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Review on the preparation process and properties of copper/graphene composites

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Abstract:

Copper/graphene composites have excellent mechanical properties, electrical conductivity, thermal conductivity, and it may also be applicable to sensors, aerospace and other fields. Due to the dispersibility of graphene, the addition of graphene will weaken the toughness and ductility of the material and other issues, it is still difficult to achieve industrialization, and currently remains in the laboratory stage. Thanks to the research of scholars recently, the preparation process of copper/graphene composites has been continuously improved. This paper summarizes some of the copper/graphene composites preparation process, and compares the capability of composites obtained by different processes simultaneously, and looks forward to the future research focus on copper/graphene composites.

Keywords: copper/graphene composites, graphene, overview, preparation process

1. Introduction

Graphene is a kind of honeycomb crystal structure that is only one atom thick and consists of tightly arranged sp2 hybridized carbon atoms.In 2004, Geim and Novoselov published an article about graphene in Science [1], using the "micromechanical exfoliation method" to obtain graphene, which has transformed graphene from a theoretical existence to a reality. Graphene has become a reality from theoretical existence. However, this method has low yield and high cost, and has not been widely used. So far, a variety of graphene preparation methods have been researched, such as the solid-phase method of mechanical exfoliation and epitaxial growth method, liquid-phase method of redox and ultrasonic dispersion, in addition to chemical vapor deposition, etc. It can be said that the methods have been relatively perfected. With excellent optical properties, mechanical properties, thermal properties and electrical properties, it serves the purpose of making sensors, fiber lasers and so on.

Copper is an important metallic material in today's world, with a long history of process development, abundant reserves in nature, and excellent properties, thanks to which copper and its composites are widely applicated in electronics, communications, and other domain.

Recently, some researchers have successfully prepared copper/graphene composites using graphene oxide and graphene as raw materials. The introduction of graphene into the copper matrix not only enhances the oxidation resistance of copper but also improves the material's mechanical properties while maintaining outstanding thermal conductivity. The composite material has excellent performance, combining chemical stability, high strength and stiffness, excellent electrical and thermal conductivity, but

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due to the small density of graphene, poor dispersion, and interfacial bonding problems, which makes it difficult to achieve uniform dispersion of graphene in the copper matrix and a strong bonding between graphene and copper interface. In this regard, this paper will discuss the fabrication process of copper/graphene composites and the properties of composites obtained by different processes.

2. Manufacturing process and performance

2.1 Ball milling method

Ball milling (BM), i.e.,dispersed particles and metal powder are put into a ball mill, and after a period of time milling, the raw materials can be tightly mixed at the atomic level, and the metal particles encapsulate hard particles uniformly. The technique of ball milling allows homogeneous mixing of the reinforcement with the metal matrix, which has the advantage of improving the uniformity of the reinforcement particle distribution and the bonding at the interface between the reinforcement and the matrix, thus improving the material properties [2]. Cui Ye [3] placed graphene, copper powder, and zirconia balls into a ball milling jar while adding ethanol, vacuumed the ball milling jar, and ball milled using a ball mill. The composites obtained using the ball milling method had excellent dispersion of graphene flakes in the copper matrix and had a yield strength of 378 MPa.It is 2.5 times higher than that of pure copper, as well as extraordinaryelectrical conductivity.

According to the research of Wen Guofu [4] and others, as the time of ball milling increases, the microhardness of the composite material shows an overall increasing trend, the tensile strength increases, and the plasticity also improves. As the ball-material ratio increases,the elongation,tensile strength and electrical conductivity of the composite material are hoisted. However, the time of ball milling is too long and the speed of ball milling is too fast will lead to graphene agglomeration, and reduce interfacial bonding with copper substrate. The reasonable ball milling parameters it gives include a ball-to-material ratio of 3:1, the ball milling speed of 300r/min, and the ball milling time of 6-8h.

