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ON THE EFFECT OF Ti_2AlC ON THE FORMATION OF THERMALLY STABLE Mg NANO GRAINS

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Abstract

When Mg or Mg-alloys are reinforced with Ti_2AlC – using a simple pressureless melt infiltration method – the result is nanocrystalline, nc, Mg-matrix composites, with outstanding mechanical properties. As an added bonus, the nc Mg-matrix is extraordinarily thermally stable. When AZ61 is used to infiltrate the Ti_2AlC preforms, ultimate tensile stresses of 800 MPa are achieved. The reasons that lead to the formation of the nc-Mg are as of yet not understood. In this study, the different composites' microstructures are investigated by X-ray diffraction, scanning and transmission electron microscopy. A correlation was found between the presence of oxygen and the nc Mg grains. Nanometer sized Mg grains were also found in between some of the Ti_2AlC layers.

Introduction

Mg alloys have attracted a great deal of interest over the past decades due to their high specific strength, which renders them good candidates for applications in the aerospace and automotive industries [1, 2]. One method that can be used to achieve better properties is to fabricate materials wherein the grain size is at the nanometer scale [3]. The challenge for this approach, however, is that the grains tend to coarsen, even at room temperature [4]. Another approach to enhance the mechanical properties is to fabricate composites [5-7]. Herein, we show that by combining both approaches exceptional properties can be achieved.

In 2009, we reported on the fabrication of novel, near net-shape nanocrystalline-Mg, nc-Mg, composites, reinforced with Ti_2AlC [8]. The latter is a member of a large family of ternary carbides and nitrides, referred to as the *MAX phases,* with unique combinations of metal and ceramic properties. Like metals, they are electrically and thermally conductive, most readily machinable [9, 10], not susceptible to thermal shock, plastic at high temperatures, and exceptionally damage tolerant. Like ceramics, some of them are elastically rigid (Young's mod. > 300 GPa), lightweight ($\approx$ 4 g/cm^3) and maintain their strengths to high temperatures [11]. The ternaries Ti_3SiC_2 and Ti_2AlC are creep, fatigue and oxidation resistant [12,13]. The Ti-based MAX phases are also more conductive, both electrically and thermally, than Ti metal at all temperatures [14, 15].

Because of their layered structure, the MAX phases' major deformation mechanism is basal slip, which in turn results in the formation of kink bands. Due to this deformation mechanism, they have excellent low and high-cycle fatigue and damping properties [16]. The latter increase with the applied stress squared [17]. The unusual damping properties have been explained by the formation and annihilation of incipient kink bands, IKBs. IKBs are parallel, co-axial, basal dislocation loops. More details on IKB-based deformation mechanisms can be found elsewhere [17, 18].

The near net shape nc-Mg composites were made by pressureless infiltration of Mg into a 50 vol.% porous Ti_2AlC preform in a vacuum furnace at 750°C for 1 h. The fabrication details can be found elsewhere [8, 18, 19]. The resulting composites, with no additional steps, possessed outstanding properties. The best results were reported for a Mg-50 vol.% Ti_2AlC, henceforth referred to as 50Mg-211. According to X-ray diffraction, XRD, transmission electron microscopy, TEM, and differential scanning calorimetery, DSC, results, the Mg grain size was found to be $\approx$ 35±15 nm. The density of the composite was 2.9 g/cm^3. The ultimate compressive strength, UCS, was 700 ± 10 MPa [8, 20]. Although both starting components had tensile strengths lower than 300 MPa, the composite's ultimate tensile strength, UTS, was 345 ± 40 MPa. This enhancement in UTS was ascribed to the small grain size of the Mg. In contrast to most nc-Mg microstructures, the nano grains were reported to be so exceptionally thermally stable that heating three times to 700°C – i.e. even melting the nc-Mg – did not lead to grain growth [20]. When the same infiltration method was used with Ti_3SiC_2 as the reinforcement, the UCSs were not as high. The reason for this state of affairs was again related to Mg grain size, which was not at the nano scale in the Mg/Ti_3SiC_2 composites [8].

More recently, we reported on 80 vol.% nc-Mg composites, reinforced with 20 vol.% Ti_2AlC. In that case, the Mg average grain size was 90±15 nm. The density was 2 g/cm^3 [18]. The UCS was 350±10 MPa. Although this composite was comprised of 80 vol.% Mg, the nano grains were still thermally stable up to 700°C.

The aim of this study is to explore: i) the reasons for the formation of the nc-Mg, and, ii) what keeps the grains from coarsening. XRD, scanning electron microscopy, SEM, and TEM results are discussed below.

