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Effects of A-site atoms in Ti$_2$AlC and Ti$_3$SiC$_2$ MAX phases reinforced Mg composites: Interfacial structure and mechanical properties

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ABSTRACT

AZ91D magnesium composites reinforced by Ti$_3$SiC$_2$ MAX phase were fabricated by the stir casting technique. Tensile tests reveal that the reinforced effects of Ti$_3$SiC$_2$ and Ti$_2$AlC on Mg matrix are different. Unlike Ti$_2$AlC-AZ91D composite for which Ti$_2$AlC delamination happens during the fracture, Ti$_3$SiC$_2$-AZ91D composite fractures by interfacial debonding mechanisms. Transmission electron microscopy characterization shows that few nanometric Mg grains form in the vicinity of Ti$_3$SiC$_2$ particles, while huge amount of nanometric Mg grains form along with Ti$_2$AlC particles. Elements mapping confirms that Al atoms of Ti$_2$AlC diffuse into Mg matrix. In contrast, no outward diffusion of Si of Ti$_3$SiC$_2$ is observed. This outcome points out that it is possible to regulate the mechanical properties of their relevant Mg composite through adjusting the content of Al and Si in MAX phases, such as Ti$_3$SiAlC$_2$ solid solution.

1. Introduction

Magnesium alloy is regarded as one of the most promising structural materials candidates in the aerospace and automobile industry, especially in applications subjected to strong acceleration and high speed [1, 2], due to its lightweight, high specific strength and high damping capacity [3,4]. It is reported that light-weighting offers up to a 7% improvement in fuel economy for each 10% reduction in vehicle weight [5]. However, the poor elevated temperature tensile strength of Mg-based materials restricts their wide utilization for applications [6,7], especially in the area, where high stiffness, high wear resistance and damping capacity are strongly desired. The only way for optimizing these properties is to introduce reinforcement into Mg alloy.

Recently, ternary and nano-layered compounds, named as MAX phases (M$_{n+1}$AX$_n$, where M is early transition metal, A belongs to group IIIA or IVA element, X is C and/or N, N = 1–3) [8,9], were introduced into Mg alloy due to their unique combination of metal-like and ceramic-like properties [10–12]. In comparison with traditional binary ceramic particles (e.g. TiC and SiC) [13–15], Barsoum et al. [8] found that MAX phases could dissipate energy capacity due to its kinking nonlinear elastic (KNE) mechanism. Anasori et al. reported that Mg composites reinforced with 20 vol% Ti$_2$AlC could dissipate 30% mechanical energy during each compressive load at 250 MPa [16]. Yu et al. [17–20] systematically investigated Ti$_2$AlC-AZ91D magnesium composite fabricated by semi-solid stirring method and processed with hot extrusion. Unlike SiC-AZ91D composite for which interfacial decohesion is found after tensile test, the in-situ tensile tests have revealed that micro-cracks are initiated from the Ti$_2$AlC basal planes rather than from the Ti$_2$AlC-Mg interface. The high damping capacity of Ti$_2$AlC-AZ91D magnesium composite comes from the high dislocation density contained in Ti$_2$AlC and Mg matrix at room temperature. Furthermore, Ti$_2$AlC-AZ91D magnesium composite simultaneously exhibits high wear resistance and self-lubricated capacity. Unlike hard ceramic particles, such as SiC, no severe grooves and scratches were found on the magnesium matrix surface due to the easy pulling out of hard ceramic particles [13]. Even though the introduction of lubricant graphene, graphite and MoS$_2$ could decrease the coefficient of friction, such as B$_4$C-Graphite/Mg [14] and SiC-Graphene/Mg [15], graphite and MoS$_2$ degrade rapidly at above 350 °C in an oxidizing environment.

MAX phases contain more than 70 different species and A elements are easily out-diffused from MAX unit cell. For example, migration energy of Si in Ti$_3$SiC$_2$ (0.9 eV) [21,22] is higher than that of Al in Ti$_2$AlC (0.83 eV). This means that it is possible to regulate the interfacial structure of MAX-Mg by replacing Ti$_2$AlC with Ti$_3$SiC$_2$. As reported in

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our previous study [19], the interfacial friction could not be activated until 200 °C. In addition, Al₂O₃ and MgO were detected on the surface of Ti₂AlC-AZ91D magnesium composite during the dry-slide test, which is detrimental to the tribological properties. Furthermore, the formed nano Mg grains did not coarsen in Ti₂AlC-Mg composite under heating 3 times to 700 °C, while this phenomenon is not found in Ti₃SiC₂-Mg composite [23]. Herein, in order to clarify this phenomenon and characterize their reinforcement capacity in magnesium composite, we fabricated two composites Ti₂AlC-AZ91D and Ti₃SiC₂-AZ91D. Then we compared their mechanical properties and investigate their interfacial evolution.

