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ARTICLE

Influence of TiC Content on Microstructure and Properties of W-30Cu/TiC Composites

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Abstract: W-30Cu/xTiC(x=0~4, wt%) composite powders were prepared by electroless plating with simplified pretreatment. The composite powders were formed by cold compaction under 400 MPa using a tablet machine and green compactions were sintered at 1300 °C for 1 h. Micromorphology of the original W and TiC powders, simple-treated W and TiC powders, and as-received W-30Cu/xTiC (x=0~4) composite powders after electroless plating were characterized by field emission scanning electron microscopy (FE-SEM). Microstructures of the W-30Cu/xTiC (x=0~4) composites were also investigated by FE-SEM. The effect of TiC content on the properties of W-30Cu/xTiC (x=0~4) composites (such as relative density, hardness, electrical conductivity, and compressive strength) were studied. Results show that W-30Cu/TiC composite powders with uniform structure are obtained by simplified W and TiC powder pretreatment, followed by electroless copper plating. When TiC content is less than 1 wt%, the compressive strength and hardness of composite materials obviously increase and the electrical conductivity of composite materials decreases with TiC content increasing. However, the electrical conductivity of composite materials is still higher than that of the national standard value. With a certain amount of TiC content to W-30Cu/xTiC (x=0~4) composites, the composites exhibit good comprehensive performance.

Key words: simplified pretreatment; electroless plating; W-Cu/TiC composites; performance

W-Cu composite materials are widely used as electrode, contact, electronic packaging, and target materials because of the combined excellent properties of W and Cu. W-Cu composites exhibit high strength and hardness, good electrical and thermal conductivity, low heat expansion coefficient, arc erosion resistance, high-temperature oxidation resistance, and welding resistance [1-5]. Electric contact materials require not only good mechanical and physical performance but also good chemical stability; W-Cu composite materials are currently in increasing demands as the electric contact materials[6]. TiC has unique properties such as high melting point, high elastic modulus, and extreme hardness[7, 8]. Dispersed TiC nanoparticles can inhibit grain growth during sintering, hinder grain boundary sliding, and stabilize microstructure when exposed to high temperature. These nanoparticles can act as annihilation points for radiation-induced defects, leading to improved irradiation resistance of materials. Therefore, the hardness, fracture strength, and room-temperature ductility of the TiC-dispersed W-Cu composites were effectively improved[9]. Nanopowder can significantly reduce sintering activation energy of the powder, enable the composite powder to exhibit excellent sintering activation, reduce sintering temperature, and shorten the sintering time effectively. Mechanical alloying and precipitation-coating processes were available to prepare superfine/nano composite powders[10-12]. The mechanical alloying process produced a detrimental phase on the wear of the milling equipment and media. The precipitation-coating process is very complex and incapable of mass production.

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Electroless plating is an autocatalytic method in which the reduction of metallic ions in the solution and film deposition can be carried out by oxidizing the present chemical compound in the solution. Basic requirements for an electroless bath include metal ions/their concentration, reducing agent(s), complexing agent(s), bath stabilizer(s), and control of pH and temperature. In electroless deposition, metal ions were reduced to metal by the action of chemical reducing agents which were simple electron donors. The metal ions were electron acceptors that react with electron donors[13,14]. The method does not require a current supply and sets no limits on the shape and type of substrate. Electroless plating produced composite powder with even phase dispersion and high purity. Many types of composite powder, including Ni-WC, Ag-Al_2O_3, Co-Al_2O_3, Ni-Cr_3C_2, Cu-Ag, and Ni-W/SiC, had been successfully prepared in the past through electroless plating[15-20]. Interactions of W-Cu and TiC-Cu are weak to enable excellent catalytic activity on the surface of the powder to be coated in case of uneven coating, rough coating layer, poor tightness, and even difficult coating. Pretreatment of W and TiC should be performed prior to electroless plating. Precious metal activation is a pretreatment method that produces the optimal results. However, the cost of this method is high because of the high price of palladium and other precious metals[21, 22].

The present paper aimed to study the influence of TiC contents on microstructure, relative density, hardness, and compressive strength of W-Cu composite after simplified pretreatment of W and TiC powders at room temperature.

1 Experiment

Simplified pretreatment of W (grain diameter of 1.16 μm) and TiC (grain diameter of 500 nm) was performed before electroless plating to produce a surface with catalytic activity. The produced W and TiC powders from simplified pretreatment were placed in a pre-made Cu plating solution for electroless plating Cu. The W-30Cu/TiC composite powders were compacted into 40 mm × 8 mm dimension under pressure of 400 MPa by a tablet machine. The as-reserved green samples were sintered at 1 300 °C for 60 min in a flowing hydrogen atmosphere.

