Microstructure and Interface Characterization of CP-Mg and AZ91 Composite Alloys

M.T. Abou El-Khair[1]*, F.M. Fairouz[1], A.M. El-Sheikh[2] and A.N. Abdel Azim[3]

[1]Composite Materials Laboratory, Central Metallurgical Research and Development Institute, Cairo, Egypt

[2]Mining, Petroleum and Metallurgical Engineering Dep., Cairo University, Cairo, Egypt

[3]Non-Ferrous Laboratory, Central Metallurgical Research and Development Institute, Cairo, Egypt

Abstract

Commercial pure magnesium and magnesium-9 aluminum-1 zinc (CP-Mg and AZ91) and their composites were prepared by using flux cover. Magnesium composite alloys containing Al_2O_3 or SiC particulates of different volume fractions (7-15% V_f) were successfully produced using stir-casting technique. The fabrication processes and controlling parameters of Mg composites produced by this technique were investigated. AZ91 and its composite alloys were solution treated at 420°C for 20 hrs and aged at 170°C for 30 hrs. Addition of 2 wt.% mish metal (MM) was also studied in this work. Addition of either reinforcements or MM to these alloys resulted to a considerable grain refinement of the matrix alloys and the degree of refinement increases as the volume fractions of reinforcement increased. The microstructure was investigated by optical microscope. The interface reaction was analyzed using EDS and X-ray diffraction. The results of the X-ray diffraction reveal the presence of MgO and Mg_2Si in the CP-Mg besides $Mg_{17}Al_{12}$ in the AZ91 alloy.

Introduction

Metal matrix composite (MMC) systems are currently under various stages of development. Composites based on aluminum and magnesium matrices reinforced with ceramic particles are of great interest to the automotive and aerospace industries. In the last two decades much of the research has enveloped around cast aluminum based MMCs. In contrast, research efforts on the processing and properties of magnesium based MMCs have been rather limited [1]. The particulate reinforced Mg composites have attracted considerable attention as a result of their relatively low cost and isotropic properties. In general, MMCs based on magnesium and its alloys reinforced with ceramic particulates have been produced by stir casting [2], powder metallurgy [3] squeeze casting, and spray forming [4].

Among the processes investigated, stir casting process has shown to effective processing scheme with acceptable economics. Improvement factors of considered for manufacturing these composites are bonding, distribution of reinforcement, wettability and metal reinforcement interface characteristics. Various methods have been suggested for improving wetting and controlling reactions between the melt and reinforcements.

The present work was undertaken to synthesize two Mg-alloys: CP-Mg and AZ91 and their composites reinforced with Al_2O_3 and SiC particulates of size (45-180, 65-120 μm respectively) and different volume fractions using conventional casting technique. Effect of addition of mish metal (MM) on either CP-Mg or AZ91 composite alloys was also studied. Microstructural characterization studies were conducted using optical microscope. The interface characteristics were studied by XRD and EDS.

Experimental Procedures

Materials

Commercial pure magnesium (CP-Mg) with purity of 99.9% Mg and magnesium aluminum zinc (AZ91) alloy were used in this investigation. The

*corresponding author. E-mail: malak310@yahoo.com

chemical composition of AZ91 alloy is: 10.08% Al, 0.604% Zn, 0.0611 others, and the rest is Mg. Mish metal (MM) was also added by 2 wt.% to the matrix and composite alloys. The standard chemical composition of the used MM is 50% Ce, 30% La, 15% Nd, and 5% Pr.

Alumina (Al_2O_3) particulates in the size range of 45-180 μm and also silicon carbide (SiC) particulates in the range of 65-120 μm were used as reinforcements. The particulates were activated before adding to the melt by preheating them to a temperature of 200°C before adding them to the melt.

Composite Preparation

Sufficient amount of (500 mg) of the matrix alloy (CP-Mg or AZ91) was placed in the crucible and heated to 100°C above its liquidus temperature. To overcome the problem of oxidation and burning of molten Mg and AZ91 alloys, a flux cover was used during melting. After fluxing, and degassing with argon gas, the surface of the melt was cleaned by skimming. A vortex was created in the melt by using a steel impeller stirrer connected to a variable speed motor. The speed of the stirrer was gradually increased to 700 rpm and the preheated ceramic particulates were gradually added to the vortex. When all the particulates had been added, stirring was continued for 5 minutes more and then the composite immediately poured into preheated cast iron mould (200°C) at pouring temperature of (700°C) for the CP-Mg composites and (670°C) for the AZ91 composites alloys.

Testing and Examination

Heat treatment was carried out for AZ91 and its composites. The heat treatment cycle consists of two stages. The first one is solution treatment (at 410°C for 20 hrs, and then air cooling) and the second is aging (at 170°C and still at this temperature for 30 hrs to reach maximum hardness).

Specimens from the middle of the casting for both CP-Mg and AZ91 alloy were cut and prepared for metallographic investigations. The prepared specimens were etched with 3% HNO_3 (*conc.*), 95% ethyl alcohol. All the specimens were investigated by optical microscope. Some specimens were examined by X-ray diffraction technique, and Philips apparatus carried out this examination. Also, some specimens were analysis by EDS using a Jeol 5410 scanning electron microscope.

