STRENGTHENING OF MG/WS_2 AND AL/WS_2 INORGANIC NANOTUBES METAL MATRIX COMPOSITES

Song-Jeng Huang,[1] Wei-Yi Peng[1], Bojana Visic[2], Alla Zak[3],
Chia-Han Ho[1], Yishay Feldman[2] and Reshef Tenne[2], Addisu Negash Ali[1]
[1]Dept. of Mechanical Engineering, National Taiwan University of Science and Technology
[2]Dept. of Materials and Interfaces, Faculty of Chemistry, Weizmann Institute of Science
[3]Holon Institute of Technology

Abstract

In the present work, advanced magnesium and aluminum metal matrix composites reinforced by nanomaterials are reported. The materials used for the experiments are Mg-alloy (AZ31) and aluminum alloy (AA6061) with inorganic nanotubes (INT) and nanoparticles of WS2. Metal matrix composite with a different weight percentage of the WS2 INT was prepared using stir casting method. Both Mg-alloy (AZ31) and aluminum alloy (AA6061) metal matrix nanocomposites (MMCs) were re-melted by the stirring-casting method. Mechanical properties and microstructure analysis of the nano-MMCs were conducted. The measurements have shown that the yielding strength, ultimate tensile strength, and ductility were improved compared to the pure Mg-Al alloys. Metallography microstructure analysis showed that increasing the WS2 INT weight percentage resulted in more refined grains. As a result, the grain size of the composite matrix was reduced.

Keywords: Metal Matrix Composite, Casting, WS_2 Nanotube, Mechanical Property

Introduction

Magnesium (Mg) and aluminum (Al) alloys are gaining more recognition as a light structural material for light-weight applications, due to their low density and high stiffness-to-weight ratio [1, 2]. AZ31 and Al6061 have good mechanical properties and good weldability. Metals reinforced with hard particles are known to exhibit enhanced mechanical properties such as: hardness, Young's modulus, yield strength and ultimate tensile strength. This reinforcement effect nevertheless comes with a penalty of a reduced ductility, i.e. lower fracture toughness. Hence, many researchers have attempted to fabricate Mg and Al-based metal-matrix composites (Al MMCs) utilizing different additives and techniques in order to obtain light-weight MMCs with excellent mechanical properties[3, 4]. In recent years, ceramic nanoparticles, such as SiC, Al_2O_3 and others, have been used to reinforce different metallic materials and form new metal matrix composites. Various mechanisms for strengthening metal-matrix composites (MMCs) were proposed, including thermal expansion mismatch, Orowan looping, Hall-Petch relation and the shear-lag model. Due to the high processing temperatures of the MMC, the thermal expansion mismatch between the nanoparticles and the matrix results in increased dislocation density, increasing thereby the yield strength of the nano-MMCs. The nanoparticles in the matrix can impede dislocation motion during tensile testing.

The proposed new INT-WS_2-based Mg and Al nanocomposites which were prepared by melt-stirring with no further mechanical or chemical processing revealed stronger and tougher properties compared with the pure Mg and Al alloys. In the present work, the effect of adding WS_2 IF and WS_2 INT on the mechanical properties of Mg and Al MMCs were investigated.

Experimental details

The Mg-alloy studied in this work is AZ31 with ~3.0 at% aluminum- available commercially (Taiwan Mach Technology (LINYI) Co.). Its chemical composition cited by the manufacturer is presented in Table 1. The Al-alloy studied in this work AA6061 was purchased from Taiwan Ta Cheng Aluminium Co. and its chemical composition as cited by the manufacturer is presented in Table 2.

Table 1. Chemical composition (in wt%) of the AZ31 alloy (Mg is about 94.5 wt%).

Elements	Al	Zn	Mn	Si	Fe	Cu	Ni	Mg

wt %	3.08	0.908	0.393	0.022	0.001	0.002	0.01	Balance

Table 2. Chemical composition (in wt%) of the AA6061 alloy

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
0.70	0.09	0.27	0.004	0.90	0.10	0.01	0.008	Bal.

