Trace Scandium addition on the strength and thermal stability of TiB₂ particles reinforced Al-4.5 Cu composites

Yunliang Zhang¹, Wentao Yu¹, Xinliang Wang², Yanqing Xue³∗

¹ School of Mechanical & Material Engineering, Shaanxi Key Laboratory of Surface Engineering and Remanufacturing, Xi’an University, Xi’an, Shannxi, 710065, China
² State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an, Shaanxi, 710072, China
³ Xi’an University of Posts and Telecommunications, Xi’an, Shaanxi, 710121, China

* Corresponding author: yqxue666@163.com

Abstract. Strategies employed for developing ultrahigh strength and scalable ductile particles reinforced aluminium-copper matrix composites (AMCs) are highly desirable and grandly challenging. In the present paper, the Scandium (Sc) micro-alloying TiB₂ particles reinforced Al-4.5 Cu composites were successfully fabricated by the optimized salt-metal reaction method. The observed microstructures displayed that Sc addition could remarkably ameliorate the dispersion of TiB₂ particles, enlarge equiaxed α-Al grain zone and refine the grains on the basis of TiB₂ heterogeneous nucleation. In particular, for the 0.4 wt.% Sc microalloyed 5%TiB₂/Al-4.5Cu composites, more than a 20 %, 87 %, and 118 % increase in the ultimate tensile strength (UTS), fracture strain elongation (%) and microhardness (HV), respectively were found with respect to the 3 %TiB₂/Al-4.5Cu composites at room temperature (298K). The improved mechanical properties of strength-ductility synergy were mainly thanks to the homogeneous distribution of TiB₂ particles and modification of Al₂Cu phase. Moreover, proper Sc also enhanced the elevated-temperature mechanical properties of the composites with the aid of the accelerated precipitation of θ′ phase and much lower coarsens rate.

1. Introduction

Aluminum matrix composites (AMCs) are regard as one of the encouraging materials for various utilization especially in the fields of aerospace, weaponry, transportation, etc., on account of the excellent physical and mechanical properties like high specific strength, excellent resistance to corrosion and small thermal expansion coefficient, along with good machinability [1-3]. Among the various AMCs, the TiB₂ particles reinforced aluminum-copper composites (Shortened to TiB₂/Al-4.5Cu composites, all components are mass fractions unless otherwise mentioned) exhibit integrated merits of super-high strength Al-Cu alloy and stiff-thermal TiB₂ ceramic particles preferentially due to the clean interfaces structure and stable interfacial bonding [4-7]. The in-situ salt-metal reaction method with K₂TiF₆, KBF₄ and Al melts makes use of the existing casting technology and controlled chemical reaction has shown a prefect application in the composite materials processing because of the simple process, short preparation cycle and low cost[8-11]. However, for the salt-metal reaction method, the obstinate problem is the reaction-generated TiB₂ particles are prone to agglomerate as coralline clusters due to the strong Van der Waals forces between TiB₂ particles [3, 12]. Besides, previous reports had indicated that it was very difficult to regulate the morphology of TiB₂ particles, and the unavoidable
fractional clusters may lead to local stress concentration, which not only given rise to defects such as cracks or holes at the interface, but also resulted in lower strength, plasticity and toughness [13, 14]. More recently, large documents had proved that rare earth (RE) elements could alter the shape, and distribution of TiB₂ particles in manufacturing process, hence possessed good mechanical properties and excellent high-temperature service capacity. Xue et al.[14, 15] indicated that the Ce element could visibly ameliorate the agglomeration of TiB₂ clusters, ulteriorly modify the primary silicon to be small and granular feature. Yang et al.[13] exhibited that the La element lowered the solidification rate and decreased the nucleation temperature, they attributed the positive effect to intensive transformation temperature of Al–Cu eutectic. Zhang et al.[16] investigated the influence of partial rare earth (RE) elements on the microstructure and wear properties of TiB₂ reinforced 6061 aluminum composites, They adopted first principle calculations to calculate the negative adsorption energy and the largest charge transfer, the calculated values disclosed that Sc elements showed the most positive effect in comparison with other element, their microscopic observation and friction experiment also confirmed the obtained conclusions.

