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Improving the strength-ductility trade-off of TiB$_2$/Al-4.5%Cu composites via Mg-Ag microalloying and multi-step heat treatment

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Abstract

To surmount the longstanding puzzle of strength-ductility trade-off, efforts had been made to apply Mg - Ag microalloying on 5%TiB$_2$/Al-4.5%Cu composites by in situ molten salt reaction and subsequent heat treatment. The obtained composites achieve an eye-catching tensile elongation ($\delta$) of 6.1 ± 0.4%, while maintaining elevated ultimate tensile strength (UTS) of 497 ± 4 MPa and yield strength (YS) of 401 ± 3 MPa. Comprehensive characterization demonstrated that the uniformly distributed TiB$_2$ particles together with semi-coherent grain boundaries between the $\alpha$-Al matrix and reinforcement phase (TiB$_2$ particles, $\Omega$-Al$_2$Cu, $\sigma$-Al$_3$Cu$_6$Mg$_2$) facilitated the dislocation motion integrally, which eliminated the stress concentrations, may be the main reason for amelioration in the strength-ductility trade-off of the composites when subject to rigorous multi-step heat treatment.

1. Introduction

The precipitate-strengthened Al-Cu alloys with high specific strength and excellent machinability are of technological importance for structural applications such as aerospace and transportation [1–3]. Moreover, the everlasting thirst for fuel-saving and cost-efficient materials has aroused enormous interest in particles reinforced aluminium matrix composites (AMCs) owing to their prominent mechanical properties such as high specific strength, low density, small thermal expansion coefficient and stable high temperature performance [4, 5]. Nevertheless, these composites typically suffer from a hard limitation—absence of tensile ductility (elongation is normally less than 5% at atmosphere temperature), which is the Achilles heels of metal matrix composites [6, 7]. Countless efforts have been made to improve the long-standing dilemma of strength-ductility trade-off, such as electromagnetic stirring [8], bimodal and hierarchical structures [9]. Despite some encouraging findings, these technologies are usually complicated and with limited strengths because of the incorporation of some coarse-scale microstructures. More recently, an innovative and economically feasible micro-alloying strategy, mainly adding trace rare elements (Sc, Zr, La, etc) and other compatible metallic elements (Cu, Zn, Mg etc) to the TiB$_2$-Al system during melting process, have been recognized as potential technology to overcome the strength-ductility trade-off of particle reinforced AMCs [6, 10–18]. Furthermore, it has been suggested that $\Omega$(Al$_2$Cu, formed on the {111}$_{\alpha,Al}$ planes other than $\theta$(Al$_3$Cu, formed on the {100}$_{\alpha,Al}$ planes), $\sigma$(Al$_3$Cu$_6$Mg$_2$), and some small dispersed (GP zones and Mg–Ag co-clusters) are semi-coherent with the Al matrix in the heat treated Al-Cu-Mg-Ag alloys, which exhibit superior performance [19–22]. Inspired by the above notions, one novel strategy is proposed in this work to conquer the strength-ductility trade-off of TiB$_2$/Al-4.5%Cu composites by multi-step heat treatment and micro-alloying with Mg and Ag.

2. Experiment procedures

Composites with nominal composition of 5% TiB$_2$/Al-4.5% Cu-x% Mg-x% Ag (all compositions are in wt. % unless otherwise specified) were prepared by in situ molten salt reaction [8, 23]. The matrix alloys used in our
experiment were pure Al, Al–50.18% Cu alloy, Al–10.37% Mg alloy, Al–10.46% Ag alloy with purity higher than 99.9% (Shanghai Qichen Metal Product Co., Ltd) and chemical salts K₂TiF₆, KBF₄, C₂Cl₆ (Shanghai Aladdin Biochemical Technology Co., Ltd), the details were described as followed.

