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Effects of thermal cycling on thermal expansion behaviors of β-$LiAlSiO_4$ reinforced copper matrix composites

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Abstract: β-$LiAlSiO_4$ reinforced Cu matrix composites (Euc/Cu) were fabricated by hot-pressed sintering process. Thermal expansion behaviors of Euc/Cu composites were studied during the thermal cycling process. Upon twice thermal cycle, the temperature dependence of the coefficients of thermal expansion (CTE) for Euc/Cu composites tends to be stable. The CTEs of the composite can be obviously decreased by the releasing of the thermal mismatch stress (TMS) in thermal cycling process. The TMS induces the irreversible phase transition of Li^+ order−disorder of Euc particles in the composite. Meanwhile, the relaxation of TMS during thermal cycling causes the twins deformation of matrix in the Euc/Cu composites.

Key words: copper matrix composite; thermal expansion; residual stress; phase transition

1 Introduction

Metal matrix composites (MMCs) have been identified as candidates for applications where the high thermal conductivity of metals and the low thermal expansion of ceramics are simultaneously needed, e.g., in electronic packaging or in electronic heat sinks requiring high heat dissipation and low thermal expansion mismatch with the silicon chip or its alumina substrate [1−4]. Copper has a very high thermal conductivity, up to 400 W/(m·K) [5], and thus is an attractive matrix material for MMCs in electronic industry except its high coefficient of thermal expansion (CTE) [6] and high density. The CTE and density of Cu can be reduced by forming MMCs containing appropriate volume fractions of ceramic materials. Although the CTE of MMCs can be reduced through the increasing of ceramic content, the thermal conductivities of the composites are generally decreased. Therefore, ceramics with low CTE have been preferably used as the reinforcements of copper matrix composites, such as SiC [2] and TiB_2 [7]. ZrW_2O_8 with isotropic negative CTE has received much interests for the reinforcement of Cu matrix composite [8−9]. However, because of phase transition induced by thermal mismatch stress of ZrW_2O_8 particle in Cu matrix composite, the CTE of ZrW_2O_8 particle reinforced Cu matrix composite (ZrW_2O_8/Cu) is much higher than that predicted from thermoelasticity theory [8]. In this work, β-$LiAlSiO_4$ with very low CTE is selected as the reinforcement of Cu matrix composite to reduce the CTE of the copper matrix composite.

β-$LiAlSiO_4$ (β-eucryptite, denoted by Euc), with a hexagonal crystal structure, has a low density (2.35 g/cm^3) and nearly zero volume CTE, and its linear CTEs are α_a=8.6×10^{-6}°C^{-1}, α_c=−18.4×10^{-6}°C^{-1} [10]. The Euc particles have been successfully used as the reinforcement to reduce the CTE of aluminum and copper matrix composite in Ref.[11]. The Euc reinforced copper matrix composites have retained the low thermal expansion and high thermal conductivity at lower volume fraction of Euc [12], but the in-depth study on Cu matrix composite reinforced by Euc particles (Euc/Cu) is still very limited.

In this work, the Cu matrix composites reinforced with Euc particles were fabricated by hot-pressed sintering method. The CTE, phase compositions and microstructure of Euc/Cu composite with thermal cycling process were studied. More importantly, this work shows that although the Euc phase transition exists

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in Euc/Cu composite, the low and stable CTE can be obtained in the Euc/Cu by thermal cycling.

2 Experimental

The Euc particles with size of 5−10 μm were produced with a mass production method [13]. Pure copper powders (mesh number, 500) were used as matrix material of Euc/Cu composite. For improving the wetting ability between Euc particles and Cu powders, the surface of Euc particles was coated by electroless plating of silver. The Euc/Cu composites with Euc volume fraction of 40% were fabricated firstly by mixing the Ag-coated Euc particles and copper powder together and then by hot-pressed sintering in an electrical vacuum furnace at 950 °C with a vacuum level of 3.0×10^{-3} Pa. The pressure of 50 MPa was held during the whole sintering and cooling processes.