Bingwei Wei [5] found in graphene obtained by mechanical exfoliation method using a ball mill that although copper powder is uniformly dispersed in the composite copper-graphene composite powder, there is a large amount of agglomeration of graphene, and the graphene sheets are tightly bound to each other. It can be shown that the mechanical exfoliation method using a ball mill cannot overcome the van der Waals forces between graphene. In this regard, before ball milling, he utilized the XC-CD series ultrasonic cell pulverizer to ultrasonically disperse the copper-graphene composite powder. After 45 min of ultrasonic dispersion, the graphene flakes were effectively separated, the transparency of graphene was good, and the composite powder would not be agglomerated, confirming the feasibility of the method of separating graphene using ultrasonic dispersion technology. At the same time, the optimal parameters for hot pressing (HP) were determined to be: a sintering temperature of 800°C, a sintering pressure of 25 MPa, and a sintering atmosphere of vacuum.

2.2 Chemical vapor deposition

Chemical vapor deposition (CVD), i.e., using carbon-containing organic matter as a carbon source and a metal matrix (copper base) as a catalyst, catalyzed the growth of graphene on the surface of the metal matrix.Wang et al. [6] grew high-quality graphene on copper nanoparticles directly with the method of CVD, and then selectively corrupted magnesium oxide and copper, and sintered to obtain a copper/graphene composite material. The hardness of the composite obtained by this method is 2.53 GPa, which is about 2.5 times that of pure copper, and the coefficient of friction (0.2) is lower than that of pure copper (0.34), while the resistivity is as low as that of pure copper. Guan Zhenhong [7] et al. used Cu-Mn alloy as raw material and de-alloying treatment to obtain nanoporous copper,then used CVD to cultivate graphene on the surface of nanoporous copper, and then obtained copper/graphene composites after roller pressing and sintering. The electrical properties of the composites obtained by this method were tested to maintain a hardness of 55.2 HV and a tensile strength of 330 MPA at 93.5% IACS, which is an increase of 38% and 34.69%, respectively, compared to pure copper.Li et al [8] mixed graphene particles with copper powder by using a rapid mixer, placed the mixed powder into a CVD chamber, and heated and reduced it by passing it through H2 , and the copper/graphene hybrid material was obtained after cooling. The samples were immersed in a copper corrosion solution for corrosion resistance testing, and the copper/graphene composites were measured to have excellent corrosion resistance.

Compared with the mechanical stripping method, the graphene distribution of composites made by CVD is more uniform, the interface between graphene and copper matrix is well bonded, and copper nanoparticles can be highly reduced on graphene, which improves the quality of the material. However, it faces the problems of cumbersome steps, easy wear of graphene layer, and growth of copper grains at high temperature.

Graphene is hydrophobic and easy to agglomerate due to strong van der Waals forces and its special molecular structure. At this point, scholars focused on a derivatives of graphene, namely graphene oxide, and found that graphene oxide overcame some of the imperfection of graphene. In comparison with graphene, graphene oxide exfoliates easily after being mingled with polymers or small molecules[9]. Graphene oxide is commonly prepared by oxidizing graphene materials with strong acids, but the traditional method is hazardous and produces toxic gases. Hummers method [10] proposes to replace concentrated sulfuric and nitric acids with potassium permanganate, which overcomes the above mentioned drawbacks and at the same time reduces the time required for the reaction. Recently Daniela C. Marcano et al [11] modified the Hummers method by eliminating the use of sodium nitrate and increasing potassium permanganate in dosage, and the reaction was carried out at H2SO4/H3PO4 of 9:1, which can improve the reaction efficiency and obtain more hydrophilic graphene oxide. So far, the modified Hummers method is still the main way to prepare graphene oxide.

2.3 Electrochemical deposition

Electrochemical deposition is the preparation of copper/graphene composites using graphene oxide as the raw material. Electrochemical deposition is a chemical reduction process that applies pulsed alternating current (AC) or direct current (DC) power supply to reduce the metal ions in the plating solution and deposit them on the surface of the substrate. Zhao X et al [12] fabricated graphene oxide by Hummers' method [10], and after that, they uses ultrasonic waves to prepare the graphene oxide solution, and the electrochemical deposition was carried out with the copper foil as the cathode and the copper rods as the anodes in a beaker, and then sintered to copper/graphene composites were obtained. The electrical conductivity of the composites obtained by this method is basically the same as that of copper, but the strength and modulus of elasticity are improved, and the graphene is uniformly dispersed, which effectively avoids graphene agglomeration. Compared with CVD, this method reacts at a lower temperature, solves the problem of grain growth in CVD, and is an atypical method to prepare copper/graphene composites.