For the preparation of 5% TiB₂/Al–4.5% Cu-x% Mg-x% Ag composites, pure Al and Al-Cu alloys were melted in a graphite crucible of an electric furnace at around 790 °C and held for around 30 min with proper stirring. Later, degasser (hexachloroethane, C₂Cl₆) was added to release any dissolved gases. After that, a mixture of intensive mixing salts: K₂TiF₆ and KBF₄ (the ratio between Ti and B was kept as 2:2.1) preheated to 250 °C to remove any moisture content, were added to the molten metal, followed by removing reaction residue from the melt surface (KAlF₄ and KAlF₆). The temperature during the entire operation was maintained at 760 °C and reaction time was controlled within 10 min, thereafter, added the quantified Al–Mg, Al–Ag alloys into the mixture and maintained at 820 °C with 30 min, in the end, cast the refined and degassed mixture molten into a preheated permanent mould after removed the remaining scum. During the process of experiment, temperature and time step control unit equipped with stir casting setup was used to control the reaction temperature and time respectively. Repeated melting was carried out four times to ensure the chemical homogeneity. The resulting exothermic reaction between molten metal and salts was given below.

\[ 3K_2TiF_6 + 8KBF_4 + 10Al \rightarrow 3TiB_2 + 9KAlF_4 + K_2AlF_5 \]

Of particular note was the calculation of percentage of salt K₂TiF₆, KBF₄, C₂Cl₆ used for the fabrication of composites, the mass fraction of C₂Cl₆ was obtained by experience which was about 1%. As has been highlighted by Shaik Mozammil et al [23, 24], A higher ratio would have led to the formation of Al₃Ti while with lower ratios, AlB₂ would have been formed, based on the atomic ratio of 2:1, the mass fraction ratio between Ti and B was kept as 2.2:1, owing to the Ti has an atomic mass of 47.87 while B has an atomic mass of 10.81.

Assuming that the weight of the composite was W, then the weight of TiB₂ required for the test was W×5%. The calculation formulas of the raw materials needed for the test were as follows:

\[ m_{Al-50.18\%Cu} = \frac{W \times 4.5\%}{50.18\%} \]
\[ m_{Al-10.37\%Mg} = \frac{W \times 0.6\%}{10.37\%} \]
\[ m_{Al-10.46\%Ag} = \frac{W \times 0.1\%}{10.46\%} \]
\[ n_1 = \frac{W \times 5\% \times 2.21}{3.21} \]
\[ n_2 = \frac{W \times 5\% \times 2.21 \times 1}{47.87} \times 2 \]
\[ m_{K_2TiF_6} = n_1 \times \frac{(39.10 \times 2 + 47.87 + 19 \times 6)}{3.21} \]
\[ m_{KBF_4} = n_2 \times \frac{(39.10 + 10.81 + 19 \times 4)}{47.87} \]
\[ m_{Al} = W - m_{Al-50.18\%Cu} - m_{Al-10.37\%Mg} - m_{Al-10.46\%Ag} - m_{TiB_2} \]

W is the total weight of the composite; \( m_{Al-50.18\%Cu} \) is the required mass of Al–50.18% Cu alloy; \( m_{Al-10.37\%Mg} \) is the required mass of Al–10.37% Mg alloy; \( m_{Al-10.46\%Ag} \) is the required mass of Al–10.46% Ag alloy; \( m_{K_2TiF_6} \) is the required mass of chemical salts K₂TiF₆; \( m_{KBF_4} \) is the required mass of chemical salts KBF₄.

Standard tensile samples were cut from equal-axis ingot and subjected to T6 heat treatments (Solid-solution at 540 °C for 10 h + water quenching + Artificial aging at 165 °C for 24 h), multi-step heat treatment (Homogenization at 450 °C for 4h, Solid-solution at 540 °C for 10 h, water quenching, pre-aging at 250°C for 8h and aging at 165 °C for 24 h), respectively. For comparison, three types of samples were prepared, the first types were TiB₂/Al–4.5%Cu composites subject to T6 heat treatment (referred to as the ‘conventionally processed composites’), the second types were TiB₂/Al–4.5%Cu–0.6%Mg–0.1%Ag composites also subject to T6 heat treatment (referred to as the ‘Mg and Ag micro-alloying composites’), and the third types were TiB₂/Al–4.5%Cu–0.6%Mg–0.1%Ag composites subject to multi-step heat treatment (referred to as the ‘modified processed composites’).

