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ARTICLE

Effect of Rare Earth Oxide Addition on the Microstructure and Properties of Ultrafine Grain W-20Cu Composites

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Abstract: Ultrafine W-20wt%Cu (W-20Cu) powders doped with 0 wt%~0.8 wt% rare earth oxides $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) were synthesized by the EDTA-citrate method using ammonium metatungstate and copper nitrate as raw materials, and the resultant powders were pressed and sintered at 1250 °C in H_2 atmosphere for 2 h to obtain SDC/W-20Cu composites. Morphology of the SDC/W-20Cu powders and microstructure of the sintered SDC/W-20Cu composites were observed by SEM, and density, physical and mechanical property of sintered SDC/W-20Cu composites were also tested to investigate the influence of rare earth addition. The results show that the SDC/W-20Cu powders are irregular in shape with particle size ranging from 100 nm to 200 nm. The addition of SDC has slight influence on the electrical conductivity, but obviously refines the grain size and improves the mechanical properties of the W-20Cu composites. The sintered SDC/W-20Cu samples have relative density above 97%. Bending strength and micro-hardness HV of the SDC/W-20Cu specimens are 1128 MPa and 3180 MPa with the addition of 0.6 wt% SDC, respectively, and the highest tensile strength reaches 580 MPa and 258 MPa at room temperature and 600°C, respectively.

Key words: SDC/W-20Cu composites; ultrafine powders; rare earth doping; microstructure; property

W-Cu materials have been widely used in electronic packaging, electrical contacts, heat sinks and some other industrial applications because they can combine the intrinsic properties of W and Cu, i.e. excellent thermal and electrical conductivity, low thermal expansion coefficient, high resistance to erosion and arc welding, etc [1-4]. At present, W-Cu composites are mainly prepared by powder metallurgy processes, such as infiltrating tungsten skeleton by liquid Cu and liquid phase sintering of W-Cu powder compacts[5,6]. However, due to the high hardness and poor formability of W powders, it is difficult to prepare a W skeleton with desired pores. Moreover, the poor wettability and low solubility between W and Cu make the W-Cu system have poor sinterability. Thus, it is difficult to fabricate W-Cu composites with high relative density and homogeneous microstructure by the method of liquid phase sintering[7,8].

Recently, more severe service conditions have been put forward for the electrical and electronic devices, which consequently raise rigorous requirements for the W-Cu components used in the fields. To meet these requirements, W-Cu composites with fine grains and full density are often needed, and much work has been done in the preparation and characterization of ultrafine or nanosized W-Cu powders, as well as their composites, and some wet chemical synthesis routes and doping with some rare earths have shown to be effective ways[9-11]. Some researches have shown that the addition of rare earth oxides into W-Cu materials can obviously refine the grain size and improve the mechanical properties, and prolong their service life[12,13]. Samaria doped ceria ($Ce_{0.8}Sm_{0.2}O_{1.9}$, SDC) is a kind of rare earth compound oxide, which has relatively high electrical and ionic conductivity, and has shown potential for improving the electrical conductivity and other properties of the

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electrolytes of solid oxide fuel cell (SOFC) and in some other applications[14]. Up to now, however, there are few reports on employing SDC as dopants in W-Cu materials.

The preparation methods also have obvious influence on the particle characteristics of the synthesized W-Cu powders, which in turn affect the sinterability of the powders, as well as the microstructure and properties of the sintered W-Cu composites. So many attempts such as co-precipitation, sol-gel, spray-drying and other wet chemical processes have been tried to prepare W-Cu powders with ultrafine particles and homogeneous composition distribution[15-17]. EDTA-citrate method is a wet chemical method for preparing inorganic ceramic powders, which has the advantages of simple operation, low equipment requirements, relatively inexpensive raw materials and high compositional homogeneity[18]. In this work, the EDTA-citrate method was employed to synthesize W-20Cu composite powders doped with different amounts of rare earth oxides $Ce_{1.9}Sm_{0.2}O_3$ (SDC). Density, microstructure and performances of the SDC/W-20Cu composites were tested to investigate the influences of rare earth addition.

