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EFFECT OF COOLING RATE AND CHEMICAL MODIFICATION ON THE TENSILE PROPERTIES OF Mg–5wt% Si ALLOY

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Abstract

Hypereutectic Mg–Si alloys are a new class of light materials usable for aerospace and other advanced engineering applications. In this study, the effects of both cooling rate and bismuth modification on the microstructure and tensile properties of hypereutectic Mg–5wt% Si alloy were investigated. It was found that the addition of 0.5% Bi, altered the morphology of primary Mg_2Si particles from bulky to polygonal shape and reduced their mean size from more than 70 μm to about 30 μm. Also, the tensile strength and elongation of the modified alloy increased about 10% and 20%, respectively, which should be ascribed to the modification of Mg_2Si morphology and more uniform distribution of the primary particles. Moreover, an increase in tensile strength value with increase in cooling rate were observed which is attributed to finer microstructure of alloy in higher cooling rates. It was observed that Bi addition is significantly more effective in refining the morphology of primary Mg_2Si particles than applying faster cooling rates.

Introduction

In recent years, the growing demand for more fuel-efficient vehicles to reduce energy consumption and air pollution is a challenge for the automotive industry. Aluminum and magnesium based composites, reinforced with particulates of Mg_2Si have been recently introduced as a new group of particulate metal matrix composites that offer attractive advantages such as low density, good wear resistance and good castability [1-5]. Hypereutectic Mg–Si alloys can be considered as in-situ Mg matrix composites containing hard particles of Mg_2Si [1, 3, 4], since a maximum solid solubility of Si into Mg is only about 0.003 at.%, thus Si atoms react with Mg atoms and are precipitated as an intermetallic compound of Mg_2Si. Despite the fact that Mg_2Si intermetallic particles exhibit a high melting temperature, low density, high hardness, low thermal-expansion coefficient and equilibrium interface [4, 5], their undesirable morphology (size, shape and distribution) in the Mg matrix, during conventional casting, has led to the low ductility and strength observed in these alloys and has limited these alloys for use in high performance applications.

Various efforts have been made to modify the microstructure and improve the mechanical properties of the Mg–Si alloys. Other than expensive methods of rapid solidification and mechanical alloying [2, 5, 6]; high cooling rates and impurity modifications are well known techniques, which have been used so far for modifying the undesirable morphology of Mg_2Si in Al–Mg–Si and Mg–Si alloys. Many of these studies have been focused on the modification of Al–Mg–Si alloys [7, 8], while less works has been done on the modification of Mg_2Si morphology in Mg–Si alloys.
So far, several modifying agents such as Ca, P, Sb and Sr, have been used to modify the coarse primary Mg_2Si in Al–Mg_2Si composites [7, 8]. It is noticeable that both P and Sb are in the VA group of the periodic table of the elements. The element Bi belongs to the VA group of the periodic table like P and Sb. Therefore, on the basis of similar physical and chemical properties between elements in the same group of the periodic table, Bi seems to be effective for morphology modification of Mg_2Si phase in Mg–Si alloys.

The objective of the present study is to improve the mechanical properties of a hypereutectic Mg–Si alloy through the modification of morphology of primary Mg_2Si particles by applying high cooling rates and Bi addition.

Experimental

Industrially pure magnesium ingot, with the composition is shown in Table I, and Si powder (99.4wt% purity) were used as starting materials to prepare Mg–5wt.% Si alloy, which corresponds to a composition of Mg–15wt% Mg_2Si in-situ composite. To study the effects of cooling rate on tensile properties, a special casting assembly shown in Figure 1 was used. It was designed in such way that the heat extracted only through the water-cooled system at the bottom, promoting vertical upward directional solidification. A steel mould was used having an internal diameter of 60 mm, height of 150 mm and wall thickness 2 mm. The lower part of the mould was closed with a water-cooling jacket made of stainless steel, with a wall thickness of 1 mm. An electric heater was used to preheat the peripheral side of the mould to about 700 °C, which was suitable for preventing lateral heat transfer and guaranteeing directional solidification from the bottom to the top of the mould.