Results and Discussion

Microstructure

Commercial Pure Magnesium (CP-Mg)

The microstructure of the as cast commercial pure magnesium CP-Mg is shown in Fig. 1a it consists mainly of α-Mg solid solution. The addition of mish metal (MM) to CP-Mg is shown in Fig. 2a. It had a dendritic cast structure, the coarse intergranular phase, shown in Fig. 2a expected as $Mg_{12}MM$. The dendrites were fairly inhomogeneous and some coarse precipitation occurred within them after solidification had taken place. Generally, when MM is added to the CP-Mg, grain refinement occurs. The main reason for such grain refinement is the formation of fine dispersoides such as Mg-Re [5].

CP- Mg Composites

The microstructure of cast CP-Mg/composite alloys show cellular dendritic structure, Fig. 1b,c. It is possible that the presence of reinforcement particles change the morphology of the growing interface from dendrites in CP-Mg into cellular dendrite interface in Mg-composites [6]. Increasing the amount of Al_2O_3 from 7% to 15 vol.% made the grain structure of the matrix finer, Fig. 1b,c. Distribution of Al_2O_3 particulates are not completely uniform in the as cast composites, and resulted in significant fraction of porosity in the bulk composite. The CP-Mg composite exhibited to same extent presence of Al_2O_3 particulate clusters. Also, the addition of MM to CP-Mg + Al_2O_3, CP-Mg + SiC composites results in additional grain refinement Fig. 2b,c.

Mg-Al-Zn (AZ91) Alloy

The microstructure of cast (AZ91) alloy is shown in Fig. 3a. It consists of α-Mg solid solutions and mainly intergranular particles of the β-$Mg_{17}Al_{12}$ phase. The eutectic is divorced and the β-$Mg_{17}Al_{12}$ forms as discrete particles each surrounded by a pool of α-Mg that is richer in Al than the primary α-Mg. Significant micro structural changes were found to take place during heat treatment. These changes of the microstructure were an extensive precipitation of β-$Mg_{17}Al_{12}$ occurred during this heat treatment, Fig. 3b. The structure of AZ91 alloy after adding MM is shown in Fig. 4a,b. Two types of intermetallic phase,
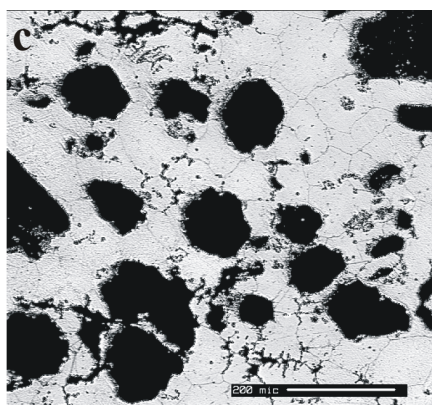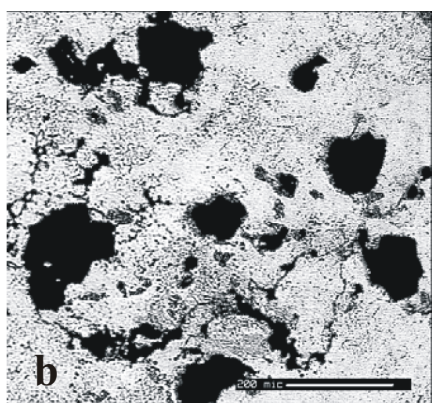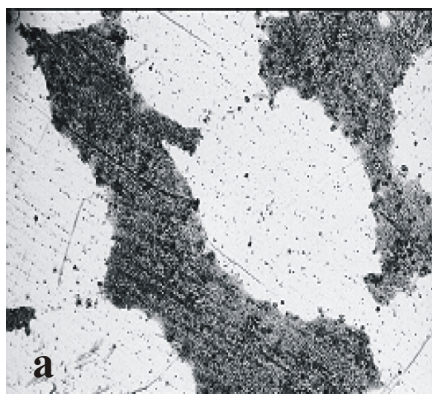
Fig. 1. Microstructure of cast CP-Mg and its composites: (a) CP-Mg, (b) CP-Mg + 7% V_f Al$_2$O$_3$, and (c) CP-Mg + 15% V_f Al$_2$O$_3$.
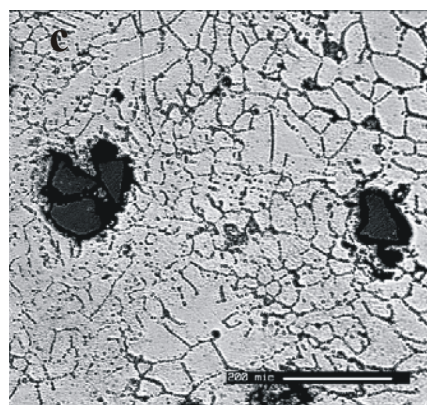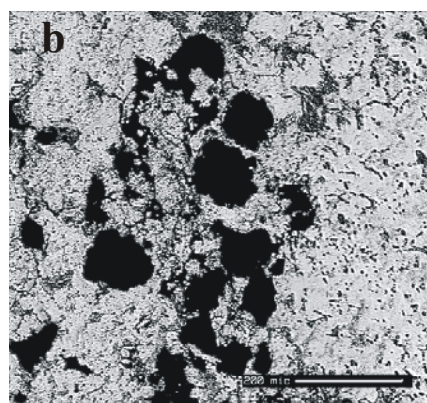

Fig. 2. Microstructure of cast CP-Mg and its composites + 2 wt.% MM, (a) CP-Mg, (b) CP-Mg + 10% V_f Al$_2$O$_3$, and (c) CP-Mg + 10% V_f SiC.

