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Atomic-scale investigation of the interface precipitation in a TiB_2 nanoparticles reinforced Al-Zn-Mg-Cu matrix composite

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Abstract

The effects of nanosized reinforcement particles on precipitation reactions in age-hardenable Al alloy matrix composites have been largely unknown. In this work, an Al-Zn-Mg-Cu matrix composite reinforced with uniformly distributed TiB_2 nanoparticles was successfully produced. The solid-soluted, peak-aged and overaged materials were then characterized, at the atomic scale using (high-resolution) scanning transmission electron microscopy, to provide a fundamental insight into the interface precipitation. Our results demonstrated that the facetted TiB_2 nanoparticles have a significant impact on the precipitation in matrix areas adjacent to the TiB_2/Al interfaces. The interfaces after solid-solution treatment are tightly-bonded and oxide-free, and display two orientation relationships (ORs): the well-reported $[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$, $(0001)_{TiB_2}//(\bar{1}11)_{Al}$ (OR1) and the new $[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$, $(01\bar{1}0)_{TiB_2}//(11\bar{1})_{Al}$ (OR2). The interface precipitates (i.e. interphase) having the size of several tens of nanometers were formed after ageing and were determined to be $(Zn_{1.5}Cu_{0.5})Mg$ phase. Their formations were only related to the initial OR1 and OR2 where the mutual ORs between the TiB_2, interphase and Al matrix were further developed. Periodically spaced misfit dislocations were revealed at the semi-coherent TiB_2/Al interfaces, which are generally considered beneficial to the heterogeneous precipitation. They not only reduced nucleation energy barrier, but also acted as short-circuit diffusion paths for transporting solute atoms and vacancies, accelerating growth rate. However, the growth of interphase at the interface parallel to close-packed {111} Al planes was suppressed by the ultra-low accommodation factor. In addition, such an interface precipitation reduced the mismatch of the TiB_2/Al interface, increasing the overall coherency and being potential for effective interface strengthening.

Keywords: Metal matrix composites, Aluminum alloys; Precipitation; Interface structure; STEM HAADF

1. Introduction

Age-hardenable Al alloys (e.g., 2xxx, 6xxx and 7xxx series) have been widely applied as structural materials in aerospace and automobile industries, due mainly to their high specific strength and excellent processability [1-3]. Commonly, one of the most effective strengthening mechanisms involves precipitation hardening, i.e., a homogenous distribution of nanosized precipitates originating from solid-state precipitation reactions during aging treatments [4-6]. In addition, micron- (or submicron-) sized reinforcement particles (MRPs), such as SiC and B_4C, have successfully been introduced to Al alloys, providing an alternative approach to further enhance their mechanical performance, particularly in case high Young's modulus is necessary [7-9]. It has been largely recognized that MRP/Al interface structure critically influences the precipitation reactions to promote the formations of coarse precipitate zone (CPZ) and precipitate free zone (PFZ) in the surrounding matrix [10-20], This, in turn, has a significant impact on overall mechanical properties of the Al-based metal matrix composites (MMCs) [21-23].

It has been well established that the CPZ is caused by thermoelastic stress induced dislocations (TSIDs) near the MRP/Al interface [10-13]. The interaction between solute atoms and TSIDs leads to a solute flux towards dislocations resulting in faster and coarser precipitation on them [11-13]. When it comes to the PFZ formation, particularly in Al-Zn-Mg(-Cu) matrix composites, the underlying mechanism remains controversial. Some researchers have claimed that the PFZ formation is related to vacancy depletion [14-16]. As proposed, precipitation reactions at the MRP/Al interface are analogous to those at high-angle grain boundaries (GBs) in (unreinforced) Al alloys. The weakly-bonded and incoherent MRP/Al interface as well as TSIDs can act as ideal sinks to absorb and cause the annihilation of vacancies during the solution treatment [14-16]. Considering the nucleation of *Guinier-Preston* (GP) zones in Al alloys requiring a critical vacancy concentration [24, 25], the precipitation process in the vicinity of MRPs is thereby hindered leading to the PFZ formation. On the contrary, some studies revealed that the number of quenched-in vacancies has no influence on the GP zone formation in Al-Zn-Mg(-Cu) alloys [26, 27]. It was thus indicated that the PFZ formation is likely attributed to the solute atoms rather than vacancy depletion [17-19]. For example, Hong *et al.* [17] observed the formation of numerous MgO particles with the size of tens of nanometers at the SiC/Al interface in the A1-Zn-Mg-Cu matrix composite reinforced with 20 vol.% SiC particles. They proposed that this results in the depletion of Mg atoms in the surrounding matrix and then the suppression of precipitation in the vicinity of SiC particles during the aging process [17].

In addition to the two well-documented CPZ and PFZ mentioned above, Strangwood *et al.* [20] reported that the MRP/Al interface can play the role as an ideal nucleation substrate to promote interracial segregation and precipitation on it in the SiC particles reinforced 2xxx and 7xxx matrix composites. They also found that the heterogeneous interfacial precipitations have a close correlation with the aging conditions [20]. In the case of 7xxx matrix composite, it was found that, in the underaged composite, the SiC/Al interface was covered by a continuous precipitate layer which extended the thickness of around 10-20 nm into the Al matrix. Within the precipitate layer, discrete η particles ($MgZn_2$) with 24-40 nm in diameter and spaced at approximately 70-80 nm intervals were discerned. However, in the overaged composite, the diffuse interfacial η’/η layer dissolved, giving rise to a series of fairly regularly (45-70 nm) spaced T phase ($Mg_{32}(Al, Zn)_{49}$) with the size ranging from 20 to 30 nm in dimeter surrounding the interface.

In parallel with the developments in nanotechnology, the dimensions of reinforcement particles (RPs) have decreased from micron/submicron scale to nanoscale (≤ 100 nm) over the last decades [28, 29]. Accordingly, volume fraction of the particle/matrix interfaces increases proportionally as: $V_2 = (r_1/r_2)^3 V_1$, where r_1 and r_2 are the radius of spherical reinforcements, V_1 and V_2 are corresponding interface volumes of the spherical reinforcements [30]. Thus, it is expected that structure evolution of nanosized reinforcement particle (NRP)/Al interfaces during the aging treatments can play a more important and critical role in influencing mechanical properties of the Al-based MMCs. Furthermore, considering interfacial structure of the NRP/Al interface being very different compared with that of the MRP/Al one, one realized that the presence of NRPs should have a disparate influence on the precipitation reactions in the Al alloy matrix. But, up to now no experimental evidences, at the nano- and atomic scales, have been properly disclosed, which constitutes one of the most important fundamental problems still unclear in the NRPs reinforced Al-based MMCs.