Inspired by these abovementioned researches, this study fabricated the Sc micro-alloying 5%TiB₂/Al-4.5%Cu composites via the optimized salt-metal reaction method, aimed at systematically investigating the influence of Sc element on their microstructure characteristics and mechanical properties. In particular, the strength and thermal stability of 5%TiB₂/Al-4.5%Cu composites at elevated temperature were implement at 473 K and 523 K. We also discussed the strengthening mechanisms in detail. The main purpose of this paper is to offer a new avenues to promote the high-temperature performance of AMCs.

2. Experimental procedure
As a study object, the 5% TiB₂/Al-4.5% Cu-x% Sc were provided by the optimized salt-metal reaction method [12, 17]. The crude materials were commercial Al, Al–50.18% Cu alloy, Al–9.86 % Sc alloy (Shanghai Qichen Metal Product Co., Ltd) and chemical salts of K₂TiF₆, KBF₄, C₂Cl₆ (Shanghai Aladdin Biochemical Technology Co., Ltd.). The specific details of the experiment were as followed: The Al ingots, Al-Cu alloy and Al–Sc alloy were smelted in a graphite crucible and heated to be 760 °C by using an electrical resistance furnace. After holding 10 minutes, an agitation impeller inserted at the crucible was used at a speed of 100 rpm to homogenize the Al melt. After the above procedure, the specially designed argon gas bubbles were injected through a graphite diffuser into the Al melt during the whole reaction process. Then, the preheated and well-mixed K₂TiF₆ and KBF₄ (stoichiometric of Ti:B ratio was 1:2) were added to the molten metals, the reaction time was maintain in 10 minutes. Finally, cast the mixture molten into a preheated permanent mould after remove the scum with the help of slaggling agent (C₂Cl₆). Repeated melting was proceeded three times to ensure the chemical homogeneity. Fig. 1 displays a schematic illustration of the optimized salt-metal reaction method.

![Fig. 1. Schematic illustration of the optimized salt-metal reaction method](image)

Standard tensile test and microscopic observation samples were cut from as-cast ingot and subjected to amended T6 heat treatments (Homogenization at 480 °C for 2h, Solid-solution at 525 °C for 12 h,
water quenching, pre-aging at 300 °C for 2h and aging at 165 °C for 10 h). For comparing, four group of samples were prepared, the first kinds were 5% TiB2/Al-4.5%Cu composites, the second kinds were TiB2/Al-4.5%Cu-0.2% Sc composites, the third kinds were TiB2/Al-4.5%Cu-0.4%Sc composites, and the fourth kinds were TiB2/Al-4.5%Cu-0.6%Sc composites.

X ray diffraction (XRD) were operated using a X'Pert PRO with Cu Kα radiation (λ = 0.154 nm) to study phase formation. Required samples for scanning electron microscope (SEM) microstructure and fractography observation were investigated using a MLA FEG650, operated at 15kV. More details are observed using Themis Z spherical aberration correction scanning transmission electron microscopy to acquire Transmission Electron Microscope (TEM) images operated at 200kV. A TV-PHS30 Vicker's hardness tester was used to test the microhardness of the samples at a load of 9.8N for a duration time of 15s. The tensile test is proceed with a speed of 0.5 mm/min by electronic universal testing machine (GNT100) in accordance with ASTM E8 standards. Every sample was tested five times and taken the average value as the valid value.

3. Results and discussions

3.1. Microstructure

Fig. 2 exhibites the X-ray diffraction (XRD) patterns of the prepared composites, which confirmed the occurrence of α-Al, Al2Cu and TiB2 within the composites. In addition, as displayed in Fig. 2(B, C), the diffraction peak matching the Al3Sc phase could be clearly seen by reason of the addition of Sc element. With the increase of Sc composition, the diffraction peaks were somewhat turned to the lower 2θ, the reason is the Sc atoms caused the deflection of diffraction peaks owing to lattice distortion. It is worth to note that when the Sc content surpassed 0.6 % in Fig. 2(D), AlCuSc peaks appear and this indicates that appropriate amount of Sc can play a positive role, and it is of practical significance to control its content.