Mg$_{17}$Al$_{12}$ and Al$_4$MM, were found in the as cast alloys. Generally, when MM are added to the AZ91, the grain size is reduced in descending order and the microstructure of AZ91 + MM shows considerable grain refinement, Fig. 4a. The main reason for such grain refinement is the formation of fine dispersoids, which are formed during casting and hinder the grain growth, resulting in the overall improvement of the fine grain structure [5].
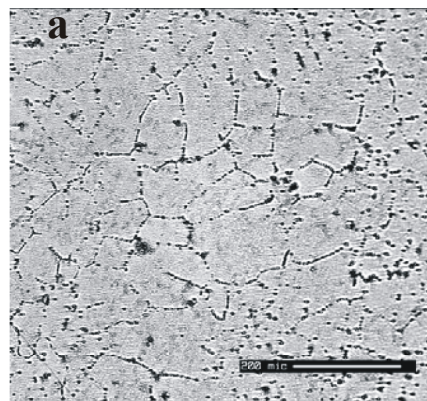
AZ91 Composites

Representative microstructure of AZ91 composites in the cast condition is shown in Fig. 3c,d. The AZ91 composites have finer grains than that of unreinforced alloy. However, for the composite reinforced with either SiC particulates or Al$_2$O$_3$ particulates, small matrix grains were presented especially near the reinforcement particulates, Fig. 3c,d. Fine grains
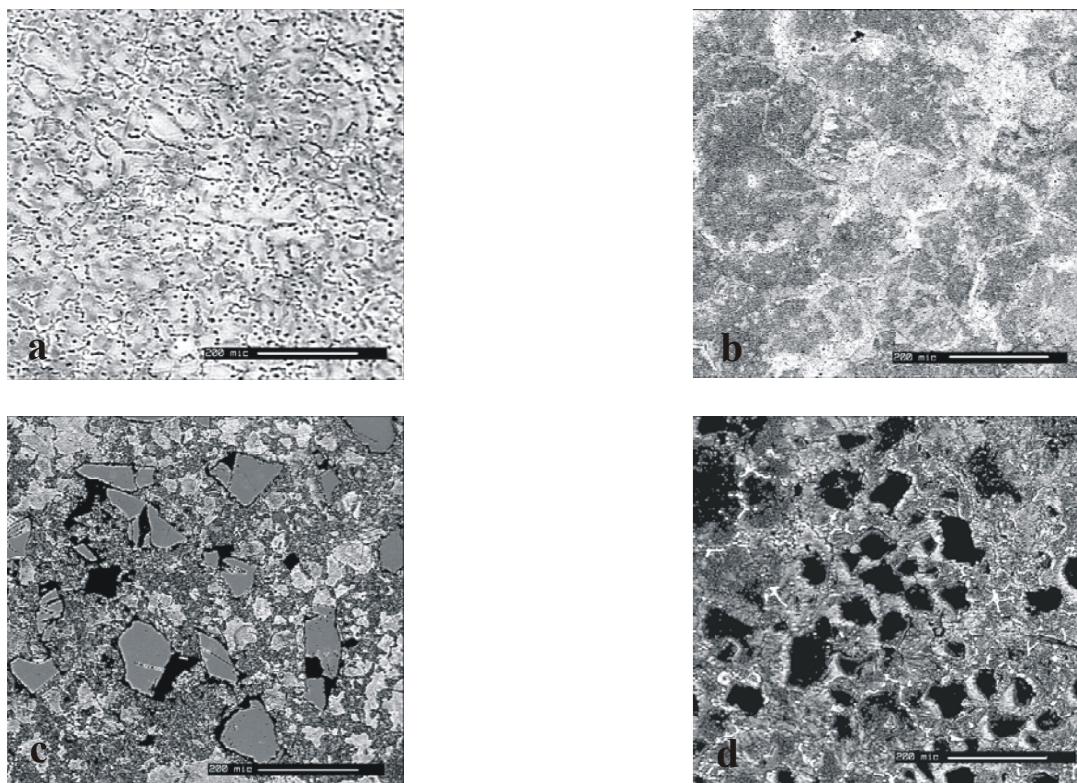
Fig. 3. Microstructure of cast AZ91 alloy and its composites, which reinforced by SiC and Al_2O_3: (a) AZ91 before heat treatment, (b) AZ91 after heat treatment, (c) AZ91 + 15% V_f SiC, and (d) AZ91 + 15% V_f Al_2O_3.
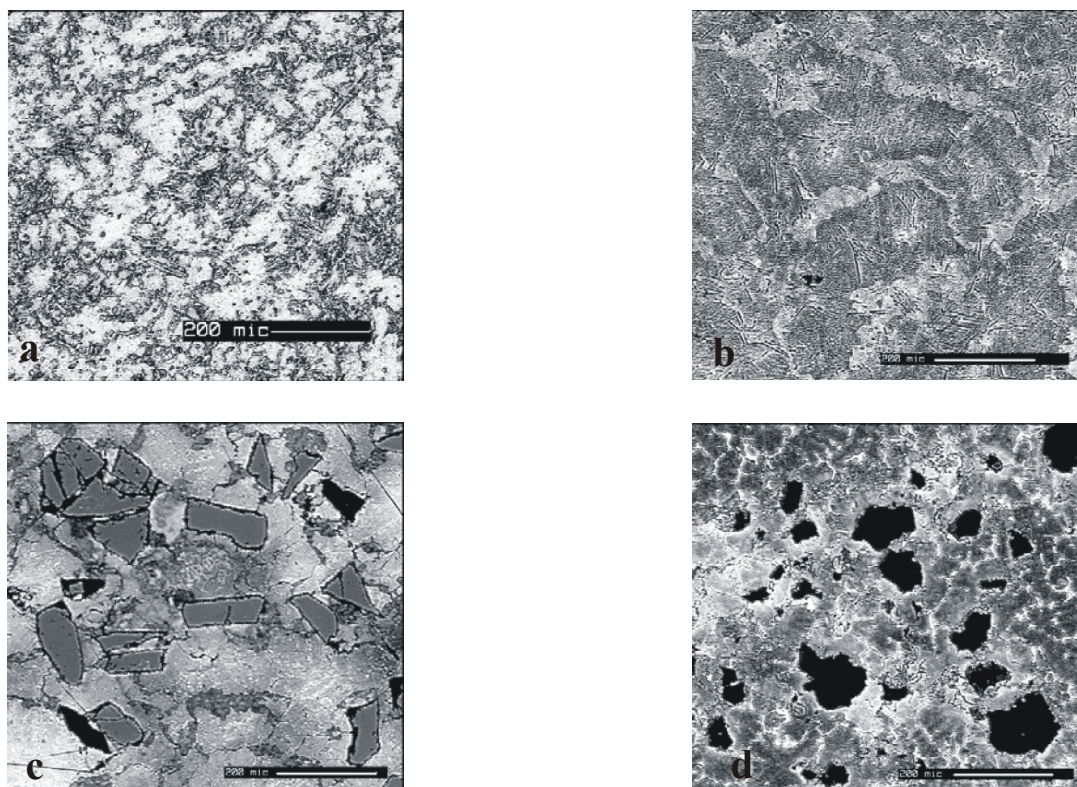