FE-SEM was used to characterize the morphology of the TiC powders before and after simplified pretreatment and W-30Cu/TiC composite powder after electroless plating. The relative density of W-30Cu/TiC composites were measured based on the Archimedes' principle. Vickers micro-hardness test and compression test composite materials were used to characterize the mechanical properties of W-30Cu/TiC composites.

2 Results and Discussion

2.1 Characterization of powders

Chemical deposition on the surface of the powder is related to the catalytic capability of the plated surface. Considering the chemical inertness of W and TiC particles, W and TiC powders were pretreated to form the surface with good catalytic activities. To compare the changes in morphology after pretreatment, Fig.1a shows the surface morphology of the original TiC powder prior to pretreatment. There are no obvious defects on the surface of the original TiC particles. Fig.1b shows the surface morphology of the TiC powder after simplified pretreatment and some obvious steps on the surface. Catalytic capability is exhibited during activation. The activation on the surface of the solid is related to the number of active centers on the solid surface. These centers pertain to surface defects, such as step (e.g., obvious steps on the surface of the TiC powder after simplified pretreatment). These positions easily adsorb foreign matter bonding. Conventional electroless plating does not produce ceramic powder with catalytic activation on the coated surface. The simplified pretreatment process forms obvious steps on the surface of TiC powder after simplified pretreatment (Fig.1b). The existence of surface steps in TiC powders increases their specific surface areas and surface catalytic activities remarkably. These features are beneficial to the adsorption, nucleation, and growth of Cu particles during electroless plating.

In electroless deposition, metal ions are reduced to metal by the action of chemical reducing agents which are simple electron donors. The metal ions are electron acceptors that

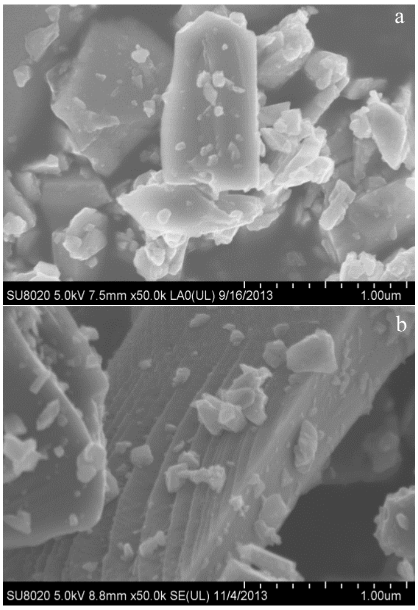

Fig. 1 FE-SEM morphologies of original TiC powders (a) and TiC powders after pretreatment (b)

react with electron donors. FE-SEM micrographs of W and TiC complex powders after electroless Cu plating through simplified pretreatment are displayed in Fig. 2. The Cu coating on the surface of W and TiC particles shows a cell structure and uniform distribution. Almost no Cu uncoated particles are developed. The active surface enhances the wettability of the powders in aqua solutions of metalion species. The Cu^{2+} ions in the electroless plating solution are dispersed on the activated catalytic surface of the W and TiC powders. Hydrogen bubbles are observed during plating. The reacting substance is adsorbed on the defective surface with catalytic activation to produce an oxidation-reduction reaction for depositing Cu grains. Subsequently, the Cu particles grow. Through this reaction, the Cu grains are adsorbed on the surface defect of W and TiC powders to nucleate and grow. Therefore, the surface steps of the pretreated W and TiC powders are the active centers of nucleation and growth of the Cu particles.

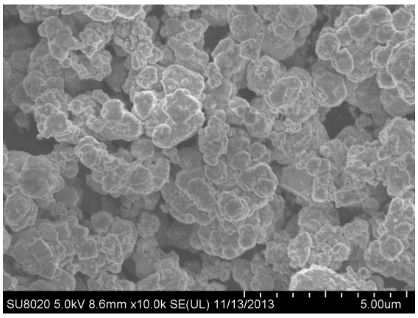

Fig. 2 FE-SEM morphology of the W and TiC complex powders after electroless Cu plating

2.2 Characterization of sintered samples

Table 1 shows the relationship between relative density and TiC content in the composite. As the TiC content increases, the relative density decreases. This finding may be attributed to the following reasons. The density of TiC (4.93 g/cm^3) is lower than those of W and Cu. Therefore, the density of the W-Cu composite decreases with the increased TiC content. The sintered process is performed at 1300 °C; however, the melting temperature of Cu is 1083 °C. During the sintering process, the Cu melt and become liquid. In liquid phase sintering, densification of the W-Cu composite depends mainly on the rearrangement of the W particles. However, the addition of TiC hinders the rearrangement of the W particles to a certain extent, thus affecting the densification of the composite. Therefore, the more content of TiC are added, the more rearrangement of the W particles are hindered. At high temperature, the wettability between TiC and Cu is poorer than that between W and Cu. Therefore, with the increased TiC contents, relative density of the composite material decreases.