Experimental Details

Both a 50Mg-211 and a Mg-50 vol.% Ti_3SiC_2 composite, henceforth referred to as 50Mg-312, were fabricated. The processing method is detailed elsewhere [8, 18, 19]. XRD was carried out on a diffractometer (Model 500D, Siemens, Karlsruhe, Germany) and the patterns were collected using step scans of 0.01° in the range of 10°–80° 2θ and a step time of 2 s. Scans were made with Cu Kα radiation (40 kV and 30 mA). The polished surfaces were observed in a SEM (Zeiss Supra 50VP, Germany) and elemental maps were taken using the energy-dispersive spectroscope (EDS) (Oxford Inca X-Sight, Oxfordshire, UK) in the SEM.

TEM samples were prepared first by cutting ~300 μm thick slices from the bulk samples with a low speed diamond saw. Small 3 mm diameter disks were then made using an ultrasonic disk cutter (Model 170, Fischione, Export, PA). Both sides were polished with a dimpling grinder (Model 200, Fischione, Export, PA) using 3 μm, 1 μm and 0.1 μm diamond pastes successively. The disk

thickness after dimpling was about 25 μm. Final perforation was made with an ion mill (Model 1010 Fischione, Export, PA) at 5 kV. TEM characterization was performed using a field emission TEM (JEOL JEM-2010F, Akishima, Japan) operating at 200 kV. Images were collected with a multi-scan CCD digital camera. EDS analysis in the TEM was carried out with an attached EDAX ultra-thin window X-ray energy dispersive spectrometer.

Results and Discussion

As reported in our earlier studies on these composites [8, 18], Mg peaks from the XRD patterns of all samples were compared with those of pure Mg powder ($d_{av} \approx 150$ μm). Figure 1 compares the main XRD peak of Mg in 50Mg-211, 50Mg-312 with that of pure Mg. Comparing the full width at half maximum, FWHM, of the Mg peaks revealed that peak broadening occurred only for the 50Mg-211 composite. Applying the Scherrer formula [21], the Mg grain size is estimated to be 35±15 nm, in agreement with previous work [8, 18]. The FWHMs of the 50Mg-312 composite are comparable to those of the initial Mg powder (Fig. 1).

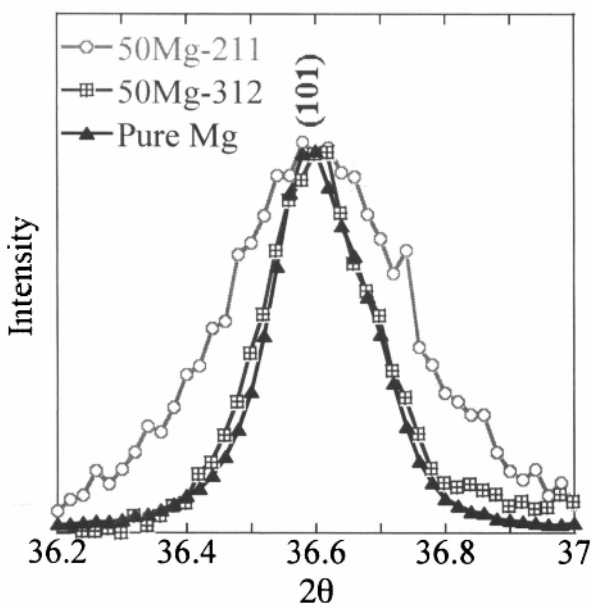

Figure 1. XRD diffractograms of the main Mg peak in the 50Mg-211, 50Mg-312 composites and pure Mg.

SEM micrographs of 50Mg-211 polished surfaces revealed that Mg infiltrated all the Ti_2AlC particles and penetrated into some of the smallest cracks and fissures in the original Ti_2AlC grains. EDS across different Ti_2AlC grains (Fig. 2) showed the presence of Mg even in cracks/delaminations of the order of a few nm (Fig. 2b). This implies that the molten Mg wets the Ti_2AlC grains exceptionally well and infiltrates all the preform. It is worth noting that the as-received Ti_2AlC powder particles are more micro-cracked and delaminated than the Ti_3SiC_2 powder particles.

