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Fabrication of Mo-Cu Functionally Graded Material by Combustion Synthesis and Centrifugal Infiltration

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Abstract: Mo-Cu functionally graded material was fabricated by a method which combines combustion synthesis with centrifugal infiltration. During the process, Cu melt produced by combustion reaction was infiltrated into a homogeneous Mo powder bed under high gravity. The as-prepared sample shows gradually-varying properties in terms of relative density, thermal diffusion coefficient and hardness. The content of heavy Mo phase decreases gradually from 75 vol% to 40 vol% along high gravity direction. The relative density of Mo-Cu FGM decreases from 97.6% to 96.5%, which can be attributed primarily to the increase in shrinkage cavity along high gravity direction. The thermal diffusion coefficient of Mo-Cu FGM increases from 43.2 to 66.6 $mm^2 s^{-1}$ due to the increase in Cu content along high gravity direction. The hardness of Mo-Cu FGM decreases gradually from 1390 to 710 MPa, as the content of Cu and porosity increases along high gravity direction.

Key words: functionally graded materials; combustion synthesis; high gravity field

Mo-Cu functionally graded material (FGM) with a gradual transition of composition and microstructure has been introduced to match the thermal and mechanical demand of the high-power electronic devices[1]. Several methods have been employed to fabricate Mo-Cu FGM, such as liquid phase sintering, spark plasma sintering, resistance sintering, plasma spraying and melt infiltration[1-5]. But, due to the low solubility and the high contact angle between Mo and Cu, it is still difficult to obtain high-dense Mo-Cu FGM by these methods[6]. It has been reported that the sinterability of Mo-Cu powder mixtures can be effectively improved by the addition of a small amount of transition element (such as Fe, Co, or Ni), or the use of ultra-fine and well-dispersed starting powders[7-9]. However, transition element additions are detrimental to the electrical and thermal properties of the resulting Mo-Cu composites. Many attempts have been made to prepare ultra-fine and well-dispersed Mo-Cu powders by different methods, such as mechanical alloying process, spray drying and reduction process, metal injection molding, electroless plating technique, and gelatification-reduction process[9-11]. Although some successful experimental results have been reported, it is still desirable to develop a simple process to fabricate Mo-Cu FGM.

Recently, we have developed a new method to fabricate W-Cu FGM by combining combustion synthesis with centrifugal infiltration[12]. Compared with the conventional sintering method and infiltration approaches, combustion synthesis and centrifugal infiltration offers a fast and furnace-free way to prepare W-Cu FGM. Since Mo-Cu system is chemically similar to the W-Cu system, it is expected that Mo-Cu FGM may also be fabricated by combustion synthesis and centrifugal infiltration.

In this study, Mo-Cu FGM was prepared by combustion synthesis and centrifugal infiltration. The phase and microstructural evolution, thermal and mechanical properties of the prepared Mo-Cu FGM were investigated. The effect of high gravity field on the formation of graded structure was discussed.

1 Experiment

Commercial powders of Al (100 μm, 99.9% purity), CuO (45 μm, 99.9% purity), and Cu (45 μm, 99.9% purity) were used as raw materials. The raw materials were mixed according to the molar ratio of Al:CuO:Cu=2:3:4 and homogenized well to prepare a thermite powder. A batch of 200 g thermite powder was pressed into a compact with a diameter of 40 mm and porosity about 50%. Commercial Mo powder (5 μm, 99.9% purity) of 50 g was loaded into a quartz tube with a diameter of 40 mm to prepare a powder bed with porosity about 60 vol%. The thermite compact was placed

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above the Mo powder bed in the quartz tube. The quartz tube was put into a graphite crucible with a heat insulation layer between them. The crucible was then coated with a carbon cap and then put into a steel vessel, which was mounted into a reaction chamber in centrifugal equipment[13]. The reaction chamber was evacuated to a vacuum of ~100 Pa. The combustion reaction was triggered by passing an electric current about 10 ampere through a tungsten coil closely above the thermite compact in a high gravity field with an acceleration of 1000 *g* (g=9.8 m s^{-2}) induced by centrifugation. During the preparation process, a large amount of heat was generated by the combustion reaction and molten Cu and Al_2O_3 were produced and separated in the high gravity field due to their density difference[13]. The separated high temperature Cu melt was rapidly infiltrated into the Mo powder bed to form the Mo-Cu composite. After cooling and solidification ceramic and metal ingots were obtained. The metal ingots were machined and polished for later characterization.