The preparation of the present Mg and Al MMCs were by using the melt-stirring furnace (Figure 1) described in great details [5]. The AZ31 and the WS_2 nanotubes were placed inside a stainless crucible and heated to 400°C in a resistance-heating furnace. The Al6061 and the WS_2 INT (or IF) were placed inside a stainless steel crucible and heated to 250-300°C (the WS_2 IF/INT are stable at these temperatures).

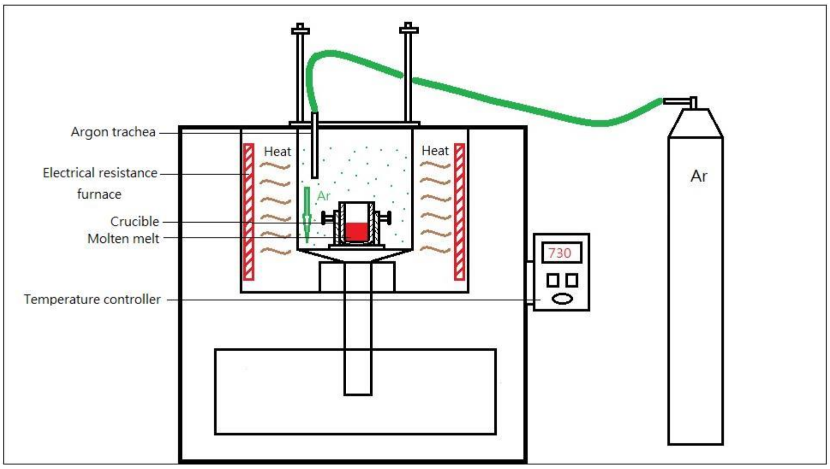

Figure 1. Schematic of stir casting furnace used for the fabrication of the Mg and Al MMCs.

Optical microscopy was carried out by Zeiss Axiotech 25HD microscope. Micro-Vickers hardness tester associated with VHPro Express software was used for the hardness measurements. A vertical theta-theta diffractometer (TTRAX III, Rigaku, Japan) equipped with a rotating Cu anode operating at 50 kV and 240 mA was used for XRD studies. The following electron microscopes were used in this work: SEM model LEO model Supra, 7426.

Results and discussion

As shown in Figure 2(a), pictures of a few ingots of AZ31Mg MMCs obtained after the melt stirring in different temperatures. Noticeably, the ingots which were prepared at temperatures of 700 °C and above looked more uniform compared to those prepared at lower temperatures. One major obstacle for this study was the need to protect the reactive mixture, and especially the nanotubes, against high-temperature oxidation. Similarly, Al MMCs ingot was cut into 3 sections for metallographic analysis; tensile and hardness tests as indicated in Figure 2(b).

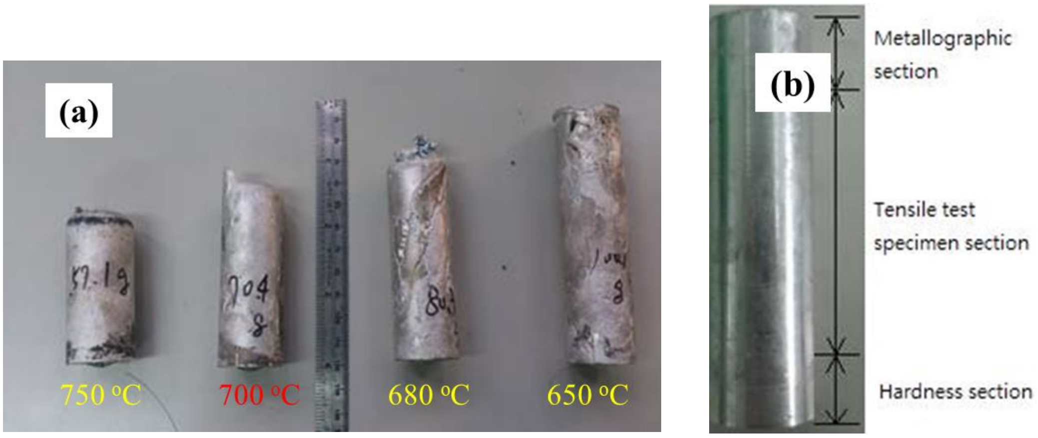

Figure 2. (a) Ingots of AZ31 at different temperature and (b) ingot sections for metallographic, tensile and hardness tests.

