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ARTICLE

Mechanical Properties and Thermal Shock Resistance of Zr, Cr Doped WCu Composite

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Abstract: WCu composites were fabricated by infiltrating Cu alloys doped with Zr and Cr into W skeleton in order to strengthen the W/Cu interfaces. The effects of Zr and Cr on the mechanical properties including flexural strength and impact toughness, and thermal shock resistance of WCu composites were investigated. The results show that the addition of a small amount of Zr and Cr can increase the flexural strength and the impact toughness of WCu composites. With the increase of thermal shock temperature, the flexural strength of WCu composites decreases. However, the addition of Zr and Cr in WCu composite can reduce the effect of thermal shock on mechanical properties obviously, improving the thermal shock resistance of WCu composites.

Key words: WCu composite; microstructure; flexural strength; impact toughness; thermal shock resistance

Considering the high thermal conductivity of copper and the excellent high-temperature strength of tungsten, WCu composites have been widely used in a variety of fields, such as electrical contacts especially at high voltage, welding electrodes, electric discharge machine, electronic packaging materials and heat sinks^[1-4]. Moreover, the good combination of Cu and W elements leads to the optimization of material properties, such as ductility, mechanical strength, corrosion and wear resistance at elevated temperature. As WCu composite is usually applied under a thermal shock load, the surface is subjected to fracture derived from internal thermal stress^[5]. Therefore, a number of investigations have been made on the improvement of the mechanical behaviours of WCu composite by doping some extra elements [6, 7], enhancing sintering temperature^[8], refining W particle size^[9-12], tungsten fibre-reinforced^[5,6] and so on. Among these methods, the addition of some extra elements is convenient to control and beneficial for the improvement of mechanical behaviours. With the addition of Cr, W-Cr solid solution transition layer is formed between the W grain boundaries^[13], and then W skeleton is strengthened. As

mentioned in Ref.^[14], cracks appear mostly at the interface of W/Cu under external load. Therefore, it is necessary to strengthen W/Cu interface by some methods including the addition of some extra elements.

Previous studies demonstrated that the addition of Group VIII transition metals, including Ni, Pd, Pt, Co, Fe, Cu, and Cr can enhance the sintering kinetics of W powder, thus reducing its sintering temperature^[15]. On the other hand, the transition metals (Ni, Cr, Nb, Zr, Mo, W, Ta) will form solid solution phase probably among the interfaces each other. In order to strengthen the W/Cu interfaces, Zr, Zr and Cr were doped in WCu composite, and then mechanical properties and thermal shock resistance of WCu composite were analyzed.

1 Experiment

WCu composites used in the present study were fabricated by infiltrating the copper alloys into tungsten skeleton. Tungsten powder (purity>99.8%, 4~6 μ m) was used to prepare skeletons, CuZr (0.15wt%~0.3wt%Zr) and CuCrZr (0.8wt%~1.2wt%Cr, 0.1wt%~0.2wt%Zr) alloys were used for infiltration. Tungsten powder mixed with

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activated element Ni was first pressed into cylindrical compacts under a pressure of 340 MPa in a hydrostatic machine, and then copper alloy blocks were placed above each compact in the graphite crucibles followed by activated sintering and infiltrating at a hydrogen atmosphere in a sintering furnace. Tungsten skeletons were sintered at 1000 $\$ for 2 h, and then held at 1350 $\$ for 2 h to infiltrate copper alloys. After annealing at 450 $\$ for 4 h, WCu composites were obtained.

The flexural strength and the impact toughness were tested by a HT-2402-100KN Computer Servo Control material testing machine and a JB-300 Charpy impact test machine, respectively. For flexural tests, the specimens were machined into the dimensions of 3 mm×4 mm×35 mm. In each case, three-point bending loading tests were performed with a span of 30 mm. Flexural test procedures were performed at room temperature and with a load rate of 0.5 mm/min. For the flexural properties analysis, the load versus displacement curves were obtained directly and the stress was calculated by a linear bending beam relationship. Charpy impact tests were performed using square 10 mm×10 mm notched specimens. A sharp notch with 2 mm depth and at a 45° flank angle was machined in each specimen. Afterwards, the tests were carried out on a 50 mm span. The absorbed energy was directly measured by the difference in potential energy between the starting and the after-impact highest position of the pendulum. Then the

impact toughness value was obtained by the absorbed energy divided by the cross-section area of specimen.

For the thermal shock tests, firstly, flexural specimens of WCu alloys were placed into an electrical resistance furnace and held for about 1 min at the temperature of 400, 600, 900 \mathbb{C} , respectively, and then the specimens rapidly were put into 20 \mathbb{C} water for about 1 min. After thermal cycling 10 times, the flexural tests were conducted at room temperature.

2 Results and Discussion

2.1 Microstructures of WCu composite

Fig.1a~Fig.1c are the SEM images of the WCu composites without Zr and Cr addition, doped with Zr and doped with Zr and Cr, respectively, in which the light region is W phase and the rest region is Cu phase. It can be seen that the sintered necks bonded between W grains are formed after sintering and the Cu phase is surrounded by tungsten matrix skeleton throughout the microstructure. Hence, there is no obvious difference in microstructure of the three WCu composites.