![XRD patterns of 5%TiB2/Al-4.5Cu-x Sc composites](image)

The optical micrographs of the samples with different Sc content are demonstrated in Fig. 3. With regard to the 5%TiB2/Al-4.5Cu composites, It can be found that most of TiB2 particles existed along the α-Al grain boundary in the type of agglomeration as coral-like clusters, and most of the grains present as irregularity dendrites. Our previous studies have indicated that the granular size of in situ fabricated TiB2 particles are usually less-than 1 μm, which result in van der Waals forces thus causing the coral-like agglomeration [12, 17]. Xue et al.[14, 15] also indicated that the TiB2 clusters in A356 melt were pushed by the front edge of solidified interface, and ultimately were assembled to be irregularly shaped agglomerations dominatingly along the grain boundary. When added Sc element to the mixed system, remarkable changes can be found in the modified 5%TiB2/Al-4.5Cu-0.4Sc, in evidence that the TiB2 particles distributed more homogeneous, a large number of TiB2 particles have been found in the interior of α-Al grains and existence isolated. In addition, the morphologies of α-grains transformed from columnar to equiaxed crystals.
Fig. 3. Optical micrographs of 5%TiB₂/Al-4.5Cu-x Sc composites, (a) Sc free, (b) 0.2% Sc, (c) 0.4% Sc, (d) 0.6% Sc.

Fig. 4 gives the SEM morphologies of the composites. Distinctly, some slag inclusion and TiB₂ agglomerates were observed in the 5%TiB₂/Al-4.5Cu composites, along with irregular shape Al₃Ti (Fig. 4(a)). After adding Sc to the composites, the serious reunion phenomenon of TiB₂ agglomerates was apparently improved and the slag inclusion also reduced remarkably, mainly because of interfacial energy reduction reduces of the whole system. Zhang et al. [16] had pointed out that Sc was one of the most efficient microalloyed element for TiB₂ particle reinforced aluminum matrix composites. The primary cause is Sc will give high priority for composition segregation on higher index single crystal surface of TiB₂, in consequence restrain the rapid growth of preference orientation, as well as reduce the interface energy. These calculated results by first principle calculations played a positive role in designing and analysing morphology evolution and variation of TiB₂ particles. However, when Sc addition is 0.6 wt%, some slag inclusion appeared again in spite of relatively evenly distributed TiB₂ particles. This is because redundant Sc results in unnecessary AlCuSc phase, which not only consumed expensive Sc but also produced unnecessary brittle phases.

Fig. 4. SEM morphologies of 5%TiB₂/Al-4.5Cu-x Sc composites, (a) Sc free, (b) 0.2% Sc, (c) 0.4% Sc, (d) 0.6% Sc.

Fig. 5(a) shows the TEM images of the 5%TiB₂/Al-4.5Cu composites, inserted image is corresponding selected-area electron diffraction (SAED) pattern of TiB₂, some large agglomerates are
observed along the crystal boundary while other small ones were dispersive coarse $\theta'$-Al$_2$Cu phases and TiB$_2$ particles. Fig. 5(b) shows the 5%TiB$_2$/Al-4.5Cu-0.4 Sc composites, indicating refined $\theta'$-Al$_2$Cu precipitates and discrete TiB$_2$ and Al$_3$Sc precipitation. Fig. 5(c) shows the TEM picture of the 5%TiB$_2$/Al-4.5Cu-0.4 Sc composites implemented the tensile test at 523 K. It is evident that high density of dislocation and severe lattice distortion were observed anywhere. The HRTEM image and SAED of Al$_3$Sc is shown in Fig. 5(d). It was found that in the case of the composites without Sc, TiB$_2$ particles distribute heterogeneously along the grain boundary regions as coralline clusters, and exist in coral-like clusters. However, as illustrated in Fig. 5(b), significant microstructure changes can be observed in the present of Sc addition, noticeably, the TiB$_2$ particles are evenly distributed and exist in isolation within grains, moreover, $\theta'$-Al$_2$Cu precipitates had been significantly refined and notably the density of the ensemble. In addition, it is worth noting that with the action of Sc, a large amount of $\theta'$-Al$_2$Cu and Al$_3$Sc precipitated phase with strong coarsening resistance contributes greatly to improving the mechanical properties of composites at high temperature.