Table I. Chemical Composition of Magnesium Ingot Used in the Present Work.

Elements	Content (wt.%)
Mn	0.144
Al	0.127
Zn	0.126
Si	0.045
Cu	0.005
Mg	Balance

The charge was melted in an electric resistance furnace using a steel crucible under argon protective atmosphere. After stirring, the melt was degassed using pure dry argon, injected into the melt by means of a steel pipe. Then, the molten alloy with temperature of about 800 °C was poured into the mould whose bottom plate was cooled down with the cooling jacket, and directionally solidified.

In order to evaluate the effects of Bi-modification on tensile properties, the alloy containing 0.5wt.% Bi was prepared. Pure elemental Bi was wrapped in aluminum foil and added to molten

Mg–5wt.% Si alloy. When the temperature reached about 800 °C, alloys with different compositions were poured into cylindrical moulds (60 mm in diameter and 80 mm in height) to prepare castings for metallographic studies and tensile testing.

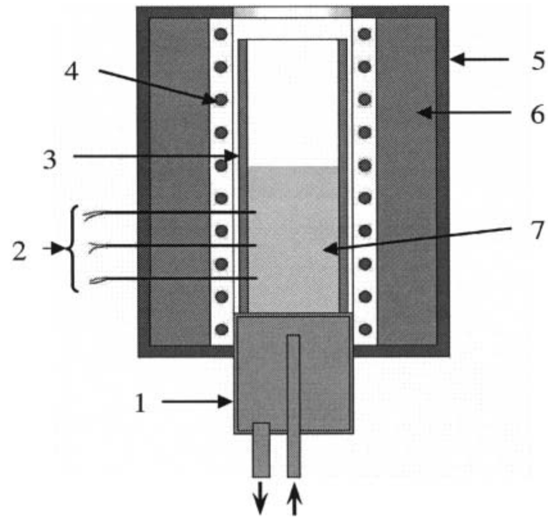

Figure 1. Schematic representation of the directional solidification apparatus: 1) cooling jacket, 2) thermocouples, 3) steel mould, 4) electric heater, 5) furnace cover, 6) heat insulator and 7) casting.

To evaluate the effect of cooling rate on tensile properties, tensile test bars were cut from the solidified ingots at different distances from the bottom of mould. Tensile test bars machined, according to ASTM-B577 standard for each condition. Tensile tests were carried out at room temperature with a constant cross-head speed of 1 mm/min. Specimens for microstructural characterization were sectioned from the same position as tensile test bars. Metallographic specimens were polished and etched with a solution of 5vol.% nitric acid + ethyl alcohol for 10-12 s at room temperature. Quantitative data on microstructure were determined using an optical microscope equipped with an image analysis system (Clemex Vision Pro. Ver.3.5.025). Also, scanning electron microscopy (SEM, Phillips XL30) and X-ray diffractometer (XRD, Philips Xpert) were used to investigate the microstructure characteristics of the specimens and phase analyses.

Results and Discussion

According to the Mg–Si binary phase diagram [9], the Mg–5wt.% Si alloy is a typical hypereutectic alloy and, therefore, the as-cast microstructure should be consisted of primary Mg_2Si and eutectic Mg_2Si + α-Mg phases. Figures 2a and b show a typical as-cast microstructure and XRD pattern of the alloy, respectively. XRD result reveals that the obtained alloy components are only Mg_2Si and Mg phases as expected. It should be mentioned that the bulky crystals are primary Mg_2Si, while the Chinese script type particles [4, 10] are eutectic Mg_2Si, as shown in Figure 2a. However, an interesting microstructural feature observed in Figure 2a is that all the primary Mg_2Si particles are surrounded by a layer of α-Mg halos, around which the fine eutectic structures of Mg_2Si + Mg are formed. The existence of α-Mg halos is related to non-equilibrium solidification of the alloy, which leads to the limited diffusion rate of Si in the liquid around the primary Mg_2Si particles and allows the formation of the Mg-rich phase. These non-equilibrium conditions, as described by Kurz and Fisher [11], could lead to a skewed coupled zone in the binary eutectic diagrams especially when one of the phases shows anisotropic growth characteristics such as Mg_2Si. As the temperature decreased to eutectic temperature, the fine eutectic structures of Mg_2Si + Mg were then formed around the α-Mg halos. This result is similar to some of the experimental findings in other hyper-eutectic systems, such as Al–Si [12] and Al–Mg–Si [13] alloys.

