The effect of Zinc on the morphology and wear resistance of Mg2Si-reinforced magnesium matrix composites

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Abstract: Using a simple cast route, Mg composite reinforced by in situ fabricated Mg2Si particles was prepared. The modification effect of zinc element on microstructure and wear resistance of composite samples was investigated. The results revealed that by addition of 1wt. % Zn the average size of the primary Mg2Si became significantly decreased and their morphologies changed to polyhedral shapes. By increasing the amount of modifier over modification occurred and many primary Mg2Si particles became coarse again. The wear sliding test disclosed that modified morphology enhanced wear property of the composite at the load of 10 N and distances greater than 0.5 km.

1- Introduction
In recent years, researches and developments of aluminum and magnesium alloys have been greatly promoted by the lightweight requirement in the automotive and aerospace industries [1, 2]. The use of magnesium alloys, however, has been restricted by their poor mechanical properties such as Young’s modulus, tensile strength, hardness and heat resistance [3]. In particular, when applying them to friction materials, the wear easily occurs by contacting with the counter. Some information concerning to the wear behavior of Mg-based MMCs reveals that tribological properties of Mg alloys can be improved by the addition of hard ceramic fiber or particulate reinforcements [4]. Currently, the Mg–Si alloys containing in situ Mg2Si particles with high hardness of 350–700 Hv have a great potential as structural materials [3, 5, 6]. Unfortunately, though this composite offers attractive properties and advantages, Mg2Si compounds which are produced via a simple conventional casting route are prone to forming undesirable coarse Chinese script morphologies, which would deteriorate the properties of the material [7-8].

Many studies mentioned that refinement of microstructure is responsible for the improvement of the mechanical and wear resistance in materials [9]. The morphologies of primary Mg2Si were improved through several different methods such as incorporating modifying agents (e.g. Lanthanum, Yttrium, Strontium, K2TiF6, KBF4 and KBF4 + K2TiF6, Sb, Ca, P), hot extrusion, rapid solidification and mechanical alloying. Among these techniques, modifying treatment during common gravity casting is a more practical method, because it is commercially available at low production cost and can be accepted by the engineering community for general applications [3, 7, 8]. In view of the above, an attempt has been made to refine microstructure of the in suit composite of Mg-5Si by adding different amounts of Zinc as the chemical modifier and the dry sliding wear behavior of Mg2Si particle-reinforced MMC was evaluated.
2- Experimental procedure

2.1- Samples preparation

Commercially pure magnesium (99.6 Wt% purity), pure silicon (99.4 Wt.% purity) and different amounts of 0.75, 1, 1.2, and 1.5 (mass fraction) pure zinc powder (99.8Wt.% purity) were used as starting materials to melt Mg-5Wt.%Si alloy. The charge was melted inside a low carbon steel (st 37) crucible by an eclectic resistance furnace under protective argon gas atmosphere. In spite of this precaution, it was found necessary to add 10% additional Mg to the melt to ensure that the target composition was reached. As soon as the charge was melted, an argon gas was steam blown to create turbulence in molten metal causing faster dissolution of silicon powder in the magnesium melt while providing a protective atmosphere against the air. Consequently, the prepared melt was poured into a cylindrical steel mold preheated at 200°C. Mg/Mg2Si composite was prepared according to a same process. Specimens were cut from a standard location on the ingots at 110 mm from the bottom of the castings. The samples were ground and polished through standard routines and etched with 5 ml HNO3 + 45 ml water for 10 seconds at room temperature. Microstructural analyses were carried out using optical microscopy (OM) and the phase of the samples were analyzed by X-ray diffraction.

2.2. Wear behavior

Pin-on-disk wear test equipment was used to evaluate the tribological properties of the samples. The wear tests were conducted at low sliding speed of 0.1 m/s for 300, 500, 800 and 1000 m at two loads of 3 and 10 N. Electronic weighting balance (accuracy of 0.1 mg) was used to measure the weight loss due to sliding distance. Wear rate was calculated using weight loss per unit sliding distance (gr/m).