In spite of this, some hypotheses based on the pioneer works can be proposed. Firstly, Kim *et al.* [31] proposed that the intensity of TSIDs shows a strong particle size dependence. It increases significantly only when the size of RPs reaches the micron level. At the finer scales the thermoelastic stress can be lower than the effective yield stress such that no TSIDs and no CPZ (caused by TSIDs) in the surrounding matrix should be generated [32, 33]. Secondly, in contrast to the incoherent MRP/Al interface [34, 35], semi-coherent NRP/Al interface is more analogous to low-angle GBs, becoming inefficient vacancy sinks [36-39]. The NRP/Al interface is thus incapable to lead to vacancy depletion in the surrounding matrix. It was also reported that no oxide particles or amorphous layers have been found at the NRP/Al interface, suggesting no solute depletion caused by interfacial oxide formation [40-42]. Consequently, no PFZ shall generate in NRPs reinforced Al-based MMCs whatever its formation mechanisms due to vacancy or solute depletion. Thirdly, unlike the MRP/Al interface, it has been well established that NRPs generally have preferential crystallographic orientation relationships (ORs) with the Al alloy matrix [28, 35].

As such, it is of theoretical possibility to have ORs in between the NRPs, interfacial precipitates and Al alloy matrix in order to minimize the nucleation energy barrier [43, 44]. Finally, considering the NRP/Al interfacial precipitation reactions being analogous to those at low-angle GBs, the transformation of precipitates from η to T phases observed at the SiC/Al interface (being analogous to high-angle GBs) during the ageing treatments [20], can most probably occur in a different way in NRPs reinforced 7xxx matrix composites [25, 39].

In view of the discussions above, the present work aims to provide a fundamental insight into the influences of NRPs on the precipitation reactions in Al-based MMCs. With high melting point (3173 K), high modulus (565 GPa), high hardness (2500 HV) and good thermal stability [45], TiB_2 nanoparticles have widely been used as one of the most ideal NRPs in Al-based MMCs [46-48]. In this work, an Al-Zn-Mg-Cu matrix composite reinforced with homogenously distributed TiB_2 nanoparticles was successfully fabricated and heat treated at different conditions, including solid-solution, peak-ageing and over-ageing treatments, followed by comprehensive characterization. Probe-corrected (high-resolution) scanning transmission electron microscopy ((HR)STEM), in particular, high-angle annular dark-field (HAADF) imaging associated with energy dispersive spectrometer (EDS) mapping was used, which provides access to the nature of the precipitation reactions with spatial resolution at the nano- and atomic scales. We found significant microstructural evolutions at the TiB_2/Al interface during the aging treatments. The interface was initially clean after solid-solution treatment. Heterogeneous interfacial precipitates (hereafter referred to as interphase, abbr. IP), determined to be $(Zn_{1.5}Cu_{0.5})Mg$ phase, were only formed at the preferential TiB_2/Al interfaces during ageing. The crystallographic ORs between the TiB_2 nanoparticle, interphase and Al matrix were determined. The atomic structure of the Al/interphase/TiB_2 multi-interfaces was systematically characterized and analyzed. Based on these experimental evidences, the kinetics of the TiB_2 nanoparticles exerted to the interface precipitation, including nucleation, growth rate, preferential precipitation TiB_2/Al interfaces, effects of aging conditions are discussed in detail.

2. Experimental procedure

An *in-situ* mixed salt method was used to produce the TiB_2 nanoparticles (6 wt.%) reinforced Al-Zn-Mg-Cu composite ingot using high-purity reactive salts of K_2TiF6 and KBF_4 [47]. Composite melts were synthesized at 900 °C in an electrical resistance furnace, and then cast into a graphite mould. 200 × 100 × 16 mm plates were then cut from the equal-axis grain zones of the ingot and homogenized at 465 °C for 24 h. Subsequently, a 4-pass friction stir processing (FSP) process was carried out with a tool rotation rate of 600 rpm, a tool tilt angle of 2.5°, a traverse speed of 80 mm/min and a processing depth of 8 mm [49]. Afterwards, hot extrusion with an extrusion ratio of 20:1 was carried out on the samples cut from the nugget zone. Finally, the as-extruded samples were subjected to T6 (470 °C/70 min + water quenching + 120°C/20h) and T76 (470 °C/70 min + water quenching + 120°C/5h + 160°C/18h) heat treatments. The as-quenched and both aged samples were characterized in more details using STEM. The hardness curves as a function of ageing time at the T6 and T76 states were plotted in Figs. S1(a) and (b), respectively. The hardness increased by increasing the ageing time in the range 0-10h at 120 °C. A plateau of the highest hardness of around 205 HV was reached after ageing for more than 10h. The peak hardness of around 208 HV was obtained after ageing at 160 °C for 6h, and then the hardness gradually reduced by extending the ageing time.

STEM specimens with 3 mm in diameter were prepared through mechanical polishing and final ion milling in a GATAN precision ion polishing system, operated at - 150 °C. A state-of-the-art FEI Titan Themis 300 microscope equipped with a probe aberration corrector, operated at 200 kV, was used to acquire (HR)STEM images. The probe size was set to 0.1 nm with a convergence semi-angle of 22.5 mrad. Collection angle of the HAADF detector was in the range 80-150 mrad. Contrasts in an HAADF image is proportional to $Z^{\sim 1.7\text{-}2}$, meaning that the bright contrast indicates relatively heavy atomic composition [50]. In this case, the bright and dark contrasts can be considered as Zn (Cu)-rich and Mg-rich areas in the Al matrix, respectively. The equipped highly efficient (4 quadrant) EDS system was used for chemical analyses of possible precipitates formed at the TiB_2/Al interface. Interface characterization was done by tilting the Al matrix to the [101] orientation in terms of the well-documented preferential ORs of the TiB_2/Al interfaces [51]. JEMS software was used for generating theoretical electron diffraction patterns by considering the kinematic approximation [52]. Dr. Probe software was used for simulating atomic-scale HRSTEM-HAADF images [53]. VESTA, a 3-D visualization program for structural models, was used to construct interfacial atomic structure configurations [54]. Note that quantitative estimations of compositions by STEM/EDS are inevitably affected by the channeling of electrons along atomic columns in zone axis conditions. The composition results were hence presented as semi-quantitative.