The microstructure was examined by a FEI technical transmission electron microscope (TEM). The samples for TEM observations were finally thinned by ion milling. The phase composition of composite was analyzed using X-ray diffraction (XRD) with a Philips X'Pert X-ray diffractometer with Cu K_α radiation. The in-situ XRD analysis at elevated temperature was carried out on a Rikagu D/max2500 diffractometer with Cu K_α radiation. Thermal expansion experiments were performed on a Netzsch DIL 402C dilatometer with a heating rate of 2 °C/min. The dimensions of the specimens for thermal expansion measurement were *d* 6 mm×15 mm. A heating process with a rate of 2 °C/min and a cooling process in the furnace during the temperature range of room temperature (RT) to 350 °C was denoted as one thermal cycling. The composites without and with four thermal cycles for CTE measurements (from RT to 350 °C) were marked by as-sintered composites and thermal-cycled composites, respectively.

3 Results and discussion

3.1 Thermal expansion behaviors

The microstructure of the as-sintered β-$LiAlSiO_4$/Cu composite was firstly observed by SEM (not given here), which shows that the distribution of β-$LiAlSiO_4$ particulates are uniform in the copper matrix [12]. Figure 1 shows the thermal expansion behaviors of the Euc/Cu composite in the heating process for multiple thermal cycling processes. As shown in Fig. 1(a), with the times of thermal cycling increasing, the elongation of the composite decreases. In the first thermal cycle process, the elongation increases equably at first and then quickly after about 200 °C. In the second thermal cycle, the elongation still increases equably and then quickly

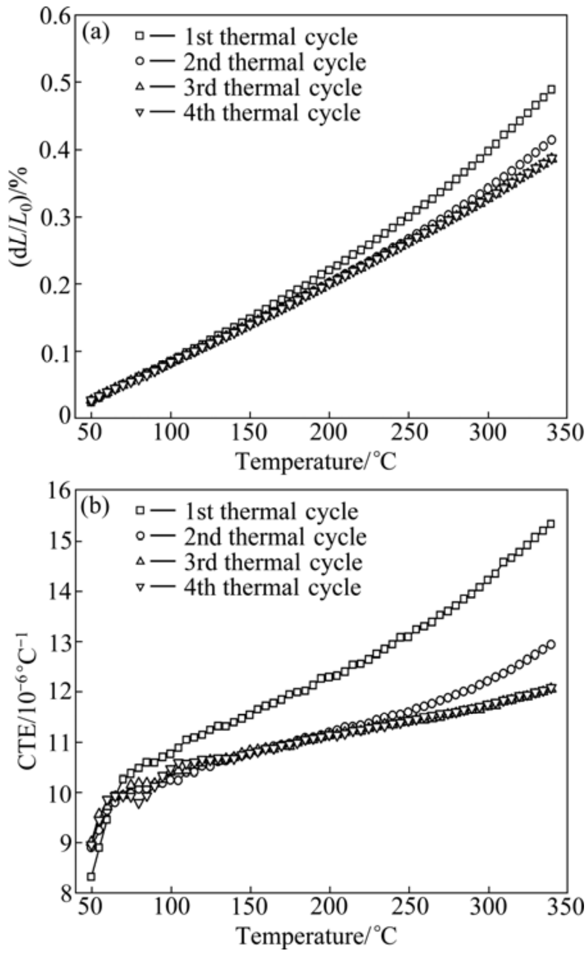

Fig. 1 Thermal expansion behavior of Euc/Cu-Ag composites in thermal cycling process: (a) Relative elongation; (b) Coefficient of thermal expansion

after 300 °C. But for the last two thermal cycle, the elongation tends to be linear and stable with temperature increasing. Figure 1(b) shows the relationships between CTE and temperature in the heating process. The CTE of the composite in the first thermal cycle is the largest among the four times of thermal cycle. The CTE of the composite in the second thermal cycle is obvious lower than that in the first thermal cycle, but a little higher than that of the last two thermal cycles after 250 °C. While in the third and fourth thermal cycle, the CTEs of the composite tend to be overlapped and are linear to temperature. After the first thermal cycle, the CTE of the composite obvious decreases over the temperature range. So it can be thought that the first thermal cycling process has the largest effect on the CTE of the composite. Because of the different CTE between reinforcements and matrix, it will generate a large thermal residual stress in the composites during cooling from the fabrication temperature. In the heating process, the CTE of the composites can be obviously affected by the changing of TMS in the composites [14].