1 Experiment

To synthesize the SDC/W-20Cu powders, ammonium meta-tungstate, copper nitrate, cerium nitrate and samarium nitrate were used as raw materials. Stoichiometric chemicals were added into an aqueous solution containing edetic acid and citric acid to form a mixed solution, and aqueous ammonia was added into the solution to maintain the pH value. The mixed solution was heated to 80 °C to form wet gels. After drying and calcining, the gels were reduced at 800 °C in H_2 to obtain SDC/W-20Cu composite powders with 0 wt%~0.8 wt% SDC. X-ray diffraction (X'Pert PRO MPD) and field emission scanning electron microscope (SU8020) were used to analyze the phase composition and the morphology of SDC/W-20Cu composite powders.

The as-prepared SDC/W-20Cu powders were pressed at a pressure of 400 MPa in a cylindrical die of 20 mm in diameter, and a 5 mm×45 mm square die. The green compacts were subsequently sintered at 1250 °C in H_2 atmosphere for 2 h. Relative density of the sintered SDC/W-Cu samples was measured by the Archimedes' method, and microstructure was observed by field emission scanning electron microscopy coupled with energy dispersive spectroscopy. Electrical conductivity of the sintered SDC/W-Cu samples was measured by DC four-probe method, and thermal conductivity was measured by a piece of laser-flash thermal conductivity apparatus (LAF457). Bending strength and tensile strength of the sintered samples were tested in Axial/Torsional test system machine (MTS-809) at room temperature and 600 °C, and Vickers hardness of polished SDC/W-Cu samples was also measured under a maximum load of 100 g (MH-6).

2 Results and Discussion

2.1 Characterization of the SDC/W-20Cu powders

Fig. 1 shows XRD patterns of the SDC/W-20Cu powders with different amounts of SDC dopants (0 wt%~0.8 wt%). The powders contain W and Cu phases, and no residual metallic oxides are found. No diffraction peaks of SDC are detected owing to the low amount of SDC addition less than 1 wt%.

Fig. 2 shows FE-SEM images of the SDC/W-20Cu powders with 0.8 wt% SDC reduced at 800 °C in H_2. The particles exhibit irregular shapes with particle size of 100~200 nm (Fig. 2a). The powders are liable to agglomerate owing to their ultrafine size. Results of the EDS analysis reveal that the weight ratio of W to Cu in the powders corresponds with the designed value, and oxygen, cerium and samarium signals are also detected (Fig. 2b).

2.2 Sintering densification and microstructure of the SDC/W-20Cu composites

Fig. 3 shows the effects of SDC addition on the sintering densification of the W-20Cu composites. Density and relative density of the samples decrease slightly with the increase of SDC addition. The addition of SDC results in the decrease of the theoretical density of the W-20Cu composites owing to the relatively low density of SDC (theoretical density is 7.12 g/cm^3). On the other hand, as shown in Fig. 4, there are more gaps on the surface of the W-20Cu composites with the increase of SDC addition, which also lead to the decrease of the relative density. This can be ascribed that the SDC particles, as a secondary phase, will impede the rearrangement of W particles and the flow of the Cu liquid phase during the sintering.

Fig.5 shows fracture surfaces of the sintered SDC/W-20Cu composites with different SDC additions. It reveals that W and Cu phases are distributed homogeneously and each W particle is wrapped by continuous copper network.

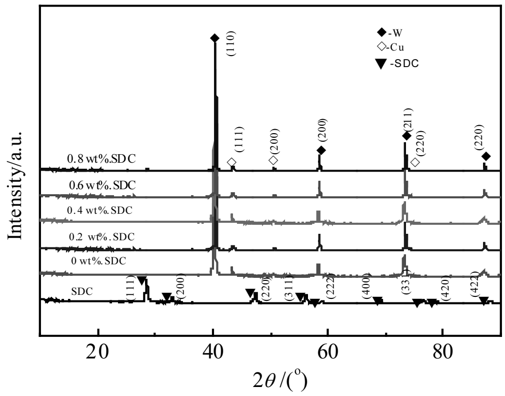

Fig.1 XRD patterns of the SDC/W-20Cu powders with different doping amount of SDC

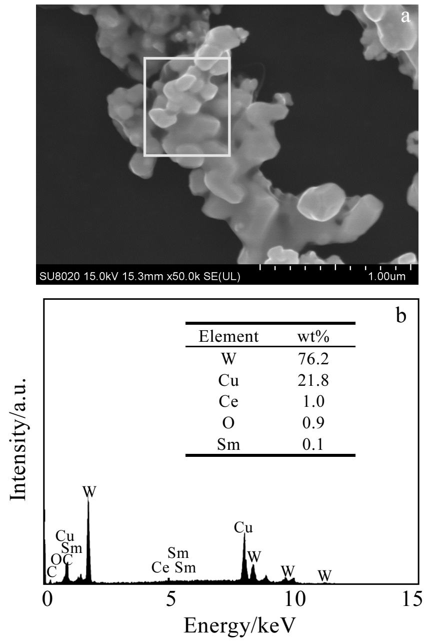

Fig. 2 SEM morphology (a) and EDS analysis (b) of SDC/W-20Cu powders added with 0.8 wt% of SDC