3. Results

3.1. The TiB_2/Al interface structure in the solid-solution treated composite

Our previous studies of the TiB_2/Al-Mg-Si [55] and TiB_2/Al-Zn-Mg-Cu composites [49] demonstrated that the fabrication process combining casting (*in-situ* reaction), FSP and extrusion is efficient to acquire a desired microstructure in the nugget zone. It is featured with a fine equiaxed grain structure (a few micrometers in the average size) and uniformly distributed TiB_2 nanoparticles. Fig. 1a shows the uniform distribution of the majority TiB_2 nanoparticles within an Al grain. Fig. 1b shows the typical TiB_2 nanoparticle that has a facetted shape with identified basal $\{0001\}$, prismatic $\{01\bar{1}0\}$ and pyramidal $\{01\bar{1}1\}$ facets, which is illustrated in Fig. 1c. This is consistent with the previous results [56, 57]. The TiB_2/Al interface is tightly bonded and free of oxide particles, where solute-enriched zones having a size of several nanometers are present.

Fig. 2 presents two typical HRSTEM images and the associated fast Fourier transform (FFT) patterns, showing two ORs between the TiB_2 nanoparticle and the Al matrix, namely OR1 (Figs. 2a-c) and OR2 (Figs. 2d-f). The majority of TiB_2 nanoparticles have the OR1 with the Al matrix being consistent with the previous results reported in Refs. [51, 58]. Only a few of them show the new OR2 with the Al matrix. From Figs. 2a and 2d one can also observe the periodically-spaced misfit dislocations next to the TiB_2/Al interface for both ORs, which are highlighted in red.

OR1: $[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$, $(0001)_{TiB_2}//(\bar{1}11)_{Al}$, $(01\bar{1}1)_{TiB_2}$ 3^{o} from $(020)_{Al}$, $(0\bar{1}12)_{TiB_2}$ 3^{o} from $(\bar{2}02)_{Al}$

OR2: $[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$, $(01\bar{1}0)_{TiB_2}//(11\bar{1})_{Al}$, $(0\bar{1}12)_{TiB_2}$ 3^{o} from $(020)_{Al}$, $(01\bar{1}1)_{TiB_2}$ 3^{o} from $(\bar{2}02)_{Al}$

3.2. The TiB_2/Al interface structures in the peak-aged and over-aged composites

After peak ageing, interphase precipitates were largely observed in between the TiB_2 nanoparticle and the Al matrix as shown in Figs. 3a-d as well as in Fig. S2. But no discernible CPZ or PFZ were found in the vicinity of TiB_2 nanoparticle. The interphases formed on preferential facets of the TiB_2 nanoparticle with a specific contact angle (θ) of around 60° measured as the projected angle. In addition to such interphase precipitates, finer precipitates with a high density can also be seen being homogeneously distributed in the Al matrix away from TiB_2 nanoparticles, as shown in Fig. 3b. These finer precipitates are the plate-like GP zones with the diameter of ~8 nm (Fig. 3c) and rectangle η' phase on the $\{111\}_{Al}$ planes, which is roughly 2 nm in thickness and 8 nm in length (Fig. 3d). Both GP zones and η' phase are fully coherent with the Al matrix.

Similar to the peak-aged sample, neither obvious CPZ nor PFZ were observed in the over-aged sample, but interphase precipitates formed at the TiB_2/Al interface with the contact angles (θ) of around 60° and 100° measured as the projected angles, as shown in Fig. 3e. In addition, dense rectangle η (type $MgZn_2$ [59]) precipitates on $\{111\}_{Al}$ planes are found being uniformly distributed in the matrix (Fig. 3f). They are about 7 nm thick and 26 nm long (Fig. 3g). This η phase is semi-coherent with the Al matrix due to the misfit dislocations at the Al/η interface (Fig. 3h).

Results in Figs. 2 and 3 indicate that the TiB_2/Al interfaces were preferred sites for promoting the precipitation reactions. While, within the Al matrix away from the interface, the observed precipitation sequence was supersaturated solid solution → GP zones → metastable η' → stable η. This agrees with the results well-documented in the Al-Zn-Mg-Cu alloy [60].

3.2.1. Structure determination of the formed interphase precipitate

Using STEM/EDS elemental mapping, it was identified that the interphase precipitates in both the peak-aged and over-aged samples were enriched with Zn, Mg, Cu and Al as exemplified in Fig. 4. However, it was hard to figure out if Al is the constituent element considering possible overlapping with the Al matrix. To solve this problem, semi-quantitative EDS data were randomly acquired from different areas containing the interphase, and the results are listed in Table 1. Despite the variations of Al content, the elemental content ratio of Zn, Mg and Cu remains constant and presents a specific value approximately 3:2:1. This indicates the absence of Al and suggests that the interphase precipitate is possibly the $(Zn_{1.5}Cu_{0.5})Mg$ phase (*Hexagonal,* $a=5.124$ *Å,* *c=16.820 Å, P63/mmc, No. 194,* atomic coordinates given in Table S1) [61]. From a HAADF image as shown in Fig. 5 the interplanar spacing of the (0004) and $(\bar{1}\bar{1}20)$ planes were measured to be 0.421 nm and 0.256 nm, respectively, which accords with that of the $(Zn_{1.5}Cu_{0.5})Mg$ phase. The corresponding FFT pattern of the $(Zn_{1.5}Cu_{0.5})Mg$ phase matches the structure of this phase well [61]. Furthermore, the simulated HAADF image of $(Zn_{1.5}Cu_{0.5})Mg$ phase (overlapped in Fig. 5a) fits with the intensity of the experimental result of the interphase. Thus, the interphase is identified to be the $(Zn_{1.5}Cu_{0.5})Mg$ phase. Note that this method was also used to identify the interphase precipitates formed in the overaged sample, confirming the same crystal structure of the phase.

Table 1 Elemental content ratio of Al, Zn, Mg and Cu recorded from the four interphases acquired by STEM/EDS mapping.

