IOP Conf. Series: Materials Science and Engineering **170** (2017) 012017 doi:10.1088/1757-899X/170/1/012017

Strengthening in a copper composite containing graphene nanofillers

Y Song[a], W W Liu[b] and Y Chen[c]
School of Mechanical and Electric Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, 215123 Suzhou, China

E-mail:[a]songying55555@163.com, [b]liuweiwei@suda.edu.cn, [c]chenyao@suda.edu.cn

Abstract: Multi-layer graphenes (MLGs) reinforced Cu matrix composites were fabricated using spark plasma sintering in this research. Microstructure observation indicated that MLGs homogeneously disperse in the matrix to result in grain refinement. Instrumented spherical micro-indentation tests were conducted to evaluate micro-mechanical properties of the composites, and the elastic modulus and indentation yield strength of the 1.5 wt.% MLG/Cu composite increase up to ~ 36% and ~ 41% than those of the unreinforced Cu, respectively. Grain refinement, the enhanced dislocation density (EDD) due to the thermal expansion mismatch between Cu matrix and MLGs and Orowan are thought to be the main strengthening mechanisms in this research.

1.Introduction

Copper (Cu) and its alloys with excellent electrical and thermal conductivities have been widely used in machinery industries including the electric train overhead trolley frame, the blast furnace of metallurgical industry and the large capacity contactor switch[1]. However, relatively poor mechanical properties such as tensile strength and hardness limit their further applications. It is expected that addition of suit second phases might be an effective way to improve their mechanical properties, and considerable research efforts have been devoted to achieve copper matrix composites reinforced with various ceramic particles/fibers in the past decades[2-4]. However, these ceramic reinforcements used in the Cu composites are nonconductive, resulting in improved mechanical properties with sacrifice of good electrical and thermal conductivities to some extent.

Carbonaceous materials have emerged as important reinforcements in recent years because of their good mechanical properties and excellent electrical conductivity. Graphene has excellent mechanical properties and electronic and thermal conductivity [5], and very high specific surface area (~ 2630 m^2 g^{-1}). It is noted that multi-layer graphenes (MLGs) consisting few graphene layers have similar properties to the single layered graphene. Hence, MLGs reinforced metal composites have attracted a lot of attentions [6-10]. Kim et al [7] reported that yield strength and tensile strength of the 1.0 vol.% MLG/Cu composite increase ~ 14.6% and ~ 10.9%. Also, Li et al [8]found that a good dispersion and strong interfacial bonding between graphene and Cu matrix using Ni nanoparticles decorated MLGs, a significant improvement in ultimate tensile strength (~ 42%) of 0.8 vol% Ni-GPL composite was achieved. However, above research mainly focused on macro-mechanical properties, however, there is a significant difference between macro and micro-mechanical properties , the later is mainly dependent upon the localised microstrusture.

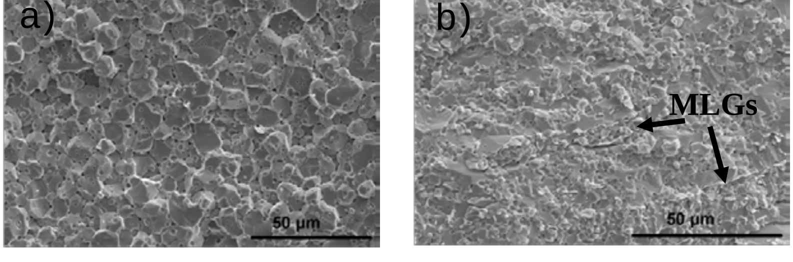
The purpose of this research is to evaluate micro-mechanical properties of the sintered composites using instrumented micro-indentation technique, and the effects of MLGs on microscopic mechanical properties of the copper composites and their strengthening mechanisms are also discussed in this research.

2.Experimentals

Copper (purity 99.5%, diameter: 60 nm) and MLGs with a thickness of ~ 1-5 nm and a length of 1-5 µm from Nanjing Xian Feng Nano Material company (China) were employed as the starting materials. MLGs were well dispersed using ultrasonic treating in distilled-water with sodium dodecyl-benzenes sulfonate (SDBS) as dispersant, and then nanosized copper powders were added into the MLG suspension for further ultrasonication. The as-obtained composite powders were mixed in the ethanol using Si_3N_4 ball milling with a speed of 350 rpm for 12 h. After fully dried, the composite powders were sintered using spark plasma sintering system (SPS, Dr. Sinter 1050, Sumitomo Coal Co. Ltd., Japan) at a temperature 900^{o}C under a uniaxial pressure of 40 MPa for 6 min with a heating rate of 150^{o}C/min. The weight fractions of MLGs in Cu matrix composite were 0.5, 1.0 and 1.5 wt.%.