Fig. 4. Microstructure of AZ91 + 2 wt.% MM and its composites that reinforced by SiC and Al_2O_3: (a) AZ91 before heat treatment, (b) AZ91 after heat treatment, (c) AZ91 + 15% V_f SiC, (d) AZ91 + 15% V_f Al_2O_3.

of the AZ91 alloy composites result from the well-distributed of fine SiC or Al_2O_3 particulates, which inhibit grain coarsening. The degree of refinement was also more pronounced as the amount of ceramic particulates was increased. Also, some voids can be seen due to the removal of some particulates during metallographic preparation. At the same time, discontinuous precipitates with smaller amount are observed on the grain boundaries and continuous precipitates inside the grains, Fig. 3b. Addition of MM to AZ91 alloy and its composite is shown in Fig. 4c,d. The intermetallic phase of Al_4MM was observed clearly as gray needles in the AZ91 matrix alloy. Also, black shadow around the particulates was observed in case of Al_2O_3 particulates microstructure.

Interface Characteristics

The results of X-ray diffraction (XRD) of CP-Mg and its composites were shown in Fig. 5a,b. The particle/matrix interface indicates the presence of an interface product, which may be MgO, which are formed during fabrication of the composite by chemical reaction of molten Mg with oxygen and/or other oxides attached at the surface of SiC particulates [7,8].

No particle/matrix interfacial reaction products were detected in CP-Mg/SiC composite by EDS analysis, Fig. 6a,b, and nearly a clean and featureless surface of SiC particulates in the CP-Mg matrix, which is consistent with the thermodynamic prediction. All these indicate good wetting between magnesi-
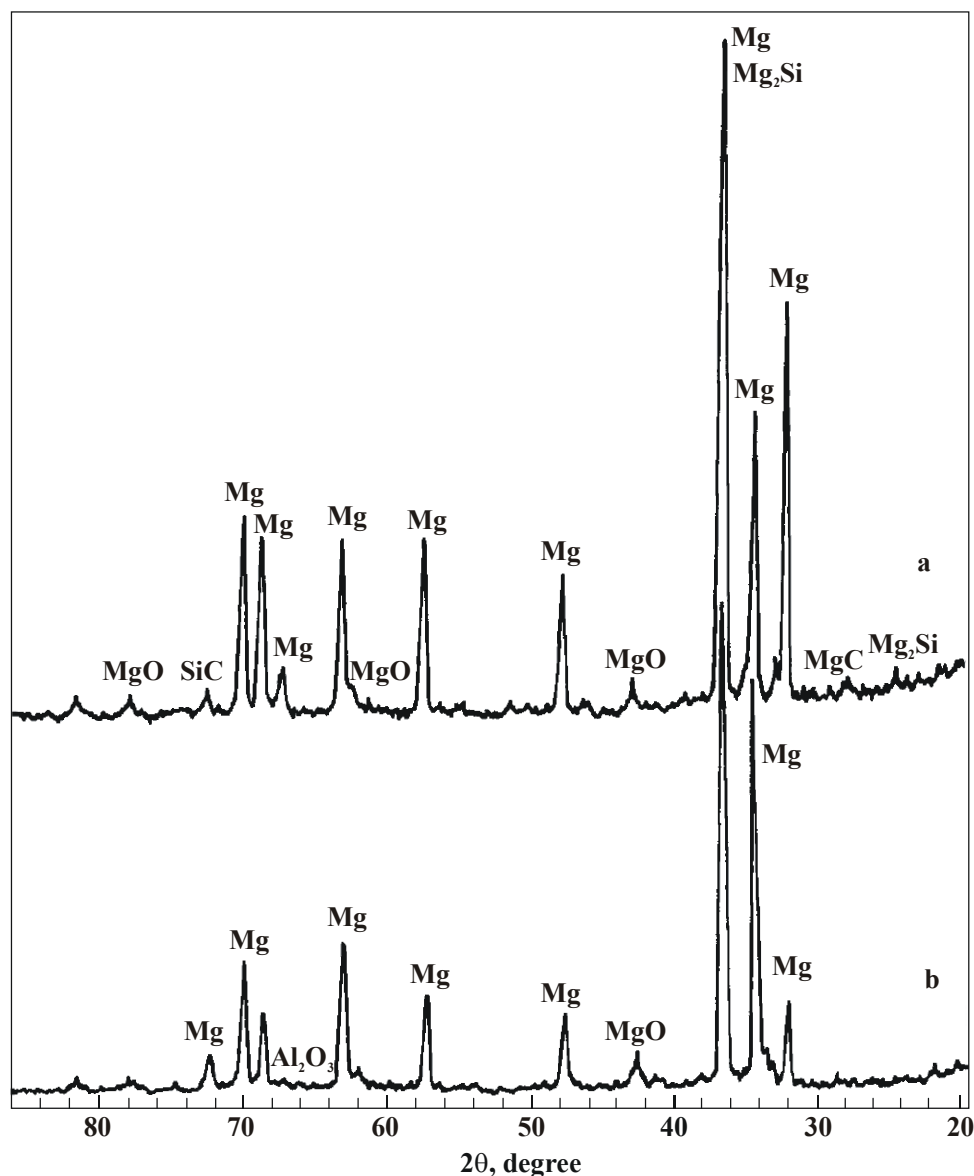