X-ray diffraction (XRD) patterns of the prepared MMC (AZ31INT0.5) are shown in Figure 3(a). A small reflection peak from the (002) plane of the INT at 13.91° (interlayer spacing of 6.36 Å) is shifted with respect to bulk 2H-WS_2. This downshift represents a 2-3% expansion in the interlayer spacing and is attributed to relaxation of the strain in the nanotubes. This lattice expansion was attributed to strain relaxation of the WS_2 layers in the nanotubes. Furthermore, the slightly larger swelling of the interlayer spacing in the present case could be attributed to Mg intercalation between the WS_2 layers. It is nevertheless not clear if the Mg intercalation occurred within the nanotubes or into portion thereof, which exfoliated during the processing. More careful inspection of some of the XRD patterns reveals two extra peaks at 30° and 35° in the MMC (black curve). The peak at 30° can be possibly assigned to the compound

Al_2CO, which is formed by the high temperature reaction between aluminum and the CO_2. XRD patterns of AA6061/ WS_2 INT MMCs and AA6061/ WS_2 IF MMCs were presented in Figure 3(b and c), respectively. Noticeably, two small reflection peaks from the Al at 38.4xx° and 44.4xx° are shifted with respect to bulk Al#04-0787. This upshift represents a 2-3% contraction in the lattice spacing and is attributed to relaxation of the strain in the Al matrix, for both AA6061/ WS_2 INT MMCs and AA6061/ WS_2 IF MMCs.