Interphase	Atomic composition (at. %)			
number	Al	Zn	Mg	Cu
1	46.16	25.30	18.29	10.26
2	59.72	19.63	12.80	7.85
3	63.32	18.71	11.64	6.33
4	69.51	15.28	9.91	5.31

3.2.2. OR-dependent precipitations at the TiB_2/Al interfaces

As shown in Fig. 6, the prismatic $\{01\bar{1}0\}$ and pyramidal $\{01\bar{1}1\}$ facets of the TiB_2 nanoparticles are the preferential heterogeneous precipitation sites at the OR1 condition (Figs. 6a-6c), while the two basal {0001} facets are the sites at the OR2 (Figs. 6d-6f). Figs. 7 and 8 show the ORs between the interphase precipitates, the TiB_2 nanoparticle and the Al matrix. At the peak-aged/OR1 condition (Fig. 7), the reproducible ORs, namely the OR3 between interphase and Al matrix and the OR4 between interphase and TiB_2 were determined. They are:

The OR3: $[1\bar{1}00]_{IP}//[101]_{Al}$, $(11\bar{2}4)_{IP}//(11\bar{1})_{Al}$, $(\bar{1}\bar{1}20)_{IP}$ 3° from $(\bar{2}02)_{Al}$, $(0008)_{IP}$ 3° from $(020)_{Al}$

The OR4: $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}$, $(01\bar{1}1)_{TiB_2}//(0008)_{IP}$, $(01\bar{1}0)_{TiB_2}//(11\bar{2}8)_{IP}$

At the overaged/OR2 condition (Fig. 8), two ORs, the OR5 between interphase and Al matrix, and the OR6 between TiB_2 and interphase, were observed. They are:

The OR5: $[1\bar{1}00]_{IP}//[101]_{Al}$, $(11\bar{2}0)_{IP}//(11\bar{1})_{Al}$, $(\bar{1}\bar{1}24)_{IP}$ 3° from $(\bar{2}02)_{Al}$, $(11\bar{2}8)_{IP}$ 3° from $(020)_{Al}$

The OR6: $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}$, $(0001)_{TiB_2}//(0004)_{IP}$, $(01\bar{1}0)_{TiB_2}//(11\bar{2}0)_{IP}$

It should be noted, in terms of extensive STEM examinations, that the ORs related to the interphase are only associated with the initial OR1 and OR2 between the TiB_2 nanoparticle and Al matrix at the solid-solution state. There is no correlation with the ageing treatments (peak- or over ageing).

3.2.3. Atomic structure of the Al/($Zn_{1.5}Cu_{0.5}$)Mg interphase/TiB_2 interfaces

At the interphase/Al interfaces (i.e. the OR3, Fig. 9), the interphase precipitate grew based on $(0008)_{IP}$ planes along the growth direction $<0001>_{IP}$. Misfit dislocations exist in the zone near the growth front of the interphase, where the measured interplanar spacing values are slightly different compared with those of the typical structure of ($Zn_{1.5}Cu_{0.5}$)Mg phase in the fully-grown zone. A most likely explanation is that this zone is out of focus regions of the interphase, due to being below the sample surface. As a result, broadening of the atomic-scale electron beam through the specimen locally resulted in a blurry image. Apart from the interphase/Al interface located at the growth front zone, it was found that the two formed interphase/Al interfaces $(\bar{1}\bar{1}20)_{IP}$ 3° from $(\bar{2}02)_{Al}$ and $(11\bar{2}4)_{IP}//(11\bar{1})_{Al}$ contain one misfit dislocation and agree with the theoretical mismatch values of 3.31 and 0.08 % (Table 2), respectively. As detailed in Fig. 10, the interphase/TiB_2

interface $(11\bar{2}8)_{IP}//(01\bar{1}0)_{TiB_2}$ contains two periodically spaced misfit dislocations (Fig. 10b) having the low mismatch of 2.94 % (Table 2). However, the interface $(0008)_{IP}//(01\bar{1}1)_{TiB_2}$ displays four misfit dislocations (Fig. 10c), suggesting that the observed interphase was not directly nucleated at this interface considering the precipitation kinetics and the very high mismatch of 60.74 % (Table 2).

At the overaged/OR2 condition (Fig. 11), the interphase grew based on the $(0004)_{IP}$ planes along the growth direction $<0001>_{IP}$, being the same as in the peak-aged/OR1 case. Only the misfit dislocations, spaced at approximately 2.7 and 1.25 nm intervals (Table 2), are observed at the arc-like (Figs. 11a and 11b) and shape interphase/Al interfaces (Figs. 11c and d), respectively. Finally, Fig. 12 shows that the interphase/TiB_2 interface displays only one misfit dislocation, being in agreement with the theoretical mismatch of 2.34 % (Table 2).

Table 2 Coherency of the Al/interphase/TiB_2 multi-interfaces at the OR1 and OR2 conditions. Note that high, intermediate and low interface coherency are defined as the interface mismatch below 5%, in the range 5-25% and above 25%, respectively.

ORs between TiB_2 and Al	Interface type	Interface planes	Interface mismatch (%)	Misfit dislocation interval (nm)	Interface Coherency
OR1 (Fig.7)	Al/IP (Fig. 9)	$(11\bar{1})_{Al}//(11\bar{2}4)_{IP}$	0.08	322.99	High
		$(\bar{2}02)_{Al}$ 3° from $(\bar{1}\bar{1}20)_{IP}$	3.31	6.35	High
	IP/TiB_2 (Fig. 10)	$(11\bar{2}8)_{IP}//(01\bar{1}0)_{TiB_2}$	2.94	11.35	High
		$(0008)_{IP}//(01\bar{1}1)_{TiB_2}$	60.74	0.68	Low
OR2 (Fig. 8)	Al/IP (Fig. 11)	Arc-shaped	9.40	2.70	Intermediate
		$(11\bar{1})_{Al}//(11\bar{2}0)_{IP}$	20.10	1.25	Intermediate
	IP/TiB_2 (Fig. 12)	$(11\bar{2}0)_{IP}//(01\bar{1}0)_{TiB_2}$	2.34	11.18	Low δ

4. Discussion

In the TiB_2/Al-Zn-Mg-Cu composite, our atomic scale investigation clearly demonstrates that the homogenous distribution of TiB_2 nanoparticles has exerted disparate influences on the precipitation reactions in the Al matrix near the TiB_2/Al interface (i.e. the NRP/Al type). Such an interface had following features: (1) No CPZs were formed (Figs. 3a and 3e) due to the absence of TSIDs (Fig. 1a). (2) The semi-coherent and clean TiB_2/Al interface (Figs. 2a and 2d) is incapable to lead to vacancy or solute depletion, and thus no PFZs formed [36-39]. It has been well documented that the formation of CPZs or PFZs is detrimental to mechanical properties of MMCs [21-23]. Thus, it is expected that their absence would be beneficial to the present MMCs. (3) The OR-dependent heterogeneous precipitations were promoted at the TiB_2/Al interface considering the much larger sizes of the interphase in comparison with those of the nano-precipitates formed in the matrix away from the interface (Fig. 3). The interphase precipitates in both the peak-aged and overaged samples were identified to be the $(Zn_{1.5}Cu_{0.5})Mg$ phase and show specific ORs with the TiB_2 nanoparticle and the Al matrix (Figs. 6-8). The corresponding underlying mechanisms of the heterogeneous precipitation reactions at the TiB_2/Al interfaces are discussed in detail below.

