Effect of Graphene Content on Microstructure and Properties of Multilayer Graphene/Silver Composite

WANG Song, WANG Saibei, XIE Ming, LIU Manmen, LI Aikun, HU Jieqiong
(State Key Laboratory of Advanced Technologies for Comprehensive Utilization,
Kunming Institute of Precious Metals, Kunming 650106, China)

Abstract: Multilayer graphene/silver electrical contact composites were prepared by powder metallurgy. Effects of multilayer graphene content on the microstructure, electrical conductivity, hardness and arc erosion of the multilayer graphene/silver composites were studied in details. Results show that the densities of the green and sintered composites decrease with increasing the multilayer graphene content. The highest electrical conductivity value of 84.5% IACS can be accomplished when the content of the multilayer grapheme is 0.5% in reinforced composite. When the amount of the multilayer graphene is higher than 2.0%, the declining rate in hardness significantly increases. The multilayer graphene/silver electrical contact composites with 1.5% the multilayer grapheme displays the best anti-arc erosion performance.

Key words: electrical contact material; graphene/silver; microstructure; hardness; arc erosion
CLC number: TG146.3+2　　**Document code:** A　　**Article ID:** 1004-0676(2016)02-0051-06

石墨烯含量对多层石墨烯/银复合材料组织和性能的影响

王　松，王塞北，谢　明，刘满门，李爱坤，胡洁琼
(昆明贵金属研究所 稀贵金属综合利用新技术国家重点实验室，昆明 650106)

摘　要：采用粉末冶金法制备了多层石墨烯/银电接触复合材料，并系统研究了多层石墨烯含量对多层石墨烯/银复合材料微观组织、导电率、硬度及电弧侵蚀的影响。结果表明，复合材料密度随多层石墨烯含量的增加而减小。多层石墨烯含量为 0.5%的石墨烯/银复合材料具有最佳的导电率，为 84.5% IACS。当多层石墨烯含量高于 2.0%以后，复合材料硬度降低幅度明显增大。多层石墨烯含量为 1.5%的多层石墨烯/银电接触复合材料表现出最优异的抗电弧侵蚀性能。

关键词：电接触材料；石墨烯/银；微观结构；硬度；电侵蚀

Graphene, which has a two-dimensional layered structure of carbon atoms, has generated great interest as a reinforcement for metal matrix composites, because of its impressive mechanical, thermal and electrical properties. Its tensile strength reaches to 130 GPa, Young's modulus is 1 TPa, and a low density is 2.2 $g \cdot cm^{-3}$. Multilayer graphene (MLG) consists of 10 ~30 sheets of graphene, are less expensive and easier to produce than single layer grapheme[1-3]. Therefore, MLG might be more suitable relative to single-layer grapheme or carbon nanotube as an effective and economical reinforcement material for the development of new-generation metal matrix composites[4].

Recently, the research of multilayer graphene reinforced metal matrix composites has attained great interest[5-10]. For example, Kim and co-workers[11]

Received date: 2016-04-13
Foundation item: National Natural Science Foundation of China (U1302272; 51267007; 51507075).
First author: WANG Song, male, engineer. Research direction: electrical contact material. E-mail: fenmoyejin@qq.com

applied high-energy ball milling and high-ratio differential speed rolling to effectively incorporate and disperse MLG into a Cu matrix and obtained MLG/Cu composite with uniform dispersion of MLG. The strength increase through the addition of MLG results from Orowan strengthening for the MLG/Cu composites and the current processing route potentially opens a new avenue for fabricating high-performance MLG-reinforced metal matrix composites in sheet form. Varol T and Canakci A[12] used flake powder metallurgy to prepare the MLG/Cu nanocomposites. The increase in agglomeration content inhibited particle-particle contact during the sintering process and therefore sintered density decreased with increasing the multilayer graphene content. Bartolucci S F and co-workers[13] fabricated a 0.1wt% MLG/Al composite using ball milling, hot isostatic pressing and extrusion. Compared to the pure aluminum and multi-walled carbon nanotube composites, the MLG/Al composite showed decreased strength and hardness. The literature has indicated that there is lots of research focused on the fabrication and characterization of MLG/Cu and MLG/Al composites. However, there has not been a comprehensive research on multilayer graphene reinforced silver matrix composite (MLG/Ag) produced by powder metallurgy.