Effect of cooling rate

Figures 3a–e show the microstructures observed in the different sections of unmodified alloy. Quantitative image analysis was used to examine the microstructural changes in the alloy in different sections. The measured particle size and volume fraction of the primary Mg_2Si phase is plotted as a function of distance from bottom of mould in Figure 4a. As it is clear in Figures 3 and 4a, a noticeable decrease is seen in primary Mg_2Si particle size in lower section corresponding to faster cooling rates although there is no obvious change in the volume fraction of the primary Mg_2Si phase in different sections. Therefore, the number of primary Mg_2Si particles per unit area, increased with increasing cooling rate. Also, the eutectic structure in different sections remains mainly fibrous while it becomes finer with increasing cooling rate. The observations follow the general rule that faster cooling corresponding to lower sections results in higher undercoolings, which subsequently leads to faster nucleation and growth thus creating a finer microstructure.

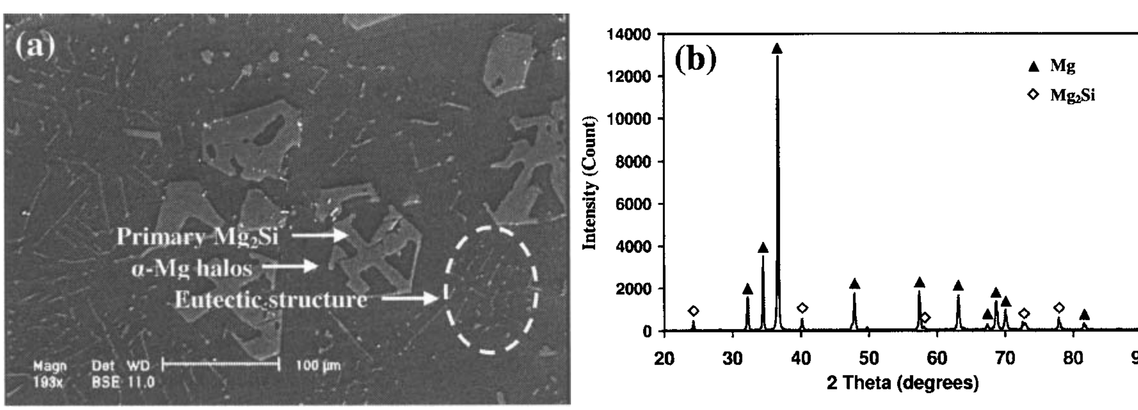

Figure 2. (a) Typical SEM micrograph and (b) XRD pattern of as-cast Mg–5wt.% Si alloy.