2.4 Molecular level mixing method

Cha et al [13] studied the conventional powder metallurgy process and discovered that they fabricate CNT/metal composites unsuccessfully, attributing the reason to the fact that the powdered CNTs are aggregated, and they are attracted mutually because of the van der Waals forces between the CNTs, and also using the conventional process to prepare the composites, the CNTs will be located on the surface of the metal after mixing. In this regard, they used the following process: first, CNTs were dispersed in solution to form a stable suspension, functional groups clung to the surface of CNTs, copper ions were mixed with the solution, the mixed solution was heated and dried, and finally the composite was obtained by calcination reduction. This process improves the dispersion of graphene and copper matrix while strengthening the bonding strength between graphene and copper interface, and the Young's modulus and tensile strength of the composites are much more outstanding than that of copper.

HWang et al. used the molecular level mixing method [14] i.e., mixed GOs and metal ions in water homogeneously, formation of a chemical bond between the functional groups of GOs and copper ions, NaOH was added to form Cuo/GO, which prevented the reduction of GOs functional groups before chemical bonds were formed with Cu ions, and then applied thermal reduction with hydrogen to obtain Cu/RGO powders. The Cu/graphene composites were obtained by molecular level mixing method and SPS process. The yield strength of the composites reached 284 MPa and the modulus of elasticity was up to 131 GPa, which were about 80% and 30% higher than that of pure Cu separately. Through molecular-level mixing, in the copper matrix, RGO was dispersed uniformly. The molecular level mixing method avoided the reunification of RGO effectively and increased the adhesion between copper and RGO, while the SPS process improved the contact interface between graphene and copper, resulting in a higher bonding strength between graphene and copper.

3. Summary and discussion

The methods to prepare Copper/graphene composites are multiform, each with its own strengths and weaknesses. The ball milling method is simple and operable, but the graphene is easy to agglomerate, and the CVD graphene is well dispersed, but the process is cumbersome, and the high temperature will lead to the growth of copper grains, which has great limitations. The molecular level mixing method overcomes the above drawbacks, but the material strength is lower compared to other processes. Electrochemical deposition is simple, economical and requires low temperature, but only foil composites can be prepared, not bulk composites. Nevertheless, copper/graphene composites still have extrusive electrical, mechanical and thermal [15,16] properties and can service in a wide range of applications, such as flame-retardant materials [17], electrochemical sensors, etc.

Kim et al [18] determined the mechanical properties of copper/graphene composites using nanopillar compression tests, revealing the reason for graphene's strengthening

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of the composites compared to pure copper. According to the results of the nanopillar compression test, the flow stress increased with decreasing metal layer spacing, and the strength was highest when the metal layer spacing was minimized. According to in-situ TEM, high-resolution TEM and MD simulations, the Cu/graphene interface effectively prevented dislocation propagation across the interface, the inherent high mechanical strength of graphene prevents fracture and shear, and the graphene effectively restrained dislocation propagation across the interface.

4. Conclusion

The research on copper/graphene has been relatively mature, but it is not perfect, and many technical difficulties are yet to be broken through. We still need to study how to further enhance the performance of composites, how to make graphene achieve a better dispersion in the copper matrix, how to enhance the interfacial bonding strength of graphene and copper matrix, how to reduce the cost of preparation, and achieve industrialization. The process is optimized to reduce the tediousness of the process, reduce the porosity of the composite after sintering, and improve the densification. In addition, due to the addition of graphene, destroying the integrity of the copper lattice system, causing lattice distortion, and at the same time, hindering the growth of grains, so that the area of grain boundaries increases, causing a decrease in conductivity, how to enhance the mechanical properties of composites while ensuring the conductivity of composites, and reasonably controlling the distribution of graphene in the copper matrix, is a problem worth studying.