In the present work, powder metallurgy was used for fabricating the MLG/Ag electrical contact composites. The effect of the content of MLG on the microstructure, electrical conductivity, hardness and arc erosion of the MLG/Ag composites were studied. In addition, the anti-arc erosion mechanism of the MLG/Ag composites was analyzed.

1 Experiment

1.1 MLG/Ag composites preparation

MLG/Ag electrical contact composites were prepared by powder metallurgy. The gas atomized Ag powder with 99.9% purity and 25 μm average particle size by self-preparation, and multilayer graphene sheets with 99% purity and an average thickness of 60~120 nm bought from Chengdu Organic Chemicals Co. Ltd, were used in the present study. Fig.1 shows the morphologies of the Ag powders and MLG. It can be observed from Fig.1 that the Ag powders is a spherical shape (Fig.1(a)) while the morphology of MLG is a flake shape (Fig.1(b)).

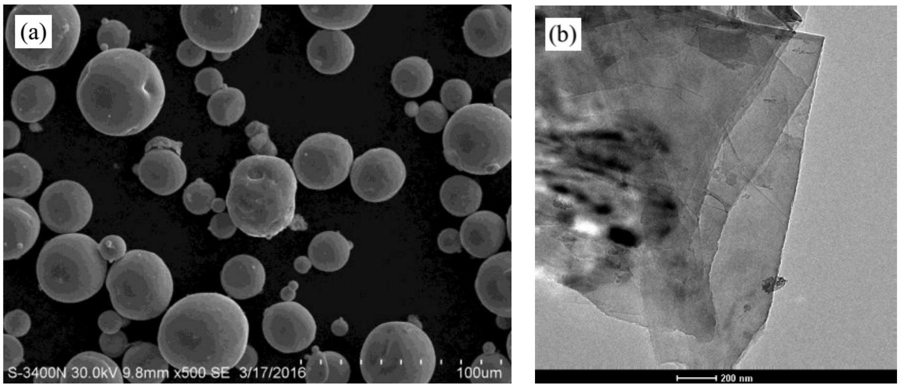


Fig.1 The morphologies of the Ag powders (a) and multilayer grapheme sheets (b)

图 1 Ag 粉末(a)和多层石墨烯片(b)的形貌

The MLG/Ag composite powders were fabricated through 10 h of ball milling using gas atomized Ag powders and multilayer graphene sheets. Different weight percentages (0.5, 1, 1.5, 2 and 2.5%) of MLG were added to the Ag matrix powders before starting the ball milling process. The ball milling speed is 280 r/min, the ball diameter is 10 mm and the ball-to-powder ratio is 5:1 (weight). The MLG/Ag composite powder was first compacted by cold isostatic pressing (100 MPa/3 min) at room temperature. Then, the powder compact was warm-pressed at 300 MPa for 1 h at 500℃. After compacting, the green ingots were sintered in a tube furnace at 800℃ for 2 h under argon atmosphere. And it was made to a wire of 8 mm in diameter by hot extrusion press (800℃/100 MPa), which was further cold drawn to a wire of 1.36 mm in diameter. The contact sample was made into the shape of a rivet shape.

1.2 Characterization method

The density of the MLG/Ag composite was measured by Archimedes' method. The theoretical density of compacts was calculated from the simple rule of mixtures taking the fully dense values for silver (10.53 $g \cdot cm^{-3}$) and multilayer graphene sheets (2.2 $g \cdot cm^{-3}$). Microstructure observations were carried out on Hitachi S-3400N scanning electron microscope. The micro-hardness was determined using HMV-FA2 micro Vickers hardness tester with a load of 1.961 N, a holding time of 10 s and each sample was measured five times to obtain the average value. The electrical conductivity was determined by measuring the alloy samples using FD101 metal conductivity tester, and every sample was tested for two times. The electrical contact experiment was held by JF04C contact tester. The arc erosion experimental parameters are showed in Tab.1.

