Effect of Cr@RGO structure on microstructure and properties of RGO/CuCr25 composite

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Abstract

CuCr alloy with high Cr content (20–50 wt.%) is the main contact material for medium voltage and high current vacuum interrupters. However, the influence of network distribution of Cr particles affect the conductivity of CuCr alloy, and its properties strongly depend on the size of Cr particles. In this paper, Cr@RGO (Cr powder coated with reduced GO) was prepared by BSA (bovine serum protein) electrostatic assembly method, and then RGO/CuCr composites with different graphene content were prepared by vacuum hot pressing sintering process. The results show that the size of Cr particles decreases with the increase of graphene content and the network of Cr particles became fractured. When the content of RGO is 3.0 wt.%, the size of Cr phase is 19.9 μm, which is 23.8% less than that of CuCr25 of 26.1 μm. The Brinell hardness and electrical conductivity of 3.0 wt.% RGO/CuCr composite are 102.5 HB and 52.9% IACS, which is increased by 8% and 6% in contrast with that of CuCr25. And the Preparation of RGO/CuCr is simple, feasible, replicable and easy to achieve the goal of the industrial preparation.

1. Introduction

CuCr (copper-chromium alloy) is a kind of immiscible alloy, it maintains the high electrical conductivity and high thermal conductivity of copper components to ensure the large working current and breaking performance of electrical contacts, and also plays the characteristics of high melting point, high hardness and oxygen affinity of chromium components, so that the electrical contact can obtain good voltage strength and resistance to fusion welding [1–3]. Therefore, CuCr alloy with high chromium content (CuCr25 ~ CuCr75) is the first choice of electrical contact material for medium voltage circuit breakers and vacuum switches [4, 5].

The solid solubility of Cr in Cu is very small and almost zero at room temperature. Therefore, the Cr rich phases in the as cast structure are connected in a network. Many studies have shown that the properties of CuCr contact alloys are strongly dependent on the Cr rich phase and the refinement of Cr phase can improve the hardness and conductivity. Therefore, refining the size of Cr is also an important research topic. Infiltration is the earliest method to prepare CuCr contact alloy, but it is difficult to prepare CuCr alloy with Cr content less than 50%. Arc melting can produce CuCr contact alloy with low Cr content with the size of Cr particles is between 15 μm and 30 μm, but Cr particles are distributed in dendrite. This is disadvantageous to the improvement of dielectric strength, in addition, its hardness is very poor [6, 7]. Rapid solidification process can reduce the composition segregation and refine the Cr particles [8–11], but the preparation process is complex, which is not conducive to large-scale production. In contrast, mechanical alloying is a common process to prepare CuCr alloy with higher hardness and conductivity [12, 13]. However, chromium particles are connected in a network in CuCr alloy with high chromium content, which undermine hardness and electrical conductivity of CuCr alloy.

In the development of new CuCr Alloys and other immiscible alloys, the concept of core-shell structure applied in catalysis, battery, medicine or sensor is used for reference, hoping to refine the size of Cr phase. Ji et al [14] synthesized Au @ polystyrene beads by electrostatic adsorption principle. Sun et al [15] coate Au
nanoparticles on ZnO by sol-gel method and synthesized Au-@ZnO core-shell composite particles. Sun et al [16] synthesized Cu@Mo composite powders with a core-shell structure via ball-milling and subsequent reduction process. The materials of core-shell structure involve metal, inorganic nonmetal and organic, etc, which are flexible. However, the formation mechanism, structure and properties of the core and shell are not very clear due to the different composition and preparation process of the core-shell. Moreover, the core-shell particles prepared by the existing synthesis technology have some problems, such as the thickness of the shell is not uniform, the coating is not compact, and the structure is not easy to control.

Aiming at the above problems in the process of shell structure construction, we consider to transform the in-situ self-generated cladding behavior into the cladding behavior using controllable structure and thickness material. Graphene has excellent thermal conductivity ($5000 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), conductivity ($100 \text{ Ms} \cdot \text{m}^{-1}$), carrier mobility ($15000 \text{ cm}^2/(\text{V} \cdot \text{s})$) and hardness, and become one of the candidates for the reinforcement of metal matrix composites [17]. In this study, Cr@RGO (Cr powder coated with reduced GO) was prepared by BSA (bovine serum protein) electrical assembly method, and then reduced graphene oxide (RGO)/CuCr composites with different graphene content were prepared by vacuum hot pressing sintering process. The effect of graphene content on microstructure and properties was studied, in addition, the evolution mechanism of refining chromium by graphene during sintering was revealed.