3- Results and discussion

3.1. Microstructure study

Considering the results of the XRD analyses presented in Fig.1, the microstructural constituents were identified as Mg, Mg2Si and eutectic phase. Microstructures of the unmodified and modified composite are shown in Fig. 1. As shown, Mg2Si appeared in different morphologies (mainly Chinese scripts, a few polyhedral shape and eutectic phases) as reported in the literature [3, 5]. No Zn or Mg-Zn compounds were found in XRD result due to its low intensity. According to Mg-Si binary phase diagram, Si has a limited solid solubility in to magnesium matrix so the Mg2Si particles were formed in melt during the solidification process. Solidification condition that leads to the change of the resultant micro structure from the equilibrium condition is studied in many researches before [3, 5, 7, 8, 11 and 12]. As it is evident from Fig.1 when 0.75 Zn was added into the melt no significant change in size of Mg2Si was observed but its morphology began to change and the arms of the dendrites separated from each other. At 1% Zn the size of the dendrites decreased from about 150 µm to 20 µm while their morphology changed to polyhedral shape. However when the zinc content exceeds 1%, it is found that coarse Mg2Si dendrites were formed again and over modification occurred. When the Zn content further increased to 1.5% a similar modification effect to the alloy with 1.2% Zn occurred. As discussed in many concerned researches before, there are two major mechanisms for modification and refinement of Mg2Si grains. The first mechanism concerns about increase of nucleation by formation of large amounts of nuclei in the melt that leads to decrease of Mg2Si grain size. Based on the second mechanism modification is responsible for inhibition of grain growth through changing the solidification condition. Therefore modification occurs due to poisoning effect of the modifier element by adsorption at the Mg2Si growing surface front [13, 14, 15, and 16].
The solubility of Zinc at 635 °C, in Mg is about 6.2%. As a result, it rules out the possibility of the Zn-containing compounds acting as heterogeneous nucleation sites for the primary Mg2Si crystals. It was relieved that segregation of Zn element at the liquid–solid interface during solidification and adsorb of their atoms in the crystal plane would change the surface energy of the Mg2Si crystals by lattice distortion due to larger size of Zn atom in comparison with Mg and Si atoms. By decreasing the temperature, the Mg–Zn compounds should be precipitated out of solution due to the segregation of Zn atoms at the liquid–solid interface, which results in decreasing Zinc content in the melts and the poisoning effect is weakened.

Fig. 1. Typical optical microstructures of Mg–5Si alloys with different contents of (a) 0, (b) 0.75, (c) 1, (d) 1.2 and (e) 1.5% Zn, respectively.

Fig. 1. XRD pattern of Mg–5Si alloys with (a): 0, (b): 0.75, (c): 1, (d) 1.2 and (e):1.5 % Zinc.
3.2. Wear behavior

Based on wear rate computed for the unmodified and modified samples, Fig. 3, (a, b) shows the effect of different distances on the wear rate at constant slide rate of 0.1 for 3 and 10 N loads. The results showed that for a constant sliding speed the wear rate increased by load as expected. The modification effect of Zinc was not clear at low load of 3 N and distances below 300m, but by increasing the load to 10 N modified composite showed lower wear rates. It could be a result of this fact that under low loads both unmodified and modified composites were capable to sustain applied loads without fracturing.

The scanning microscopy micrographs of typical worn surfaces of unmodified and modified composites at load of 10 N are presented in Fig. 4, which shows the wear track morphology of the specimens tested. Under the lower distances SEM micrographs showed dark surfaces that were covered by a thin layer of fine particles and grooves parallel to the sliding direction. Chemical analyses of surface sample in Fig. 5 shows the oxygen peak along with Mg and Si peaks which indicates that oxidation occurs in the first steps of wearing. By increasing the distance transition occurred from mild to severe wear and both modified and unmodified composites showed a mixed abrasion-plastic deformation mechanism. It is in a good agreement with the other researches that says at low loads the wear mechanism of Mg alloys is mainly abrasive wear and oxidation [17] and above a critical point the rate of removal the oxide film through sliding become greater that its rate of formation, and a transition to metallic wear occurred that caused plastic deformation and delaminating in the bulk material and increased the wear rate [18]. However in this condition the modified reinforcement did not provide a significant beneficial effect in improving the wear resistance because of the low ductility of the composite specimens. In addition to delamination, wear debris also cause abrasion of the matrix.
4- Conclusions

1. Mg/Mg$_2$Si composite was prepared by casting directly from the melt. The observed microstructure consisted of mainly coarse primary Mg$_2$Si particles in eutectic magnesium matrix.

2. Adding 1 Wt.% Zn refined the primary Mg$_2$Si, reducing the average size of it from 150 µm to ~20 µm.

3. Modification of Zinc increased the wear properties of Mg-5Si at 10 N load and distances more than 500 m to some extent but it did not have any significant influence on wear properties of composite under very low loads and distances.

Fig.5. EDS Spectrum showing evidence of the presence of magnesium oxide on worn surface of modified composite at sliding distance of 300m and load of 10 N.
References