Tab.1 Parameters of arc erosion experiment

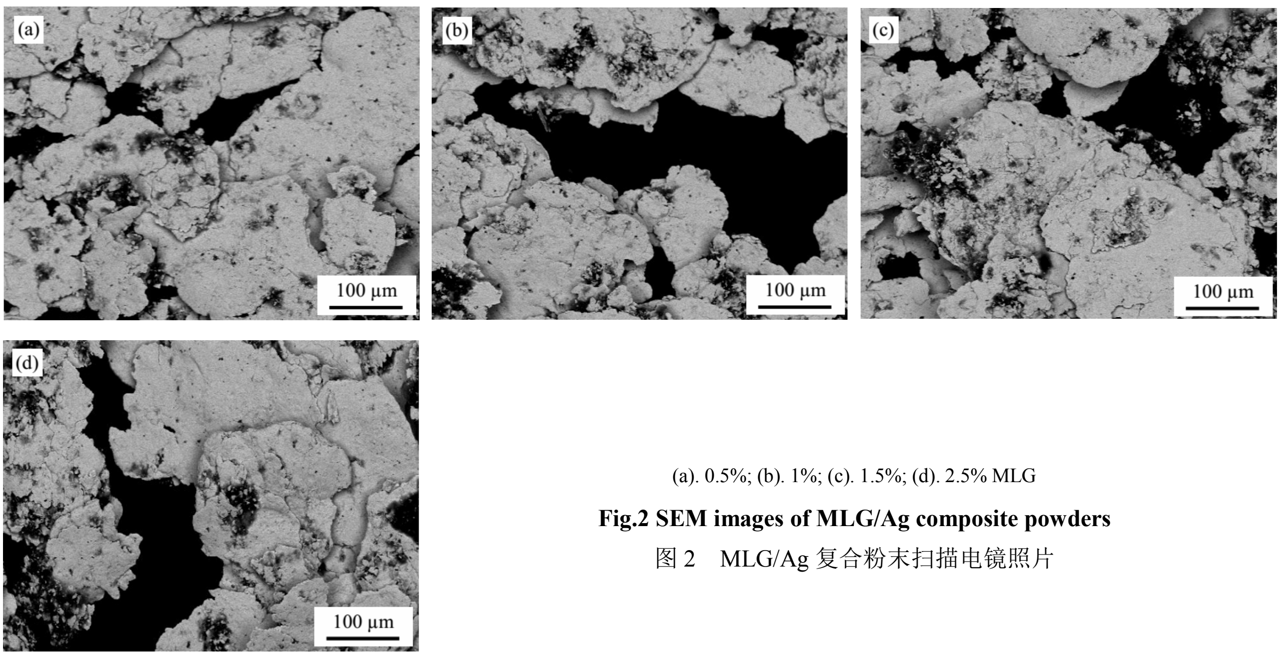
表 1 电弧侵蚀实验参数

Parameter	Value
Circuit condition	DC 25V/15A
Load condition	Resistive load
Contact pressure (N)	0.686
Contact frequency (times/min)	60
Contacts spacing (mm)	1.0
Surrounding gas	Air

2 Results and discussion

2.1 MLG/Ag composites morphology

Fig.2 showed a comparative morphological analysis for MLG/Ag composites powders with different MLG contents at the end of 10 h of ball milling. The morphology evolution of MLG/Ag composites powders during the ball milling as a function of MLG content (0.5, 1, 1.5 and 2.5%) is presented in the Fig.2. The spherical morphology of the initial Ag powders changed into the flake morphology because of the high-energy impacts resulting from the ball-powder-ball collisions. The MLG sheets were embedded and dispersed into the Ag matrix powders during the ball milling. Although the general morphology is the flake morphology in the MLG/Ag composite powders containing higher MLG sheets content, some semi-flake powders were observed, as seen in Fig.2(d). The agglomeration tendency increased due to the increase in the number of MLG sheets when increasing MLG content from 0.5% to 2.5%.



(a). 0.5%; (b). 1%; (c). 1.5%; (d). 2.5% MLG

Fig.2 SEM images of MLG/Ag composite powders

图 2 MLG/Ag 复合粉末扫描电镜照片

The apparent density of the MLG/Ag composites powders was showed in Fig.3. The apparent density of the MLG/Ag composites powders increased as MLG content increaseing up to 1.5% and then decreased with MLG content increasing further. The MLG sheets were embedded in the flake Ag powders during ball milling. The apparent density of MLG/Ag composite powders increased up to 1.5% of MLG content due to the effective embedding of MLG in the flake Ag powders. However, a sufficient MLG embedding surface area in the flake Ag matrix powders was not achieved when the MLG content is above 1.5 %, and particles rearrangement not come true by the MLG sheets, which cannot be embedded within the flake Ag powders. Therefore, the apparent density of MLG/Ag composite powders decreased after 1.5% of MLG content.