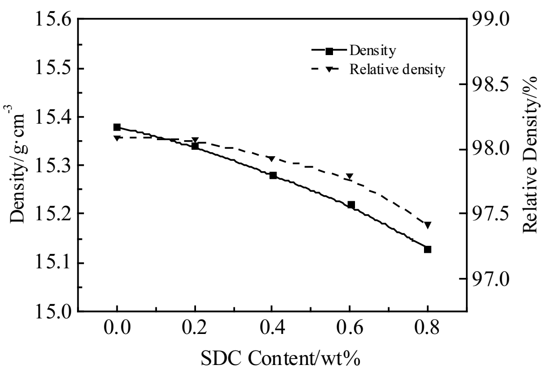

Fig. 3 Density of the SDC/W-20Cu composites containing different amounts of SDC sintered at 1250 °C

The grain size is less than 1μm, and it decreases obviously with the increase of SDC addition. This may be ascribed to the fact that the addition of SDC particles reduces the contact probability between W particles and prevents the growth of W grains during the liquid-phase sintering process. The results of EDS analysis show that Sm and Ce elements are mainly distributed in the grain boundary between W and Cu (see Fig.6).

2.3 Physical and mechanical properties of the SDC/W-20Cu composites

Table 1 lists the electrical and thermal conductivity of the SDC/W-20Cu composites as a function of SDC addition amount. The conductivity of the SDC/W-20Cu samples has no significant changes when the addition of SDC is less than 0.4 wt%, and maximum electrical and thermal conductivity reaches 41.74 IACS% and 203.85 (W/m·K) at SDC addition amount of 0.2 wt% and 0.4 wt%, respectively. Both electrical and thermal conductivity decrease slightly as SDC addition increases. The conductivity of W-Cu composites is mainly determined by the formation of the continuous copper network in the structure. As shown in Fig. 3, excessive addition of SDC may lead to the decrease in relative density and the increase in the porosity. Furthermore, the electrical conductivity of SDC is much lower than those of W and Cu. These both will depress the electrical and thermal conductivity of the SDC/W-Cu composites.

Fig. 7 shows the effects of SDC addition on the bending strength and Vickers micro-hardness of the sintered SDC/W-20Cu samples. The addition of SDC obviously increases the strength. Maximum bending strength and Vickers micro-hardness HV reach 1130 MPa and 3180 MPa, respectively, with the addition of 0.6 wt% SDC, which are 14.5% and 13.2% higher than those of the W-20Cu samples with no SDC addition, respectively. Mechanical properties of W-Cu composites depend greatly on the relative density and microstructure, especially the grain size. Addition of a suitable amount of SDC facilitates the dispersion of W and Cu, prevents the agglomeration of W phase, and obviously refines the grain size (Fig. 5). They are beneficial to the increase of the mechanical properties of the composites. However, further addition of SDC exceeding 0.6 wt% leads

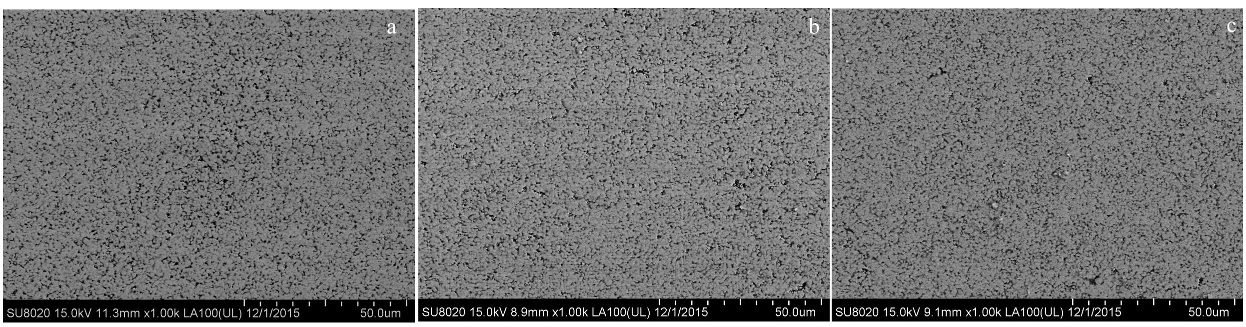

Fig. 4 Surface morphologies of the SDC/W-20Cu samples with different SDC contents sintered at 1250 °C: (a) 0.2 wt%, (b) 0.6 wt%, and (c) 0.8 wt%

