Elevated Temperature Mechanical Properties of in-situ Synthesized TiB₂/Al-4.5Cu Matrix Composites

Yanqing Xue¹,a, Qitang Hao ¹,b*, Bo Li¹,c, Xinliang Wang¹,d, Han Zhang¹,e, Dayong Wu²,f, Enpu Liang²,g, Ru Su ²,h*

¹. State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an, Shaanxi, 710072, China
². School of Materials Science and Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, China

*aemail: yqxue666@163.com, bemail: haoqitang@nwpu.edu.cn, cemail: 1096516577@qq.com, demail: 1054470459@qq.com, eemail: laraine0222@163.com, femail:wudayong_yusu@126.com, gemail:85672693@qq.com.

*corresponding author: bemail: haoqitang@nwpu.edu.cn; hemail: dywu@hebust.edu.cn

Abstract. Precipitation coarsening characteristics at elevated temperature have a powerful influence on the thermodynamics properties of TiB₂ particles reinforced aluminium-copper matrix composites (PRAMCs), aging precipitation of θ-Al₂Cu is stable at room temperature, but coarsening occurs at elevated temperature, In this paper, Al-4.5Cu matrix composites with different content TiB₂ are prepared via the molten salt reaction to evaluate the microstructures transformation and the related elevated temperature mechanical properties. Experimental results show that yield strength (YS) and ultimate tensile strength (UTS) of TiB₂/Al-4.5Cu composites increase with the augment of TiB₂ mass fraction, while the elongation decreases gradually both at elevated-temperature of 453k and 493k. The analysis suggests that the remarkable α-Al grain refinement along with pinning effect of TiB₂ particles has a great effect on the grain boundary sliding and migration at high temperature. Additionally, interface debonding also affects the damage and fracture of the composites.

1. Introduction

Aluminum matrix composites (AMCs) have prominent mechanical properties such as high specific strength, low density, small thermal expansion coefficient, stable high temperature performance and good abrasion resistance. They are prospective materials for the application in aerospace, transportation, automobile manufacturing and other fields[1, 2]. Among various reinforced particles, TiB₂ has outstanding advantages of high micro-hardness, good thermodynamic stability, strong corrosion resistance and good wettability with aluminum matrix[3]. Especially, TiB₂/Al-Cu matrix composites can be in-situ synthesized via molten salt reaction which involves adding the mixed K₂TiF₆ and KBF₄ salts with a molar ratio into molten Al or Al-Cu alloy[4, 5]. This method is simple and controllable, accordingly has great potential value in large-scale industrial application.

However, at high temperature, ultimate tensile strength (UTS) of this material tends to decrease, and plasticity tends to increase, the main cause is related to more easier movement of grain boundaries (GBs) and precipitation coarsening[6, 7]. Furthermore, during high temperature oxidation environment, not only will accelerate the initiation and propagation of cracks, but atomic activity will become stronger
and diffusion will increase drama and so on. Regrettably, there are few investigations on the elevated-temperature mechanical properties of TiB2/Al-Cu with plastic deformation, which is more important for the application. In this work, TiB2/Al-4.5Cu composite is successfully synthesized by molten salt reaction methods, our objective is to find the effect of TiB2 particles on the microstructure, elevated-temperature strength and ductility of Al-4.5Cu composite matrix.

2. Materials and Experimental Procedures
In this work, TiB2/Al-4.5Cu composite materials with various content of TiB2 (0%, 2%, 5% and 8%, all compositions are in wt.% unless otherwise specified) were prepared by molten salt reaction method [8, 9]. The raw materials used in the experiments included commercial aluminum ingot, aluminum copper alloy (Al-50wt% Cu), K2TiF6, KBF4, Na3AlF6, etc. The purity of above materials are shown in Table 1.

| Raw materials | Al | Al-50Cu | KBF4 | K2TiF6 | Na3AlF6 |
|---------------|----|---------|------|--------|---------|
| purity        | >99.9% | >99.9% | 99.99% | 99.99% | 99.99% |

Electric-resistance furnace with silicon carbide graphite crucible was used to fabricate TiB2/Al-4.5Cu in-situ composites, the fabrication process was as followed:

1. K2TiF6, KBF4 were prepared in proportion (Ti: B mass fraction is 2.21:1) and mixed fully in advance. The prepared salts were preheated to 250 ℃ and held 2 hours.

2. Put pure aluminum and Al-50Cu into the crucible, and heated to 780 ℃ rapidly, after the melting is ended completely, evaluated the temperature to 860 ℃, and held 30 minutes.