2.2 Mechanical behaviours

Fig.2 shows the flexural stress-displacement curves of WCu composites. In the case of no Zr and Cr addition, the curve shows approximately linear until failure, indicating the classic brittle behaviour. With the addition of Zr and Cr, the curves exhibit non-linear stress-displacement



Fig.1 SEM images of microstructures of WCu composites: (a) without Zr and Cr addition, (b) doped with Zr, and (c) doped with Zr and Cr



Fig.2 Flexural stress-displacement curves of WCu composites

relationship and more plastic deformation appears. As seen in Fig.2, the flexural strengths of WCu composite doped with Zr, Zr and Cr increase from 919 MPa to 1050 MPa and 1020 MPa, respectively, increase by 14.25% and 10.99%, respectively. In addition, with the addition of extra element, the bending deformation of WCu composites doped with Zr, Zr and Cr increase by 92.49% and 104.20%, respectively. Therefore, the curves show an evident improvement of strength and ductile due to the addition of Zr and Cr.

The impact toughnesses of three WCu composites are summarized in Fig.3. It is clear that the WCu composite without any element additions has an impact toughness of 0.330 J cm^{-2} , while the impact toughnesses of the WCu composites doped with Zr, Zr and Cr are both 0.368 J cm⁻²,

which is increased by 12% in comparison with that without Zr and Cr additions. However, the impact toughness of WCu composite doped with Zr and Cr has less change compared with that doped with Zr.

During fabrication, W skeleton was sintered firstly and then Cu alloys were infiltrated. The addition of Zr and Cr in Cu alloys mainly affect W/Cu interfaces. Considering the microstructure and the fabrication process of WCu composite, it seems that the improvement of composites properties is related to the strength of W/Cu interface, which leads to the improvement of strength and ductile of the WCu composites.

2.3 Thermal shock resistance

Fig.4 shows the flexural strengths of WCu composites doped with Zr and Cr after thermal shock repeated 10 times. It is evident that the flexural strength decreases significantly with the increase of temperature of thermal shock, especially for the composite without any extra element addition. Therefore, it is suggested that the addition of Zr and Cr can enhance the thermal shock resistance. The flexural strength decreases sharply after thermal shock at 600 °C, but increases after thermal shock at 900 °C. After thermal shock at 600 °C, the flexural strength of WCu composites without Zr and Cr addition, doped with Zr and doped with Zr and Cr decreases from 919, 1020 and 1050 MPa to 701.88, 873.75 and 868.75 MPa, respectively. However, there is a little bit change when compared with the WCu composite after thermal shock at 900 °C.

The fracture surfaces of WCu composites are shown in Fig.5. It can be seen that most of fracture morphologies are classified as the inter-crystalline fracture and dimple patterns. The inter-crystalline fracture indicates that the tungsten grains are separated from each other. The dimple reveals the cracking of copper adhesive tungsten grains. Occasionally some transgranular cleavage fractures present at some tungsten grains.

As shown in Fig.5, the fracture mode of W skeleton is predominantly inter-crystalline fracture after thermal shock at 600 \mathbb{C} , but more transgranular cleavage fractures of tungsten grains present after thermal shock at 900 \mathbb{C} . It reveals that the strength of WCu composite after thermal shock at 600 $^{\circ}$ C is mainly determined by the W/W interfaces while more W grains play a major role for the composite strength after thermal shock at 900 $^{\circ}$ C. Considering the large ultimate strength of pure tungsten, the strength of WCu composite increases again after thermal shock at 900 $^{\circ}$ C. The mechanism may be explained as follows.

During the period of thermal shock, the internal thermal stress is induced by the temperature gradient and the mismatch of different coefficients of thermal expansion between W and Cu phase. Therefore, damage is induced at the interfaces and the flexural strength declines after



Fig.3 Impact toughness of WCu composites



Fig.4 Flexural strengths of WCu composites after thermal shock



Fig.5 Fractographies of WCu composites with the addition of Zr and Cr after the thermal shock: (a) doped with Zr, △ T=600 °C, (b) doped with Zr, △ T=900 °C, (c) doped with Cr and Zr, △ T=600 °C, (d) doped with Cr and Zr, △ T=900 °C (Note: (i) inter-crystalline fracture, (ii) dimple, (iii) transgranular cleavage)

repeated thermal shock with the increase of temperature^[16]. As the Cu phase becomes soft and tends to be melted, most of the deformation energy is absorbed during thermal shock at 900 °C, the thermal stress among WCu composite decreases and thermal shock damage seldom occurs. With the addition of Zr and Cr, the W/Cu interfaces are strengthened, and thus the damage of WCu composite is reduced.

3 Conclusions

1) The strength and the ductility of WCu composites doped with Zr, Zr and Cr are improved compared with those without Zr and Cr addition, and the impact toughness increase as well. The addition of Zr and Cr can effectively strengthen W/Cu interfaces, and lead to the improvement of strength and ductile of the WCu composites.

2) The flexural strength of WCu composite decreases obviously with the increase of thermal shock temperature. However, there is a little change after thermal shock at 900 $^{\circ}$ C.

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WCu 复合材料掺杂 Zr、Cr 的力学及抗热震性能

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摘 要:为了强化W/Cu界面,通过在钨骨架中熔渗掺杂有Zr、Cr的铜合金,制备了WCu复合材料。研究了掺杂Zr、Cr对WCu复合材料 的力学性能(包括弯曲强度及冲击韧性)及抗热震性能的影响。结果表明,少量的掺杂Zr、Cr可以有效提高WCu复合材料的弯曲强度及 冲击韧性。随着热震温度的提高,WCu复合材料的弯曲强度降低,而Zr、Cr的掺杂可明显提高WCu复合材料的抗热震性能。 关键词:WCu复合材料;微观组织;弯曲强度;冲击韧性;抗热震性

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