4.1. Reduced nucleation energy barrier for the interphase precipitation

For the homogenous precipitation in the Al alloy matrix, the minimum activation energy barrier ΔG_{hom}^{*} can be expressed using the following equation [43]:

$$\Delta G_{hom}^{*} = -\frac{16\pi {\gamma_{\alpha\beta}}^{3}}{3(\Delta G_V - \Delta G_S)^2} \qquad (1)$$

where $\gamma_{\alpha\beta}$ and ΔG_V are the interfacial energy and difference in free energy (per unit volume) between the Al matrix (α) and the precipitate (β), respectively; ΔG_S is the misfit strain energy (per unit volume) of the precipitate. Analogously, for the heterogeneous precipitation at the TiB_2/Al interface, the equation for the minimum activation energy barrier ΔG_{het}^{*} is expressed by [43, 44]:

$$\Delta G_{het}^{*} = -\frac{4}{3}\pi\frac{\gamma_{\alpha\beta}^{3}}{(\Delta G_V - \Delta G_s)^2}(2 - 3Cos\theta + Cos\theta^3) \quad (2)$$

where $\gamma_{\alpha\beta}$, ΔG_V and ΔG_S are the same as in Eq. (1), θ is the contact angle between the nucleus of the interphase and the TiB_2 substrate.

Consequently, the relationship between ΔG_{hom}^{*} and ΔG_{het}^{*} is acquired and expressed by the following equation:

$$\frac{\Delta G_{het}^{*}}{\Delta G_{hom}^{*}} = \frac{1}{4}(2 - 3Cos\theta + Cos\theta^3) = f(\theta) \quad (3)$$

Thus, as long as the contact angle between the interphase and TiB_2 substrate is lower than 180^o, being obvious in Fig. 3, the calculated *f(θ)* is always smaller than 1. This means that the energy barrier for the heterogeneous precipitations at the TiB_2/Al interface is reduced compared with the homogeneous nucleation in the Al matrix away from the interface.

In addition, from Fig. 2, highly-dense misfit dislocations are observed at the TiB_2/Al interfaces in the sample after solid-solution treatment. The stress field generated by these misfit dislocations could be the driving force for the migration of solute atoms (Zn, Mg, Cu etc.) on the substitutional sites towards the dislocations [62, 63]. The segregation of solute atoms along the misfit dislocation lines at the TiB_2/Al interfaces therefore led to the formation of Cottrell atmospheres. This is in good agreement with the observed solute-enriched regions at the TiB_2/Al interfaces in Fig. 1b. Moreover, it has been well-documented that vacancies, being essential for the nucleation of precipitates, are readily affected by the stress field caused by dislocations [20, 64]. Vacancies could migrate towards the misfit dislocations at the TiB_2/Al interfaces during the subsequent aging treatments [64]. Solute-vacancy clusters thus form and transform to the nucleus once vacancies approach solute atoms in the solute-enriched regions located at the TiB_2/Al interfaces [65, 66].

The interactions between the solute atoms, vacancies and misfit dislocations at the TiB_2/Al interfaces can be beneficial to the nucleation of the interphase precipitates [62, 67].

4.2. Accelerated growth rate for the interphase precipitation

As proposed by the previous studies, the lattice distortion near dislocation cores effectively lower the activation energy for solute atoms diffusion [68-70]. The dislocation cores can act as fast diffusion paths for solute atoms enabling the rapid growth of precipitates on dislocations [25, 71] and promoting the precipitation of nanoscale precipitates [72, 73]. In this case, the accelerated growth of the interphase (Fig. 3) is also attributed to the misfit dislocations presenting at the semi-coherent TiB_2/Al interface (Fig. 2).

As a diffusion-controlled phase transformation, the precipitation in Al-Zn-Mg(-Cu) alloys depends on the diffusion of solute atoms, i.e., Mg, Zn (Cu) in the Al matrix [44]. For the ideal crystal structure with no defects, the solute atoms diffuse randomly by substitution, advancing a radial distance according to the following equation [74]:

$$\begin{cases} x = \sqrt{6Dt} \\ D = D_0 exp\dfrac{-Q}{RT} \end{cases} \tag{4}$$

where D is the bulk diffusivity with units (m^2/s); D_0 is a material constant; Q is the activation energy for substitutional diffusion; R is the universal gas constant (=8.3145 J/mol K); and T is the absolute temperature in Kelvin. According to the reports of Ma *et al.* [75], the bulk diffusivity rates of Mg and Zn (Cu) are 1.7×10^{-21} m^2/s and 7.4×10^{-22} m^2/s at the aging temperature of 120 °C, respectively. Zn (Cu) thus is the diffusion-rate limiting elements in Al-Zn-Mg(-Cu) alloys.

For the homogenous precipitations in Al-Zn-Mg(-Cu) alloys, the radius of the initially nucleated embryo can be illustrated by the Zener-Hillert model [44]:

$$\frac{dr}{dt} = \frac{D(c - c_e)}{r_p(c_p - c_e)}\left(1 - \frac{r_c}{r_p}\right) + \frac{1}{N}\frac{dN}{dt}(\alpha r^* - r) \tag{5}$$

where r is the radius of the η' phase; c is the current solute concentration of the matrix; c_e is the equilibrium solute concentration of the matrix and c_p is the solute concentration at the equilibrium precipitate/matrix interface; r_p is the radius of platelet tip and r_c is the critical platelet tip radius at which growth would stop for capillarity effects reducing the driving force for solute diffusion to zero; N is the precipitate density; α is the numerical factor accounts for the fact that nucleated precipitates can grow only when their radius is slightly larger than the radius r*, (r > r* and dN/dt > 0), otherwise, they dissolve into the matrix.

When dislocations are involved, the growth rate of the precipitate is accelerated by an enhancement factor expressed as [76, 77]:

$$f = 1 + \frac{b\sqrt{2}}{\pi r}\sqrt{f(t')}\frac{\sqrt{D_p}}{\sqrt{D}} \tag{6}$$

where f is the enhancement factor that pipe diffusion enhancing the precipitate growth rate, D is the bulk diffusivity of the rate-controlling solute species; D_p is the diffusivity of the rate-limiting species along the dislocation core; b is the Burgers vector; the core width of the dislocation is assumed to be equal to $2b$; $f(t')$ can be expressed by the following equation:

$$f(t') = \int_0^\infty \frac{\exp(-t'x^2)}{x[J_0^2(x) + Y_0^2(x)]}dx \tag{7}$$

where $J_0(x)$ and $Y_0(x)$ are the zeroth-order Bessel functions of the first and second kind.