3.2 In-situ XRD analysis

In order to discuss thermal expansion behavior in the thermal cycling process, the in-situ XRD analysis of the as-sintered composite at elevated temperature was carried out. On the foundation of Gauss fitting for diffraction peaks and the Bragg equation, the relationships between $d_{Euc(202)}$, $d_{Cu(200)}$ and temperature in the as-sintered Euc/Cu-Ag composites are shown in Fig. 2. As shown in Fig. 2(a), with the temperature increasing, $d_{Euc(202)}$ firstly expands from RT to 100 °C and then contracts from 100 to 450 °C. It is interesting to see that the contraction rate of $d_{Euc(202)}$ occurs a fluctuation at 300 °C, which is abnormal to be higher than the expectation. The relationship between $d_{Cu(200)}$ and temperature in the heating process is shown in Fig. 2(b). It could be seen that $d_{Cu(200)}$ expands with the temperature increasing, but the expansion rate of $d_{Cu(200)}$ also appears a inflection point at about 200 °C, the expansion rate of $d_{Cu(200)}$ before 200 °C is obviously lager than that after 200 °C.

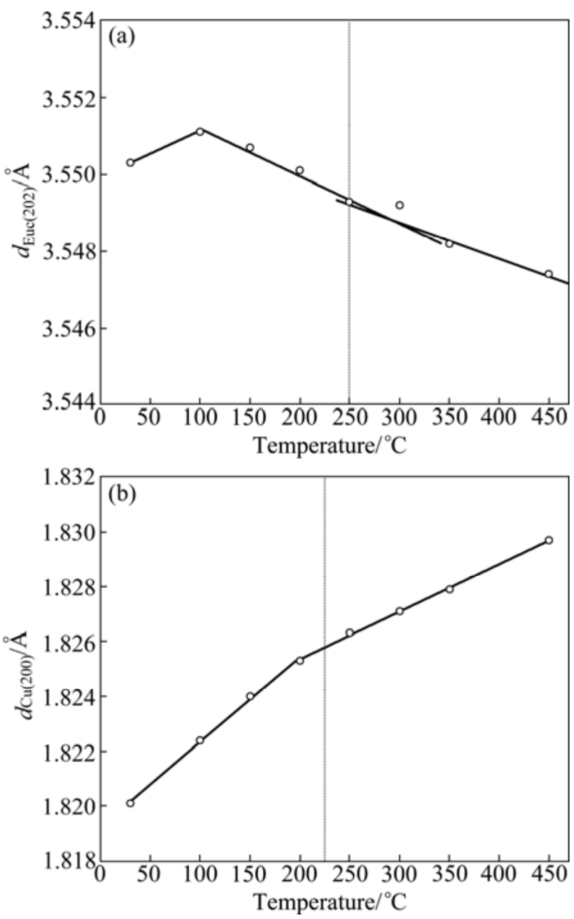

Fig. 2 Changing of plane spacing with temperature in as-sintered Euc/Cu-Ag composites by in-situ XRD analysis at elevated temperature process: (a) $d_{Euc(202)}$; (b) $d_{Cu(200)}$