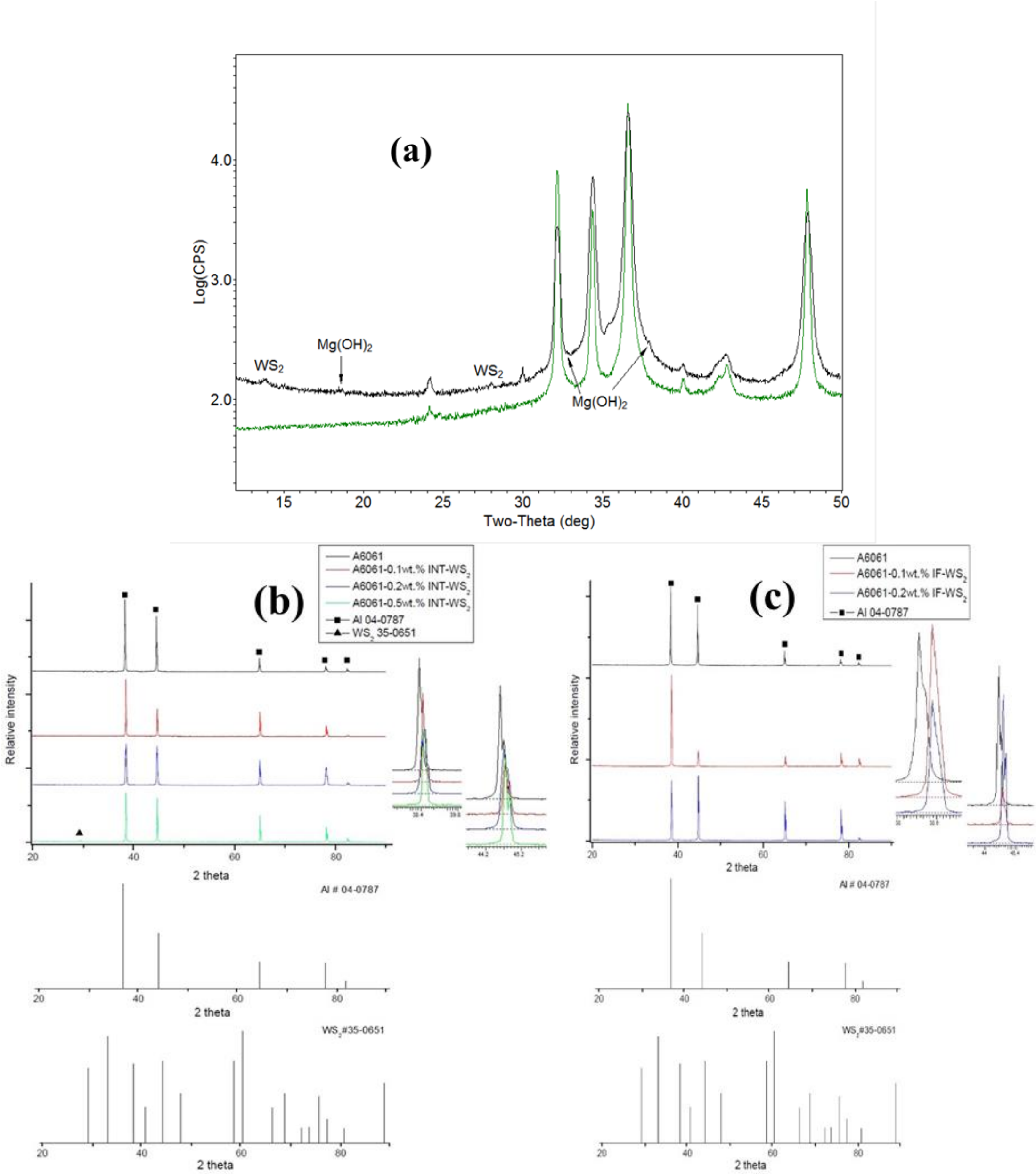

Figure 3. (a) XRD patterns of the AZ31INT0.5-1 sample and a pristine Mg alloy (green), (b) XRD patterns of AA6061/ WS_2 INT MMCs and (c) XRD patterns of AA6061/ WS_2 IF MMCs.

Numerous tensile tests were carried out for the AZ31INT samples. Figure 4(a) shows a typical result of such tests for the AZ31 alloy filled with 1 wt% INT-WS_2. Two obvious conclusions can be drawn from this figure: 1. there exists some scattering in the data, which therefore necessitated to average over many repetitive measurements. 2. the addition of the nanotubes had a relatively minor effect on the stiffness and yield strength of the samples. Figure 4(b) shows the stress-strain curve of AA6061/ WS_2 INT MMCs and AA6061/ WS_2 IF MMCs. The strain-stress curves of the pure Al-alloy and some of the nanocomposites studied in this work.

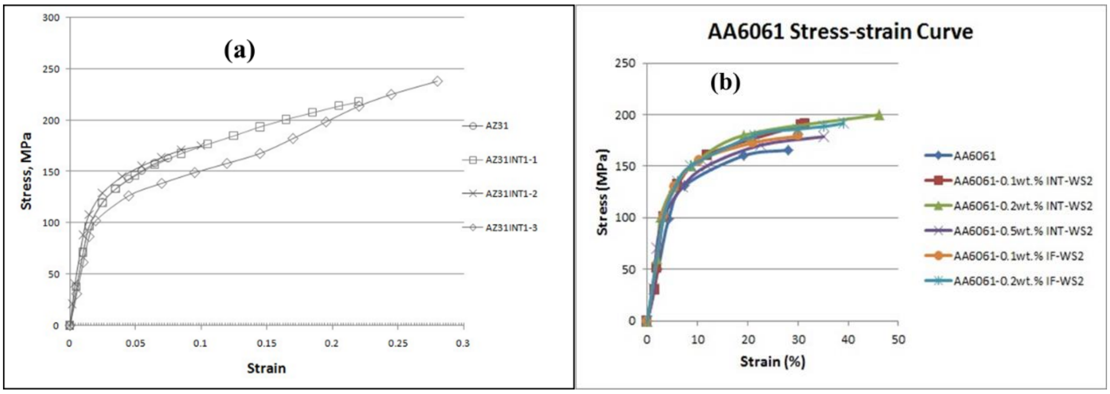

Figure 4. (a) Stress-strain curve (tensile test) of the pure Mg-ZA31 alloy and the Mg MMC with 1 wt% nanotubes (AZ31INT1-x; x=1-3) and (b) Stress-strain curve of AA6061/ WS_2 INT MMCs and AA6061/ WS_2 IF MMCs.