2. Experimental method

In this work, AZ91D magnesium alloy (Al: 9.0, Zn: 0.81, Si: 0.1, Mn: 0.24, Fe: 0.022, Cu: 0.030, Ni: 0.005, Mg: rest) reinforced by laboratory-made Ti₃SiC₂ particles (diameter below 10 μm) was fabricated by semi-solid stirring method. The Ti₃SiC₂ powders were synthesized from starting powders of Titanium (Ti, 99.5% purity) and titanium carbide (TiC, 99.5% purity) powders with a molar ratio of 3Ti: 1.1Si: 1.9C by pressureless sintering at 1500 °C during 20 min under Ar gas protection. The AZ91D alloy ingots were heated to be 700 °C under the protection of CO₂/SF₆ gas and cooled to the semi-solid condition (590 °C). Then, the preheated Ti₃SiC₂ particles were poured into the high speed stirred (1000 rpm) semi-solids. After homogeneous stirring, the melt was reheated to be 700 °C and poured into a preheated metal mold (450 °C). Finally, the 100 MPa was applied on a servo press machine during solidification. More details can be found in our previous study about Ti₂AlC-AZ91D composite [24].

Uniaxial tensile tests were performed through a universal servo-hydraulic mechanical testing machine (Instron 5600, Norwood, MA) with a strain rate of 0.5 mm/min at room temperature. The specimens were prepared with the dimension of 18 mm long (gauge), 3 mm wide and 2 mm thick in reference to the ASTM E8M – 03 flat specimen standard.

Phase identification was performed by X-Ray Diffraction (XRD) using a Bruker (Karlsruhe, Germany) D8 diffractometer with CuKα radiation. Microstructural observation was carried out by Scanning Electron

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**Fig. 1.** Backscattered electron (BSE) micrographs of (a) as-cast AZ91D alloy and the composites reinforced with (b) 5 vol% Ti₃SiC₂, (c) 5 vol% Ti₂AlC and (d) 15 vol% Ti₃SiC₂.

**Fig. 2.** XRD diffractograms of as-cast (a) Ti₃SiC₂-AZ91D and (b) Ti₂AlC-AZ91D [24] composites.
Elasticity moduli (E) and ultimate tensile strengths (UTS) of Ti2AlC and Ti3SiC2, including Elasticity moduli (E), 0.2% yield strengths (YS), and ultimate tensile strengths (UTS), as summarized in Table 1.

Table 1: Mechanical properties of the as-cast A91D alloy and its composites reinforced by Ti2AlC and Ti3SiC2, including Elasticity moduli (E), 0.2% yield strengths (YS), and ultimate tensile strengths (UTS).

<table>
<thead>
<tr>
<th>Materials</th>
<th>E (GPa)</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A91D</td>
<td>40 ± 1</td>
<td>70 ± 2</td>
<td>175 ± 5</td>
<td>this work</td>
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<tr>
<td>5 vol% Ti3SiC2-A91D</td>
<td>46 ± 1</td>
<td>178 ± 3</td>
<td>195 ± 6</td>
<td>this work</td>
</tr>
<tr>
<td>10 vol% Ti3SiC2-A91D</td>
<td>55 ± 1</td>
<td>173 ± 3</td>
<td>180 ± 6</td>
<td>this work</td>
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<td>15 vol% Ti3SiC2-A91D</td>
<td>66 ± 2</td>
<td>–</td>
<td>120 ± 4</td>
<td>this work</td>
</tr>
<tr>
<td>20 vol% Ti3SiC2-A91D</td>
<td>76 ± 2</td>
<td>–</td>
<td>105 ± 4</td>
<td>this work</td>
</tr>
<tr>
<td>5 vol%Ti2AlC-A91D</td>
<td>52</td>
<td>108</td>
<td>200</td>
<td>[24]</td>
</tr>
<tr>
<td>10 vol%Ti2AlC-A91D</td>
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<td>135</td>
<td>215</td>
<td>[24]</td>
</tr>
<tr>
<td>15 vol%Ti2AlC-A91D</td>
<td>62</td>
<td>145</td>
<td>185</td>
<td>[24]</td>
</tr>
<tr>
<td>20 vol%Ti2AlC-A91D</td>
<td>69</td>
<td>160</td>
<td>165</td>
<td>[24]</td>
</tr>
</tbody>
</table>

Fig. 3. The room temperature tensile stress-strain curves of the as-cast A91D and its composites reinforced by Ti2AlC and Ti3SiC2.