3. Added the prepared salts to the molten, and stirred slowly to make the salt and molten alloy reacted fully, this process must be proceeded at least 30 minutes. Then removed the reaction residue staying on the molten surface and degassed the as-reacted molten with Na3AlF6 for 30 minutes, after that, raised the temperature to 780 ℃ and held 10 minutes, poured the well-prepared molten composite into preheated metal mold.

The heat treatment was done with solution temperature at 510℃ for 4h and aging temperature at 170℃ for 24h, water quenching, controlled transferring time within 10s.

Phase determination of the samples was done by X-ray diffraction (XRD, D8 DISCOVER) with Co target (power is 3kw) and scanning speed of 2°/min.

The microstructures were examined using scanning electron microscope (SEM, ZEISS Gemini 500 field emission scanning electron microscope) and transmission electron microscope (TEM, Themis Z spherical aberration correction scanning transmission electron microscopy operated at 300 kV).

According to the ASTM-E8M standard, the dog-bone tensile testing bars were machined and performed on an electronic universal testing machine (GNT100) at a loading rate of 1 mm/min, At least three specimens were used for each tensile test condition, the standard deviation were also given.

3. Results and Discussions

3.1. Microstructure Characterization
Fig. 1 is XRD analysis results of matrix alloy and composites. It can be seen that the phase composition of composites is mainly α-Al, TiB2 and Al2Cu. XRD spectrum shows a smooth state without any peak between 39.0 ° and 39.5°, in which range, the strongest peak of Al3Ti phase often appears [10]. It indicates that this experiment effectively avoided the formation of these common intermediates in the preparation process of composites, and ensures that the microstructure and properties of composites will not be affected by the intermediates.
Fig. 1 XRD pattern of in-situ TiB2/Al-4.5% Cu composites and matrix alloy

Fig. 2 shows the optical micrographs of Al-4.5Cu and various amounts TiB2/Al-4.5Cu composites. As can be seen in Fig. 2(a), the microstructure of Al-4.5Cu matrix alloy is composed of relatively coarse α-Al grains and Al2Cu phase, the average size of α-Al grains is 171.5 μm. With the addition of TiB2, the α-Al grains are obviously refined. For 2%, 5% and 8% TiB2/Al-4.5Cu, the average grain size is 134.4μm, 92.2μm and 67.5μm, respectively. The effect of grain refinement is remarkable. However, for 8% TiB2/Al-4.5Cu composite, TiB2 agglomeration appears to some extent, as shown in Fig. 2 (d). The agglomeration may weaken the strengthening effect of particles on metal matrix[11].

Fig. 2. Optical microstructure of: (a) Al-4.5Cu Matrix, (b) 2% TiB2/Al-4.5Cu, (c) 5% TiB2/Al-4.5Cu, (d) 8% TiB2/Al-4.5Cu

Fig. 3(a–e) show the TEM and HRTEM micrographs of 5% TiB2/Al-4.5Cu after the tensile test at 493K. As seen in Fig. 3(a) and (c), nanosized TiB2 particles are distributed at the grain boundaries (GBs) and in the interior of the α-Al grains. Fig. 3(b) inserted in the Fig. 3(a) is the selected area electron
Diffraction (SAED) pattern of TiB₂. The corresponding HRTEM image of the interface between TiB₂ and α-Al is shown in Fig. 3(e). The dislocations around the TiB₂ particles are shown in Fig. 3(d), which is aroused by the discrepancy of thermal expansion (CTE) in the Al matrix and TiB₂. These dislocations can act as heterogeneous nucleation sites for precipitates[12]. It has been well documented that TiB₂ hinder the coarsening of the α-Al grains by pinning at the GBs [7, 13]. At elevated temperatures, the strengthening of the TiB₂ particles and θ-Al₂Cu precipitates are the main strengthening mechanism of the TiB₂/Al-4.5Cu composites. As the TiB₂ content increase, the strengthening effects correspondingly increase, which contribute to the enhancement of strength and ductility of the composites at high temperatures.

![Fig. 3 TEM micrographs of TiB₂ in the TiB₂/Al-4.5Cu composite](image)

3.2. Mechanical Properties

Tensile engineering stress-strain curves of Al-4.5Cu and TiB₂/Al-4.5Cu are shown in Fig. 5. The result turns out that Al-4.5Cu alloy has a lower strength and higher elongation than fabricated composites, all curves show a similar trend. At 453K, with the increase of TiB₂ content, the yield and tensile strengths of TiB₂/Al-4.5Cu composites show a similar growing trend, when TiB₂ content is up to 8%, the yield and tensile strengths reach to 312MPa and 374MPa. However, the elevated-temperature elongation of TiB₂/Al-4.5Cu shows a downward trend, when the content of TiB₂ reaches to 8%, its elongation is decreased from 12.1% to 4.6%. This may be due to the fact that atoms are more active, and inter-atom binding force is weakened at the elevated temperature, which leads to the decrease of critical shear stress.
of dislocation on atomic plane, what's more, under small external stress, deformation gets easy, which shows enhancement of plasticity and decrease of tensile strength [14, 15]. When experimental temperature gets to 493K, 8% TiB₂/Al-4.5Cu shows the highest yield and tensile strengths, increased to 289MPa and 335MPa respectively while elongation decreases from 13.2% to 5.5%.