5. Reference

[1] Novoselov, K.S.; Geim, A.K.; Morozov, S.V. Electric field effect inatomically thin carbon film. Science 2004, 306 (5296), 666–669.

[2] Joy, J., Krishnamoorthy, A., Tanna, A., Kamathe, V., Nagar, R., & Srinivasan, S. (2022). Recent developments on the synthesis of nanocomposite materials via ball milling approach for energy storage applications. Applied Sciences, 12(18), 9312.

[3] Cui Ye. Preparation of graphene/copper composite powder and the organization and properties of its composites[D]. Harbin Institute of Technology,2015.

[4] Wen Guofu,Liang Yanjuan,Wang Xufei,et al. Effect of ball milling parameters on the properties of graphene reinforced copper matrix composites[J]. Lubrication and Sealing,2021,46(01):103-110.

[5] Wei B.W.. Research on the preparation and properties of copper-graphene composites[D]. Chongqing University of Technology,2014.

[6] Shuangyue Wang,Shaobo Han,Guoqing Xin,Jianliang Lin,Ronghua Wei,Jie Lian... & Qingkai Yu.(2018).High-quality graphene directly grown on Cu nanoparticles for Cu-graphene nanocomposites.Materials & Design181-187.

[7] Zhenhong Guan, Zhenyang Yu, Zhijun Qiao, et al. Preparation of in situ-grown three-dimensional graphene/copper matrix composites by chemical vapor deposition[J]. Journal of Materials Science and Engineering, 2018,12(4):340-346

[8] Shuangyi Li,Baosen Hou,Dan Dai,Shengcheng Shu,Mingliang Wu,Ao Li... & Cheng-Te Lin.(2018).CVD Synthesis of Monodisperse Graphene/Cu Microparticles with High Corrosion Resistance in Cu Etchant. Materials(8),1459-1459.

[9] Gao, Wei. “The chemistry of graphene oxide.” Graphene oxide: reduction recipes, spectroscopy, and applications (2015): 61-95.

[10] Hummers,W.S.;Offeman,R.E. Preparation of graphitic oxide.Journal of The American Chemical Society 1958, 80,1339–1339.

[11] Marcano D C, Kosynkin D V, Berlin J M, et al. Improved synthesis of graphene oxide[J]. ACS nano, 2010, 4(8): 4806-4814.

[12] Zhao X, Tang J, Yu F, Ye N. Preparation of graphene nanoplatelets reinforcing copper matrix composites by electrochemical deposition. Journal of Alloys and Compounds. 2018 Oct 25;766:266-73.

[13] Cha, S. I., Kim, K. T., Arshad, S. N., Mo, C. B., & Hong, S. H. (2005). Extraordinary strengthening effect of carbon nanotubes in metal-matrix nanocomposites processed by molecular-level mixing. Advanced Materials (Deerfield Beach, Fla.), 17(11), 1377-1381.

[14] Hwang, Jaewon, et al. “Enhanced mechanical properties of graphene/copper nanocomposites using a molecular-level mixing process.” Advanced materials 25.46 (2013): 6724-6729.

[15] Hu, Z., Tong, G., Lin, D., Chen, C., Guo, H., Xu, J., & Zhou, L. (2016). Graphene-reinforced metal matrix nanocomposites–a review. Materials Science and Technology, 32(9), 930-953.

[16] Cakir, D., Caylan, O. R., & Cambaz Buke, G. (2024). Synthesis and characterization of homogeneously dispersed graphene–copper heterostructures with enhanced thermal properties. Journal of Materials Science, 59(1), 105-113.

[17] Zhang, W., Wang, L.-G., Wang, L.-T. & Zhang, T.. (2022). Graphene reinforced copper matrix composites with flame retardant technology. Materials of Information Record (10), 63-66. doi:10.16009/j.cnki.cn13-1295/tq.2022.10.012.

[18] Kim, Y., Lee, J., Yeom, M. S., Shin, J. W., Kim, H., Cui, Y., ... & Han, S. M. (2013). Strengthening effect of single-atomic-layer graphene in metal–graphene nanolayered composites. Nature communications, 4(1), 2114