Phase identification of the sample was characterized by powder X-ray diffraction (XRD, D8Focus, Bruker, Germany) using Cu-Kα radiation with a scanning rate of 6 °/min. The microstructure was examined by scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The room temperature thermal diffusion coefficient was measured by laser flash using a transient thermal flash technique (LFA 457, Netzsch, Germany). The bulk density was measured according to the Archimedes principle. The hardness was tested by the Vickers indentation method with a load of 98 N.

2 Result and Discussion

2.1 Phase and microstructure

The XRD patterns of the prepared sample were analyzed along high gravity direction, as shown in Fig.1. It can be seen clearly that it is composed of two different layers. Pure Cu phase is on the upper layer of the sample and Mo-Cu phases on the bottom. The existence of an extra pure Cu layer suggests that the Al_2O_3 ceramic phase produced by the combustion reaction is completely separated from the Cu phase. The Mo-Cu layer is formed by the infiltration of Cu melt into the bottom Mo powder bed with the assistance of applied high gravity field. The diffraction peak intensity of Mo and Cu phases show a gradual changes along high gravity direction in the bottom Mo-Cu layer. While the intensity of diffraction peak (110) at 2θ=40.515 ° of Mo phase decreases along high gravity direction, the intensity of diffraction peak (200) at 2θ=50.433 ° of Cu phase shows a reverse trend. This may be caused by a gradual reduction of Mo content along high gravity direction in the Mo-Cu layer. Considering that Mo powder bed was homogeneously designed with a porosity about 60 vol%, the gradual change of composition along high gravity direction may be a result of the applied 1000 g high gravity field during the infiltration process.

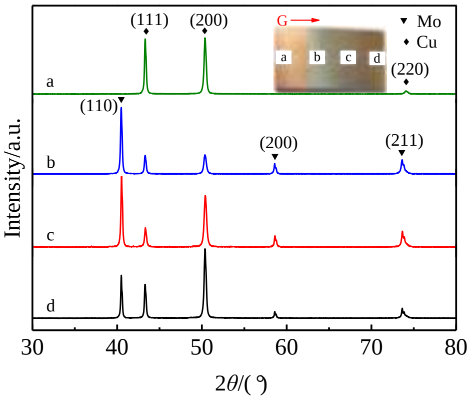

Fig.1 XRD patterns of the prepared sample recorded along high gravity direction (the positions of examined sections are pointed out in the inset photograph)

The microstructure of Mo-Cu layer was analyzed along high gravity direction, as shown in Fig.2. The brighter phase is Mo, which has a higher atomic weight than the darker Cu phase. It can be seen obviously from the SEM images that the microstructure of Mo-Cu layer shows a gradual transition along high gravity direction. The content of Mo phase decreases gradually from 75 vol% to 40 vol% along high gravity direction, as determined by an image analysis software. Pores on the Mo-Cu layer can be observed from the SEM images, and its content is increased along high gravity direction. The gradual transition of composition in Mo-Cu layer is in agreement with the result of XRD mentioned above.

Compared with the W-Cu FGM prepared by the same method, we are amazed to find that Mo-Cu FGM can be fabricated without the use of pre-designed graded Mo powder bed. Moreover, the content of the heavier Mo phase is gradually decreased along high gravity direction, which runs counter to that observed in W-Cu FGM. The formation of this graded structure may be caused by the different densification rates of the Mo powder bed along high gravity direction. It is considered that the sintering of Mo powder was carried out under influence of the high temperature liquid Cu and the pressure produced in high gravity field. The instantaneous temperature of liquid Cu can reach about 2000 ℃, high enough for Mo sintering[14,15]. By calculation, the pressure applied on the Mo powder bed by the thermite compact placed above is 1.56 MPa in high gravity field. When liquid Cu is infiltrated into the Mo powder bed with the assistance of high gravity field, the temperature of liquid Cu and the pressure on Mo powder bed are decreased along high gravity direction[16,17]. The densification rates of Mo powder are thereby reduced along high gravity direction. Fig.2e shows the SEM image of etched upper Mo-Cu layer by a mixture of 5wt% $FeCl_3$ solution and 2wt% HCl solution for 1 min. It can be seen that Mo particles are sintered together to form a continuous Mo

