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ARTICLE

Fabrication of W/Cu Graded Heat-sink Materials by Electroless Plating and Powder Metallurgy

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Abstract: The W/Cu graded heat-sink materials with high density were fabricated by electroless plating and powder metallurgy. The microstructure, interface and fracture of the graded heat-sink materials were observed using the field emission scanning electron microscope (FESEM). The mechanical properties of the materials such as bending strength and hardness were determined. The results show that the structure of each layer is uniform and dense. The components of the cross-section present a graded distribution. There is no obvious interface among layers. The relative density of three-layer W/Cu graded heat-sink materials reaches 99.2%. The average values of microhardness HV of the radiating layer, the transitional layer and the sealing layer are 2000, 2100, 2400 MPa, respectively. It is indicated through the experimental results of bending strength that the bending strengths of the sealing layer and the radiating layer as the load-bearing surfaces are 428.5 and 480.7 MPa, respectively.

Key words: electroless plating; powder metallurgy; W/Cu graded heat-sink materials

The plasma facing components (PFC) are mainly composed of two parts, plasma facing materials (PFM) and heat sink materials (HSM). Meanwhile, a good contact between them is required [1-3]. With the characteristics of high-melting point, low vapor pressure, low sputtering rate and low retention of tritium, tungsten is used for the plasma facing materials [4,5]. In addition, due to their excellent thermal conductivity, copper and its alloys are used for the heat sink materials. However, owing to the great difference of the properties between tungsten and copper and mutual immiscibility [6-9], the bonding strength of them at the interface of PFC W/Cu is low. Two kinds of thermal load stresses[10] emerge under high thermal load. Therefore, a suitable transition layer is necessary between the two layers in order to relieve the thermal stress and to increase the heat-transfer effect. The W/Cu graded heat-sink materials are considered as the most effective method to solve this problem [10,11]. The advantage of the W/Cu graded heat-sink materials is the excellent relief of the thermal stress because of the mismatching of thermal properties between W and Cu. Generally, this kind of graded material has excellent properties such as mechanical property, ablation resistance and thermal shock resistance, which enables the maximization of the respective advantages of W and Cu. The selection and design of the W/Cu functionally graded materials as an interlayer have been extensively studied. For example, W/Cu functionally graded materials were manufactured by plasma spraying process to reduce the thermal stress[12]. The researchers put forward three methods, diffusion bonding to CuCrZr after plasma spraying of oxygen-free copper in the tungsten rod, diffusion bonding to CuCrZr after casting of oxygen-free copper and direct diffusion bonding to CuCrZr [13]. The use of W/Cu graded heat-sink materials is most reported in literatures. The joined interface of W/Cu would disappear with the use of the materials, and the thermal stresses are

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well relieved. Therefore, the service life of PFC is prolonged[14-16]. Presently, the fabrication methods of W/Cu functionally graded materials mainly include a conventional powder metallurgy method [17-19], a ultra-high pressure sintering method[20,21], a microwave sintering method[22], plasma spraying method [23,24], etc. In the present study, the W-10Cu, W-30Cu and W-50Cu powders were first fabricated by electroless plating, and then the W/Cu graded heat-sink materials with high density were obtained by the conventional powder metallurgy method. The microstructure, interface and anti-bending fracture of the graded heat-sink materials were observed by the FESEM. The mechanical properties and fracture mechanism were studied.

1 Experiment

1.1 Fabrication of W-Cu composite powder

The W powders used in the experiment were manufactured by Xiamen Golden Egret Special Alloy Co., Ltd. The average particle size was 3 μm, and the purity was greater than 99.9%. The morphology of the W powders was polygon, as shown in Fig.1. The W-10Cu, W-30Cu and W-50Cu powders were fabricated by electroless plating. The chemical activation was required for W powders before electroless plating to obtain the surface with catalytic activity. The detailed activation process is described in Ref.[25]. The W powders after chemical activation was put into the prepared copper-plating solution. The formulation of the plating solution is shown in Table 1, including main salt, reductant, complexing agent, stabilizer and modifier. The copper sulfate was the main salt, and the formaldehyde was the reductant. The EDTA was the complexing agent, and the 2, 2'-bipyridine was the stabilizer. During the process of electroless plating, the pH value of the plating solution was controlled to be in the range of 11~13 using sodium hydroxides. The W-Cu composite powders with different contents of copper were obtained by controlling the amounts of main salt in the plating solution. The electroless plating was performed in the thermostat water bath, and the temperature during the process was controlled at 60 ℃. The plating solution was stirred continuously to ensure a uniform dispersion of W powders. The whole process took approximately 50 min. After electroless plating, the W-Cu composite powders obtained were cleaned with deionized water for several times until the residual liquid was clear. Then, the mixture was dried in the vacuum drying oven at 70 ℃ for 4 h.