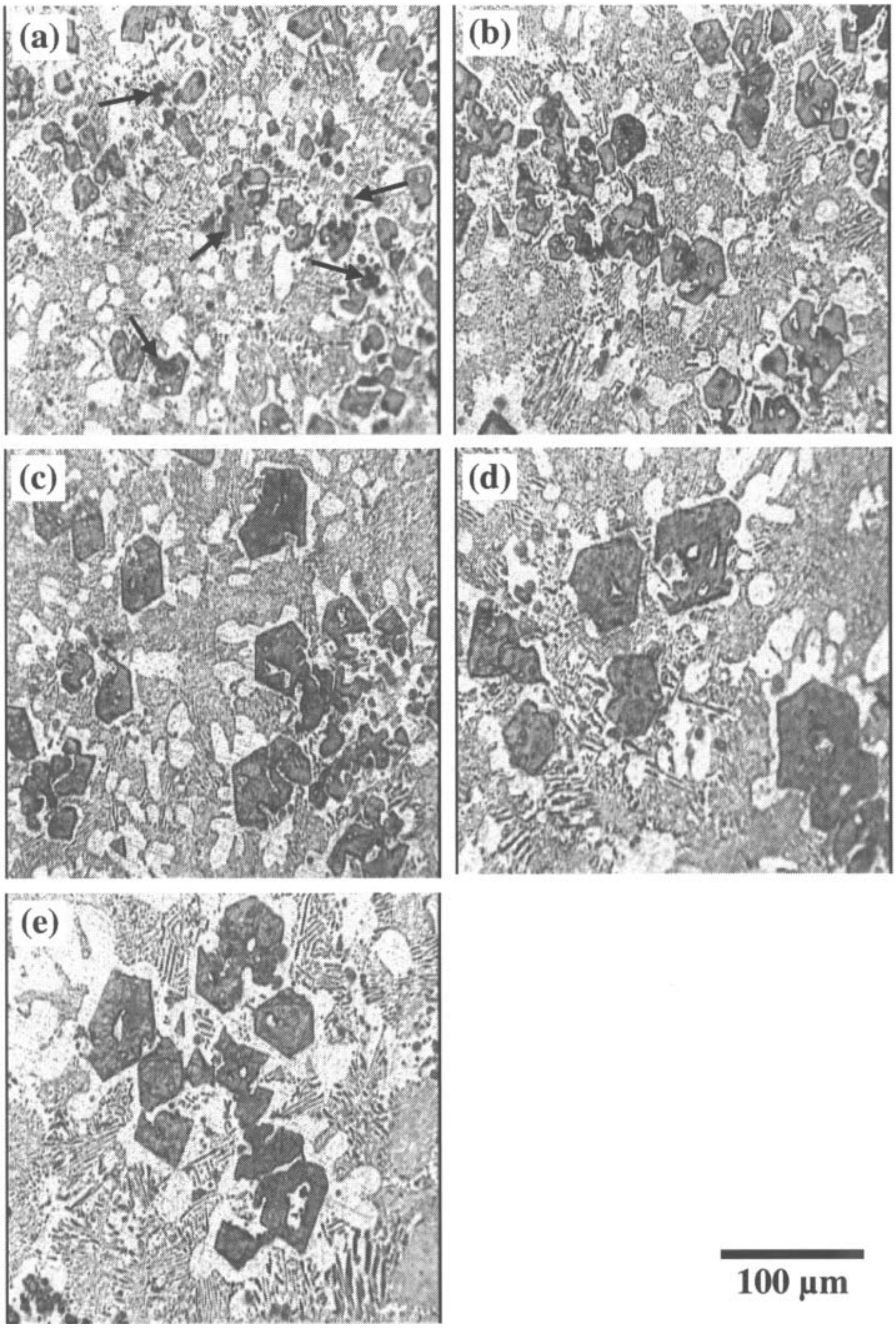

Figure 3. Effect of cooling rate on microstructure of Mg–5wt.% Si alloy without Bi modification. (a) 5 mm, (b) 15 mm, (c) 30 mm, (d) 50 mm and (e) 75 mm sections from bottom of mould. Arrows indicate the gas porosities.

Despite degassing treatment, the alloy still contains gas porosity, which is clearly seen in Figure 3a. Since Mg–5wt.% Si alloy enjoys a wide range of solidification, dispersed shrinkage porosity is more likely. In samples with major casting defects, fracture is initiated at the defects, and cracks tend to propagate from these defects, even bypassing Mg_2Si primary particles.

The ultimate tensile strength (UTS) values of the specimens are plotted against the distance from bottom of mould in Figure 4b. It is evident from the diagram that in general there is an increasing trend in the strength of the composite in lower sections corresponding to higher cooling rates. Thereby, this confirms expectations based on metallographic results. However, some scattered results are observed within 5mm section. The 5mm section result is an exception to the observed trend of improved UTS with increasing cooling rate. It seems reasonable to attribute the unexpected low tensile strength value for the 5mm section to presence of casting defects, which are exaggerated in this section (Figure 3a). The presence of casting defects implies that in addition to microstructural modification by applying high cooling rates, casting process improvement is also necessary to obtain higher tensile properties for this alloy. Also, bulky morphology of primary Mg_2Si particles and their clustering behavior, however, can result in stress concentration at sharp edges and corners of Mg_2Si and lead to anisotropic tensile properties. Therefore, in order to improve the tensile properties, a more isotropic microstructure is preferred.