The basic optical microscopy (OM) was performed on a Leica Microsystems CMS GmbH, more microstructural details were well characterized using ZEISS Gemini 500 field emission scanning electron microscope (SEM) operated at 25 kV, the test samples were deep etched by using electrolytic polishing in a CH₃OH solution with a concentration of 5 vol% HClO₄ at 24 V and 15 s. A Themis Z spherical aberration correction scanning transmission electron microscope equipped with a probe aberration corrector, operated at 300 kV, was used to acquire (HR) TEM images, which equipped highly efficient EDS system was used for chemical analyses, specimens with 3 mm in diameter were prepared through mechanical polishing and final ion
milling by GATAN precision ion polishing system, operated at -150 °C. Tensile test was performed with a constant tensile speed of 1 mm min⁻¹ in electronic universal testing machine (GNT100) according to ASTM E8 standards, each sample was tested at least three times, and the average value was taken.

3. Results and discussion

3.1. Tensile properties

Tensile tests at ambient temperature (AT) were investigated to measure the mechanical properties of the designated three types of composites, as shown in figure 1, the modified processed composites exhibited outstanding combination of tensile strength and large uniform ductility. The yield strength reached as high as 401 ± 3 MPa, and the ultimate tensile strength came up to 497 ± 4 MPa, increased by 15.6% and 10.2% compared with the conventionally processed composites. More encouragingly, the modified processed composites showed a large tensile ductility, with a uniform elongation of 6.1 ± 0.4%, which was more than twofold than that of the conventionally processed composites (2.8 ± 0.4%).

3.2. Microstructural characterization

To understand the admirable mechanical properties of the modified processed composites, we studied the underlying microstructures in detail. Figure 2 exhibited the representative microstructures of three types composites. Figures 2(a), (d), (g) shown the conventionally processed TiB₂/Al-4.5%Cu composites, the microstructures was mainly comprised of the refined α-Al grains with average grain of 161 μm and the Al₂Cu phase at the grain boundaries. It was obvious in the figure 2(g) that most of the TiB₂ particles with irregular profile adhere to each other and present as the form of agglomeration. As one of the most commonly used heterogeneous nucleating agent, TiB₂ can lead to large-scale grain refinement, nonetheless, because of the submicron-sized particles have large surface area-to-volume ratio, which gives rise to van der Waals and adhesion forces thereby causing the particles to aggregate into clusters, consequently, the seriously agglomerated TiB₂ particles may cause stress concentration and become the crack source during the process of stress deformation [15].

When the 0.6%Mg and 0.1%Ag additive was added in the composites, as shown in figures 2(b), (e), (h), in spite of fractional TiB₂ agglomerations still existed in the matrix alloy, the average size of α-Al grains decreased gradually to 82 μm. It can be seen that the segregation of large TiB₂ agglomerates was significantly improved (figure 2(h)). The main reason is that as a type of surface active element, Mg can reduced the work of adhesion (W_{ad}) which indicates Mg segregation weakens the Al/TiB₂ interface, thus possibly inhibit TiB₂ agglomerations. Furthermore, Mg element can also reduce the interfacial energy of the whole system on account of higher oxygen affinity than Al. Large document had proved that Mg element tends to react with Al₂O₃ oxide with formation of MgO or MgAl₂O₄ [25, 26], which reduces the amount of Al₂O₃ on the surface of melt and improves the wettability of melt to TiB₂ particles, thus inhibiting the segregation of TiB₂ particle clusters.

As shown in figures 2(c), (f), (i), It was clear that the combined process of Mg-Ag microalloying and multi-step heat treatment had a great influence on the sizes of α-Al grains, the microstructure consists of fine-scale
columnar and equiaxed grains, the mean size of $\alpha$-Al grains was 66 $\mu m$, which was fairly smaller than that of $\alpha$-Al grains in the unreinforced Al-Cu alloy. It has been largely recognized that the grain sizes play an important role in the strength and ductility of material \[27\], a general relationship between grain size and yield stress can be described by the Hall-Petch equation \[11, 28\]:

$$
\Delta \sigma_y = k(d^{-1/2} - d_0^{-1/2})
$$

$\Delta \sigma_y$ is the increment of yield strength, $k$ is a constant, $d$ and $d_0$ is the average $\alpha$-Al grains diameter.

Obviously, the yield strength of the composites increases as $\alpha$-Al grains size decreases. Moreover, The refined grain structures can reduce flaw sizes and make more grains endure deformation to realize uniform deformation so as to increase the resistance to crack propagation and enhance the ductility \[9, 29\].