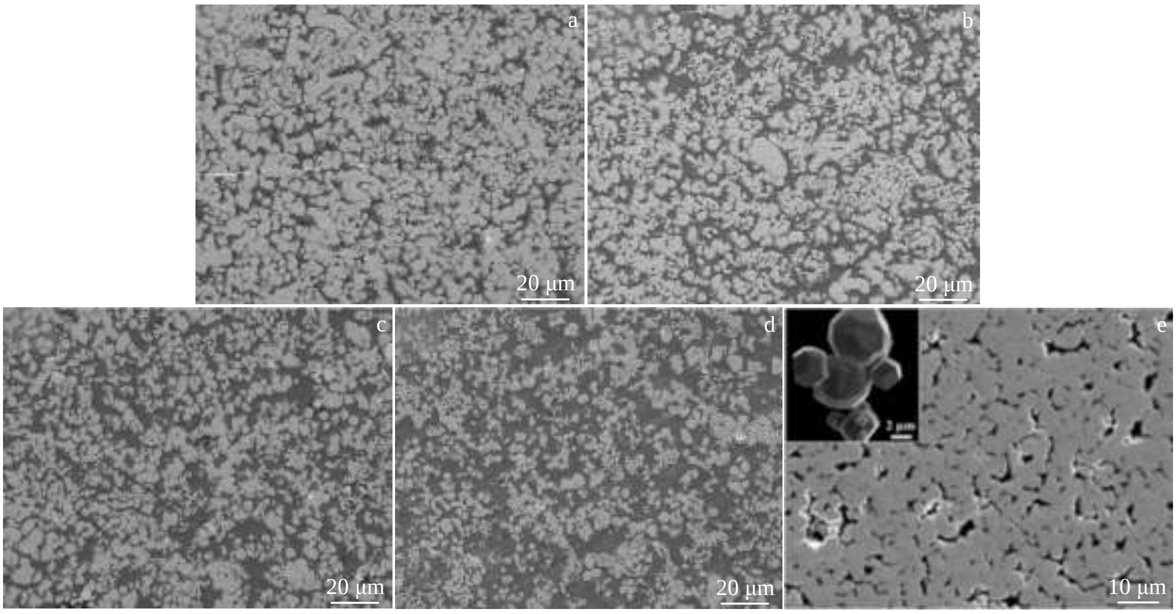

Fig.2 (a~d) SEM images of Mo-Cu layer examined along high gravity direction, showing the gradual transition in the microstructure; (e) SEM image of etched upper Mo-Cu layer (the inset shows the SEM image of Mo powder)

skeleton. With reducing densification rates of Mo powder, the content of Mo in Mo-Cu layer is consequently decreased along high gravity direction.

2.2 Thermal and mechanical properties

The relative density and thermal diffusion coefficient of Mo-Cu FGM were examined along high gravity direction, as shown in Fig.3a. The relative density of Mo-Cu FGM decreases from 97.6% to 96.5%, which may be caused by an increase in porosity along high gravity direction, as confirmed by SEM. There are two types of pores in Mo-Cu FGM, i.e., closed pores formed in sintered Mo skeleton and shrinkage cavity. The increase in porosity along high gravity direction can be attributed primarily to the increase in shrinkage cavity, as the viscosity of infiltrated liquid Cu increases with decreasing temperatures. The thermal diffusion coefficient of Mo-Cu FGM increases from 43.2 to 66.6 $mm^2\ s^{-1}$, which can be attributed to the increase in Cu content along high gravity direction. The relative density and thermal property of the prepared Mo-Cu FGM are comparable with that prepared by other methods[7,8].

The hardness of Mo-Cu FGM along high gravity direction is presented in Fig.3b. It can be seen that the hardness decreases gradually from 1390 to 710 MPa along high gravity direction. The decrease in hardness along high gravity direction can be attributed to the increase in Cu content and porosity in Mo-Cu FGM. The gradual transition in composition, structure, thermal and mechanical properties of prepared Mo-Cu FGM indicates that the combination of combustion synthesis with centrifugal infiltration is an effective method for the fabrication of functionally graded materials.

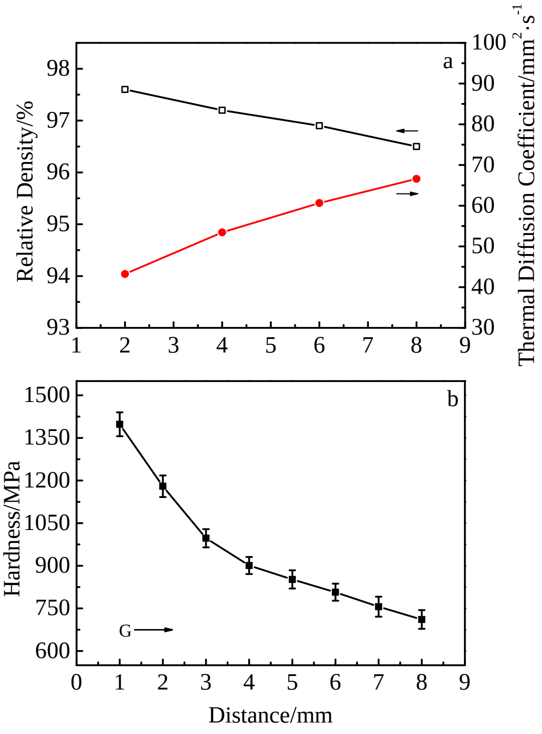

Fig.3 Relative density and thermal diffusion coefficient of Mo-Cu layer along high gravity direction (a); Hardness of Mo-Cu layer along high gravity direction (b)

3 Conclusions

1) Mo-Cu functionally graded material is prepared by a

method which combines combustion synthesis with centrifugal infiltration.