From tensile data tested under 453K and 493K, it can be concluded that tensile and yield strengths of the composite shows a downward trend, while plasticity increases slightly. From previous analyses, it can be seen that active atom leads to the weakening of atomic binding force and make deformation easy. In addition, yield and tensile strengths of 8% TiB₂/Al-4.5Cu are higher than that of Al-4.5Cu, and the improvement is also obvious. Under 493K, tensile and yield strengths of 8% TiB₂/Al-4.5Cu can increase by 95% and 94% compared with that of Al-4.5Cu, respectively. High-temperature mechanical properties show that TiB₂ is very important to TiB₂/Al-4.5Cu, and further investigations of 8% TiB₂/Al-4.5Cu under high temperature can benefit from above data.

![Graph](image)

**Fig 4** High-temperature engineering stress-strain of TiB₂/Al-4.5Cu (a) yield strength (YS), (b) ultimate tensile strength (UTS), (c) elongation (δ)

### 3.3. Fractography

Fig. 5 shows SEM fracture morphology of Al-4.5Cu and 8% TiB₂/Al-4.5Cu, which is obtained under room temperature, 453K and 493K respectively. As can be seen, some deep equiaxed dimples exist on fracture surface of Al-4.5Cu alloy (Fig. 5(a-c)), indicating the occurrence of large plastic deformation just before failure, and the fracture of Al-4.5Cu alloy is deduced to be ductile by micro-voids formation and coalescence. It is proved that during tensile testing at different temperatures, micro-voids are initiated under local stress state and grow with the increase of tensile load. On the end, the voids reach to a critical size and fracture is occurred by such micro-void coalescence. The fracture surfaces of 5% TiB₂/Al-4.5Cu composites consist of deep dimples, indicating a higher amount of plastic deformation before fracture and cleavage facets at some area (Fig. 5(d-f)). It is concluded that cracks are initiated firstly on the interface between matrix and TiB₂ particles and propagate along the boundary. Inspection of the fracture surface of 5% TiB₂/Al-4.5Cu (Fig. 5(h-j)) shows shallower dimples, indicating a lower plastic deformation before fracture. Therefore, fracture surfaces of TiB₂/Al-4.5Cu composites show a ductile feature of Al-4.5Cu matrix. Also, there are some cleavage features indicating crack development at the interface of aluminum matrix and TiB₂ particles due to stress concentration at these regions. From above observations, TiB₂ ceramic particles are visible that is the evidence of the growth of cracks from reinforcement and matrix interface. It is concluded that the ductility of composites is decreased by increasing mass fraction of TiB₂ reinforcement particulates.
4. Conclusion
In the present work, Ti$\text{B}_2$/Al-4.5Cu composites with mass fractions of 0%, 2%, 5% and 8% were synthesized by molten salt reaction. Microstructure and mechanical properties of fabricated composites were analyzed and the result can be conclude as:

(1) OM and SEM results showed remarkable grain refinement effect, average grain size of $\alpha$-Al in matrix material was 167.5μm, while in 2%, 5%, 8% Ti$\text{B}_2$/Al-4.5Cu, the average grain size was 110.4μm, 87.2μm, 75.2μm, respectively.

(2) The mechanical properties of Ti$\text{B}_2$/Al-4.5Cu composites at high temperature were investigated. The fracture morphology was observed by SEM, while the microstructure was observed by TEM and HRTEM, the effect of Ti$\text{B}_2$ content on the fracture mechanism was studied, the results were compared with that of room temperature strengthening. Dimples observations indicated that ductile rupture was predominant fracture mechanism and dimple depth decreases with the increment of volume fraction of reinforcement particles, some cleavage facets were also observed in the fracture surface of Ti$\text{B}_2$/Al-4.5Cu.

(3) Compared with matrix Al-4.5Cu alloy, mechanical properties improvement of Ti$\text{B}_2$/Al-4.5Cu benefited from higher load bearing capacity of reinforcement particle, smaller matrix grain size, and the effect of dislocation pinning.

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