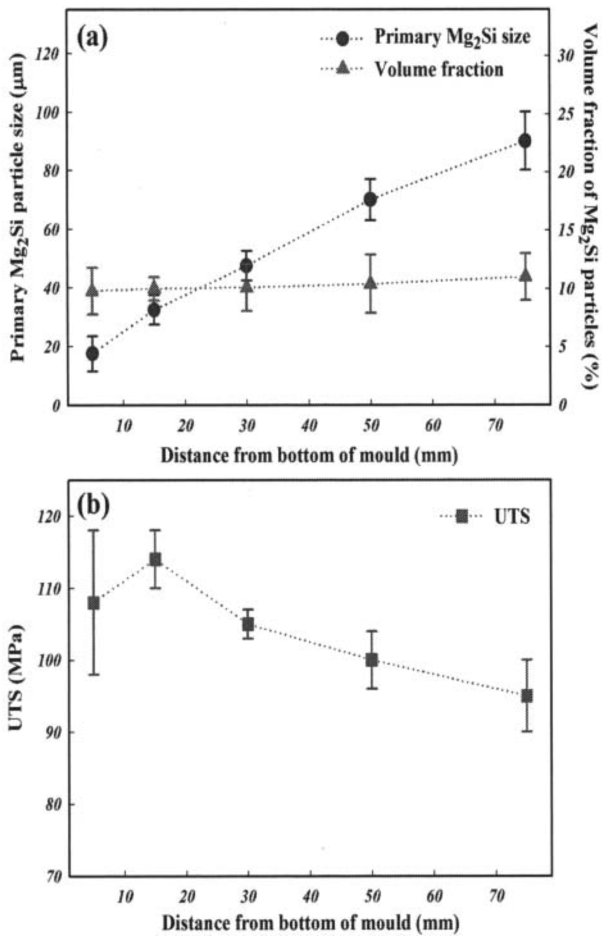

Figure 4. (a) Size and volume fraction of primary Mg_2Si particles and (b) UTS value vs. distance from bottom of the mould.

Effect of Bi addition

In Figures 5a and b, the general microstructures of unmodified and Bi-modified alloys are compared. As compared to the base alloy shown in Figure 5a, considerable microstructural refinement is obtained by the addition of Bi (Figure 5b). According to quantitative image analysis results, the mean size of primary Mg_2Si particles was about 70 µm in unmodified alloy. Modification by Bi reduced their size to about 30 µm, formed an even distribution of particles in the matrix and decreased reinforcement clustering (Figure 5b). Other than refinement of size and distribution, the morphology of the bulky primary Mg_2Si particles changed to a polygonal character after Bi addition. Comparing Figures 3 and 5b, it can be inferred that Bi addition is significantly more effective in refining the morphology of primary particles than the faster cooling rates applied in this study. Furthermore, it is interesting to note that addition of Bi has a considerable influence on eutectic structure and the eutectic Mg_2Si fibers exhibit modified morphology as a finer size (Figure 6). Also, some white point-like phases are observed in the eutectic microstructure of Bi-modified alloy (Figure 6b). The EDS analysis confirmed that the white point-like compound in modified alloy is a Bi-containing compound. According to Mg–Bi binary phase diagram [9], it may be presumed that the compound is Mg_3Bi_2.