2. Experimental

2.1. Preparation of Cr@RGO structure

Cu powders (300 mesh, 99.9% purity, from Sinopharm Group Chemical Reagent Co., Ltd), Cr powders (1000 mesh, 99.9% purity, from Sinopharm Group Chemical Reagent Co., Ltd), bovine serum protein (analytical pure, from Sinopharm Group Chemical Reagent Co., Ltd), GO (graphene oxide) is prepared by Hummer’s method. The micro morphology and Raman analysis of GO are shown in figure 1 and indicate that the thickness of GO is as thin as translucent, and its surface has a certain amount of folds, because the repulsion between different layers caused by the oxygen functional groups on the surface of GO. Raman spectrum shows that the peaks of D and G are produced at 1340 cm$^{-1}$ and 1585 cm$^{-1}$ by GO. And $I_d/I_g = 1.14$, which indicate that GO has some defects and functional groups.

Figure 2 shows the schematic illustration of the preparation process of Cr@RGO (Cr powder coated with reduced GO) by BSA (bovine serum protein) electrostatic assembly method. The Cr powder was dispersed in 200 ml of alkaline cleaning solvent ($20 \text{ g} \cdot \text{l}^{-1} \text{NaOH}, 50 \text{ g} \cdot \text{l}^{-1} \text{Na}_2\text{SiO}_3, 25 \text{ g} \cdot \text{l}^{-1} \text{Na}_3\text{PO}_4$ and residual deionized water) under magnetically stirred at 70 °C for 10 min, then filtered and vacuum-dried 60 °C for 6 h. After that the hydroxylated chromium powder was dispersed in 500 ml of BSA solvent ($0.3 \text{ g} \cdot \text{l}^{-1} \text{BSA}, 0.2 \text{ mol} \cdot \text{l}^{-1} \text{PB buffer solution concentration and the pH} = 3$) under magnetically stirred at room temperature for 1 h to obtain Cr@BSA (Cr powder coated with BSA). GO was dissolved in Cr@BSA solvent under sonication for half an hour and magnetically stirred for half an hour to obtain Cr@BSA@GO with different mass fractions of GO. Then, Cr@BSA@GO and 1 g NaBH4 were dissolved in 500 ml distilled water under magnetically stirred for two hours at room temperature to obtain Cr@BSA@RGO.

2.2. Preparation and characterization of RGO/CuCr Composites

The Cu and Cr@RGO mixture powders were mechanically milled with a speed of 200 rpm in ethanol for 2 h and the ball powder ratio of 10:1. After ball milling, the mixed power loaded into graphitic die with the inner
diameter of 40 mm and a piece of graphite paper was placed between the die and the powder to facilitate the removal of sintered samples, thus prolonging the service life of the die. Then, the different GO mass fractions of RGO/CuCr25 (1.0 wt.%, 3.0 wt.% and 4.5 wt.%) was consolidated by hot pressing and sintering at 1173 K for 2 h under a pressure of 30 MPa in vacuum.

HORIBA LABRAM Soleil high-resolution ultra-sensitive intelligent Raman imager was used to characterize graphene oxide, and SupNIR Model 2750 near infrared analyzer analyzes the reduction degree of graphene oxide. Metallographic structure of the sample was performed by using optical microscope (DMM-440C) and the microstructure of Cr@RGO was observed by field emission scanning electron microscope (Nava400nano). The density of the sample is measured by Archimedes drainage method and the density is calculated. The hardness test was measured using a Brovie optical durometer at a load of 613 N for 10 s on clean surface of the CuCr25 and RGO/CuCr25 composites. The hardness of each sample was tested for 10 times, and the hardness value was calculated and averaged. The conductivity of the samples were measured on a four-probe conductivity tester.

3. Results

3.1. Structure of Cr@RGO and Cr@GO

Figure 3 shows the SEM images and the FTIR pattern of the Cr@RGO. Curve 1 and curve 2 represent the absorption vibration curves of Cr@GO and Cr@RGO, respectively. It is observed that transmittance is very high in the region of 3250 cm\(^{-1}\)–3500 cm\(^{-1}\) which arises due to stretching vibrations of –OH groups. In case of curve 1, the peak at 3250 cm\(^{-1}\)–3500 cm\(^{-1}\) widens because water absorption of GO and chromium powder and the oxygen affinity of chromium lead to water vapor and CO2 doping into the samples. Accordingly, the peak at 1635 cm\(^{-1}\) is due to stretching vibrations of –OH. The peaks near 2930 cm\(^{-1}\) and 2850 cm\(^{-1}\) correspond to the antisymmetric and symmetric stretching vibrations of –CH\(_2\), respectively. In case of curve 1, the peaks at 1110 cm\(^{-1}\), 1264 cm\(^{-1}\) due to stretching vibrations of C–OH of alcohol and C–O–C in surface of GO, respectively, which confirms the presence of GO.