In order to illuminate the morphology change of TiB$_2$ particles, we have carried out the SEM observation, as observed in figure 3(a), TiB$_2$ particles in the conventionally processed composites were distributed unevenly and exist in severely agglomerations. With the addition of Mg and Ag, significant improvement of distribution can be found in the composite, as shown in figure 3(b). From figure 3(c), we observed the agglomerations of TiB$_2$ particles were mitigated greatly, and distributed more uniformly in the modified processed composites, moreover, the average size of TiB$_2$ particles declined obviously. The agglomeration of particles was mainly attributed to high surface energy of TiB$_2$ particles. With Trace additive Mg and Ag, the interfacial tension
between $\alpha$-Al and TiB$_2$ particles can be reduced which results in the increase of wettability of TiB$_2$ particles in aluminum melt [12].

Figure 4 displayed the TEM micrograph of the modified processed composites, figure 4(a) revealed that with the addition of Mg and Ag, the TiB$_2$ particles exhibits a uniform distribution of ultrafine equiaxed grains with an average size of 478 nm. The EDS mappings showed that the element Mg and Ag were mainly presented in the TiB$_2$ particle and preferentially segregated to the interface. Figure 4(b) was the corresponding selected area diffraction (SEAD) patterns of TiB$_2$. Figure 4(c) showed two types of precipitates that can be identified as $\Omega$-Al$_2$Cu and $\sigma$-Al$_5$Cu$_6$Mg$_2$, according to the available literature [20]. Indexing of the SEAD in figure 4(d) suggests that highlight phase were $\Omega$-Al$_2$Cu formed on the $\{111\}$ $\alpha$-Al planes other than $\theta$-Al$_5$Cu which normally formed on the $\{100\}$ $\alpha$-Al planes. Figures 4(e)–(h) indicates that the cubic precipitate was $\sigma$-Al$_5$Cu$_6$Mg$_2$ with cubic parameters of $a = 0.831$ nm. Obviously, Trace additive Mg and Ag along with multi-step heat treatment alters the precipitation process in the TiB$_2$/Al-4.5%Cu composites by modifying the dispersion, morphology and crystal structure of precipitates.

3.3. Discussion

Characteristic of dislocations in modified processed composites at different strain of plastic deformation were observed to analyze the intrinsic mechanisms for the unusual tensile ductility. At the strain of $\sim$1% (figure 5(a)), the dislocation slipping was activated in the appearance of random orientation around TiB$_2$ particles, indicating an early stage of planar dislocation slip across the grain boundaries. With further increasing strain to $\sim$3% (figure 5(b)), more dislocation were activated and with a much higher density. Further increasing the strain to 6.2% (figure 5(c)), it can be seen that dislocation networks were formed and appeared hexagonal mainly, it is generally accepted that dislocations rearranged and transformed to dislocation networks are beneficial to lower the defect energy so as to enhance the ductility [30].

The modified processed composites exhibited an advisable comprehensive mechanical properties, several major contributions can account for the mechanism. First, nanoparticles of TiB$_2$ in low concentrations can be easily engulfed during solidification thereby greatly mitigated the agglomerations of TiB$_2$ particles [6]. Second, plentiful $\sigma$-Al$_5$Cu$_6$Mg$_2$ and $\Omega$-Al$_2$Cu phase were precipitated when subject to multi-step heat treatment with addition of trace Mg and Ag. Third, the dislocations rearranged and transformed to dislocation networks along with the recrystallized and uniform microstructure promotes the homogeneous deformation were also beneficial to lower the defect energy.
4. Conclusions

In contrast with the common dilemma of strength-ductility trade-off in traditional particle reinforced AMCs, the yield strength and elongation to fracture of the TiB$_2$/Al-4.5%Cu composites were simultaneously and significantly improved by multi-step heat treatment and microalloying process in the present work. Underlying mechanisms responsible for the elevated deformation properties and considerable ductility of the modified composites were also discussed. The ultrafine grains and uniformly distributed reinforcement phases coherent with $\alpha$-Al were key to unlocking the full potential of metal matrix composite, consequently, combined utilization of the micro-alloying and multi-step heat treatment strategy can potentially open a new avenues for designing ultrahigh yet ductile materials.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Conflicts of interest

The authors declare no conflicts of interest.

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Figure 5. Deformation morphology of modified processed composites at strain of (a) 1%, (b) 3%, (c) 6.2%.
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