Figure 5**(**a**)** presents a summary of the mechanical properties of the pure AZ31 alloy and the WS_2 nanotubes-based Mg MMCs after averaging. Indeed, the addition of small amounts of INT-WS_2, with no additional mechanical processing, leads to significant improvements in the mechanical behavior of the Mg-alloy (AZ31). In particular, both the strength and strain of the Mg MMC was ameliorated, which produced a remarkable improvement in its fracture toughness. The yield strength

(YS), ultimate tensile strength (UTS) and elongation of AA6061/ WS_2 INT MMCs and AA6061/ WS_2 IF MMCs as a function of the nanoparticle concentrations are shown in Figure 5(b), sequentially. The yield strength, ultimate tensile strength, and elongation increased with increasing INT and IF content. However, there exists an optimal content of the added IF/INT, beyond which the mechanical performance is compromised, as shown for Al MMCs with 0.5 wt.% INT.

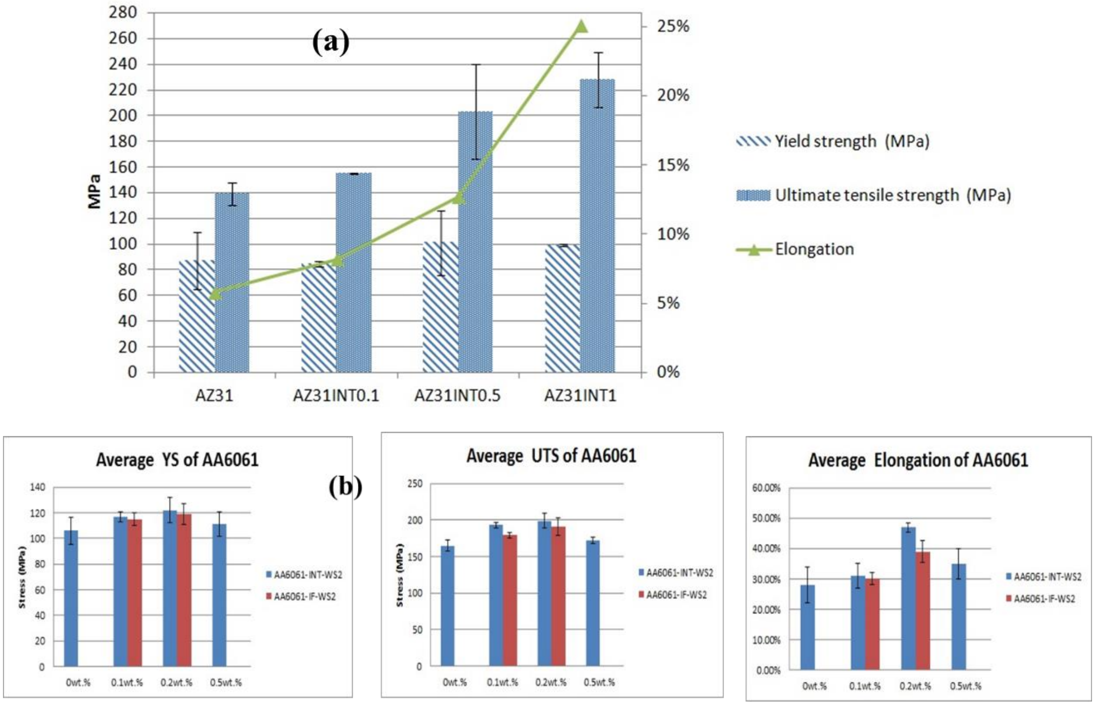

Figure 5. (a) Summary of the mechanical testing of the different Mg-alloy samples and (b) Summary of the mechanical testing of AA6061/ WS_2 INT MMCs and AA6061/ WS_2 IF MMCs.

In order to elucidate the reinforcement effect of the nanotubes, the metallographic analysis was carried-out for the MMCs. Figure 6 (a) shows a typical optical micrograph of the surface of three AZ31INT1 samples and pure AZ31 alloy. Visibly the nanotubes-containing MMC possess smaller grains. Figure 6(b) show the metallography of AA6061 MMCs with (a) 0.1 wt.% INT, (b) 0.2 wt.% INT, (c) 0.5 wt.% WS_2 INT, while Figure 6(c) shows the results for AA6061 MMCs with 0.1 wt.% and 0.2 wt.% WS_2 IF; consecutively. It can be observed that the grain size of both AA6061/ WS_2 INT MMCs and AA6061/ WS_2 IF MMCs decreased with increasing INT and IF concentrations.