Table 1 Relative density of W-30Cu/xTiC composite

x	0	0.25	0.5	1	2	3	4
Density/%	97.58	94.68	92.43	88.28	83.38	82.40	78.84

Fig.3 shows the metallographic micrographs of the W-30Cu/TiC composite. Fig. 3a~3c show that the composites have uniform and homogenous microstructures with fine particles when the TiC content is within a certain range. The addition of TiC reduces the contact between W and W, thus promoting the refinement of particles after sintering. However, the composite is characterized by the formation of agglomerated particles and Cu pools when the TiC content is 2 wt% (Fig.3d). This characterization may be ascribed to the poor wetability between TiC and Cu. Consequently, the increase of TiC content hinders the flow of Cu liquid, resulting in a sintered bulk with composition segregation and low density.

Fig. 4 shows the FE-SEM morphologies of the fractured W-30Cu/TiC composites. Some thin Cu layers exist as a network between W and TiC particles, and the network becames more intact with the TiC content increased to 1 wt% (Fig.4a~4d). TiC served the role of dispersion strengthening. However, the network becomes discontinues with the TiC content increasing to 2 wt%. It is ascribed to the reinforcing particles which start to gather on the grain boundary with the TiC content increasing to 2 wt%, which significantly reduces the bonding strength between particles. And some voids and holes in the cross section are found in the W-30Cu-2TiC (wt%) composites with very low density.

The electrical conductivity, Vickers microhardness and the room temperature compressive strength of W-30Cu/xTiC composites are shown in Table 2. As the TiC content increases, the electrical resistivity of W-30Cu/xTiC composites also increases. This change in the values may be attributed to the electrical conductivity of TiC which is lower than those of W and Cu. Despite the electrical conductivity decreasing, when the TiC content is 1 wt%, the electrical conductivity (as percent of the International Annealed Copper Standard) of the composite reaches 49.78%, which is higher than the national standard value (electrical conductivity of GB/T 8320-2003 is 42%) of 18.53%. However, when the TiC content is 4 wt%, the electrical conductivity of the composite reaches 45.61%, which is higher than the national standard value of 8.60%. And the Vickers microhardness of composite increases with the TiC content increasing. This finding may be attributed to that the hardness of TiC is higher than those of W and Cu, and the addition of TiC particle reduces the connection between the W and W particles. As Table 2 shows, when the TiC content is less than 1 wt%, the compressive strength of the composite increases with the TiC content increasing.

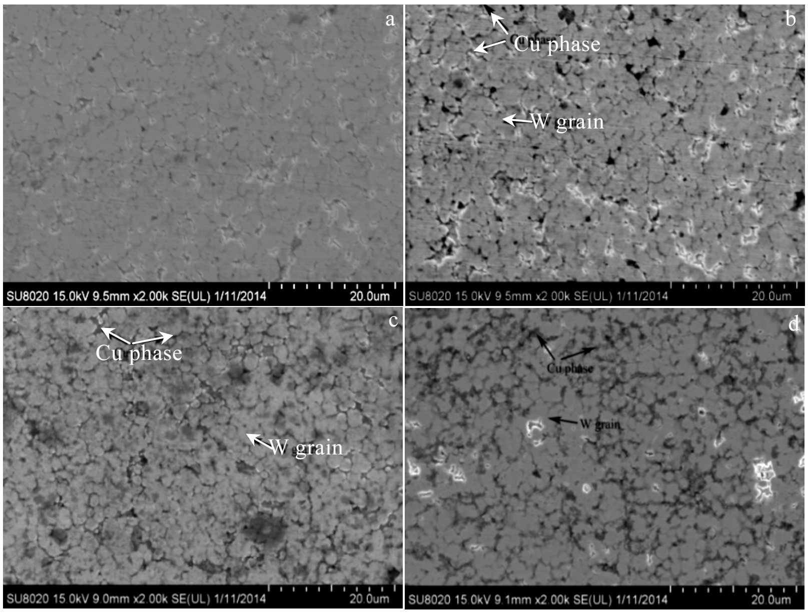

Fig.3 FE-SEM micrographs of W-30Cu/xTiC composites: (a) x=0, (b) x=0.5, (c) x=1, and (d) x=2