Microstructural refinement could be attributed to a change in diagram due to high constitutional undercooling. There is also a hypothesis that a change in surface energy of Mg_2Si crystals caused by Bi atoms on its surface or entering its lattice may also be responsible for the change in growth morphology. Tani and Kido [14] reported that there is a high solubility limit of Bi in Mg_2Si and Bi atoms are primarily located at the Si sites in Mg_2Si lattice. Therefore, during solidification of the melt with Bi addition, some of Bi atoms should dissolve in the Mg_2Si lattice and thus change the surface energy of the Mg_2Si crystals by lattice distortion due to the larger atomic radius of Bi compare with Si (about 30%). This may poison the growth manner of primary Mg_2Si in preferred directions and significantly influence and suppress the growth of the undesirable morphology of primary Mg_2Si. Further observations of Figure 5b depict the volume fraction of α-Mg halos increased with addition of Bi but the eutectic structure area was appreciably reduced. The refining mechanism of eutectic Mg_2Si phase needs further study. But, one possible explanation is that the precipitation of Bi-containing compound around the surface of eutectic Mg_2Si rods results in restriction of growth in radial direction, leading to their finer size as shown in Figure 6b.

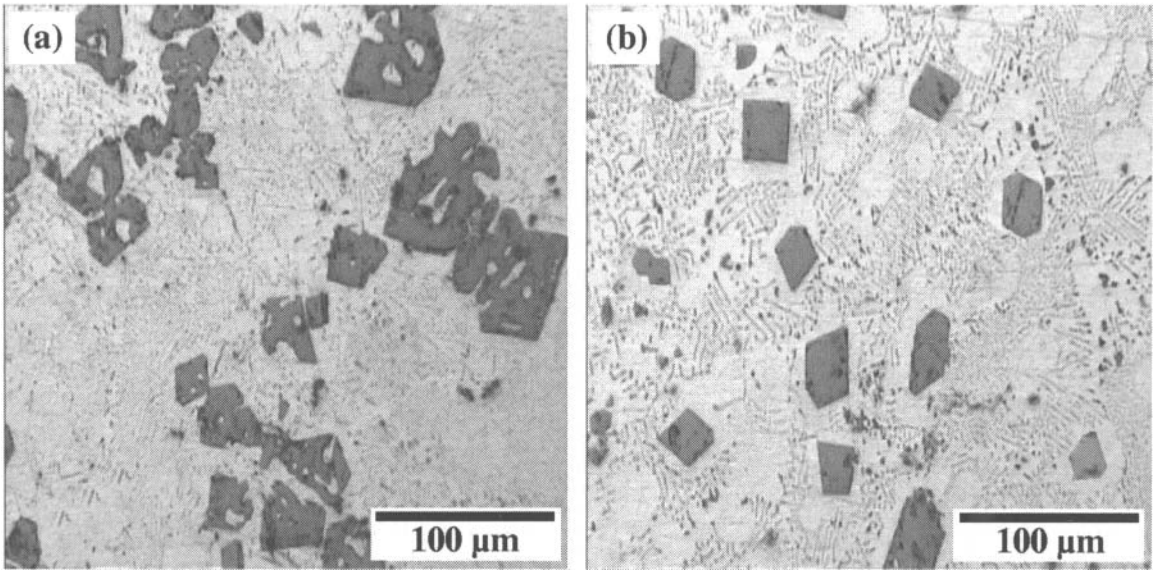

Figure 5. (a) Typical optical microstructure of as-cast Mg-5wt.% Si alloy and (b) the microstructure after modification with 0.5% Bi.