Fig. 5. XRD pattern of CP-Mg composites, (a) CP-Mg + 10% V_F SiC + 2 wt.% MM, (b) CP-Mg + 10% V_f Al_2O_3 + 2 wt.% MM.

um melt and SiC particle under processing conditions employing in present studies. On the other hand the addition of Al_2O_3 particulates reveals the presence of MgO in XRD pattern, Fig. 5b. This indicates that the presence of oxygen in the composite system will play a key role in the formation of MgO. The formation of MgO is possible from the following reaction:
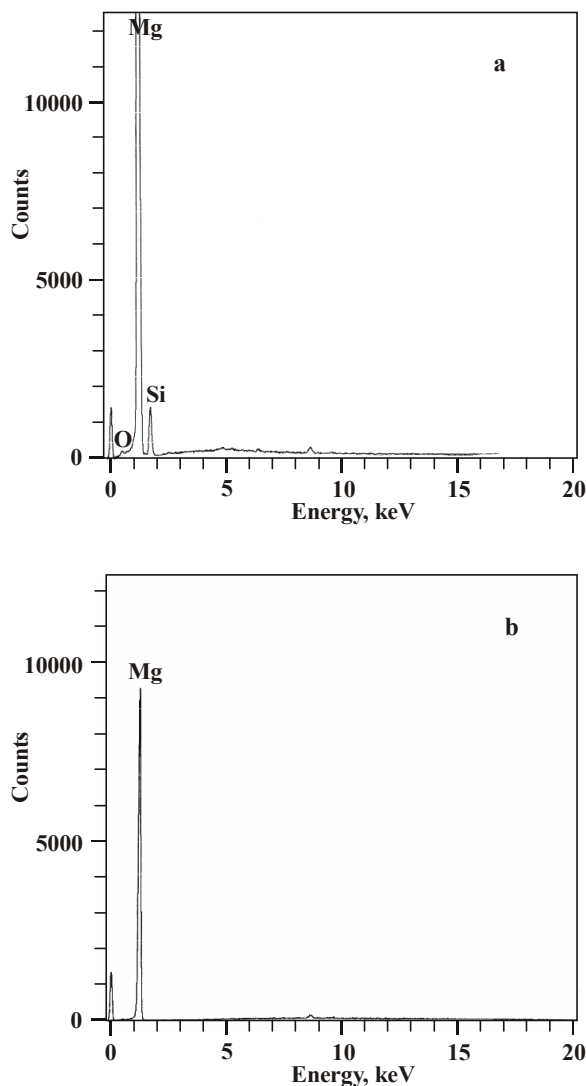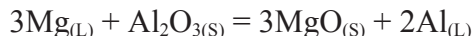
$$3Mg_{(L)} + Al_2O_{3(S)} = 3MgO_{(S)} + 2Al_{(L)}$$

Fig. 6. EDS of CP-Mg + 10% V_f SiC + 2 wt.% MM, (a) at particle/matrix interface, and (b) at the matrix.