According to the XRD patterns shown in figure 4, the peaks at 2\(\theta\) = 44°, 64° and 82° correspond to (100), (200) and (211) crystal face of Cr, respectively. A short and wide peak corresponding to the (001) crystal face of GO was observed in the three samples near 2\(\theta\) = 10°. In addition, the XRD pattern shows that the Cr@GO prepared in this study does not contain other impurities such as chromium oxide and chromium carbide.

3.2. Microstructure of RGO/CuCr25

Figure 5 shows the metallographic images of CuCr25 and RGO/CuCr25 prepared by vacuum hot pressing. The metallographic image of CuCr25 alloy shows that the Cr phase after sintering process has a large size, which is distributed in the matrix as a network structure, and many Cr phases are connected and overlapped with each other to form a larger Cr phase in figure 5(a). The Cr phase of this kind of connector accounts for a larger proportion in the matrix compared with the dispersed fine Cr phase, which results in a coertain degree of Cr segregation. The particle size of Cr phase of RGO/CuCr25 decreases and the dispersed fine Cr phase increases in the matrix in figures 5(b)–(d). The network structure of Cr phase in RGO/CuCr25 composites is broken, which greatly alleviates the agglomeration and connection of large-scale Cr phase, and effectively avoids the segregation of Cr phase. Figure 6 shows the size of Cr phase in RGO/CuCr25 composite with different RGO mass fractions.
It can be seen that the size of Cr phase in RGO/CuCr25 composite decreases with the increase of RGO amount, because RGO hinders the diffusion and growth of Cr during sintering. When the mass fractions of RGO are 1.0 and 3.0 wt.%, the average size of Cr phase are 23.32 and 19.87 μm, respectively. When the mass fractions of RGO is 4.5 wt.%, the average size of Cr phase reduce to 18.65 μm, and reduce by 17.7% compared with CuCr25 alloy.

Figure 7(a) is the SEM image of 4.5 wt.% RGO/CuCr25. Graphene are mainly distributed around Cr particles. Figure 7(b) shows the TEM image of interface between Cu and Cr. It can be seen that graphene exists at the interface between Cu and Cr and black precipitated phase produces near Cu or Cr. The interface structure of RGO/CuCr25 composites was further studied by HRTEM and the corresponding fast Fourier transform (FFT) and inverse Fourier transform (IFFT). Figure 7(c) shows compact interfacial adhesion between Cr and Cu matrix without voids or cracks. The FFT (figure 7(d)) shows (110), (021) and (131) diffraction spots of Cr7C3. Figure 8(a) is another HRTEM image of specially shaped black phase and shows a good interface. Figures 8(b) and (c) are FFT and IFFT recorded form the marked box (red box in (a)) shows (020), (001) and (021) diffraction spots of Cr7C3 and lattice fringes with the measured inter-planar spacing of 0.61 nm, which corresponds to the plane of (020) (Orthorhombic, a = 0.7015 nm, b = 1.215 nm, c = 0.4532 nm, PDF card #36-1482).

3.3. Properties of RGO/CuCr25

Figure 9(a) shows the relative density of RGO/CuCr25 and indicates the relative density of RGO/CuCr25 changed little with the increase of RGO content (0 ~ 3.0 wt.%). The relative densities of 1.0 wt.%RGO/CuCr25 and 0.3 wt.%RGO/CuCr25 are 98.31% and 98.08% respectively, which are very close to the relative density of
CuCr25 of 98.48%. The relative density of RGO/CuCr25 decreased obviously when the amount of RGO was 4.5 wt.%, and the relative density was 96.5%. Therefore, the addition of micro amount of RGO (0 ~ 0.3 wt.%) has no significant effect on the density of RGO/CuCr25. When the mass fraction of RGO is more than 4.5 wt.%, RGO overlap and agglomerate into impurity phase in the matrix, which increase the number of defects and holes in the matrix, and reduce relative density of the material. At the same time, these defects was the source of microcracks, leading to the decrease of material strength and fracture, and also undermine the conductivity of RGO/CuCr25 [18, 19].

Figure 9(b) shows that Brinell hardness and conductivity of RGO/CuCr25 with different mass fraction of RGO, and indicate that Brinell hardness and conductivity of RGO/CuCr25 composite prepared by vacuum hot pressing sintering have an increasing trend with the increase of trace amount RGO content. When the mass fraction of RGO is 3.0 wt.%, the maximum Brinell hardness of RGO/CuCr25 composite is 124.5, which is 8.3% higher than that of CuCr25 alloy of 115.0; when the mass fraction of RGO is 4.5 wt.%, the Brinell hardness of RGO/CuCr25 composite is 120.6, which is lower than 3.0 wt.%RGO/CuCr25, but is still higher than that of CuCr25 alloy without RGO. The electrical conductivity of 1.0 wt.%RGO/CuCr25 composite is 56 IACS%, and the improvement rate is 12%. When the mass fraction of RGO is 3.0 wt.% and 4.5 wt.%, the electrical conductivity of RGO/CuCr25 composite can be increased by 5.8% and 3%, to 52.9 and 51.8 IACS%, respectively. The Brinell hardness and electrical conductivity of RGO/CuCr25 composites after structure pretreatment meet the application requirements of CuCr25. RGO is used as the reinforced phase to strengthen CuCr, and the comprehensive properties of RGO/CuCr25 composite are improved by composite strengthening and refinement of Cr phase. However, the agglomeration and overlapping behavior can not be completely avoided with the increase of RGO, which has a bad effect on the relative density, Brinell hardness and electrical conductivity of RGO/CuCr25 composite.