The integral in Eq. (7) is time dependent but for typical values of time from 100-1000 s has a value from 0.85 to 0.62 [77]. Deschamps *et al.* [71, 77] have estimated that in Al-Zn-Mg(-Cu) alloys D_p is on the order of 10^{-17} m^2/s at the aging temperature of 120 °C. D for the rate-limiting solute species Zn(Cu) is 7.4×10^{-22} m^2/s [75]. b is 0.286 nm for Al [78]. r is approximate to 4 nm as shown in Fig. 3b. Substituting these parameters to Eq. (6), the enhancement factor is approximated to be ~3.95. According to Fig. 3a, the radius of the interphase heterogeneously precipitated at the TiB_2/Al interfaces is around 17 nm. Consequently, the enhanced precipitate growth factor observed experimentally at the peak-aged state is calculated to be 4.25, which is approximate to the enhancement factor of 3.95 acquired by Eq. (6).

4.3. Preferential TiB_2/Al interfaces for suppressing the interphase precipitation

As shown in Fig. 6, the precipitation depended on the ORs between the TiB_2 nanoparticles and the Al matrix. For the OR1, the interphase preferentially formed on the prismatic $\{01\bar{1}0\}$ and pyramidal $\{01\bar{1}1\}$ facets of the TiB_2 nanoparticle. But, the OR2 resulted in the precipitation on the basal {0001} facets. The common feature is that the TiB_2/Al interface was parallel to the close-packed {111} planes of the Al matrix and remained ‘clean’ after the ageing treatments, i.e. the suppression of the interphase precipitation.

It has been well established that the precipitation in the Al-Zn-Mg(-Cu) alloys is caused by diffusional nucleation followed by effective growth [6, 79]. As discussed above (Section 4.1), the TiB_2/Al interfaces are the favorable sites for nucleation of the interphase. Indeed, a closer look confirm that, for example for the OR1 (Figs. 13a and 13b), the interphase has nucleated at the TiB_2/Al interface being parallel to the basal {0001} facets of the TiB_2 particle, while its growth has been suppressed. It is well-known that the growth of precipitates is essentially the process where a nucleus/matrix interface migrates into the surrounding parent phase by transferring atoms across the moving interface [43]. In this case, the suppression of the precipitation can be understood by the fact that a coherent close-packed interface between the embryo of the hcp interphase and the fcc Al matrix was formed during the nucleation stage (Fig. 13a). As schematically illustrated in Figs. 13c and 13d and was reported in Refs. [80-82] that the atom on a C site in the fcc Al matrix must change into a B position to make the interphase growth happen. This should result in a very high energy and unstable configuration with two atoms directly above each other on B sites [43]. In addition, a loop of Shockley partial dislocation should be necessarily created around the atom [82]. An atom attempting such a jump will, therefore, be unstable and be forced back to its original position [43, 82]. Thus, the suppressed growth at the coherent close-packed interphase/Al interface can be explained by very low accommodation factors and low mobility.

4.4. Crystallographic ORs between TiB_2 nanoparticles, interphase and Al alloy matrix

In order to further understand the experimentally determined ORs, the edge-to-edge matching (E2EM) model is used to predict/calculate the possible ORs between the phases based on the basic crystallographic data, including lattice parameters and actual atomic positions, of the phases [83-85]. The E2EM calculation process includes: (a) identifying the closed-packed (CP) atomic row pairs and the CP plane pairs in phases; (b) calculating the values of interatomic spacing misfit (f_r) and interplanar spacing mismatch (f_d); and (c) predicting and refining the ORs between any two phases based on the rules that the matching directions must be on the matching planes and the parallel $\mathbf{\Delta g}$s conditions [86, 87]. The lattice parameter of pure Al metal is used in the present work. It is a = 0.40494 nm [88]. As a simple FCC structure, there are three possible close packed or nearly close packed directions. They are $<110>_{Al}$, $<100>_{Al}$ and $<112>_{Al}$. The close packed plane for FCC is $\{111\}_{Al}$ and this contains the $<110>_{Al}$ directions and the $<112>_{Al}$ directions. $\{200\}_{Al}$ is the second close packed plane and this contains the $<110>_{Al}$ directions and the $<100>_{Al}$ directions.

The third close packed plane is $\{220\}_{Al}$, and this contains all three of the above directions. TiB_2 has hexagonal lattice structure with a = 0.3038 nm and c = 0.3262 nm [88] and belongs to *P6/mmm* space group. There are four possible close or nearly close packed directions and planes of TiB_2. They are $<11\bar{2}0>_{TiB2}$, $<10\bar{1}0>_{TiB2}$, $<11\bar{2}3>_{TiB2}$, $<0001>_{TiB2}$ and $\{10\bar{1}1\}_{TiB2}$, $\{10\bar{1}0\}_{TiB2}$, $\{0001\}_{TiB2}$, $\{11\bar{2}0\}_{TiB2}$. The interphase $(Zn_{1.5}Cu_{0.5})Mg$ (IP) also has an hexagonal lattice structure with lattice parameters a = 0.5124 nm and c = 1.682 nm and space group of *P63/mmc* [61]. Each unit cell contains 12 Zn atoms, 8 Mg atoms and 4 Cu atoms. This interphase has three possible close or nearly close packed directions, $<11\bar{2}0>_{IP}$, $<10\bar{1}0>_{IP}$, and $<0001>_{IP}$ and five close packed or nearly close packed planes, $\{22\bar{4}0\}_{IP}$, $\{11\bar{2}0\}_{IP}$, $\{0008\}_{IP}$, $\{11\bar{2}4\}_{IP}$ and $\{11\bar{2}3\}_{IP}$. Based on these crystallographic data, the E2EM calculation predicted following ORs.

The predicted ORs between the Al matrix and the TiB_2 nanoparticles are:

The OR-A: $[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$, $(01\bar{1}1)_{TiB_2}$ 0.6^o from $(020)_{Al}$

The OR-B: $[1\bar{1}00]_{TiB_2}//[\bar{1}\bar{1}2]_{Al}$, $(11\bar{2}0)_{TiB_2}$ 1.2^o from $(\bar{2}20)_{Al}$

The OR-C: $[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$, $(0\bar{1}10)_{TiB_2}$ 1.5^o from $(\bar{1}\bar{1}1)_{Al}$

Considering the inherent error in FFT, the OR-A can be regarded as the OR1 and the OR-C as the OR2. The predicted OR-B was not experimentally observed in the present work.

