquad (5)$$

where

$$E(m) = \int_0^{\pi/2}(1-m\sin^2\theta)^{1/2}\,d\theta$$

is the complete elliptic integral of the second kind.

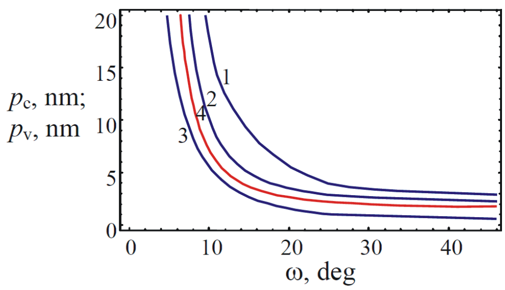

Fig. 2. Dependences of the critical values of the dipole arm, p_c (curves 1-3) and p_v (curve 4), for the formation of a nanovoid and a nanocrack, respectively, on the disclination dipole strength ω at the different values of the external shear stress τ=100 MPa (curve 1), 500 MPa (curve 2), and 1000 MPa (curve 3).

In first approximation, the energy W_{gb} of the GB fragments that disappear due to nanovoid is given by the formula:

$$W_{gb} \approx \gamma_{gb} s. \qquad (6)$$

The relation $(\partial \Delta W / \partial s)\big|_{s=s_e} = 0$ allows to calculate the equilibrium nanovoid length $s=s_e$ at t=1 nm and at a given value of the strength ω. Therefore, the necessary condition $s_e \geq p$ for nanovoid formation can be rewritten as $p \geq p_v$, where p_v is defined by the relation $s_e(\omega p_v)=p$.

5. RESULTS

Using formulas (1)-(6) calculate the dependences $p_c(\omega)$ and $p_n(\omega)$ in the exemplary case of bimodal Ni-graphene composite. To do so, we have used the following parameter values typical of Ni composite: [11,14]: G=73 GPa, ν=0.31, γ_s=1.725 J/m^2, γ_{gb}=0.69 J/m^2. Other parameters are taken as d=1000 nm, L=300 nm, and t= 1 nm. The dependences $p_c(\omega)$ (curves 1-3) and $p_n(\omega)$ (curve 4) are shown in Fig. 2 for different values of the external shear stress τ=100 MPa (curve 1), t = 500 MPa (curve 2), and τ=1000 MPa (curve 3). The formation of a nanocrack and a nanovoid is favorable in the parameter plane (p,ω) region located above the dependences $p_c(\omega)$ and $p_v(\omega)$ and unfavorable in the region located below these dependences. As follows from Fig. 2, at τ=100 MPa and τ=500 MPa, $p_c > p_v$ for any ω, which means that the formation of a nanocrack at -ω-disclination of the disclination dipole AB is much more difficult than the formation of a nanovoid around this dipole. In contrast the above result, at τ=1000 MPa the formation of a nanocrack is energetically more favorable than the formation a nanovoid for any ω (Fig. 2).

6. CONCLUSIONS

Thus, following the results of our theoretical analysis, the generation of nanovoids and nanocracks at the GB disclination dipoles which formed near the graphene inclusions are in competition depending on parameters of the defect system in bimodal metal-graphene composites. According to our estimates, the nanovoids formation is more energetically preferred than that of brittle nanocracks in deformed bimodal Ni-graphene composite in wide ranges of their parameters. The formation of nanocracks is energetically favorable at the very high values of the external shear stress < 1000 MPa only. Nanovoids can serve as nuclei for viscous dimple structures experimentally observed in work [5] at fracture surfaces of bimodal Ni-graphene composite. The presented theoretical model explains experimental observation [5] of the ductile fracture of bimodal Ni-graphene showing good ductility compared to the most metal-graphene composites which exhibit brittle fracture and demonstrate low ductility. Thus, the formation of nanovoids in bimodal metal-graphene composites can improve the toughness of these composites.

ACKNOWLEDGMENTS

The work was supported by the Russian Fund of Basic Research (grant 18-29-19086).

