Study on Graphene Reinforced Copper Contact Material

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Abstract. Cu is widely used to contact materials because of its excellent electrical conductivity and economical efficiency, but its high temperature strength is slightly insufficient. In this paper, the less layers of graphene oxide were dispersed in deionized water by ultrasonic treatment, then copper acetate aqueous solution was added to the graphene oxide suspension with mixing. Then add NaOH aqueous solution into the blend solution. With graphene as a substratum, Cu $(OH)_2$ precipitations were generated so that a molecular level dispersion can be achieved. The precipitations were isolated by filtering, rinsing and drying, and then, these powders were reduced at 400℃ under a hydrogen atmosphere to form the homogeneously dispersed Cu/graphene composite powders. Sinter powders by spark plasma sintered and we obtained Cu contact materials strengthened by graphene. Under the sintering pressure of 250 Mpa, the hardness of Cu/graphene composite was 171.4 HV, which was 4.3 times than that of annealed copper; the electrical conductivity of Cu/graphene only decreased 5% and can still meet the contact demand.

1 Introduction

Electrical contact is one of the most important elements in instruments and electric switches. It is mainly responsible for the switch-on and switch-off of load current and circuit [1]. Due to the fusion welding, oxidation, and the bridge can happen in the process of repeated disconnect the closure, electrical contact materials should meet these demands [2]: high electrical conductivity, high thermal conductivity, good plasticity and toughness, high strength and hardness, resistance to arc erosion, welding and small tendency of bridging.

Cu is widely used to contact materials because of its excellent electrical conductivity and economical efficiency, but the high temperature strength is slightly insufficient. Graphene has high electrical conductivity [3], high hardness and mechanical properties, it's hardness reaches 110-120Gpa, tensile strength reaches 125GPa, Young's modulus is about 1100GPa, thermal conductivity is about 5000J/(m·K·s), carrier mobility is 2×10^5 $cm^2/(V\cdot s)$. Graphene also has good chemical stability and physical structural stability, which provides the driving force for the development of composite materials. We believe that graphene is a very good nano-filler to strengthen copper contact [4].

2 Experimental method

2.1 Preparation of Cu/graphene composite

First, graphene oxide was weighed and added to deionized water. After ultrasonic treatment for 2 hours in ultrasonic cleaning machine, we got uniform and stable monolayer oxide graphene solution [5]. Then copper acetate solid was weighed to prepare $Cu(CH_3COO)_2$ solution. Heated the copper acetate solution to 80℃ and mixed it with the dispersed grapheme [6]. Then, added NaOH solution and kept stirring, a blue flocculent precipitate was formed in the solution.

Because the graphene was uniformly dispersed in the solution, it would be the nucleating agent and $Cu(OH)_2$ would be adsorbed onto the monolayer grapheme [7], thereby CuO/graphene composites were formed. After standing, the precipitate was filtered, washed and dried to obtain a dried CuO/graphene composite. The dried powder was placed in a planetary ball mill and grinded to obtain a fine CuO/graphene composite powder [8]. Finally, CuO was heated in a hydrogen atmosphere and reduced to Cu. So we can obtain Cu/graphene composite materials.

2.2 Preparation of graphene reinforced contact materials

After graphene composite powder qualified was by XRD analysis, we used SPS320MKⅡspark plasma sintering system to perform low temperature high pressure SPS sintering. SPS sintering mold was WC mold and Sintering process was that sintering pressure was 250MPa, heating rate was 50℃ /min, sintering temperature was 600℃, holding time was 5 min. Conventional SPS sintering molds are typically made of graphite, they can only withstand the pressure below 80 MPa. So we used a special WC mold for sintering.

3 Results and discussion

3.1 XRD scanning

Using XRD to scan prepared Cu/graphene composite powder, the results obtained are shown in Figure 1

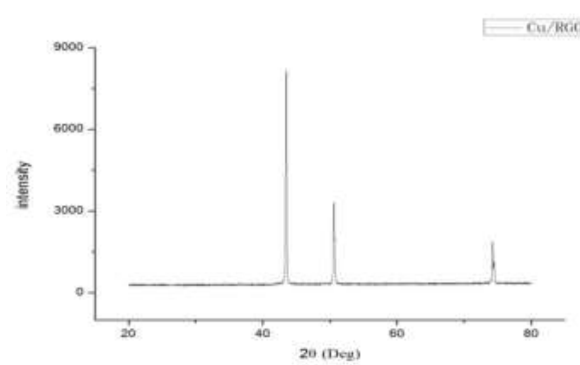

Fig.1. Results of XRD scanning of Cu/graphene composites.

Figure 1 shows that in the Cu/graphene composite powder, the characteristic peak of Cu is in full accordance with the PDF card result. The reduction process is sufficient.

By Debye-Scherrer formula ($D = \frac{K\lambda}{\beta\cos\theta}$) and using jade 6 software to draw the characteristic peak image of reduced copper, we calculated that D=79.5nm. That means the average thickness of the reduced Cu grains was 79.5nm, which shows in the Cu/graphene composite powder prepared by hydrogen reduction, Cu is nanometer.

3.2 Conductivity measurement

Conductivity was measured using an FQR-7501 eddy current conductivity meter. The conductivity is expressed in% IACS. The results are shown in Table. 1.