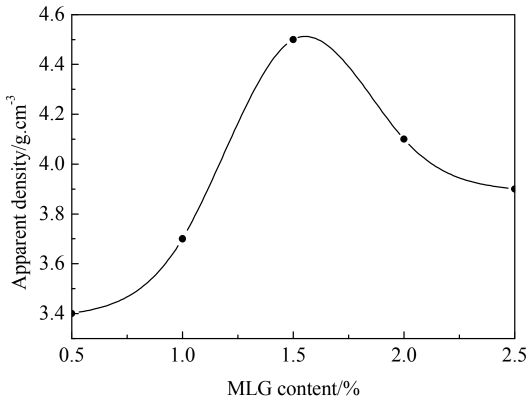


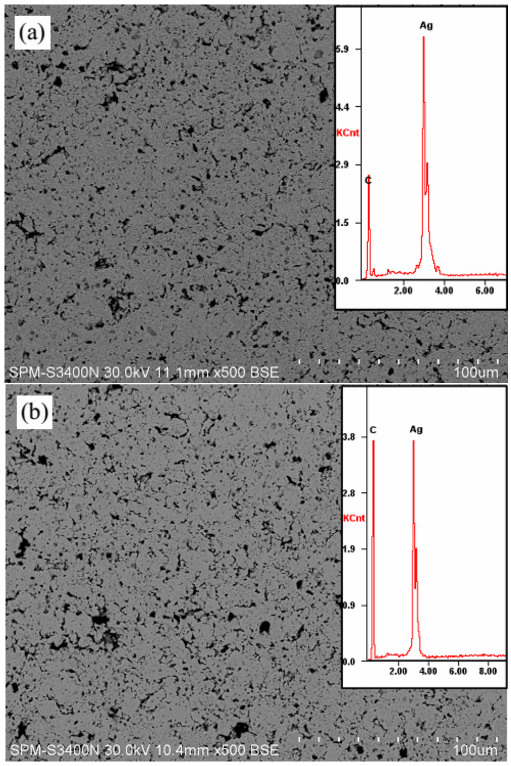
Fig.3 Apparent density of the MLG/Ag composites powders

图 3 MLG/Ag 复合粉末的松装密度

Fig.4 shows the cross-section SEM images and EDS pattern of the 1% MLG/Ag and 2% MLG/Ag electrical contact composites, where MLG sheets were uniformly distributed on silver matrix. Moreover, it can be seen from Fig.4, there are no clear visible pores in the MLG/Ag composite sample. This proves that the powder metallurgy method is a very promising technique for uniformity and high densification of MLG/Ag electrical contact composites.

2.2 Density of MLG/Ag composites

The effect of MLG content on the density of MLG/Ag composites is shown in Fig.5. As can be seen in Fig.5, the density of sintered and green MLG/



(a). 1% MLG; (b). 2% MLG

Fig.4 Cross-section SEM images and EDS pattern of MLG/Ag composite

图 4 MLG/Ag 复合材料横截面扫描电镜照片与 EDS 图谱

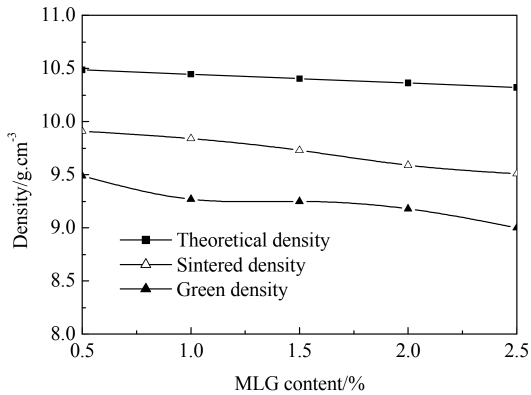


Fig.5 Density of MLG/Ag composites with different MLG content

图 5 不同 MLG 含量 MLG/Ag 复合材料的密度

Ag composites decreased with increasing the weight percentage of the MLG sheets. The highest density values were 9.91 g·cm^{-3} and 9.49 g·cm^{-3} for sintered and green 0.5% MLG/Ag composite respectively while the lowest density values were 9.51 g·cm^{-3} and 9.01 g·cm^{-3} for sintered and green 2.5% MLG/Ag composite respectively. Sintered density mostly depends on the distance between matrix powders in the particle reinforced composites. When MLG sheets were added to the MLG/Ag composites, the distance between Ag powders increased, and the sintering ability was reduced. The agglomeration of the MLG sheets reduced the sintered density of the MLG/Ag composites because the agglomeration regions acted as a resistant barrier to particle boundary diffusion during the sintering process.