1.2 Fabrication of W/Cu graded heat-sink material

The compacts of W/Cu graded heat-sink materials were obtained by segmented compaction of the prepared W-10Cu, W-30Cu and W-50Cu powders under YP-40C sheeting mill. Then, the compacts were placed for 1 h under the hydrogen atmosphere in the tubular sintering furnace at 1100 ℃ and then sintered. The samples were cooled to the room temperature in the furnace. The W/Cu graded heat-sink materials obtained in the experiment consisted of three layers, the sealing layer, the transitional layer and the radiating layer. The components were W-10Cu, W-30Cu and W-50Cu, respectively. The thickness of each layer (after sintering) was 0.8, 0.8 and 0.8 mm, respectively.

1.3 Microstructure and performance detection

The relative density of W/Cu graded heat-sink materials was determined by a drainage method. The microstructure and fracture morphology of the powders and graded materials were observed by SU8020 FESEM. The hardness was determined by Vickers hardness tester. The bending strength of the sample was determined by a three-point bending method on the DCS-3000 Shimadzu tester. The size of the sample was 45 mm×8 mm×2.4 mm. The loading rate was 0.2 mm/min, and the span was 25 mm. The sealing layer and the radiating layer served as the load-bearing surface of the sample.

2 Results and discussion

2.1 Morphology analysis of W-Cu composite powder

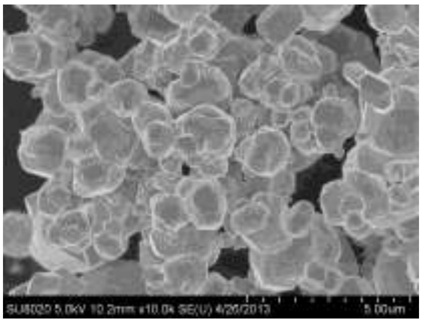

Fig.1 SEM morphology of W powders used in experiments

Table 1 Composition of the electroless copper plating solution

Chemical	Formula	Effect	Concentration
Copper sulfate	$CuSO_4$ $5H_2O$	Main salt	10~20 g/L
Formaldehyde	HCHO	Reducing agent	15~30 g/L
Sodium EDTA	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	Complexing agent	30~50 g/L
2, 2 '- Dipyridyl	$C_{10}H_8N_2$	Buffer agent	0.01~0.06 g/L
Sodium hydroxide	NaOH	Regulator	pH: 11~13

The SEM surface morphologies of W-Cu composite powders of different compositions are shown in Fig.2. As shown in Fig.2, three kinds of W-Cu powders with different copper contents all have the core-shell structure. The shell is made of Cu particles, and the core is W particles. There is no simple substance of W existing in the three kinds of composite powders. We discover through the EDS analysis that the surface of W-10Cu composite powders has Cu particles in different sizes (represented by arrows A and B in Fig.2a). The Cu particles are uniformly coated on the surfaces of W particles in W-30Cu and W-50Cu composite powders. The size of the particles is 200~500 nm (represented by arrow C in Fig.2b and in Fig.2c). When the three kinds of powders are compacted and sintered, the direct contact between W particles is avoided. The contact is all between Cu particles, which are favorable for the formation of W/Cu alloy with high density after sintering. Meanwhile, ultra-fine Cu particles inhibit the growth of W particles in the process of sintering, which is beneficial for the structural property of the bulk materials after sintering.