![Fig. 5 TEM images of the 5%TiB$_2$/Al-4.5Cu-x Sc composites, (a) Sc free, (b) 0.4% Sc, (c) 0.4% Sc composites after the tensile test at 523 K, (d) HRTEM image and SAED of Al$_3$Sc.](image)

3.2. Mechanical properties

The microhardness of Sc microalloyed TiB$_2$/Al-4.5Cu-0.4Sc composites are demonstrated in Fig. 6(a). It is clearly that the hardness of the composites increases from 74 HV to 139 HV from free to 0.6 % Sc addition, and the optimum addition level was 0.4% Sc, which was corresponding to the observation of microstructure. Whereas added more than 0.6% Sc content, the microhardness starts to decline to some extent. The promotion of microhardness can be attributed to the uniformly distributed TiB$_2$ particles and contributions from Al$_3$Sc phase. However, inappropriate over addition Sc will cause exacerbating phenomenon of aggregation, therefore leads to the decrease in hardness.

The tensile test performed on the 5%TiB$_2$/Al-4.5Cu-x Sc composites was done in accordance with the ASTM E8 standard. Fig. 6 (a) shows the Young’s modulus of the 5%TiB$_2$/Al-4.5Cu-x Sc composites while Fig. 6 (b) gives the engineering stress-strain curves of the 5%TiB$_2$/Al-4.5Cu-x Sc composites at 298 K, 473K, and 573 K, respectively. The tests demonstrated that as the temperature increased, the ultimate tensile strength (UTS) was decreasing gradually while the fracture strain (elongation %) was increasing markedly. In particular, at all three tested temperatures, the optimal strength-ductility synergies were obtained in the present 5%TiB$_2$/Al-4.5Cu-0.4 Sc composites compared with other
counterparts with less or free Sc elements. The higher strength was derived from the refined dispersion of 0\textsuperscript{th}-Al\textsubscript{2}Cu and Al\textsubscript{3}Sc phase, this microstructure has strong resistance to coarsening. The improved elongation coming from Sc microalloying can be explained by the homogeneous distribution of TiB\textsubscript{2} particles and continuance interface adhesion between strengthening phase and \(\alpha\)-Al matrix during plastic deformation. This phenomenon was mainly gained by ameliorated critical interfacial strength by refined coarsening-resistance precipitate dispersion to reduce stress-strain concentration and Sc segregation to decrease the interfacial energy.

Fig. 6. (a) Vicker’s hardness values and Yong’s modulus, (b) Tensile engineering stress-strain curves of the 5%TiB\textsubscript{2}/Al-4.5Cu-x Sc composites.

Fig. 7 shows the SEM fractography of 5%TiB\textsubscript{2}/Al-4.5Cu-x Sc composites after tensile test at 523K. In Fig. 7(a), the 5%TiB\textsubscript{2}/Al-4.5Cu composites characterized by the brittle cleavage fracture induced by the agglomerated TiB\textsubscript{2} particles and some inclusion. With the Sc content increasing up to 0.4%, the ductile dimples distributed more uniformly and became much shallower, this was in step with the improved ductility, as shown in Fig. 7(c), which demonstrates that the fracture mode of composites at high temperature is principally plastic fracture. Besides, the irregularly shallow dimple on the fracture surface of the 5%TiB\textsubscript{2}/Al-4.5Cu-0.6 Sc composites was observed. Based on the observations, the fracture surface of composites with 0.4%Sc was well-distributed compare with the other composites.

Fig. 7. SEM fractography of 5%TiB\textsubscript{2}/Al-4.5Cu-x Sc composites after tensile test at 523K, (a) Sc free, (b) 0.2% Sc, (c) 0.4% Sc, (d) 0.6% Sc.