Four ORs between the interphase and Al were calculated. They are:

The OR-D: $[0001]_{IP}//[101]_{Al}$, $(\bar{4}220)_{IP}$ 1.0^o from $(1\bar{3}\bar{1})_{Al}$

The OR-E: $[1\bar{1}00]_{IP}//[101]_{Al}$, $(11\bar{2}3)_{IP}$ 1.2^o from $(1\bar{1}\bar{1})_{Al}$

The OR-F: $[1\bar{1}00]_{IP}//[101]_{Al}$, $(0008)_{IP}$ 3.7^o from $(020)_{Al}$

The OR-G: $[1\bar{1}00]_{IP}//[101]_{Al}$, $(11\bar{2}\bar{4})_{IP}$ 1.3° from $(20\bar{2})_{Al}$

Although the OR-D and the OR-E were not experimentally observed in the present work, one can see that the OR-F consists with the OR3 and the OR-G agrees well with the OR5.

From the OR-A and the OR-F, following OR can be deduced.

The OR-H: $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}$, $(01\bar{1}1)_{TiB_2}$ < 4.3° from $(0008)_{IP}$

This OR-H actually is consistent with the OR4. Similarly, the OR6 can also be deduced from the OR-C and the OR-G.

The above crystallographic analysis indicates that the interfaces in between the TiB_2 nanoparticles and the Al matrix in the composite produced using the *in-situ* mixed salt method were either coherent or semi-coherent. Such interfaces acted as preferred sites for precipitation of the $(Zn_{1.5}\ Cu_{0.5})Mg$ interphase during ageing treatment, this in turn impact on the mechanical properties of the composites.

4.5. Effect of the aging conditions on the interphase evaluation

It was reported that the precipitation of T phase requires a high vacancy boundary diffusivity, i.e., at high-angle GBs or MRP/Al interface [20, 24, 25]. Different from as observed in the SiC/Al MMC [20], no transformation of the interphase from η to T phases is found when the aging condition is shifted from the peak-aged to overaged states (Figs. 4 and 5). This is due to the low boundary diffusivity of the semi-coherent TiB_2/Al interface being unfavorable for promoting this transformation. Further, it is well known that the precipitation in Al-Zn-Mg(-Cu) alloys involves the formation of precipitates with a different composition compared to the matrix, and therefore long-range diffusion is required [43]. This is a continuous and time-consuming phase transformation process featured by thermally activated atomic movements [43, 44]. As such, a metastable transitional zone should always exist at the growth front as long as the phase transformation process has not completely accomplished, although it cannot be confirmed in this work. It would be interesting in the future to carry out in-situ TEM heating tests, starting from the as-quenched state, to track the whole interface precipitation process.

5. Conclusions

In this work, the TiB_2/Al-Zn-Mg-Cu nanocomposite component produced by casting (in-situ reaction), FSP and hot extrusion was used as the model material for (HR)STEM characterization at the atomic scale. The specific structures of the TiB_2/Al interface and the matrix away from the interface at the as-quenched, peak-aged and overaged states were revealed. The results indicate the significant effects of the TiB_2 nanoparticle on the precipitation reactions in the Al matrix surrounding the TiB_2/Al interfaces, the formation of the interphase in particular depends on the ORs between the TiB_2 and Al matrix. The following conclusions can be drawn.

(1) The majority of TiB_2 nanoparticles are uniformly dispersed inside Al grains, featured with the basal {0001}, prismatic $\{01\bar{1}0\}$ and pyramidal $\{01\bar{1}1\}$ facets. At the as-quenched state, the well-documented crystallographic OR1 ($[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$, $(0001)_{TiB_2}//(\bar{1}11)_{Al}$) as well as the new OR2 ($[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$, $(01\bar{1}0)_{TiB_2}//(11\bar{1})_{Al}$) at the TiB_2/Al interface are determined. Periodically spaced misfit dislocations and solute-enriched regions and no obvious TSIDs are observed in the surrounding Al matrix next to this interface.

(2) Preferential heterogeneous interface precipitates are closely related to the OR1 or OR2 conditions between the TiB_2 and Al matrix, while being independent on the ageing conditions.

The interphase is identified to be the $(Zn_{1.5}Cu_{0.5})Mg$ phase both at the peak-aged and overaged states. At the OR1, The ORs between the TiB_2 nanoparticles, interphase and the Al matrix are: $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}//[101]_{Al}$, $(01\bar{1}1)_{TiB_2}//(0004)_{IP}$ 3° from $(020)_{Al}$, $(01\bar{1}0)_{TiB_2}//(11\bar{2}8)_{IP}$, $(11\bar{2}4)_{IP}//(11\bar{1})_{Al}$, $(\bar{1}\bar{1}20)_{IP}$ 3° from $(\bar{2}02)_{Al}$. At the OR2, the ORs are: $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}//[101]_{Al}$, $(01\bar{1}0)_{TiB_2}//(11\bar{2}0)_{IP}//(11\bar{1})_{Al}$, $(0001)_{TiB_2}//(0004)_{IP}$, $(\bar{1}\bar{1}24)_{IP}$ 3° from $(\bar{2}02)_{Al}$, $(11\bar{2}8)_{IP}$ 3° from $(020)_{Al}$. These determined ORs agree with the predictions using the E2EM calculation.

(3) At the peak-aged and overaged states, the mismatch of the $Al/(Zn_{1.5}Cu_{0.5})Mg$ interphase/TiB_2 multi-interfaces formed at the OR1 condition are generally very low (below 5 %) except the $(0008)_{IP}//(01\bar{1}1)_{TiB_2}$ interphase/TiB_2 interface planes. Comparatively, when formed at the OR2, the Al/interphase and interphase/TiB_2 interfaces show very low (below 5 %) and intermediate mismatch values (in the range 5-25 %), respectively.

(4) The energy barrier for the heterogeneous precipitations at the TiB_2/Al interface is considerably reduced compared to the homogeneous nucleation in the Al matrix away from such an interface. Highly-dense misfit dislocations at the TiB_2/Al interfaces are beneficial for the nucleation and effective growth of the interphase since they provide short-circuit diffusion paths for solute atoms and vacancies. The growth of the precipitates at the TiB_2/Al interfaces parallel to the close-packed {111} planes of the Al matrix is severely suppressed due to the ultra-low accommodation factor.