3.3 Phase analysis and microstructures observations

The phase analysis of Euc/Cu composites is shown in Fig. 3. By the XRD investigation in Fig.3, no reaction has taken place between Euc and Cu matrix. But the diffraction peak of Euc (200) at 19.5° has disappeared in the thermal-cycled composites. According to Ref.[14], pressure can induce the Li^+ disordering of the Euc particles, it can be suggested that the Li^+ disordering due to the TMS makes the diffraction peaks of Euc(200) disappear. At room temperature, the TMS of Euc particles is compressive stress, which means that the phase transition of Li^+ order−disorder in the Euc particles is caused by tensile stress, so there should be a changing of TMS in the Euc particles state from compression stress to tensile stress during the heating process. The tensile stress induces the phase transition of Li^+ order−disorder of Euc particles. After thermal cycle, the TMS of Euc particles reverts to compression stress, the diffraction peaks of Euc(200) disappears, which means that the phase transition of Li^+ order−disorder in the composites is irreversible.

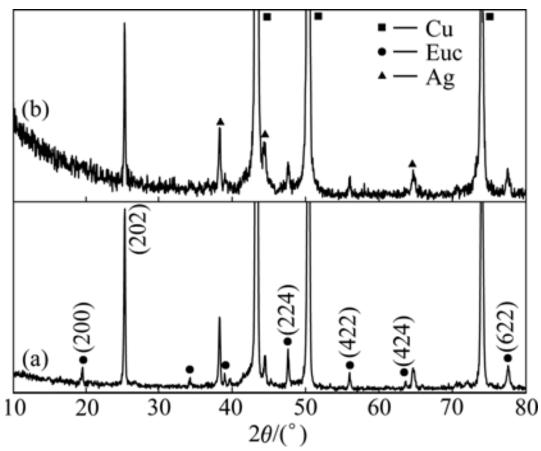

Fig. 3 XRD patterns of Euc/Cu-Ag composites: (a) As-sintered composite; (b) Thermal-cycled composite

Combining the results of Fig. 2, the changing of TMS in Euc particles in the composites during the heating process can be concluded. At the beginning stage of heating, the quick releasing of large compression stress makes $d_{Euc(202)}$ increase. With the temperature further increasing, the compression stress decreases, then the $d_{Euc(202)}$ starts to contract due to the intrinsic negative thermal expansion of Euc. At about 250 °C, the compression stress has been fully relaxed and the tensile stress is generated, which makes the CTE of Euc/Cu-Ag composite increase quickly. With the tensile stress generating, the contraction rate of $d_{Euc(202)}$ decreases. Accordingly, the TMS of Cu matrix changes from the relaxation of tensile stress to the generation of compression stress, which makes the expansion rate of $d_{Cu(200)}$ decrease after 250 °C, as shown in Fig. 2(b). On the foundation of the above analysis, the fluctuation of $d_{Euc(202)}$ occurring at 250 °C is caused by the phase transition of Li^+ order−disorder of Euc particles.

The TEM observations of the as-sintered and thermal-cycled Euc/Cu-Ag composites are shown in Fig. 4. It can be obviously found that there are a lot of dislocations in the matrix of the as-sintered composites, which illustrates that large hot-mismatch exists in the interface of Euc/Cu-Ag composites. After thermal-cycle, the morphology of the matrix in the thermal cycled Euc/Cu-Ag composites has transformed to twins. Since many dislocations exist in the lamella of the twins, the twins should belong to mechanical twins. The result illustrates that the plastic deformation is one way of TMS releasing, and the releasing rate of TMS is very high.