The EDS analysis showed that the interface contained excess O and Al compared to the matrix alloy. This indicates that the Al_2O_3 particulates has reacted with the molten CP-Mg during processing, Fig. 7a,b. This is consistent with the results obtained by Karlson [9], who has reported that the formation of either MgO or $MgAl_2O_4$ spinel depends on the Mg content

in the melt. If the Mg content is higher than 7 wt.% like in the present work, the formation of MgO is more favored.
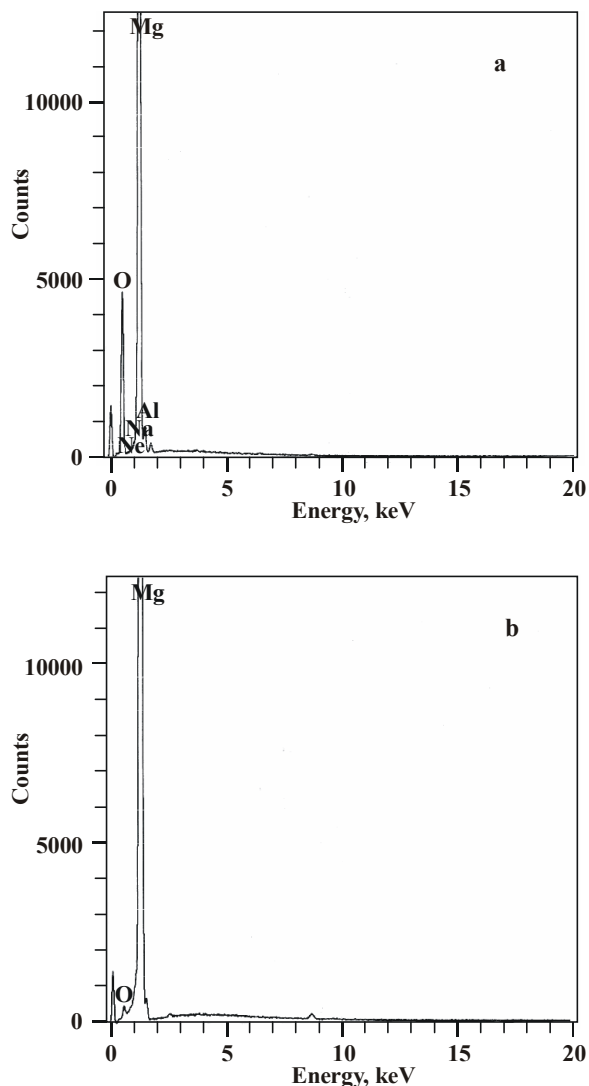

Fig. 7. EDS of CP-Mg + 15% V_f Al_2O_3, (a) at the particle/matrix interface, and (b) at the matrix.

On the other hand, the results of the XRD for AZ91 alloy reveals the presence of $Mg_{17}Al_{12}$ and α-Mg, Fig. 8a,b,c. At the same time, XRD results of the alloy AZ91 + 15% V_f SiC show two important compounds, which may be responsible for the interface product. These compounds are Mg_2Si and MgO. The absence of thermodynamically stable Mg_2C limits the nature of attack of the reinforcement interface even though molten Mg readily wets the SiC when ensures good reinforcement integration [10]. Previous work on similar systems identified the presence of fine Mg_2Si reaction products [11,12]. The alloy-

ing elements such as aluminum in AZ91 can react with SiC to form Al_4C_3:

$$4Al + 3SiC \rightarrow Al_4C_3 + 3Si$$
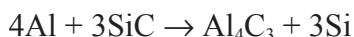
In addition, the silicon liberated by this reaction can react further with the molten magnesium to form Mg_2Si [13]:

$$Si + 2Mg \rightarrow Mg_2Si$$
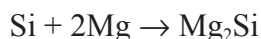
The reaction product, Mg_2Si was detected by XRD, Fig. 8b results and EDS analysis, Fig. 9. On the other hand, the MgO found in the alloy was identified by XRD pattern Fig. 8c and EDS analysis Fig. 10. It is noticed that MgO was formed during the fabrication of the composites by chemical reaction of magnesium with oxygen and/or other oxides. Also, the results of AZ91 + 15% $V_f Al_2O_3$ alloy, showed all of those compounds except Mg_2Si, because the interface compound in the case of Al_2O_3 is MgO, Fig. 10b. It is noticed from all previous studies [14] that the MgO is the interfacial reaction product in case of Al_2O_3/Mg composite. The reaction may be:

$$Al_2O_{3(S)} + 3\ Mg_{(L)} \rightarrow 3MgO$$

This interfacial product agrees with the results of XRD and EDS in the present study, Fig. 8c and Fig. 10. It is observed that MgO will be formed around the Al_2O_3 particle as an interface compound.
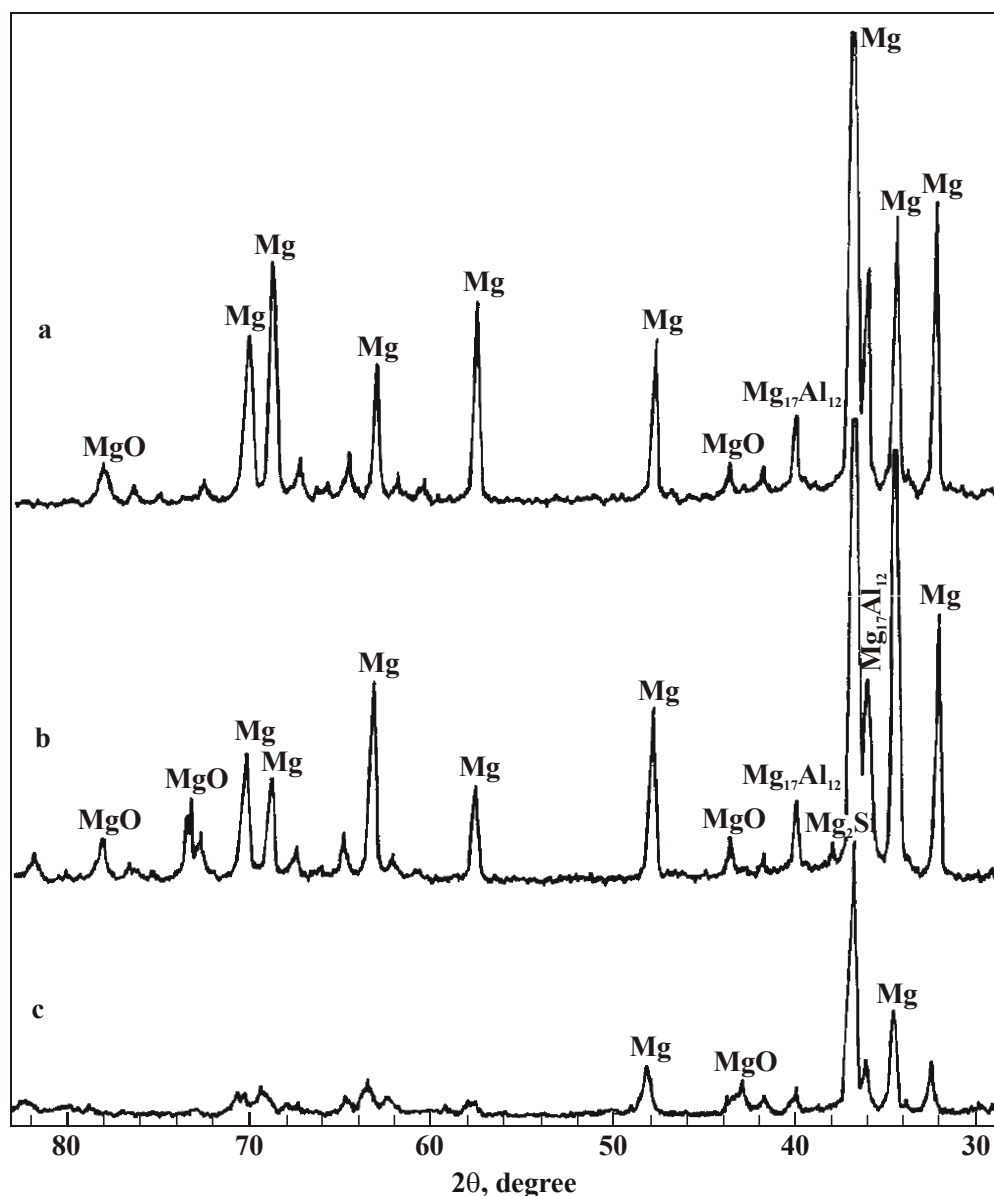

Fig. 8. XRD pattern of AZ91 composites, (a) AZ91, (b) AZ91 + 15% V_f SiC, and (c) AZ91 + 15% V_f Al$_2$O$_3$.
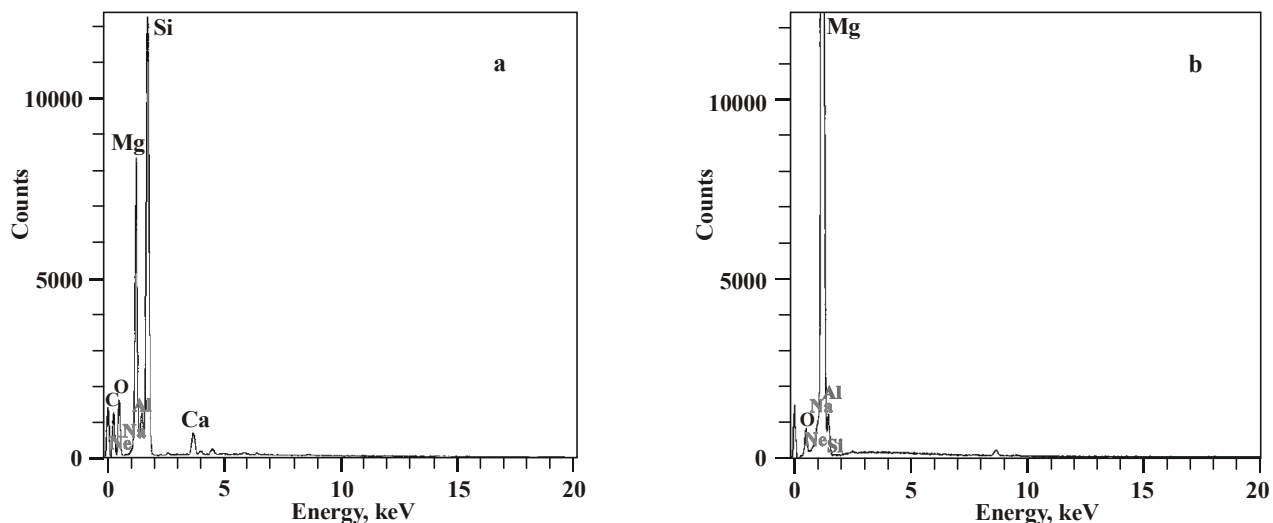
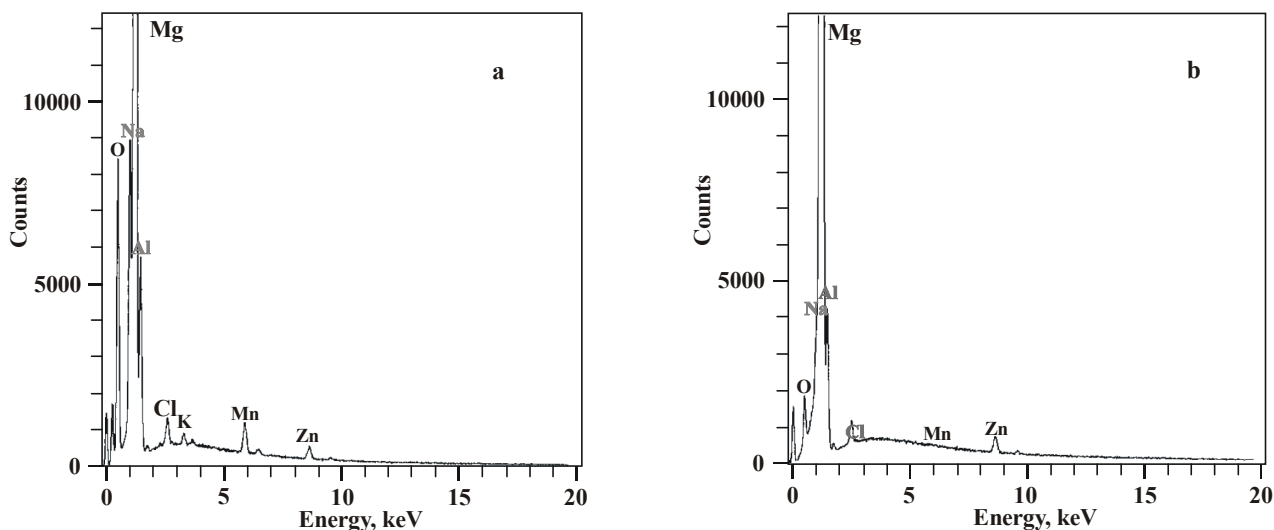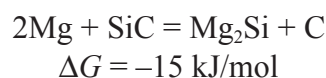Fig. 9. EDS of AZ91 + 15% V_f SiC + 2 wt.% MM, (a) at the particle matrix/interface, and (b) at the matrix.