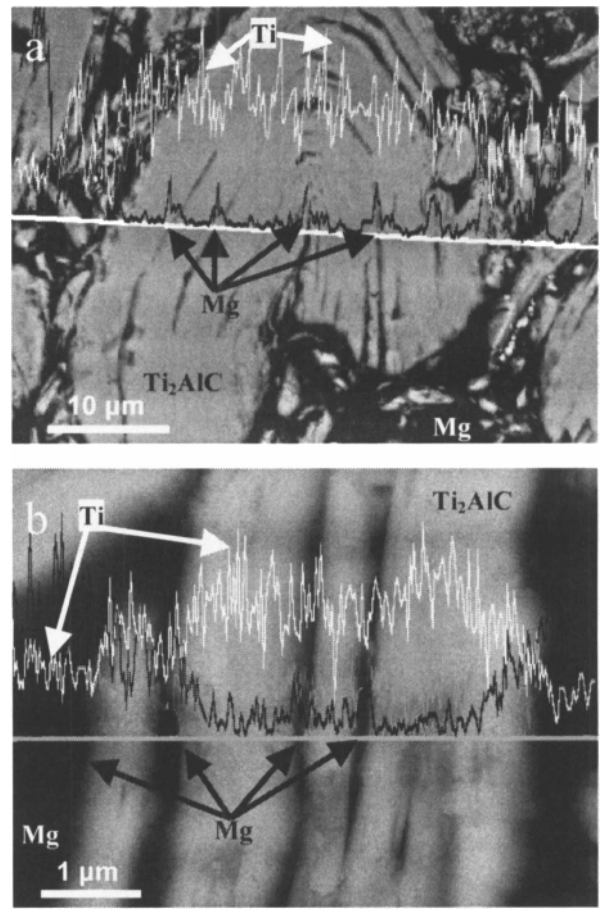

Figure 2. a) SEM micrograph of polished 50Mg-211 surface superimposed with elemental line scans (solid line) showing the presence of Mg in between delaminations in individual Ti_2AlC grains, b) same as a, but at higher magnification. In these maps, black represents Mg; white Ti.

The presence of Mg in between delaminations, cracks and fissures in individual Ti_2AlC grains is also confirmed when fractured surfaces are examined (Fig. 3a). Here two morphologies were observed. Some surfaces (see arrow in Fig. 3a) were not decorated with Mg, but were simply Al or Ti-terminated surfaces typical to those present when bulk Ti_2AlC samples are fractured. Other surfaces, on the other hand, were covered in small (<100 nm) dimples that EDS identified as Mg (see Fig. 3b and bottom inset). The Mg was also found stretched between two Ti_2AlC surfaces (top inset in Fig. 3b). The presence of Mg in such narrow regions is important because it could at least partially explain the broadening observed in the XRD patterns. More importantly, these thin Mg layers would also explain the exceptional mechanical properties obtained in some of these composites, since such thin metallic layers would be difficult to deform. For example, when AZ61 50 vol.% Ti_2AlC composites were fabricated, their UTSs ranged from 600 to 800 MPa.

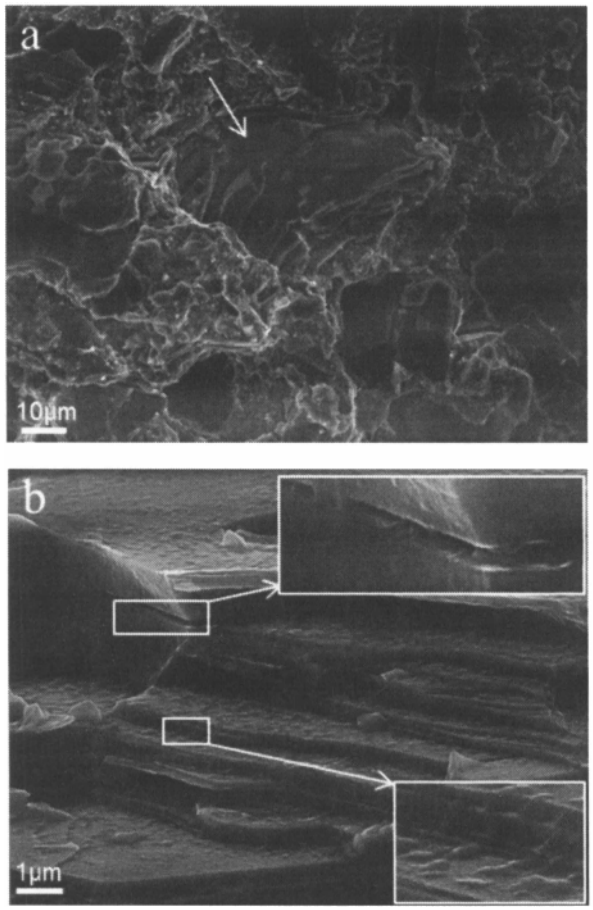

Figure 3. SEM fractographs of 50Mg-211 showing, a) a fracture surface mostly covered with Mg, which also surrounds the Ti_2AlC particles, and b) fractured Ti_2AlC particle covered with a thin layer of Mg. Insets show higher magnification micrographs of select regions on the image. Arrow in (a) point to a Ti_2AlC fractured surface that is not decorated with Mg.