2.3 Electrical conductivity and hardness of MLG/Ag composites

Fig.6 shows the effect of the MLG content on the electrical conductivity of the green and sintered MLG/Ag composites.

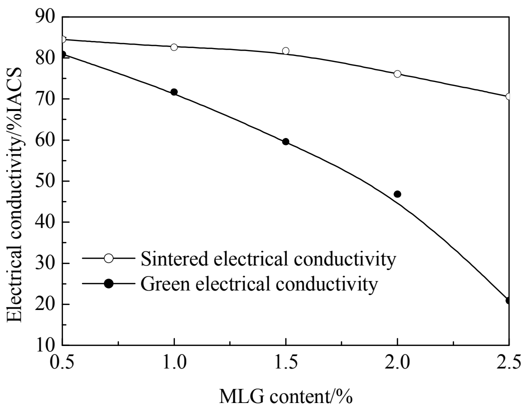


Fig.6 Electrical conductivity of MLG/Ag composites with different MLG content

图 6 不同 MLG 含量 MLG/Ag 复合材料的导电率

It can be seen from Fig.6, the electrical conductivity of green MLG/Ag composites decreased with the addition of MLG sheets to the Ag matrix. The electrical conductivity of the green 0.5% MLG/Ag composite was 80.9%IACS while that of the green 2.5% MLG/Ag composite was 20.8%IACS. The decreasing trend of electrical conductivity with MLG content in the green MLG/Ag composites can be attributed to an increase in the amount of porosity. After sintering, the electrical conductivity of all MLG/Ag samples increased significantly with the sintering process. The electrical conductivity of the sintered 0.5% MLG/Ag composites was 84.5%IACS, which may be attributed to microstructural change and consistency. The reduction rate of the electrical conductivity of the sintered MLG/Ag composites with increasing the MLG content is smaller than that of the green MLG/Ag composites. This can be attributed to the significantly increased porosity and agglomeration amount in the green MLG/Ag composites. The agglomeration amount increased with increasing the MLG content, and the agglomeration regions caused electron scattering within the particle boundaries.

Fig.7 shows the micro-hardness values of the sintered MLG/Ag composites with different MLG contents.

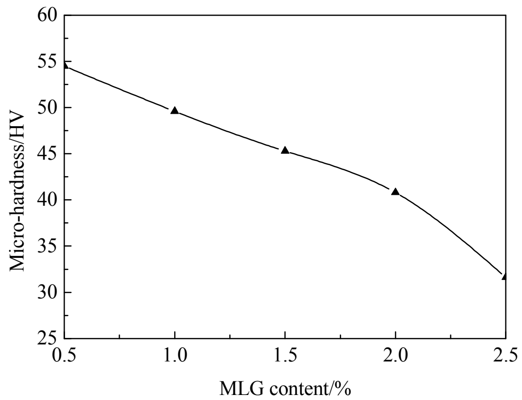


Fig.7 Micro-hardness of sintered MLG/Ag composites with different MLG content

图 7 不同 MLG 含量 MLG/Ag 复合材料的显微硬度

As we can seen from Fig.7, the micro- hardness values of the composites decreased with the addition of MLG sheets. When the amount of the multilayer graphene is higher than 2.0%, the decreasing rate in hardness significantly increases. This was due to the soft nature of the MLG sheets. The reduction rate in the hardness of the MLG/Ag composites can also be attributed to a decrease in density and the non- homogeneous distribution of MLG sheets in the Ag matrix.

2.4 Arc erosion of MLG/Ag composites

Tab.2 shows the mass changes of MLG/Ag composites with different MLG contents over 60000 times break off operations under DC 25V/15A. There is a net transfer of material from the anode to the cathode and part of the weight loss to the environment. The transfered weight and the lost weight to environment of 1.5%MLG/Ag composite contacts are only 17 mg and 15 mg, respectively, which is lower than that of other MLG/Ag composite contacts. The result indicates that the 1.5%MLG/Ag composite has the best ability of anti-arc erosion for all MLG/Ag composites. It is indicated that the appropriate content of MLG in the Ag matrix can reduce the splatter erosion of liquid silver and prevent the material transfer.