2.2 Microstructure of W/Cu graded heat-sink material

The SEM images of the interfaces between layers and the microstructure of each layer are shown in Fig.3. The white area in images represents the distribution of W, while the black area represents the distribution of Cu (arrows A and B in Fig.3c). As shown in Fig.3a~3f, the whole structure is composed of two components, W and Cu, with uniform distribution. The W is granular, and Cu is coated on W particles uniformly. No obvious defects such as pores are identified in the whole structure. The average relative density of the sample reaches over 99.2%. As shown in Fig.3a and Fig.3b, the boundaries designed originally among the three layers are quite obscured. The EDS of three areas was determined successively from the radiating layer to the sealing layer of the sample. We find that the composition of the radiating layer is W: 53.10 wt%, Cu: 46.90 wt%; that of the transitional layer is W: 68.32 wt%, Cu: 31.68 wt%; that of the sealing layer is W: 87.26 wt%, Cu: 12.74 wt%. Therefore, the W/Cu components still present an obvious graded distribution. There are few differences from the components originally designed. However, the copper content has an increase from the radiating layer to sealing layer. This is because the relocation diffusion of Cu causes the deviation of the components of each layer from the originally designed components during the process of sintering. Meanwhile, there is no obvious growth of the W particles during the process of sintering. The size of W particles is consistent with that of the original W particles. The results indicate that there is an obvious inhibitory action of nano-crystalline Cu particles on the growth of W particles in W-Cu powders prepared by electroless plating.

2.3 Mechanical properties and fracture analysis of W/Cu graded heat-sink materials

The average values of microhardness HV of the radiating layer, transitional layer and the sealing layer of W/Cu graded heat-sink materials are 2000, 2800 and 3400 MPa, respectively. The experimental results of bending strength indicate that the bending strengths of the sealing layer and the radiating layer as load-bearing surface are 428.5 and 480.7 MPa, respectively. Therefore, the mechanical properties of the sample show certain variation along the gradient direction. The hardness of the materials is decreased and the bending strength is increased from the sealing layer to the radiating layer due to the increase of Cu content.

The fracture morphology of the W-Cu graded materials is shown in Fig.4. As shown in Fig.4, the material has an excellent densified structure. There are no obvious defects. The continuous mesh structure constituted by Cu is coated on the surface of W particles uniformly. This kind of mesh structure provides a channel of rapid thermal conduction for the graded heat-sink materials. The fracture morphology of the radiating layer is shown in Fig.4a. The ductile fracture of Cu is the dominant fracture mode of the radiating layer. There is no pull-out of a large number of W particles. This indicates that W particles have excellent bonding with the ultrafine Cu layer. The fracture morphology of the sealing layer is shown in Fig.4b. The pull-out of some W particles and the fracture of some other W particles are the dominant fracture modes of the sealing layer. The fracture of W particles is beneficial for the improvement of bending strength of the materials.

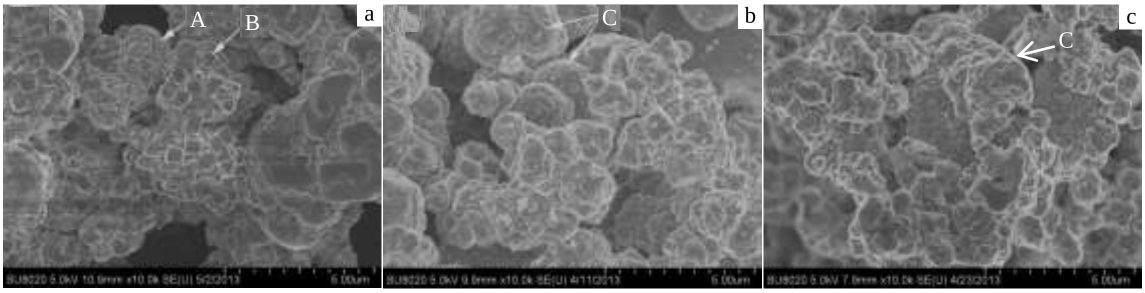

Fig.2 SEM morphologies of W-Cu composite powders: (a) W-10Cu, (b) W-30Cu, and (c) W-50Cu