X-ray diffraction (XRD, X'Pert-Pro MPD, The Netherlands) used Cu Ka radiation with a scanning rate of 2^o/min to analysis phase constituents of the sintered samples. The additive MLGs into copper composites and as-received MLGs were analyzed by Raman spectroscopy (JR HR800, France) using an Argon ion laser of wave length 514 nm and acquisition time of 20 s. Microstructures of the sintered samples were analyzed using scanning electron micrography (SEM, Hitachi S-4700, Japan). Hardness and elastic modulus of the sintered samples were tested using instrumented micro-indentation by MCT tester (CSM, Switzerland) with a load of 500 mN and a dwell time of 10 s. Spherical indenter radius was 20 µm and load-uploading rate was 1000 mN/min. Furthermore, Continuous Multi-Cycle (CMC) load-unloading technique was also conducted to achieve the indentation stress-strain curves of these sintered samples with spherical indenter radius 20 µm. The CMC process consisted of 12 cycles of load-partial unloading indentation performed on the same spot, and the applied load increased quadratically from 100 mN to 1000 mN. Ten tests were conducted at different locations for each sample.

3.Results



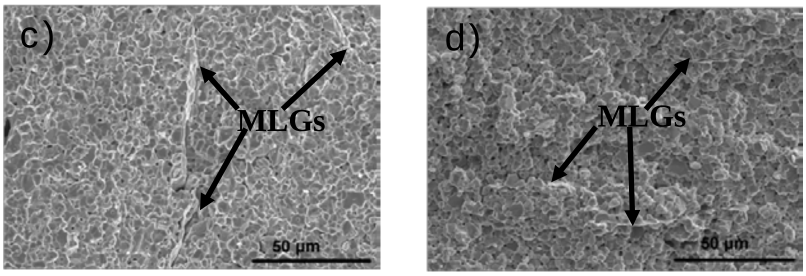


Fig. 1 SEM images of the fracture surfaces of unreinforced sample (a), and sintered composites with 0.5wt.% MLG (b), 1.0 wt.% MLG (c) and 1.5 wt.% MLG (d).

Fig.1 shows SEM images of the fracture surfaces of sintered samples, it is clear that the average grain sizes of the unreinforced sample are ~ 8 μm (Fig. 1a), while those of the samples with MLGs are all ~ 5 μm (Fig. 2b-d). The grain refinement might ascribe to MLGs dispersed in the grain boundaries restrict grain growth. Moreover, MLGs disperse homogeneously in the copper matrix (Fig. 1). As shown in Fig. 2a, it is clear the main phases of the sintered copper and MLG/Cu composites are Cu and some oxide particles, implying Cu powders underwent oxidation in the ball milling and SPS. Furthermore, the content of oxide particles decreases with increasing of MLG content in light of the peak intensity, this is due to rapid transfer of thermal energy from surface to the inner of the composites in the SPS process by means of excellent thermal conductivity associated with MLGs. Fig. 2b shows the Raman spectra of as-received MLGs and the sintered 1.5 wt% MLG/Cu composite, it is clear that D (1347 cm^{-1}) and G (1595 cm^{-1}) peaks which are related to defects in the structure and plane C-C bond stretching in graphene, respectively. The results sufficiently confirm that MLGs survive in the composites after harsh SPS process conditions.

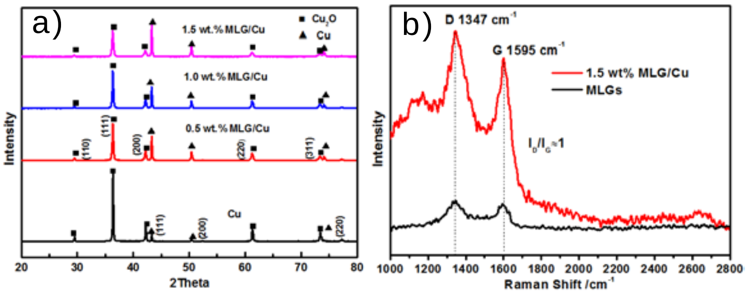


Fig. 2 XRD results of the milled powders and sintered samples (a) and Raman spectroscopy of the 1.5 wt.% MLG/Cu Composite powders and as -received MLGs (b).