Fig. 4. Elasticity moduli (E) and ultimate tensile strengths (UTS) of Ti3SiC2-A91D and Ti2AlC-A91D composites as a function of the reinforcement volume fraction.

3. Results

Fig. 1 shows the microstructure of the as-cast A91D alloy and composites reinforced with different MAX phases. As found in Fig. 1a-c, no matter the introduction of Ti3SiC2 or Ti2AlC, the composites present the similar microstructure. MAX phases particles distribute along grain boundaries of the primary α-Mg phase and coexist with eutectic α (Mg) and β (Mg17Al12) phases. As previously observed on Ti2AlC-A91D composite [24], when the introduction of Ti3SiC2 particles increased from 5 vol% to 15 vol%, the agglomeration of Ti3SiC2 particles appeared (Fig. 1d).

Fig. 2 shows the XRD diffractograms of Ti3SiC2-A91D and Ti2AlC-A91D composites. No impurities are detected in both two composites. The shift of Mg peak appeared for all of Mg peaks. For example, it is clear that the Mg peak (103) at around 2θ of 48° continuously shifts with the increasing content of Ti2AlC particles in Ti2AlC-A91D composite, while it is much less clear in Ti3SiC2-A91D composite. During the solidification, as most particles are segregated in the intergranular regions during the impingement with other growing grains [25,26], the growth of dendritic α-Mg is restricted and produces a compressive force. The difference in these two composites suggests that much higher compressive force formed around Mg grains with the increasing Ti2AlC volume in Ti2AlC-A91D composite.

Fig. 3 plots the room temperature tensile stress-strain curves of as-cast A91D and its composites reinforced by Ti2AlC and Ti3SiC2. With the introduction of more MAX particles, the ductility of composites strongly decreased, especially for Ti3SiC2-A91D composite. The composites reinforced with 15 vol% and 20 vol% Ti3SiC2 particles did not even reach the summit of yield strength before fracture. Table 1 summarizes the elastic modulus (E), tensile yield strength, and ultimate tensile strength (UTS) values of the different specimens. For clarity, E and UTS values of the two composites are plotted as a function of reinforcement volume fraction (Fig. 4). E of both composites are continuously enhanced with the increasing content of reinforcement, especially for the case of Ti3SiC2. Such a result is supposed to be the difference in E between Ti2AlC (277 GPa) [27] and Ti3SiC2 (343 GPa) [28]. Regarding UTS, the UTS of A91D alloy is enhanced when 5 vol% of Ti2AlC or Ti3SiC2 MAX phase is introduced into magnesium alloy. Similar to the results found in Ti2AlC-A91D composite [24], the addition of Ti3SiC2 could refine the grains of α-Mg and produce the Hall-Petch effect. After, the UTS of Ti3SiC2-A91D composites increases with the introduction of Ti2AlC from 5 vol% to 10 vol%, then decreases with more introduction of Ti2AlC. Differently, UTS of Ti3SiC2-A91D continuously decreases with the increasing content of Ti3SiC2 volume fraction. In addition, the UTS Ti3SiC2-A91D composite is higher than that of Ti3SiC2-A91D for each volume fraction. This phenomenon was also reported by Anasori et al. [29] who studied the MAX phases particles (50 vol%) reinforced Mg composites fabricated by pressureless melt infiltration method. In order to clarify this difference, the tensile fracture surface and interfacial evolution in these two composites were further exploited in the following part.

4. Discussion

Fig. 5a and b shows the tensile fracture morphologies of AZ91D composites reinforced by 5 vol% and 15 vol% Ti3SiC2. Tear edges in Mg matrix are strongly reduced with the increasing content of Ti3SiC2 particles in composites. However, as found in Fig. 5b and c, Ti3SiC2 and...
Ti$_2$AlC particles exhibit different fracture behavior in MAX particles. The enlarged area shown in Fig. 5d indicates that Ti$_3$SiC$_2$ particles are detached from Mg matrix due to the interfacial decohesion. However, no interfacial decohesion was observed in Ti$_2$AlC-AZ91D composite. In Fig. 5c, the clean and flat fracture surface of Ti$_2$AlC indicates that delamination occurred in Ti$_2$AlC particles.