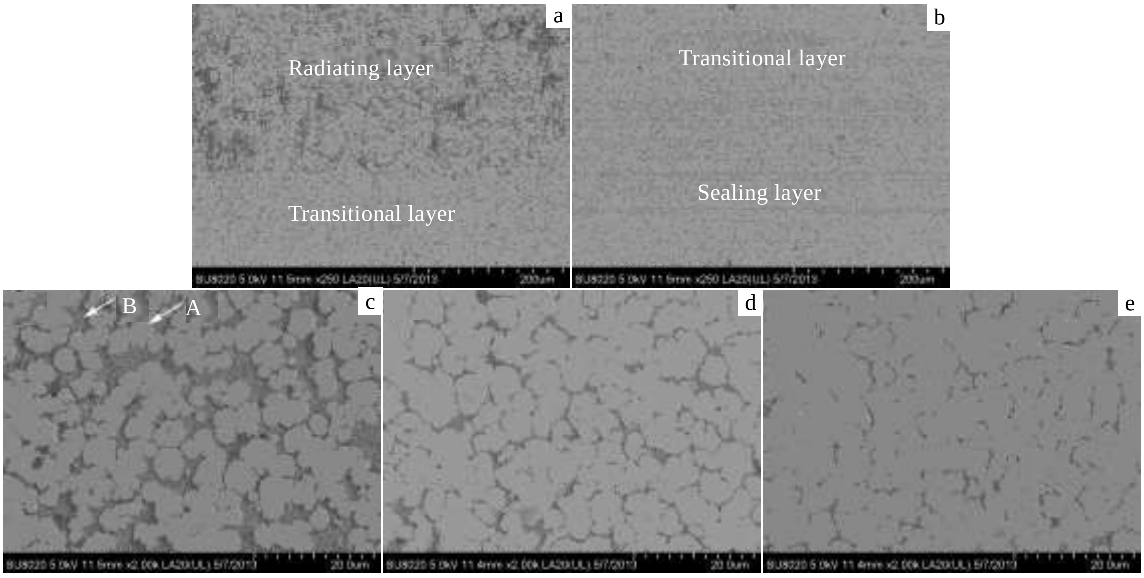

Fig.3 SEM microstructures of cross-section and interface of W-Cu gradient material: (a) interface between radiating layer and transitional layer, (b) interface between transitional layer and sealing layer, (c) cross-section of radiating layer, (d) cross-section of transitional layer, and (e) cross-section of sealing layer

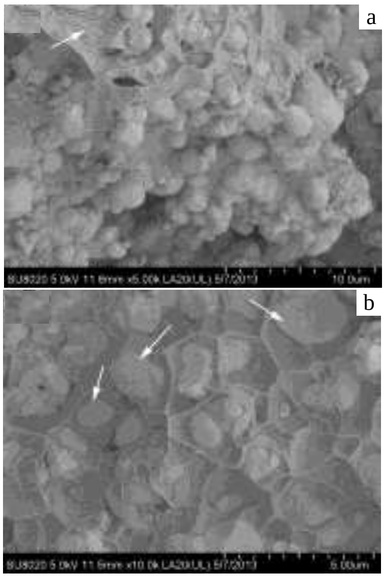

Fig.4 Morphologies of fracture surfaces of W-Cu gradient material: (a) radiating layer (W-50Cu) and (b) sealing layer (W-10Cu)

3 Conclusions

1) W/Cu graded heat-sink materials with high density are prepared by electroless plating and powder metallurgy.

2) The structure of each layer is uniform and dense, with no obvious interface among layers. The continuous mesh structure constituted by Cu is coated on the surface of W particles uniformly. Meanwhile, there is no obvious growth of W particles. The relative density of the three-layer W/Cu graded materials reaches 99.2%. Thus, the ideal microstructure of the graded heat-sink materials is obtained.

3) The mechanical properties of the sample show certain variation along the gradient direction. The fracture mode of the materials transits from the dominance of ductile fracture of copper to the dominance of pull-out of part of the W particles and fracture of some other W particles from the radiating layer to the sealing layer.

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化学镀和粉末冶金法制备 W/Cu 梯度热沉材料

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摘　要：用化学镀法和粉末冶金的方法制备高致密的W/Cu梯度热沉材料。用场发射扫描电镜观察了材料的组织结构、界面和断口形貌。对材料的力学性能也进行了表征，如抗弯强度和显微硬度。结果表明材料每一层都很致密且组织结构均匀。截面上材料成分呈梯度分布，每层之间没有明显的界面。3层W/Cu梯度热沉材料的相对密度可达99.2%。散热层、过渡层和封接层的显微硬度HV分别是2000、2100和2400 MPa。抗弯实验结果显示封接层和散热层作为承重抗弯表面时的强度分别是428.5和480.7 MPa。

关键词：化学镀；粉末冶金；W/Cu 梯度热沉材料

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