Table 1 Micro-mechanical properties of sintered samples

Samples	*Hardness(GPa)*	*Elastic Modulus(GPa)*	*Hardening Exponents*	*Yield strength (MPa)*
Cu	1.73±0.06	31.85±1.67	0.298±0.16	196±9.33
0.5 wt.%MLG/Cu	1.66±0.03	33.92±2.54	0.274±0.08	218±7.93
1.0 wt.%MLG/Cu	1.45±0.03	36.45±1.37	0.168±0.09	266±6.77
1.5 wt.%MLG/Cu	1.37±0.10	43.30±2.00	0.166±0.08	276±7.82

Fig. 3 depicts the representative load-displacement curves and the reconstructed indentation stress-strain curves of the tested samples using Field and Swain method [11] , in which indentation yield strength was defined as the minimum stress at 0.2% plastic deformation[12]. As summarized in Table 1, elastic modulus and indentation yield strength of the sintered samples show an increase with MLG content. It is clear that elastic modulus of the 1.5 wt.% MLG/Cu composite exhibits an improvement by up to ~ 36% as compared with that of monolithic copper. High elastic modulus of the MLGs gives rise to the significant increase in the elastic modulus of the composites. Also, hardness of the 1.5wt.% MLG/Cu composite decreases to ~ 1.37 GPa while that of unreinforced Cu is ~ 1.73 GPa. As mentioned above, the content of oxide particles decreases with increasing of MLGs content, consequently resulting in the decrease of the hardness. Most importantly, the indentation yield strength of the 1.5 wt.%MLG/Cu composite significantly increases up to ~ 41%. Therefore, the addition of the MLGs to the Cu matrix plays a significant role in the improvement of the mechanical properties. It should be noted that the indentation yield strength increases ~ 22% when the content of added MLGs increases from 0.5 wt.% to 1.0 wt.% , but only ~ 4% impromen occurs with further increase in MLG content (1.5 wt.%). These mainly because the MLG length of the 1.0 wt.% MLG/Cu composite is ~ 6 μm as depicted in Fig. 4a when that of the 1.5 wt.% MLG/Cu composites is apparent agglomeration (~ 20 μm, Fig. 4b). Also there are some micro-voids existing around the MLGs due to their agglomeration as shown in Fig. 4, which would decrease the stress transfer efficiency from Cu matrix to MLGs. These results show that the reinforced effect would decrease when the MLG content exceed 1.0 wt.%.

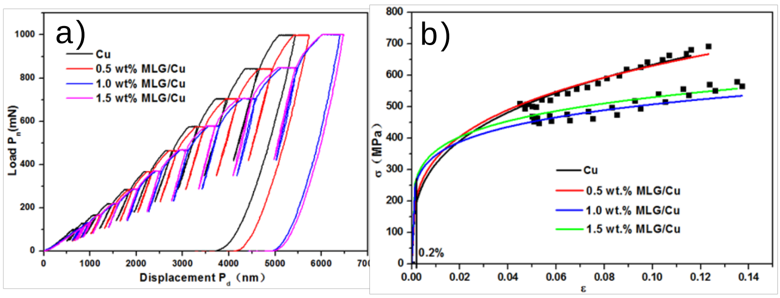


Fig.3 Typical load-displacement curves of spherical indentation Continuous Multi-Cycle (CMC) load-unloading of the sintered samples (a), and reconstructed indentation stress-strain curves of the sintered samples (b).

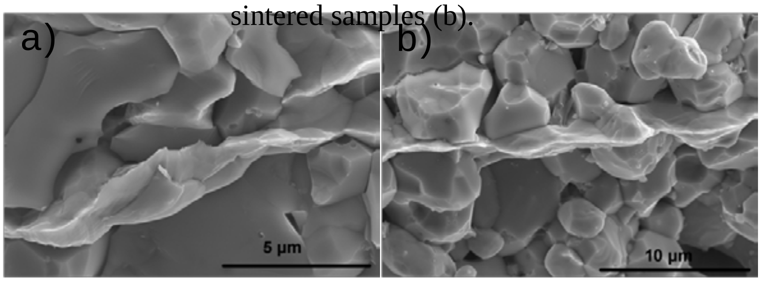


Fig. 4 SEM images of fracture surfaces of sintered composites containing of 1.0wt.% (a) and 1.5 wt.% MLG(b)s.

Hihger residual stress should exist in the sintered composites due to thermal expantion mismatches between Cu ($17\times10^{-6}K^{-1}$) [1] and MLGs ($(-8.0\pm0.7)\times10^{-6}K^{-1}$) [13] during cooling from the processing temperature to ambient temperature. Carbonaceous materials reinforced composites usually lead to enough residual thermal stresses to induce dislocation around the carbonaceous materials [14]. Therefore, the dislocation density would be increased duing the SPS to produce higher dislocation interaction and a shorter traveling distance of dislocations, subsequentely leading to an increased resistance to further plastic deformation, which will lead to the decrease of the hardening exponent. This phenomenon is similar to the fact that the strain hardening exponent of copper is controlled by dislocation density and grain size because smaller grain sizes and larger dislocation densities[15].