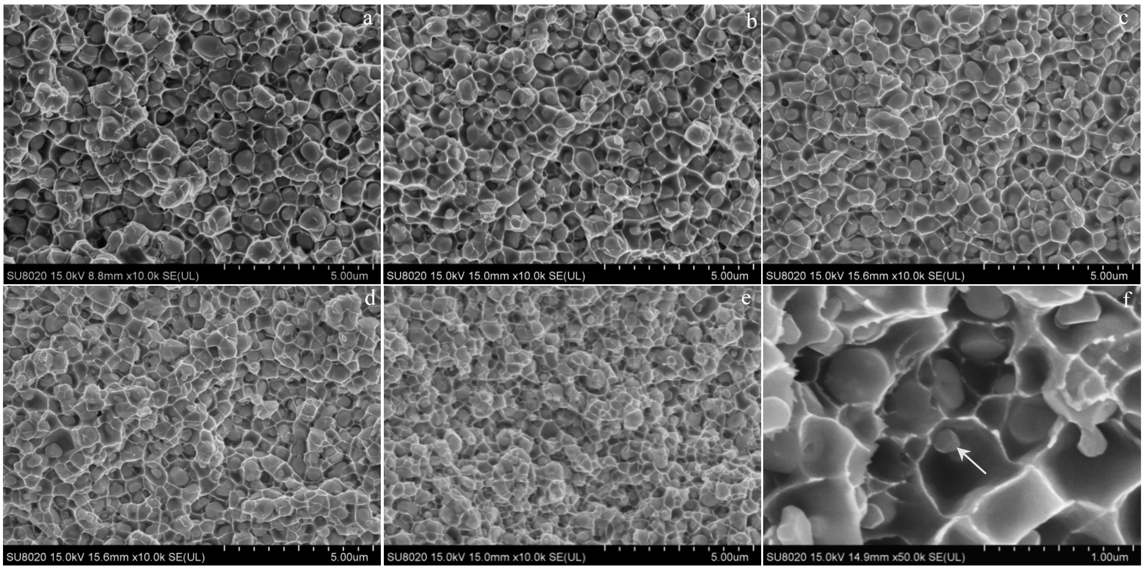

Fig.5 Fracture surface of the SDC/W-20Cu samples with different SDC contents sintered at 1250 °C: (a) 0 wt%, (b) 0.2 wt%, (c) 0.4 wt%, (d) 0.6 wt%, (e, f) 0.8 wt%

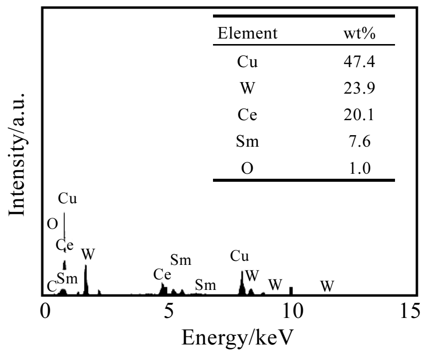

Fig.6 EDS analysis of marked arrow in Fig.5f

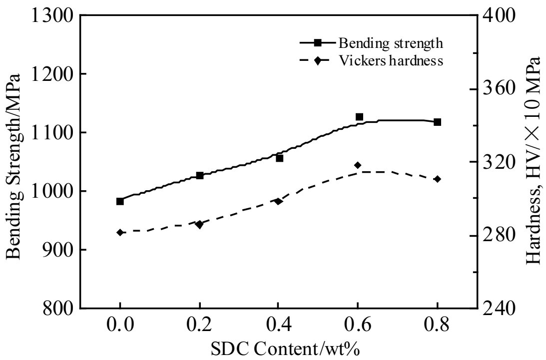

Fig.7 Bending strength and hardness of the SDC/W-20Cu composites sintered at 1250 °C versus SDC doping amounts