4. Discussion

The effect of hot pressing on the refinement of Cr phase was studied by two steps [20, 21]. The first is to affect the agglomeration behavior of Cr powder in the initial mixing process and the model of Cr@RGO particle agglomeration behavior. For the original Cr without GO coating, due to the low surface energy of submicron Cr powder, it is easy for Cr to adsorb Cr particles (that is, small particles will adhere to the surface of large particles.
Figure 6. The average of Cr phase of (a) CuCr25, (b) 1.0 wt.% RGO/CuCr25, (c) 3.0 wt.% RGO/CuCr25 and (d) 4.5 wt.% RGO/CuCr25.

Figure 7. (a) SEM image of 4.5 wt.% RGO/CuCr25; (b) TEM image of 4.5 wt.% RGO/CuCr25; (c) HRTEM result of interface between Cu and Cr; (d) FFT of Cr7C3 in (c).
to form polycrystalline particles), and Cr particles will also have some cold welding behavior in the ball milling process, which makes some Cr powder agglomerate. After sintering, the size of Cr phase in CuCr25 is larger and the distribution of Cr phase is grid like. Due to the protection of RGO shell, Cr particles can effectively avoid the local agglomeration caused by the physical adsorption of Cr particles in the mixing process, thus inhibiting the plastic deformation and growth of Cr powder in the later hot pressing sintering process. The second is that the Cr@RGO structure affects the growth behavior of the Cr sintered neck during the sintering process. The solid phase sintering of CuCr25 alloy can be divided into three processes according to the theory of powder metallurgy.
sintering at 1173 K for 2 h. The original contact point and contact surface between Cu and Cr particles began to transform into crystal combination, forming sintering neck in the initial stage of sintering. Cu and Cr grains did not change significantly, and the sintered body did not shrink significantly. Then, the sintering neck diffuses to the particle bonding surface through volume diffusion, surface diffusion, grain boundary diffusion, and plastic flow in the growth stage of the sintering neck. The distance decreases to form a network of voids, and the large pores gradually shrink and disappear. In the later stage of sintering, the pore shape gradually changes into a fine ball shape. As the sintering time increases, the pores gradually disappear, thereby increasing the density of the CuCr25 alloy.

Figure 10 is the schematics of the possible Cr7C3 formation in RGO/CuCr25 composite. During sintering, Cr and Cu atoms begin to diffuse to each other, but diffusion is difficult due to low solid solubility. The hot pressing sintering process can cause minor surface damage to RGO and form discontinuous AC layers [22]. After the formation of AC layer, Cr atoms diffused to AC layer will react with AC activated carbon atoms to form Cr7C3 nucleus when the concentration reaches a certain degree. As the sintering time increases, the Cr7C3 phase grows until all activated carbon atoms are reacted.

5. Conclusions

In this work, the Cr@RGO core-shell structure was successfully prepared by the BSA electrostatic assembly method. RGO/CuCr25 composites with different mass fraction of RGO were prepared by vacuum hot pressing method, and the effects of RGO content on microstructure and properties were studied. Research shows that the Cr@RGO structure alleviates the behavior of Cr particles cold welding agglomeration in the powder mixing process, and hinders the growth of the Cr sintering neck during the sintering process. The average size of the Cr particle is 18.6 μm when the mass fraction of RGO is 4.5 wt.%, and the refining rate is 28.5% compared with the Cr phase particle size of CuCr25 of 26.1 μm. Graphene is added to the CuCr25 matrix through the Cr@RGO structure, which has little effect on the density of the RGO/CuCr25 composite material. When the amount of RGO reached 4.5 wt.%, the relative density of the composite material has a serious effect due to the agglomeration of graphene. The Brinell hardness of 3.0 wt.% RGO/CuCr25 reaches 124.5, which is 8.3% higher than that of CuCr25. When the content of RGO is 1.0 wt.%, the electrical conductivity increases by 12% compared with CuCr25. Because the addition of RGO makes the grid like Cr particles become dispersed equiaxed Cr particles, which reduces the electron scattering and improves the conductivity.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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