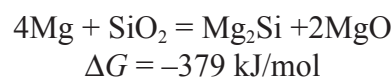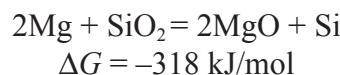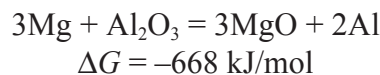

Fig. 10. EDS of AZ91 + 15% V_f Al$_2$O$_3$, (a) at the particle/matrix interface, and (b) at the matrix.

It can be concluded that the SiC or Al$_2$O$_3$/Mg-Al composite system can be thought as an Al-Mg-Si-C-O system. The possible reaction products can form at the interface of reinforcement/matrices are thus Mg$_{17}$Al$_{12}$, Mg$_2$Si, Al$_4$C$_3$, Al$_2$O$_3$, MgAl$_2$O$_4$ and MgO. Because Mg-O, Al-O and Si-O bonds are significantly stronger than the Al-C, Al-Mg and Mg-Si bonds [15], oxide phase should form in preference to other possible compounds such as Mg$_2$Si, Al$_4$C$_3$ and Mg$_{17}$Al$_{12}$ until all of the available oxygen is consumed free energy of formation [16], also dictates that the oxides are preferred thermodynamically over the other possible compounds. The study on thermodynamic stability of Mg-Al oxides in Mg-Al alloys show the formation of Al$_2$O$_3$, MgAl$_2$O$_4$ and MgO are competitive processes, with preferential MgO for-

mation for high Mg content. These thermodynamic considerations show that the most stable oxide in Mg MMCs is MgO. According to the structure and thermodynamic analysis, the fine interfacial phase of Mg-Al composites are identified as MgO (a = 0.42 μm) [13]. Some typical reaction paths are [17]:

$$3Mg + Al_2O_3 = 3MgO + 2Al$$
$$\Delta G = -668 \text{ kJ/mol}$$

$$2Mg + SiO_2 = 2MgO + Si$$
$$\Delta G = -318 \text{ kJ/mol}$$

$$4Mg + SiO_2 = Mg_2Si + 2MgO$$
$$\Delta G = -379 \text{ kJ/mol}$$

$$2Mg + SiC = Mg_2Si + C$$
$$\Delta G = -15 \text{ kJ/mol}$$

So, generally speaking we can say that the interfacial reaction between ceramics and metals improve the wetting and/or bonding between them. While CP-Mg does wet SiC particle as seen in this work, the wettability can be further improved by adding aluminum to the matrix alloy (AZ91), which creates certain interfacial reactions. However, excessive reaction due to high temperature processing may degrade the reinforcement and result in agglomerates, which give rise to particle segregation before solidification begins. High melt temperatures may also lead to extensive oxidation and gas related casting defect.

Conclusions

CP-Mg and AZ91 alloy and their composites have been fabricated by casting technique using a cover flux. The composite alloys reinforced with Al_2O_3 or SiC particulates were successfully produced by stir casting.

The microstructure of CP-Mg consists of α-Mg solid solution, while the microstructure of AZ91 alloy consists of α-Mg solid solution and mainly intergranular particles of β-$Mg_{17}Al_{12}$ phase.

The presence of either Al_2O_3 and SiC particulates or MM in the matrix alloys cause a significant grain refining in the microstructure.

For CP-Mg reinforced by Al_2O_3, the interface compound was MgO, while there are no reaction products in case of SiC particulates due to the absence of stable carbides. On the other hand, the interface compounds in AZ91 composite alloys were MgO and Mg_2Si.

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