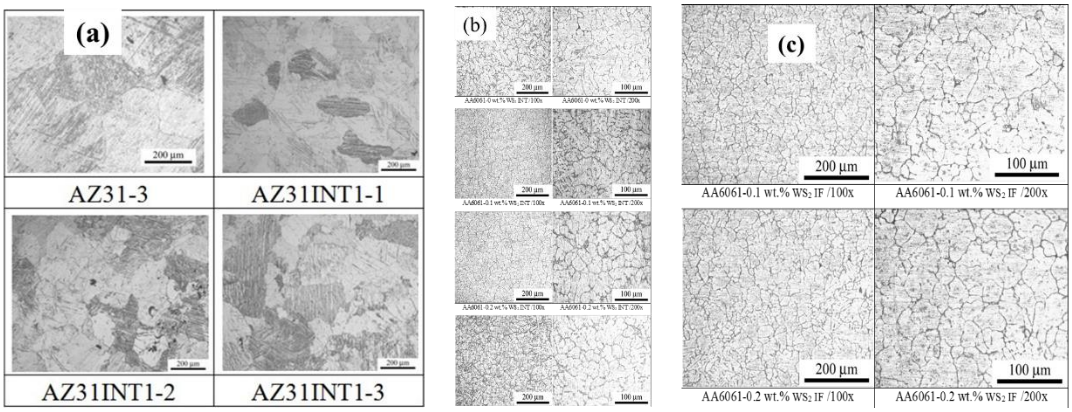

Figure 6. (a) Metallography of the pure Mg alloy and the different Mg alloys formulated with 1 wt% INT-WS_2, (b) Metallography of AA6061 MMCs with added 0.1, 0.2 and 0.5 wt.% WS_2 INT and (c) Metallography of AA6061 MMCs with 0.1 and 0.2 wt.% WS_2 IF.

Finally, metallographic analysis of quite a few Mg MMCs surfaces, with different nanotubes content, is displayed in the block diagram in Figure 7(a). Accordingly, as the nanotubes concentration goes-up, the grain size is reduced. This analysis strongly suggests a relationship between the grain-size and the mechanical properties of the MMCs. As indicated in Figure 7(b), the grain size decreases with increasing the concentration of INT or IF in the composite. Al MMCs with 0.1, 0.2 and 0.5 wt.% INT exhibits 13.1, 36.5 and 48.4% reduction in the grain size compared with neat AA6061, respectively. From these results, it can be concluded that WS_2 INT and WS_2 IF produce a remarkable reduction in the grain size of AA6061, which favorably affects the mechanical properties of the MMCs.

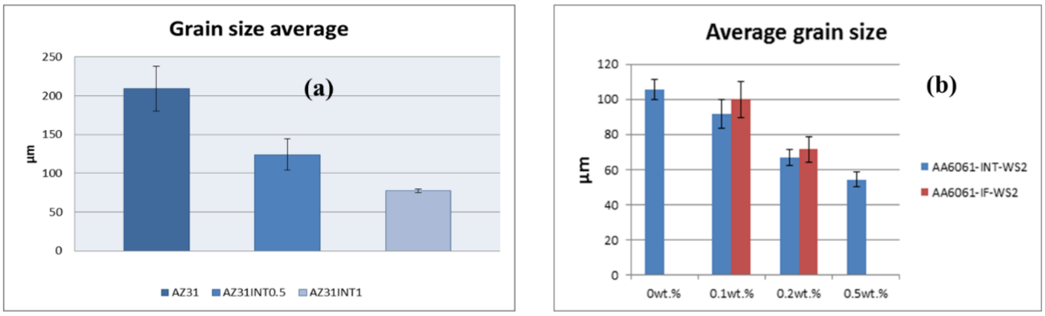

Figure 7. (a) Comparison between the grain sizes of the pristine AZ31 Mg alloy and the MMC's with 0.5 and 1 wt% of WS_2 nanotubes and (b) Grain size analysis of AA6061/ WS_2 INT MMCs and AA6061/ WS_2 IF MMCs.