REFERENCES

[1] Y.H. Zhao, T. Topping, J.F. Bingert, J.J. Thornton, A.M. Dangelewicz, Y. Li, W. Liu, Y. Zhu, Y. Zhou and E.J. Lavernia, *High Tensile Ductility and Strength in Bulk Nanostructured Nickel*, Adv. Mater., 2008, vol. 20, pp. 3028-3033. https://doi.org/10.1002/adma.200800214

[2] G. Dirras, J. Gubicza, Q.H. Bui and T. Szilagyi, *Microstructure and mechanical characteristics of bulk polycrystalline Ni consolidated from blends of powders with different particle size*, Mater. Sci. Eng. A, 2010, vol. 527, no. 4-5, pp. 1206-1214. https://doi.org/10.1016/j.msea.2009.09.050

[3] K.S. Raju, V.S. Sarma, A. Kauffmann, Z. Hegedus, J. Gubicza, M. Peterlechner, J. Freudenberger and G. Wilde, *High strength and ductile ultrafine-grained Cu–Ag alloy through bimodal grain size, dislocation density and solute distribution*, Acta Mater., 2013, vol. 61, no. 1, pp. 228-238. https://doi.org/10.1016/j.actamat.2012.09.053

[4] M.J. Shen, B.H. Zhang, X.J. Wang, M.F. Zhang, M.Y. Zheng and K. Wu, *Significantly improved strength and ductility in bimodal-size grained microstructural magnesium matrix composites reinforced by bimodal sized SiCp over traditional magnesium matrix composites*, Comp. Sci.Tech., 2015, vol. 118, pp. 85-93. https://doi.org/10.1016/j.compscitech.2015.08.009

[5] O.Y. Kurapova, I.V. Lomakin, S.N. Sergeev, E.N. Solovyeva, A.P. Zhilyaev, I.Y. Archakov and V.G. Konakov, *Fabrication of nickel-graphene composites with superior hardness*, J. Alloy. Compd., 2020, vol. 835, art. 155463. https://doi.org/10.1016/j.jallcom.2020.155463

[6] M. Khoshghadam-Pireyousefan, R. Rahmanifard, L. Orovcik, P. Švec, and V. Klemm, *Application of a novel method for fabrication of graphene reinforced aluminum matrix nanocomposites: Synthesis, microstructure, and mechanical properties*, Mater. Sci. Eng. A., 2020, vol. 772, art. 138820. https://doi.org/10.1016/j.msea.2019.138820

[7] L.L. Zhu and J. Lu, *Modelling the plastic deformation of nanostructured metals with*

bimodal grain size distribution, Int. J. Plast., 2012, vol. 30-31, pp. 166-184. https://doi.org/10.1016/j.ijplas.2011.10.003

[8] X.Guo,X.Y.Dai,G.J.Weng, L.L. Zhu and J. Lu, *Numerical investigation of fracture behavior of nanostructured Cu with bimodal grain size distribution*, *Acta Mech.*, 2014, vol. 225, pp. 1093–1106. https://doi.org/10.1007/s00707-013-1050-8

[9] A.G. Sheinerman and M.Yu. Gutkin, *Model of Enhanced Strength and Ductility of Metal/ Graphene Composites with Bimodal Grain Size Distribution*, Metall. Mater. Trans. A, 2020, vol. 51, pp. 189-199. https://doi.org/10.1007/s11661-019-05500-w

[10] H.A. Padilla and B.K. Boyce, *A Review of Fatigue Behavior in Nanocrystalline Metals*, 2010, vol. 50, pp. 5-23. https://doi.org/10.1007/s11340-009-9301-2

[11] J.P. Hirth and J. Lothe, *Theory of dislocations*, (Wiley, New York, 1982).

[12] A.E. Romanov and V.I. Vladimirov. In: Nabarro FRN, *Dislocations in Solids*. (North-Holland, Amsterdam, 1992) Vol. 9, pp. 191–302.

[13] I.A. Ovid'ko and A.G. Sheinerman, *Elliptic nanopores in deformed nanocrystalline and nanocomposite materials*, Philos. Mag., 2006, vol. 86, no. 10, pp. 1415-1426. https://doi.org/10.1080/14786430500311766

[14] C.J. Smithells, E.A. Brands, *Metals Reference Book*, (Butterworth, London, 1976).