4. Conclusion
The Sc micro-alloying TiB\textsubscript{2}/Al-4.5Cu composites were fabricated by the optimized salt-metal reaction method, which can not only avoid the large amount of TiB\textsubscript{2} particles agglomeration, but also reduce the harmful unavoidable inclusion impurities during the reaction process by the adoptive impeller stirring and argon gas bubble refining. The 5%TiB\textsubscript{2}/Al-4.5Cu-0.4 Sc composites exhibited the highest ultimate tensile strength, Yong’s modulus and fracture strain (elongation %) at all the three temperature. At room temperature of 298K, their average microhardness was 139HV and the Yong’s modulus was 75.6 GPa,
Especially at 523K, the ultimate tensile and strength fracture strain were respectively 162MPa and 9.34%, which is increased by nearly 92.8% and 123% compared to the Sc free composites. Being consistent with the microscopic observation, the uniformly distributed TiB₂ particles and refined dispersion of θ'-Al₂Cu and Al₃Sc phase were the dominant strengthening mechanism of the composites at elevated temperatures.

References
[1] Y. Cui, D.J.M. King, A.P. Horsfield, C.M. Gourlay, (2020) Solidification orientation relationships between Al₃Ti and TiB₂. Acta Mater. 186 149-161.
[2] J. Li, F.S. Hage, Q.M. Ramasse, P. Schumacher, (2021) The nucleation sequence of α-Al on TiB₂ particles in Al-Cu alloys. Acta Mater. 206.
[3] Y. Ma, A. Addad, G. Ji, M.-X. Zhang, W. Lefebvre, Z. Chen, V. Ji, (2020) Atomic-scale investigation of the interface precipitation in a TiB₂ nanoparticle reinforced Al–Zn–Mg–Cu matrix composite. Acta Mater. 185 287-299.
[4] B.-X. Dong, Q. Li, Z.-F. Wang, T.-S. Liu, H.-Y. Yang, S.-L. Shu, L.-Y. Chen, F. Qiu, Q.-C. Jiang, L.-C. Zhang, (2021) Enhancing strength-ductility synergy and mechanisms of Al-based composites by size-tunable in-situ TiB₂ particles with specific spatial distribution. Composites Part B 217.
[5] Q. Gao, S. Wu, L. Lü, X. Duan, P. An, (2016) Preparation of in-situ 5 vol% TiB₂ particulate reinforced Al–4.5Cu alloy matrix composites assisted by improved mechanical stirring process. Mater. Des. 94 79-86.
[6] Y. Han, Y. Dai, D. Shu, J. Wang, B. Sun, (2006) First-principles calculations on the stability of Al / TiB₂ interface. Appl. Phys. Lett. 89(14).
[7] J. Liu, Z. Liu, Z. Dong, X. Cheng, Q. Zheng, J. Li, S. Zuo, Z. Huang, Y. Gao, J. Xing, Q. Han, (2018) On the preparation and mechanical properties of in situ small-sized TiB₂/Al–4.5Cu composites via ultrasound assisted RD method. J. Alloys Compd. 765 1008-1017.
[8] R. Du, Q. Gao, S. Wu, S. Lü, X. Zhou, (2018) Influence of TiB₂ particles on aging behavior of in-situ TiB₂/Al-4.5Cu composites. Mater. Sci. Eng., A 721 244-250.
[9] Q. Gao, S. Wu, S. Lü, X. Xiong, R. Du, P. An, (2017) Improvement of particles distribution of in-situ 5 vol% TiB₂ particulates reinforced Al-4.5Cu alloy matrix composites with ultrasonic vibration treatment. J. Alloys Compd. 692 1-9.
[10] Y. Li, G. Lian, J. Geng, C. Song, D. Chen, H. Wang, (2021) Effects of ultrasonic rolling on the surface integrity of in-situ TiB₂/2024Al composite. J. Mater. Process. Technol. 293.
[11] C. Mallikarjuna, S.M. Shashidhara, U.S. Mallik, K.I. Parashivamurthy, (2011) Grain refinement and wear properties evaluation of aluminum alloy 2014 matrix-TiB₂ in-situ composites. Mater. Des. 32(6) 3554-3559.
[12] Y. Xue, Q. Hao, B. Li, X. Wang, C. Yin, H. Zhang, (2021) Improving the strength-ductility trade-off of TiB₂/Al-4.5%Cu composites via Mg–Ag microalloying and multi-step heat treatment. Mater. Res. Express 8(5).
[13] Y. Xue, B. Li, X. Wang, X. Li, H. Zhang, Q. Hao, (2021) Effect of Mg on the microstructure evolution and mechanical properties of 5%TiB₂/Al–4.5%Cu composites. Materials Today Communications 28.