Table 3. shows a representative example using the different models and the parameters used for the calculations. It is clear from the calculations that the greatest contribution for the reinforcement effect is the increase in the dislocations density at the nanotube-Mg-alloy matrix due to the large mismatch in the thermal expansion of the two materials. In contrast to the Hall-Petch mechanism, this effect is more local and is limited to the grain boundaries in the vicinity of the nanotube-metal interface. These calculations were not particularly sensitive to the size of the nanoparticles (20-100 nm). However, models taking into account the large anisotropy of the nanotubes would be highly warranted in this case. Further research is required to optimize the process and elucidate the mechanism of the reinforcement effect- in particular using advanced electron microscopy techniques. The calculated contributions of the different mechanisms for the reinforcement of AA6061/ 0.2 wt.% WS_2 INT MMCs and AA6061/ 0.2wt.% WS_2 IF MMCs are presented in **Table 4** and **Table 5**, respectively. It is clear from the calculations that the greatest contribution for the reinforcement effect is the increase in the dislocations density at the nanotube-Al-alloy matrix due to the large mismatch in the thermal expansion of the two materials.

Table 3. Calculated contributions of the different mechanisms for the reinforcement of the AZ31 by 0.1 wt% INT-WS_2, assuming the diameter of the nanoparticles is 100 nm.

Symbol	Description	Value [MPa]	Percentage of strengthening the contribution
$\Delta\sigma_{\text{Hall-Petch}}$	enhancement of composite strength due to grain refining	6.4698	14.4%
$\Delta\sigma_{\text{CTE}}$	enhancement of composite strength due to dislocation density increase	31.2113	69.7%
$\Delta\sigma_{\text{Orowan}}$	enhancement of composite strength due to Orowan strengthening	7.0407	15.7%
$\Delta\sigma_{\text{load}}$	enhancement of composite strength due to load bearing	0.09834	0.2%

Table 4. Calculated contributions of the different mechanisms for the reinforcement of the AA6061/ 0.2wt.% WS_2 INT MMCs

Symbol	Description	Value (MPa)	Percentage of strengthening the contribution
$\Delta\sigma_{\text{Hall-Petch}}$	enhancement of composite strength due to grain refining	1.54	4.8%
$\Delta\sigma_{\text{CTE}}$	enhancement of composite strength due to dislocation density increase	22.25	68.9%
$\Delta\sigma_{\text{Orowan}}$	enhancement of composite strength due to Orowan strengthening	8.45	26.2%
$\Delta\sigma_{\text{load}}$	enhancement of composite strength due to load bearing	0.04	0.1%

Table 5. Calculated contributions of the different mechanisms for the reinforcement of the AA6061/ 0.2wt.% WS_2 IF MMCs

Symbol	Description	Value (MPa)	Percentage of strengthening the contribution
$\Delta\sigma_{Hall-Petch}$	enhancement of composite strength due to grain refining	1.30	5.8%
$\Delta\sigma_{CTE}$	enhancement of composite strength due to dislocation density increase	16.51	73.6%
$\Delta\sigma_{Orowan}$	enhancement of composite strength due to Orowan strengthening	4.57	20.3%
$\Delta\sigma_{load}$	enhancement of composite strength due to load bearing	0.04	0.2%

Conclusion

Small amounts of up to 1 wt% of WS_2 nanotubes (INT-WS_2) were added to the AZ31 Mg-alloy using a melt-stirring reactor operated at 700 °C. Despite the small amounts of added INT-WS_2 their addition led to remarkable improvements in the mechanical properties of the alloys. Surprisingly, both the tensile strength of the AZ31alloy and its elongation were largely improved. Considering composites of AA6061 MMCs with 0.1, 0.2 and 0.5 wt.% WS_2 INT and AA6061 MMCs-with 0.1and 0.2 wt.% WS_2 IF were fabricated by the stirring-casting method. The Al MMCs reinforced by WS_2 INT or WS_2 IF exhibit excellent mechanical properties. Yielding strength, ultimate tensile strength, and ductility of AA6061/ 0.2 wt.% WS_2 INT (inorganic nanotubes) MMCs were improved by 15.0%, 20.6% and 67.8%, respectively. Yielding strength, ultimate tensile strength and ductility of AA6061/ 0.2 wt.% WS_2 IF (inorganic fullerene-like nanoparticle) MMCs were enhanced by 12.3%, 15.8% and 39.3%, respectively. AA6061/ 0.5 wt.% WS_2 INT exhibited the best result in hardness, which was improved by 5.1%.

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