When the same sample was imaged in a TEM, thin Mg layers (not shown) were observed in between the Ti_2AlC layers confirming the SEM observations. In addition, relatively large regions of Mg were observed (Fig. 4a). At higher magnification (Fig. 4b), it is evident that the Mg is present at the nano scale. Selected area diffraction, SAD, of this region (not shown) confirmed that these grains are at the nanometer scale. EDS revealed the presence of oxygen in this region. Its presence can be explained by postulating that thin MgO layers somehow separate, or exist between, the Mg nano grains. This is in agreement with what was reported earlier [8, 18, 20]. The conclusion is bolstered by the facts that, i) MgO peaks are observed in the XRD diffractograms and, ii) the peaks were quite broad [8]. Using the Scherrer formula the size of the MgO grains was estimated to be ~ 3 nm [8]. The thermal stability of nano Mg grains can be explained by the presence of these MgO layers in between the Mg nano grains, as well as the presence of nano Mg layers in between the Ti_2AlC layers. These comments notwithstanding, more work – some of it ongoing – is needed to unambiguously show that thin MgO layers are present in between the Mg grains.

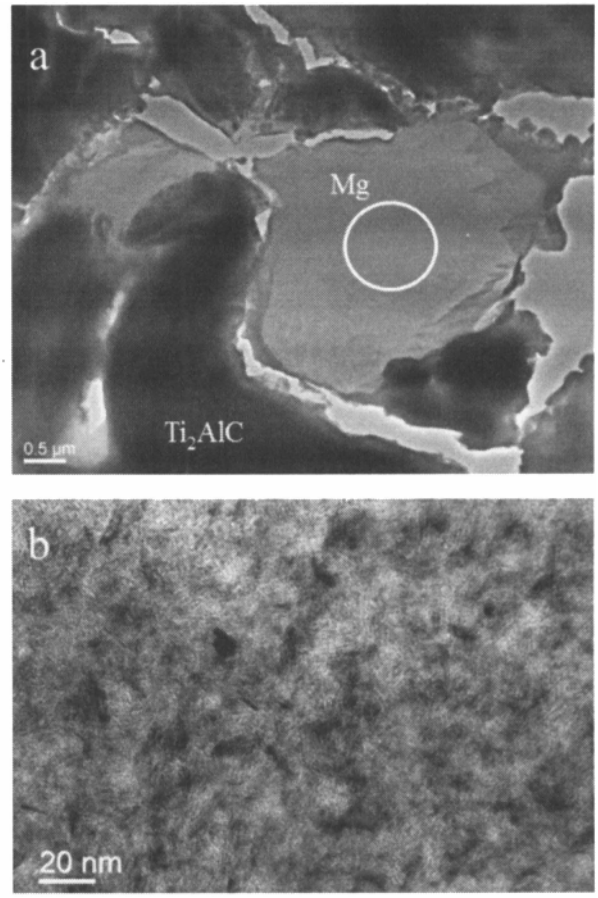

Figure 4. TEM micrographs of 50Mg-211 composite, a) showing large Mg region next to a Ti_2AlC grains, b) higher magnification of circled Mg region in (a) showing Mg nano grains.

It is important to note that not all the Mg regions are comprised of nanograins. In some regions, relatively large Mg grains have been found. The oxygen content in these regions was less than in those where the grains were at the nanoscale. Understanding what role these large grains play on the mechanical properties is ongoing as well.

Summary and Concluding Remarks

Using a simple pressureless melt infiltration method, near net shape nc-Mg composites reinforced with Ti_2AlC, that exhibit good mechanical properties were fabricated. Mg peak broadening in the XRD shows the presence of nano-Mg grains in the matrix. The latter was also confirmed by TEM images and SAD patterns. The reason for the formation of the nano-Mg grains is still unclear. However, given that oxygen is detected in all the nano-Mg regions, it is reasonable to assume that oxygen plays an important role. In addition, the wetting of Mg in these composites is excellent, which leads to Mg penetration into the thinnest of cracks and delaminations in the Ti_2AlC grains and formed nc-Mg between them. The presence of MgO in between the nano-Mg grains and the confinement of Mg in between the Ti_2AlC layers in some regions may explain the thermal stability of Mg nano grains.

Acknowledgements

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