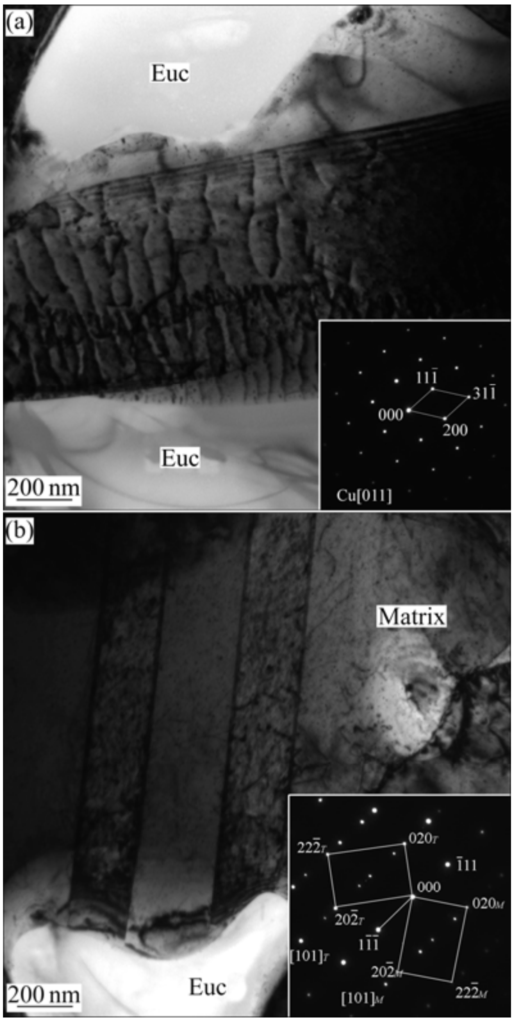

Fig. 4 TEM images of Euc/Cu-Ag composites: (a) As-sintered composites; (b) Thermal-cycled composites

In the composites, the effect of TMS on thermal expansion of composites reflects intrinsically the releasing of residual elastic strain by the TMS. The volume modulus of Euc is only 74 GPa [15], which is much lower than that of Cu. The relaxation of compression stress in the Euc particles becomes the main factor which affects the changing of thermal expansion for the Euc/Cu-Ag composites.

On the basis of the former analysis, it can be concluded that in the first thermal cycle, the releasing of the larger compression stress and the phase transition of Euc particle in the Euc particle make the elongation and CTE of the composites increase greatly. After the first thermal cycle, the plastic deformation of the matrix occurs, and the TMS in the composite decreases to a little extent. At the second thermal cycle, the effect of TMS on the thermal expansion of Euc/Cu-Ag composites decreases, so the CTEs are stable before 250 °C. With a amount of TMS releasing after 250 °C, the CTE of the composites has less increase. After twice thermal cycle, the effect of TMS on thermal expansion of the composites can be neglected, so the CTE of the composites is stable. In addition, after two times of thermal cycle, although the phase transition of Euc occurs, due to its irreversible characteristics, the CTEs of the Euc/Cu composites are still stable.

4 Conclusions

1) The effect of thermal cycle on thermal expansion behavior of Euc/Cu composites is very obvious. Upon twice thermal cycle, the CTEs of Euc/Cu composites tend to be stable.

2) The CTE of the composite can be decreased obvious by the releasing of thermal residual stress in thermal cycling process.

3) In the thermal cycling process, the TMS of Euc/Cu composites changes from compression stress to tensile stress, and tensile stress induces the irreversible phase transition of Li^+ order−disorder of Euc particles. Meanwhile, the changing of thermal residual stress causes the plastic deformation of matrix in the Euc/Cu composites.

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热循环对β-$LiAlSiO_4$/Cu 复合材料热膨胀行为的影响

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摘　要：采用热压烧结工艺制备β-$LiAlSiO_4$/Cu 复合材料。对复合材料进行多次热循环过程中的热膨胀行为测试，对烧结态复合材料进行原位高温 XRD 分析，对热循环前后复合材料的微观组织进行观察。结果表明：经过 2 次以上热循环处理后，β-$LiAlSiO_4$/Cu 复合材料获得稳定的热膨胀系数。在热循环过程中复合材料残余应力得到松弛和释放，可以显著降低复合材料的热膨胀系数。复合材料中的残余应力引起 β-$LiAlSiO_4$ 颗粒中的 Li^+从有序到无序的非可逆性的相转变。在热循环过程中复合材料残余应力的释放引起基体孪晶变形。

关键词：铜基复合材料；热膨胀；残余应力；相转变

(Edited by HE Yun-bin)