(5) No transformation of the interphase from η to T phases is found when the aging condition is shifted from the peak-aged to overaged states due to the low boundary diffusivity of the semi-coherent TiB_2/Al interface.

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FIGURE CAPTIONS

Figure 1: (a) Bright-field TEM image showing homogenous distribution of TiB_2 nanoparticles in the Al-Zn-Mg-Cu matrix grain at the as-quenched state, (b) STEM-HAADF image showing a typical TiB_2/Al interface and (c) schematic drawing illustrating the facetted shape of the TiB_2 nanoparticle. Insets in (b) at the left bottom and top right sides highlight corresponding FFT pattern of the TiB_2 nanoparticle and solute-enriched regions, respectively.

Figure 2: (a) and (d) HRSTEM-HAADF images showing TiB_2/Al interface structures at the OR1 and OR2 conditions, respectively, (b) and (e) corresponding FFT patterns of (a) and (d), and (c) and (f) corresponding simulated diffraction patterns for indexation, respectively. The projection direction is $[2\bar{1}\bar{1}0]_{TiB_2}$//$[101]_{Al}$. See the text for more details.

Figure 3: (a) and (b) STEM-HAADF images showing heterogeneous precipitates at the TiB_2/Al interfaces and finer precipitates in the matrix away from the interface at the peak-aged state, respectively. HRSTEM-HAADF images highlighting (c) plate-like GP zone and (d) elongated η' phase in (b); (e) and (f) STEM-HAADF image showing the heterogeneous precipitates at the TiB_2/Al interfaces and finer precipitates in the matrix away from the interface at the overaged state, respectively. (g) HRSTEM-HAADF image highlighting lath-like η phase in (f) and (h) corresponding inverse FFT pattern of (g) showing misfit dislocations at the Al/η interfaces. Inset in (h) shows the corresponding FFT pattern of (g). The projection direction is $[101]_{Al}$.

Figure 4: STEM-HAADF image of the Al/interphase/TiB_2 interfaces and corresponding Al, Zn, Mg, Cu and Ti elemental EDS maps.

Figure 5: (a) HRSTEM-HAADF image showing atomic structure of the interphase, (b) and (c) corresponding FFT and simulated diffraction patterns, respectively. Insets in (a) are the simulated HRSTEM-HAADF image of $[1\bar{1}00]$ $(Zn_{1.5}Cu_{0.5})Mg$ phase overlapped and intensity profiles used for measuring interplanar spacing.

Figure 6: (a) STEM-HAADF image showing interphase formed at the TiB_2/Al interface exhibiting the OR1 between TiB_2 nanoparticle and Al matrix revealed by corresponding FFT pattern (b) and schematic drawing (c). (d) STEM-HAADF image showing another interphase formed at the TiB_2/Al interfaces exhibiting the OR2 between TiB_2 nanoparticle and Al matrix revealed by corresponding FFT pattern (e) and schematic drawing (f). The projection direction is $[2\bar{1}\bar{1}0]_{TiB_2}//[101]_{Al}$. See the text for more details.

Figure 7: (a) HRSTEM-HAADF image showing the Al/IP/TiB_2 multi-interfaces at the OR1; (b), (c) and (e) corresponding FFT patterns of box areas namely b, c and e given in (a) exhibiting the mutual ORs between the TiB_2 nanoparticle, interphase and Al matrix; (d) and (f) simulated diffraction patterns corresponding to (c) and (e), respectively. The projection direction is $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}//[101]_{Al}$. See the text for more details.

Figure 8: (a) HRSTEM-HAADF image showing the Al/IP/TiB_2 multi-interfaces at the OR2. (b), (c) and (e) corresponding FFT patterns of box areas namely b, c and e given in (a) exhibiting the mutual ORs between the TiB_2 nanoparticle, interphase and Al matrix; (d) and (f) simulated diffraction patterns corresponding to (c) and (e), respectively. The projection direction is $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}//[101]_{Al}$. See the text for more details.

Figure 9: (a) HRSTEM-HAADF image showing atomic structure of the Al/IP interfaces at the OR1. (b) and (c) inverse FFT patterns of (a) using different reflection pairs selected in corresponding FFT patterns in insets and (d) simulated atomic structure model showing the Al/IP interface $(11\bar{1})_{Al}//(11\bar{2}4)_{IP}$. The projection direction is $[1\bar{1}00]_{IP}//[101]_{Al}$. See the text for more details.

Figure 10: (a) HRSTEM-HAADF image showing atomic structure of the IP/TiB_2 interfaces at the OR1. (b) and (c) inverse FFT patterns of (a) using different reflection pairs selected in corresponding FFT patterns in insets and (d) simulated atomic structure model showing the IP/TiB_2 interface $(11\bar{2}8)_{IP}//(01\bar{1}0)_{TiB_2}$. The projection direction is $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}$. See the text for more details.

Figure 11: HRSTEM-HAADF images showing atomic structure of the Al/IP interfaces at the OR2: (a) the arc-shaped interface at the growth front of the interphase and (c) interface $(\bar{1}11)_{Al}//(11\bar{2}0)_{IP}$. (b) and (d) inverse FFT patterns of (a) and (c) using different reflection pairs selected in corresponding FFT patterns in insets, respectively and (e) Simulated atomic structure models showing the Al/IP interface $(\bar{1}11)_{Al}//(11\bar{2}0)_{IP}$. The projection direction is $[1\bar{1}00]_{IP}//[101]_{Al}$. See the text for more details.

Figure 12: (a) HRSTEM-HAADF image showing atomic structure of the IP/TiB_2 interface at the OR2. (b) inverse FFT pattern of (a) using reflection pairs selected in corresponding FFT pattern in inset and (c) simulated atomic structure model showing the IP/TiB_2 interface $(0001)_{TiB_2}//(0008)_{IP}$. The projection direction is $[2\bar{1}\bar{1}0]_{TiB_2}//[1\bar{1}00]_{IP}$. See the text for more details.

Figure 13: (a) HRSTEM-HAADF image showing coherent Al/IP/TiB_2 interfaces parallel to the close-packed $(1\bar{1}\bar{1})_{Al}$ planes, (b) EDX line profiles across the interface showing the embryo of the interphase rich in Zn, Mg and Cu elements; (c) and (d) Simulated atomic structure models illustrating the precipitation suppression mechanism associated with the growth of coherent close-packed interface between the hcp embryo of the interphase and fcc Al matrix.