Table 1 Electrical and thermal conductivity of the SDC/W-20Cu composite sintered at 1250 °C with different addition amounts of SDC

SDC content/ wt%	Conductivity/ IACS%	Thermal conductivity/ $W\cdot(m\cdot K)^{-1}$
0	41.51	203.29
0.2	41.74	202.76
0.4	41.26	203.85
0.6	40.09	200.08
0.8	39.17	197.11

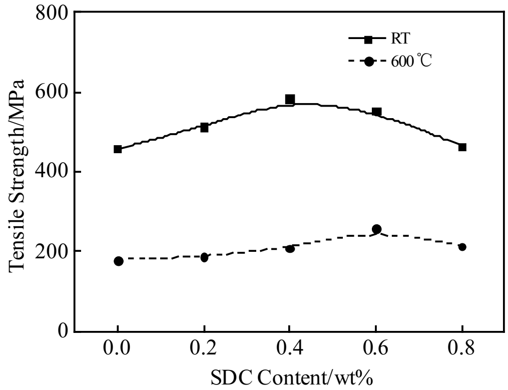

Fig.8 Tensile strength of SDC/W-20Cu composites versus SDC doping amount at room temperature and 600 °C

to the increase of the porosity obviously, resulting in the decrease of the bending strength and Vickers hardness.

Fig.8 shows tensile strength of the SDC/W-20Cu composites at room temperature and 600 °C. The tensile strength of the SDC/W-20Cu composites shows a trend of falling after rising first with the addition of SDC. Maximum tensile strength reaches 580 MPa at room temperature with 0.4 wt% of SDC addition, and 258 MPa at 600 °C with 0.6 wt% of SDC addition. The tensile strength of the

SDC/W-20Cu samples decreases obviously with the increase of temperature. The increase of temperature weakens the grain-boundary strength between phases, and leads to the softening of Cu phase because of its relatively low melting point. However, the little amount of SDC addition can improve the tensile strength of the SDC/W-20Cu composites at room temperature and 600 °C because of the refining of the grain size and reinforcement the grain-boundary strength.

3 Conclusions

1) SDC/W-20Cu composite powders with particle size of 100 nm to 200 nm were synthesized by the EDTA-citrate method.

2) The SDC/W-20Cu composite samples reach a relative density above 97% after sintering at 1250 °C for 2 h. The sintered samples have a homogeneous microstructure and the grain size is less than 1 μm.

3) The addition of SDC obviously refines the grain size and improves the mechanical properties of the W-20Cu composites. Electrical and thermal conductivity are 41.5%IACS and 203 $W\cdot(m\cdot K)^{-1}$, respectively. Bending strength and Vickers microhardness are 1128 MPa and 3180 MPa with the addition of 0.6 wt% SDC, respectively. The SDC/W-20Cu samples have the highest tensile strength of 580 MPa at room temperature and 258 MPa at 600 °C.

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掺杂复合稀土氧化物对 W-20Cu 复合材料组织与性能的影响

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摘 要：以偏钨酸铵和硝酸铜为原料，采用 EDTA-柠檬酸法制备了含有 0%~0.8%（质量分数）稀土氧化物（ $Ce_{0.8}Sm_{0.2}O_{1.9}$, SDC）的 W-20Cu 复合粉体，所制备的复合粉体经压制成形、1250 ℃烧结 2 h 后获得 SDC/W-20Cu 复合材料烧结体。对所制备复合粉体进行物相、形貌的表征；研究稀土氧化物的添加对 SDC/W-20Cu 烧结体的密度、组织结构和物理力学性能的影响。结果表明：所制备的 W-Cu 复合粉体平均粒度为 100~200 nm；同时，SDC 的添加对烧结体的密度和电导率会有轻微的影响，但能够抑制晶粒的长大并明显改善烧结体的力学性能。经 1250 ℃烧结后，SDC/W-20Cu 烧结体的相对密度均高于 97%；当 SDC 的添加量为 0.6%时，具有最大的抗弯强度和显微硬度 HV，分别是 1128 MPa 和 3180 MPa；此外，在室温和 600 ℃的测试条件下，其最大的抗拉强度分别可以达到 580 和 258 MPa。

关键词：W-Cu 复合材料；超细粉体；掺杂稀土氧化物；组织；性能

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