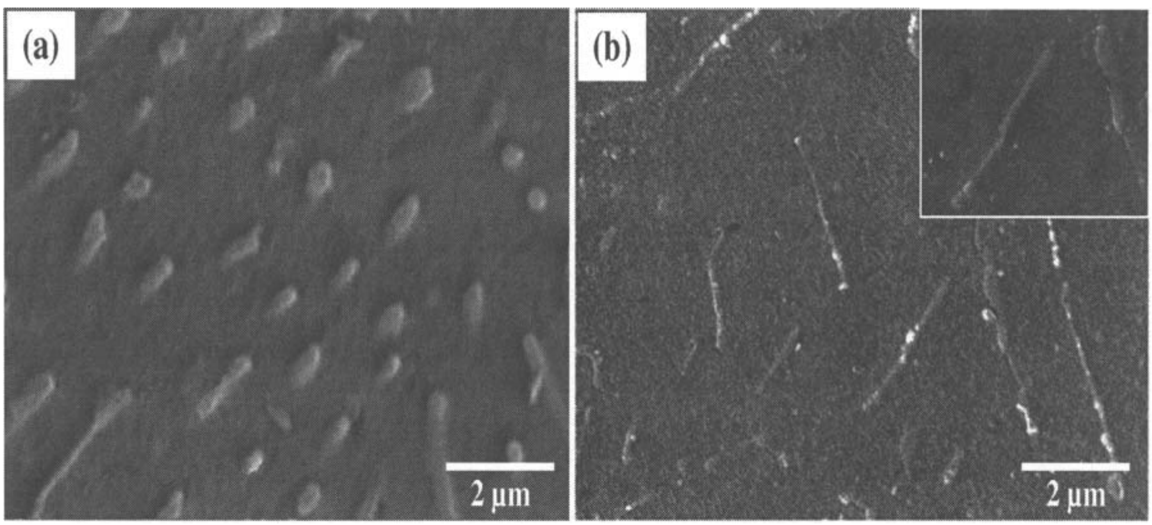

Figure 6. Typical SEM micrographs of eutectic Mg_2Si in the (a) unmodified and (b) Bi-modified alloys.

As mentioned above, the coarse Mg_2Si primary crystals in an unmodified alloy grow bulky, but the finer Mg_2Si particles in Bi-modified alloy do not show such morphology, which is considered an advantage since holes inside the particles could be potential sites for crack initiation. Therefore, Bi modification raises the tensile strength of the unmodified alloy about 10% (Figure 7). Some researchers emphasized the importance of homogeneous particle distributions to improve the ductility [15, 16, 17]. Adding Bi has clearly homogenized the structure, reducing the clustering behavior of primary Mg_2Si particles (Figure 5b) which would be expected to aid crack propagation. Large primary particles and their clusters seem to be the favored crack propagation path in unmodified alloy. Therefore, Bi addition increase the elongation of unmodified alloy about 20% as is observed in Figure 7.

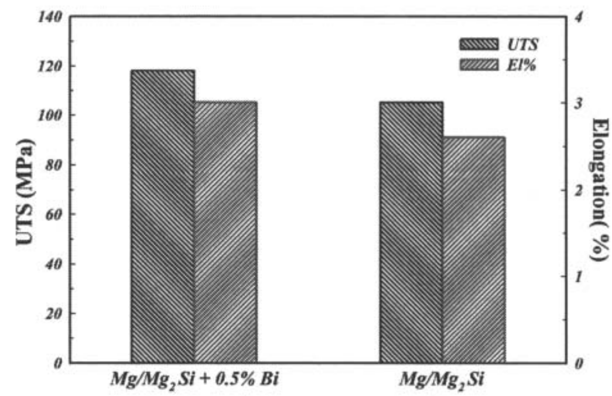

Figure 7. Comparison between tensile properties of unmodified and Bi-modified Mg–5wt% Si alloys.

Conclusions

The following conclusions may be drawn from the experiments conducted to study the influence of cooling rate and addition of Bi on the microstructure and tensile properties of Mg–5wt.% Si alloy.

1- The observed as-cast microstructure of Mg–5wt.% Si alloy consists of coarse primary Mg_2Si particles are surrounded by a layer of α-Mg halos, which is again surrounded by the eutectic Mg_2Si + Mg structures.

2- UTS values increased with increasing cooling rate. However, in the lowest cast section the UTS value showed an unexpected fall together with significant scatter in data attributed to casting defects.

3- Adding Bi refined the primary Mg_2Si morphology, reducing their mean size from more than 70 μm to about 30 μm. Furthermore, the bulky primary Mg_2Si particles exhibit modified morphology as a polygonal shape in Bi-modified alloy. In addition, the eutectic Mg_2Si also exhibits modified morphology as a fine fiber. Adding Bi also raised the UTS and elongation values of unmodified alloy about 10% and 20%, respectively.

4- Bi addition is significantly more effective in refining the morphology of primary Mg_2Si particles than the faster cooling rates applied in this study.

Acknowledgements

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