As for the nanocomposites, it is well known that grain refinement, enhanced dislocation density (EDD) and Orowan mechanism have significant effects on the mechanical properties. (i) Grain refinment. The grain refinement would lead to the strength improvement according to the Hall-Petch relationship. As depicted in Fig. 1, the grain size of the composites is ~ 5 μm, which is much smaller than that of the unreinforced Cu (~ 8 μm). Therefore, grain refinement plays a significant role in the improvement of the mechanical properties. (ii) Enhanced dislocation density mechanism (EDD), which results from the increase of the dialocation destiny due to the thermal expanation mismatches between MLGs and Cu. (iii) Orowan mechanism. MLGs are capable of restricting dislocation movement and forming loop-like configuration around the MLGs when the dislocations by-pass these MLGs on the slip plane to increase the strength. Therefore, the improvement of yield strength is ascribed to the grain refinement, EDD and Orowan mechanism.

4.Summary

Cu composites reinforced with MLGs were fabricated by SPS, in which MLGs with their pristine structure could homogeneously disperse in the composites and lead to grain refinement of the composites. Instrumented indentation results indicate that mechanical properties of the MLG/Cu composites such as elastic modulus and yield strength are improved. Analysis indicates that the grain refinement, the enhanced dislocation density (EDD) due to the thermal mismatch between copper and MLGs, and Orowan mechanism are attributed to the strengthening in this research.

5.References

[1] Tjong S C 2013 Recent progress in the development and properties of novel metal matrix nanocomposites reinforced with carbon nanotubes and graphene nanosheets, *Mater. Sci. Eng, R.* **74** 281-350.

[2] Wang T M, Zou C L, Chen Z N, Li M Y, Wang W, Li R G, et al. 2015 In situ synthesis of TiB_2 particulate reinforced copper matrix composite with a rotating magnetic field, *Mater. Des.* **65** 280-288.

[3] Li C, Feng X, Shen Y and Chen W 2016 Preparation of Al_2O_3/TiO_2 particle-reinforced copper through plasma spraying and friction stir processing, *Mater. Des.* **90** 922-930.

[4] Yin J, Yao D, Hu H, Xia Y, Zuo K and Zeng Y P 2014 Improved mechanical properties of Cu matrix composites reinforced with β-Si3N4 whiskers, *Mater. Sci. Eng, A.* **607** 287-293.

[5] Alexander S G, Balandin A, Bao W, Calizo I, Teweldebrhan D, Miao F and Lau C N 2008 Superior Thermal Conductivity of Single-Layer Graphene, *Nano Lett.* **8** 902-907.

[6] Chu K and Jia C 2014 Enhanced strength in bulk graphene-copper composites, *Physica status solidi. A.* **211** 184-190.

[7] Kim W J, Lee T J and Han S H 2014 Multi-layer graphene/copper composites: Preparation using high-ratio differential speed rolling, microstructure and mechanical properties, *Carbon.* **69** 55-65.

[8] Li M, Che H, Liu X, Liang S and Xie H 2014 Highly enhanced mechanical properties in Cu matrix composites reinforced with graphene decorated metallic nanoparticles, *J. Mater. Sci.* **49** 3725-3731.

[9] Rashad M, Pan F, Hu H, Asif M, Hussain S and She J 2015 Enhanced tensile properties of magnesium composites reinforced with graphene nanoplatelets, *Mater. Sci. Eng, A.* **630** 36-44.

[10] Wang J, Li Z, Fan G, Pan H, Chen Z and Zhang D 2012 Reinforcement with graphene nanosheets in aluminum matrix composites, *Scripta Mater.* **66** 594-597.

[11] Field J S and Swain M V 1994 Determining the mechanical properties of small volumes of material of submicrometer spherical indentation, *J. Mater. Res.* **10** 101-112.

[12] Huang Q Q, Song Y, Liu W W, Chen Y, Qi F, Zhao D, et al. 2015 Spherical indentation with multiple partial unloading for assessing the mechanical properties of ZrB_2–SiC composites, *Ceram. Int.* **41** 12349-12354.

[13] Yoon D, Son Y W and Cheong H 2011 Negative Thermal Expansion Coefficient of Graphene Measured by Raman Spectroscopy, *Nano Lett.* **11** 3227-3231.

[14] Chen Y, Balani K and Agarwal A 2012 Do thermal residual stresses contribute to the improved fracture toughness of carbon nanotube/alumina nanocomposites?, *Scripta Mater.* **66** 347-350.

[15] Fattah-alhosseini A, Imantalab O, Mazaheri Y and Keshavarz M K 2016 Microstructural evolution, mechanical properties, and strain hardening behavior of ultrafine grained commercial pure copper during the accumulative roll bonding process, *Mater. Sci. Eng, A.* **650** 8-14.