Table 1. Conductivity and Electrical Conductivity of Samples sintered at Different Pressure.

Sample / Conductivity (MS/m)	50 MPa	%IACS	250 MPa	%IACS
Reduced Cu	38	65.5	44.5	76.7
Cu/graphene composite	35	60.4	42	72.4

Table 1 shows that for reduced copper, the conductivity at 250Mpa reached 76.7%, increased by 17.1% than that of 50Mpa. For Cu/graphene composite, the conductivity at 250Mpa increased by 20% than 50Mpa. These results indicated that the increase of pressure has a positive effect on the improvement of conductivity. It is worth noting that at 50 MPa pressure, after adding graphene, the conductivity decreased by 7.9%. At 250MPa pressure, the conductivity only decreased by 5.6% and electrical conductivity also reached 75% IACS. At 20℃, the resistivity of pure copper is 1.7×10^-8Ω·m. The resistivity of samples prepared in this paper and that of pure copper are in the same order of magnitude.

After adding graphene, the conductivity of the sample decreased, the reason may be the following:

Effect of lattice distortion. In the actual crystal, impurities, defects, the structure of the interface between the grain is not complete will produce resistance and the addition of grapheme will cause lattice distortion defects which enhances the inhibition of electron motion, resulting in a decline in conductivity. But because of the high conductivity of graphene itself, the decline may be less than the other added components.

Effect of grain refinement. The finer the grain size, the more the number of grain boundaries, the stronger the resistance to electron motion, resulting in a decrease in conductivity.

3.3 Microhardness measurement

The samples obtained after SPS sintering were measured for microhardness with HXS-1000A. The results are shown in Table 2.

Table 2. Microhardness of Cu Samples sintered at Different Pressures.

Sample / Hardness (HV)	Pressure	
	50MPa	250MPa
Reduced Cu	130.6	137.5
Cu/graphene composite	163.7	171.4

Table 2 shows that at 50 MPa pressure, the hardness of the reduced copper reaches 3.3 times of the annealed copper. After adding graphene, the hardness reaches 4.1 times of annealed copper. The addition of graphene increased the hardness by 25.3%. At 250 MPa, the hardness of the reduced copper reaches 3.5 times of the annealed copper. After adding graphene, the hardness reaches 4.3 times of annealed copper. The addition of graphene increased the hardness by 24.7%. The increase in pressure has a certain effect on the hardness increase, they are 5.3% and 4.7%.But the effect of adding graphene on the hardness is obvious, reaching 25.3% and 24.7%.

The reasons are as follows. On one hand, as the strengthening phase, graphene has a very high hardness, the strengthening effect on the very soft Cu phase is obvious. On the other hand, increase in sintering pressure may reduce the voids and voids present within the sintered material, higher pressure results in a more compact material, thereby increasing the hardness.

3.4 SEM and EDS analysis

We conducted a SEM analysis of the Cu/graphene composites to observe the grain size of the samples and EDS surface scan of the Cu/graphene composites to analyze whether the dispersion of graphene was uniform. The results are shown in Figure 2 and Figure 3.

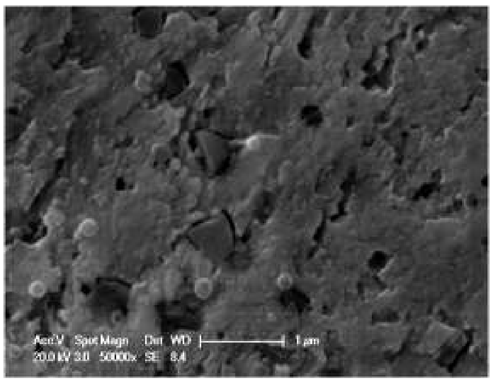

Fig.2. Cu/graphene composite SEM（50000X）scanning image.

Figure 2 shows Cu grain size is 500 nm-1µm, the Cu/graphene composites prepared in this paper are fine-grained materials.

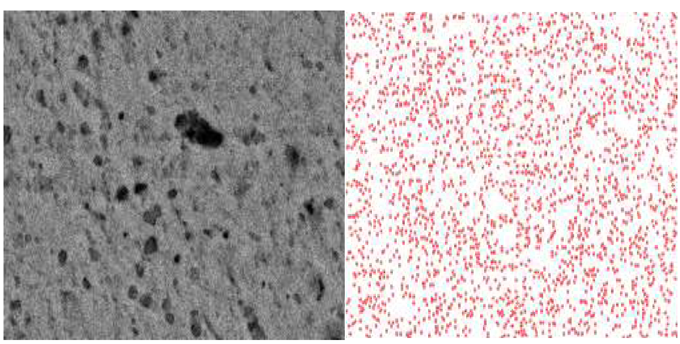

Fig.3. Micrograph of Cu/graphene composites and Carbon distribution state image.

In Figure 3, C is the graphene C is marked red. It can be seen that the distribution of graphene is uniform. Thus, we believe that the composite material is fine-grained material, graphene dispersion effect is good.

4 Conclusion

After XRD analysis, the prepared Cu/graphene composites have few impurity and high purity, Cu/graphene composites are the contact material of ultrafine grain.

The addition of graphene has a significant effect on the improvement of the hardness of copper. The conductivity of the Cu/graphene composites after graphene addition decreased only a little, still fully meet the electrical conductivity of the contact material requirements.

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