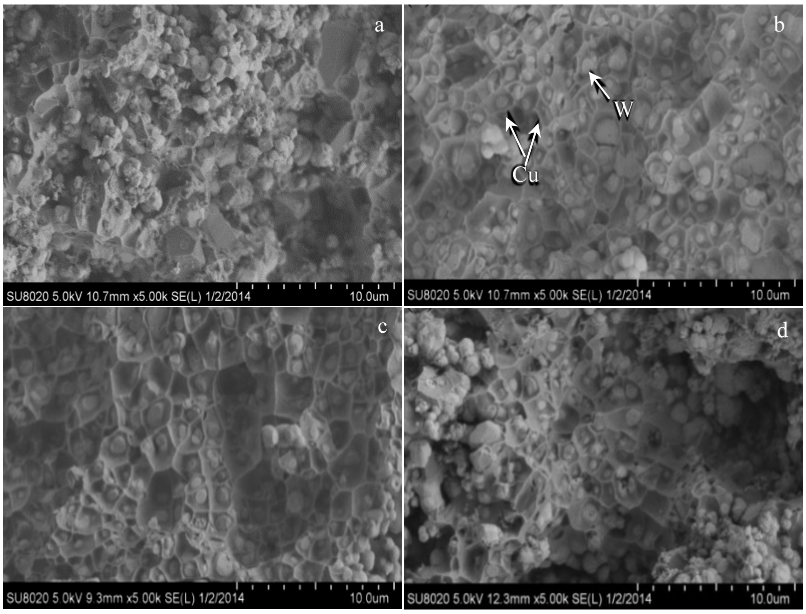

Fig.4 FE-SEM morphologies of the fractured W-30Cu/xTiC composites: (a) x=0, (b) x=0.5, (c) x=1, and (d) x=2

It is attributed to that the network becomes more intact, and the composite has uniform and homogenous microstructures with fine particles with the TiC content increasing to 1 wt%. These feature makes the compressive strength increase. However, when the TiC content is more than 1 wt%, the compressive strength of the composite decreases substantially. This phenomenon is ascribed to the reinforcing particles gathering on the grain boundary with the TiC content increasing to 2 wt%, which significantly reduces the bonding strength between particles. The addition of TiC particle to the composite decreases their density, and

Table 2 Electrical conductivity, microhardness (HV) and the room temperature compressive strength of W-30Cu/xTiC composites

x	Conductivity/%	HV/MPa	Strength/MPa
0	59.13	3584	447.3
0.25	51.65	4947	523.6
0.5	51.12	6289	602.4
1	49.78	6852	847.6
2	47.45	7402	404.2
3	46.52	7947	321.7
4	45.61	8465	250.6

some voids and holes are presented in the W-30Cu-2TiC composite.

3 Conclusions

1) W-30Cu/TiC composite powders with uniform structure are prepared by electroless plating with simplified pretreatment. W-Cu/TiC composites are fabricated via powder metallurgy.

2) The TiC content influences the comprehensive performance of the composite materials. Adding a certain amount of TiC content ($x \le 1$) increases the compressive strength and hardness of the composite effectively, while decreases their electrical conductivity.

3) When the TiC content is 1 wt%, the electrical conductivity of the composite reaches 49.78%, which is higher than the national standard of 18.53%.

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TiC 含量对 W-30Cu/TiC 复合材料显微结构和性能的影响

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摘 要：经简化预处理后，采用化学法制得 W-30Cu/xTiC (x= 0~4, 质量分数%)复合粉末，在 400 MPa 压力下，将制得的复合粉末压制成毛坯块体试样，随后在 1300 ℃下烧结 1 h 制得块体复合材料试样。采用场发射扫描电镜来表征原始 W 和 TiC 粉末、预处理后的 W 和 TiC 粉末、化学法制得的 W-30Cu/xTiC (x= 0~4)复合粉末的显微形貌，以及制得的 W-30Cu/TiC 复合材料的显微结构。对不同 TiC 含量对 W-30Cu/TiC 复合材料性能（相对密度、硬度、导电性和抗弯强度等）进行研究。结果表明：对简单预处理后的 W、TiC 粉末化学镀 Cu 所获得的 W-30Cu/TiC 复合粉末的显微结构均匀。TiC 含量低于 1%时，W-30Cu/TiC 复合材料的抗弯强度和硬度随 TiC 含量的增加而显著增大。而导电性则随 TiC 含量增加而减小，但仍高于国家标准值。添加一定量的 TiC 有利于获得综合性能较好的 W 30Cu/TiC 复合材料。

关键词：简单预处理；化学镀；W-Cu/TiC 复合材料；性能

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