Tab.2 Mass change of the contacts over 60000 times breaks

表 2 经 60000 次分断后电接点质量变化

MLG/Ag ratio	Weight of anode/mg		Weight of cathode/mg		Weight transfer/ mg	Weight loss/ mg
	Before erosion	After erosion	Before erosion	After erosion		
0.5%	5351	5299	5342	5370	28	24
1%	5305	5264	5294	5316	22	19
1.5%	5233	5201	5201	5218	17	15
2%	5199	5160	5184	5205	21	18
2.5%	5078	5031	5036	5061	25	22

3 Conclusions

1) A new MLG/Ag electrical contact composites have been successfully produced by powder metallurgy method and the MLG sheets were uniformly distributed on silver matrix.

2) The densities of the MLG/Ag composites decrease with increasing the multilayer graphene content. The 0.5%MLG/Ag composite has the highest electrical conductivity value of 84.5% IACS in studied composites. The micro-hardness values of the composites decreased with the addition of MLG sheets.

3) The MLG/Ag composite with 1.5% the multilayer grapheme presents the best anti-arc erosion performance. The transfered weight and lost weight of 1.5%MLG/Ag composite contacts after 60000 times breaks is only 17 mg and 15 mg, respectively.

References:

[1] HWANG J, YOON T, JIN S H, et al. Enhanced mechanical properties of graphene/copper nanocomposites using a molecular-level mixing process[J]. Advanced materials, 2013, 25: 6724-6729.

[2] XU P T, YANG J X, WANG K S, et al. Porous graphene: properties, preparation, and potential applications[J]. Chinese science bulletin, 2012, 57(23): 2948-2955.

[3] NOVOSELOV K S, GEIM A K, MOROZOV S V, et al. Electric field effect in atomically thin carbon films[J]. Science, 2004, 306: 666-669.

[4] RASHAD M, PAN F S, YU Z W, et al. Investigation on microstructural, mechanical and electrochemical properties of aluminum composites reinforced with graphene nanoplatelets[J]. Progress in natural science: materials international, 2015, 25(5): 460-470.

[5] STANKOVICH S, DIKIN D A, DOMMETT G H B, et al. Graphene-based composite materials[J]. Nature, 2006, 442(7100): 282-286.

[6] WEJRZANOWSKI T, GRYBCZUK M, CHMIELEWSKI M, et al. Thermal conductivity of metal-graphene composites[J]. Materials & design, 2016, 99: 163-173.

[7] YOLSHINA L A, MURADYMOV R V, KORSUN I V, et al. Novel aluminum-graphene and aluminum-graphite metallic composite materials: synthesis and properties[J]. Journal of alloys and compounds, 2016, 663: 449-459.

[8] HUANG G, WANG H, CHENG P, et al. Preparation and characterization of the graphene-Cu composite film by electrode position process[J]. Microelectronic engineering, 2016, 157: 7-12.

[9] SELVAM M, SAMINATHAN K, SIVA P, et al. Corrosion behavior of Mg/graphene composite in aqueous electrolyte[J]. Materials chemistry and physics, 2016, 172: 129-136.

[10] LIU J H, KHAN U, COLEMAN J, et al. Graphene oxide and graphene nanosheet reinforced aluminium matrix composites: powder synthesis and prepared composite characteristics[J]. Materials & design, 2016, 94: 87-94.

[11] KIM W J, LEE T J, HAN S H. Multi-layer graphene/copper composites: preparation using high-ratio differential speed rolling, microstructure and mechanical properties[J]. Carbon, 2014, 69: 55-65.

[12] VAROL T, CANAKCI A. Microstructure, electrical conductivity and hardness of multilayer graphene/copper nanocomposites synthesized by flake powder metallurgy[J]. Metals and materials international, 2015, 21(4): 704-712.

[13] BARTOLUCCI S F, PARAS J, RAFIEE M A, et al. Graphene-aluminum nanocomposites[J]. Material science and engineering A, 2011, 528(27): 7933-7937.