Fig. 6 presents the high-angle annular dark field (HAADF) micrographs of Ti$_3$SiC$_2$-AZ91D and Ti$_2$AlC-AZ91D interfaces. As shown in Fig. 6a and b, no nanometric Mg grains were found in the vicinity of Ti$_3$SiC$_2$ particles. However, Fig. 6c and d reveal the formation of nanometric Mg grains among Ti$_2$AlC particles. This agrees with the results reported by Amini et al. [30]. In addition, different contrasts can be observed in Mg matrix among Ti$_2$AlC particles. Fig. 7 shows the magnified area marked in Fig. 6c. Closed to the interface, the nano Mg grains become smaller. The corresponding diffraction patterns of selected areas confirmed this phenomenon. The polycrystalline rings were found in region 2 and 3, especially in region 2. This indicates that a finer polycrystalline magnesium tends to form on the Ti$_2$AlC surface. As the formation of nano-sized Mg grains among Ti$_2$AlC particles could strongly strengthen the metal matrix due to the Hall-Petch effect [30–32], the UTS of Ti$_2$AlC-AZ91D composite is higher than that of Ti$_3$SiC$_2$-AZ91D for each volume fraction.

Fig. 8 shows the images taken close to the interfaces of the composites accompanied with the corresponding elemental EDX maps of Ti, Al and Si. Fig. 8b-c show that maps of Ti and Si exhibit identical distribution in Ti$_3$SiC$_2$-AZ91D composite. However, Fig. 8f-g indicate that the Al zone is much bigger than that of Ti in Ti$_2$AlC-AZ91D composite. The Al distribution in Fig. 8g suggests that Al atoms in Ti$_2$AlC outwards diffused into AZ91D magnesium matrix. Finally, nano Mg grains formed among Ti$_2$AlC particles. In addition, the out-diffusion of Al atoms may arouse the formation of a thin amorphous magnesium layer between Ti$_2$AlC and nano Mg grains. This robust amorphous layer was respectively found by Yu et al. [17] and Amini et al. [30]. Khoddam et al. pointed that the robust amorphous layer could reduce the interfacial energy of incoherent interface due to large lattice mismatch and therefore promote the interfacial bonding strength [33]. Herein, interfacial decohesion happens in Ti$_3$SiC$_2$-AZ91D composite, while not found in Ti$_2$AlC-AZ91D composite.

This difference is maybe aroused by different solubility between Al and Si in magnesium matrix or by the different migration energy between Al and Si in MAX phases. First-principles calculations show that the migration energy of Al in Ti$_2$AlC (0.83 eV) is lower than that of Si in Ti$_3$SiC$_2$ (0.9 eV) [21,22], which indicates that out-diffusion of Si from Ti$_3$SiC$_2$ is much harder than Al from Ti$_2$AlC under the same conditions. It has been experimentally proved that the ratio between Al and Si in Ti$_3$(Si$_{1-x}$Al$_x$)C$_2$ solid solution can be arbitrarily regulated [34]. This means that it could be possible to control the interface bonding strength between Ti$_3$SiC$_2$ and Mg Matrix with the formation of Ti$_3$(Si$_{1-x}$Al$_x$)C$_2$ solid solution.

5. Conclusion

Both Ti$_3$SiC$_2$ and Ti$_2$AlC (5, 10, 15, 20 vol%) reinforced AZ91D magnesium composites were fabricated under 700 °C by the stir casting method and compared. As previously observed on Ti$_2$AlC-AZ91D composite [24], an agglomeration of particles occurred when the
The introduction of Ti$_3$SiC$_2$ particles is higher than 5 vol%. A slight and continuous shift of the Mg peaks appears with the increasing content of Ti$_2$AlC particles due to the formation of nanometric Mg grains, while this phenomenon was not found in the case of Ti$_3$SiC$_2$-AZ91D composite. Ti$_3$SiC$_2$ particles were detached from Mg matrix due to the interfacial decohesion. However, no interfacial decohesion has been observed in Ti$_2$AlC-AZ91D composite. Herein, the UTS of Ti$_3$SiC$_2$-AZ91D composite is much lower than that of Ti$_2$AlC-AZ91D composite. TEM analyses have revealed that the outwards diffusion of Al from Ti$_2$AlC into Mg matrix aroused the formation of the thin amorphous magnesium and nano Mg grains among Ti$_2$AlC particles. In contrast, no outwards diffusion of Si from Ti$_3$SiC$_2$ into Mg matrix was detected. This study suggests that it is possible to control the interface bonding strength between Ti$_3$SiC$_2$ and Mg matrix through the ratio design between Al and Si in Ti$_3$(Si$_{1-x}$Al$_x$)C$_2$ solid solution.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The experimental section was by State Key Lab of Advanced Metals and Materials 2021-ZD08 and the fundamental research funds for the Central Universities (Grant No. 2020YJS14S).
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