2) The content of heavy Mo phase decreases gradually from 75 vol% to 40 vol% along high gravity direction. The relative density of Mo-Cu FGM decreases from 97.6% to 96.5%, which can be attributed primarily to the increase in shrinkage cavity along high gravity direction. The thermal diffusion coefficient of Mo-Cu FGM increases from 43.2 to 66.6 $mm^2 s^{-1}$ due to the increase in Cu content along high gravity direction. The hardness of Mo-Cu FGM decreases gradually from 1390 to 710 MPa, as the content of Cu and porosity increases along high gravity direction.

References

1 Fan J L, Chen Y B, Liu T *et al. Rare Metal Materials and Engineering*[J], 2009, 38: 1693 (in Chinese)
2 Sun A K, Wang D Z, Wu Z Z *et al. Materials Chemistry and Physics*[J], 2014, 148: 494
3 Fang F, Zhou Y Y, Yang W. *International Journal of Refractory Metals and Hard Materials*[J], 2014, 42: 120
4 Wang P F, Shen W P, Zhang Q *et al. Rare Metal Materials and Engineering*[J], 2007, 36: 652 (in Chinese)
5 Kieback B, Neubrand A, Riedel H. *Materials Science and Engineering: A*[J], 2003, 362: 81
6 Aguilar C, Guzman D, Rojas P A *et al. Materials Chemistry and Physics*[J], 2011, 128: 539
7 Guo S, Kang Q, Cai C *et al. Rare Metals*[J], 2012, 31: 368
8 Zhou X L, Dong Y H, Hua X Z *et al. Materials & Design*[J], 2010, 31: 1603
9 Wang D, Dong X, Zhou P *et al. International Journal of Refractory Metals and Hard Materials*[J], 2014, 42: 240
10 Song P, Cheng J, Wan L *et al. Journal of Alloys and Compounds*[J], 2009, 476: 226
11 Sun A, Wang D, Wu Z *et al. Journal of Alloys and Compounds*[J], 2010, 505: 588
12 Sun A, Dong X, Wang X *et al. Journal of Alloys and Compounds*[J], 2013, 555: 6
13 Zhao P, Guo S B, Liu G H *et al. Journal of Alloys and Compounds*[J], 2014, 601: 289
14 Liu G H, Li J T. *Journal of Asian Ceramic Societies*[J], 2013, 1: 134
15 He G, Zhao P, Guo S B *et al. Journal of Alloys and Compounds*[J], 2013, 579: 71
16 Ohser-Wiedemann R, Martin U, Seifert H J *et al. International Journal of Refractory Metals and Hard Materials*[J], 2010, 28: 550
17 Mahmoodian R, Hassan M A, Rahbari R G *et al. Composites Part B: Engineering*[J], 2013, 50: 187

超重力场辅助燃烧合成钼铜功能梯度材料

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摘　要：采用超重力场辅助燃烧合成的方法制备了钼铜功能梯度材料。燃烧合成生成的 Cu 熔体在 1000 g 超重力场作用下渗透进入 Mo 粉坯中，随着熔体温度降低及渗透压力减小，沿超重力场方向上形成组分梯度分布的钼铜功能梯度材料。采用 X 射线衍射（XRD）、扫描电子显微镜（SEM）对样品沿超重力场方向的物相组成和微观形貌进行表征，利用激光闪射法、维氏硬度计对样品沿超重力场方向的热扩散系数的硬度值进行测试。结果表明：样品沿超重力场方向钼铜合金组分渐变，Mo 含量由 75 vol%减小至 40 vol%，相对密度相应的由 97.6%降低至 96.5%。相对密度的降低可能是由沿超重力场方向 Cu 熔体冷却体积收缩增大造成的。钼铜功能梯度沿超重力场方向的热扩散系数由 43.2 $mm^2 s^{-1}$ 增加至 66.6 $mm^2 s^{-1}$，硬度值由 1390 MPa 逐渐减小至 710 MPa。

关键词：功能梯度材料；燃烧合成；超重力场

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