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Letter

Effect of hafnium carbide on the grain refinement of Mg-3 wt.% Al alloy

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ABSTRACT

This study investigates how different amounts of hafnium carbide (HfC) powder affect the grain refinement of Mg-3 wt.% Al alloys. Even though HfC and Mg have a similar crystallography, the use of HfC powder is not a very effective means of refining pure magnesium with typical columnar grains. However, Mg-3 wt.% Al alloy can be successfully refined by the addition of HfC due to the in situ formation of Al_4C_3. The addition of 0.7 wt.% of HfC into Mg-3 wt.% Al alloy leads to the smallest grain size, and its average grain size is refined from 365 μm to 145 μm.

1. Introduction

The last decade has witnessed a significant increase in the use of magnesium alloys for engineering components in the automotive industry. Magnesium alloys are promising structural light materials due to their high specific strength and high specific stiffness. However, poor ductility and workability have limited the application of magnesium alloys. Improvements in ductility and workability are therefore desirable [1]. Grain refinement is an effective method of improving the microstructural homogeneity, mechanical properties, and workability of magnesium alloys.

Magnesium alloys can be divided into two groups: aluminum-free alloys and aluminum-bearing alloys. Zirconium is an effective grain refiner for magnesium alloys that contain little or no Al, Mn, Si, and Fe (because Zr forms stable compounds with these elements) [2]. The most commonly accepted mechanism of grain refinement by Zr is the lattice disregistry between Zr (hcp structure, $a = 0.323$ nm, $c = 0.514$ nm) and Mg (hcp structure, $a = 0.320$ nm, $c = 0.520$ nm). Therefore, Zr particles are believed to provide efficient nucleation sites. Large numbers of grain refining methods have been proposed in aluminum-containing magnesium alloys. However, there are few available commercial grain refiners for magnesium alloys. Adding chlorinated hydrocarbons (C_2Cl_6) is an effective method in industry, however, its use should be restricted due to the emission of toxic gases which are detrimental to the workplace and environment. In the recent years, many researches have been conducted on seeking alternative of C_2Cl_6. The addition of compounds, such as ZnO [3], AlN [4], Al_2Y [5] and $MgCO_3$ [6], exhibits good grain refinement effect and some master alloys, such as Ni–C [7], Al–Ti–C–Si–B [8], Al–B [9], Mg–TiB_2 [10], Al–C [11] and Mg-Sr [12] can also refine Mg–Al alloys effectively.

One new grain refiner that is not harmful to the environment is HfC (FCC structure, $a = 0.4641$ nm). It was selected by means of an edge-to-edge matching crystallographic model [13–15]. Due to the absence of any detailed observations about HfC characteristics in the literature, the effect of HfC powders on the grain refinement of aluminum-bearing magnesium alloy was investigated in this study.

2. Experimental procedures

The HfC powders (with an average particle size of 2 μm) wrapped in a pure magnesium capsule were added into the molten metal of pure magnesium and Mg-3 wt.% Al alloy at 740 °C in an electrical furnace by using a mild steel crucible in a protecting gas atmosphere (10% SF6 and 90% CO_2). Different amounts of the HfC powder were used; that is, 0.20 wt.%, 0.70 wt.%, and 1.20 wt.%. The melt was kept at 740 °C for 30 min and then poured into a mild steel mold with a size of 25 mm × 80 mm × 125 mm coated with BN and preheated to 200 °C. The 12.5 mm × 25 mm samples for microstructure observation were sectioned on the plane as shown in Fig. 1. They were then heat-treated at 380 °C for 8 h and subsequently air-cooled to delineate the grain boundaries. Finally, microstructure characterization and qualitative analysis were carried out for the selected specimens of pure magnesium and Mg-3 wt.% Al alloys with HfC. For the measurement of grain size, a Nikon EPIPHOT 200 optical microscope and an I-solution software program were used in this study.

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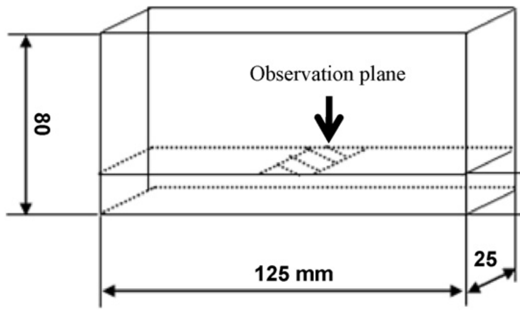

Fig. 1. Schematic illustration of sections from ingots selected for microscopy observations.

3. Results and discussion

Fig. 2 shows the macrostructures of the pure magnesium with HfC powder (for the entire observation plane in Fig. 1). The left and right-hand side of the images in Fig. 2 and Fig. 3 correspond to two edges of each specimen. As 0.2 wt.% of HfC was added into the pure magnesium, coarse columnar grains still remained, but their size tends to decrease as the amount of added HfC increases. The decrease in the size of the columnar grains indicates that HfC does have a grain refining effect on pure magnesium, though the effect is less significant than that observed in Mg-3 wt.% Al alloys.

Fig. 3 shows the optical macrostructure of a heat-treated Mg-3 wt.% Al alloy with different amounts of HfC powder. The columnar grains at the edge of the optical microscope plane and equi-axed grains at the center of the plane can be found in Fig. 3(a). As 0.7 wt.% of HfC was added to the Mg-3 wt.% Al melt, the columnar grains were replaced by homogeneous fine equi-axed grains. It is obvious that the grains were successfully refined by adding HfC powder to the Mg-3 wt.% Al melt, as shown in Fig. 4. Fig. 5 shows the average grain size of the Mg-3 wt.% Al alloys with the addition of HfC. The grains of Mg-3 wt.% Al alloy without addition of HfC have an average size of about 365 μm, and they become smaller as the amount of HfC increases. The smallest grain size (145 μm) was obtained when 0.70 wt.% of HfC powders were added into the Mg-3 wt.% Al alloy. Any excess amount of HfC over 0.70 wt.% cannot contribute to the refining effect of the powders.

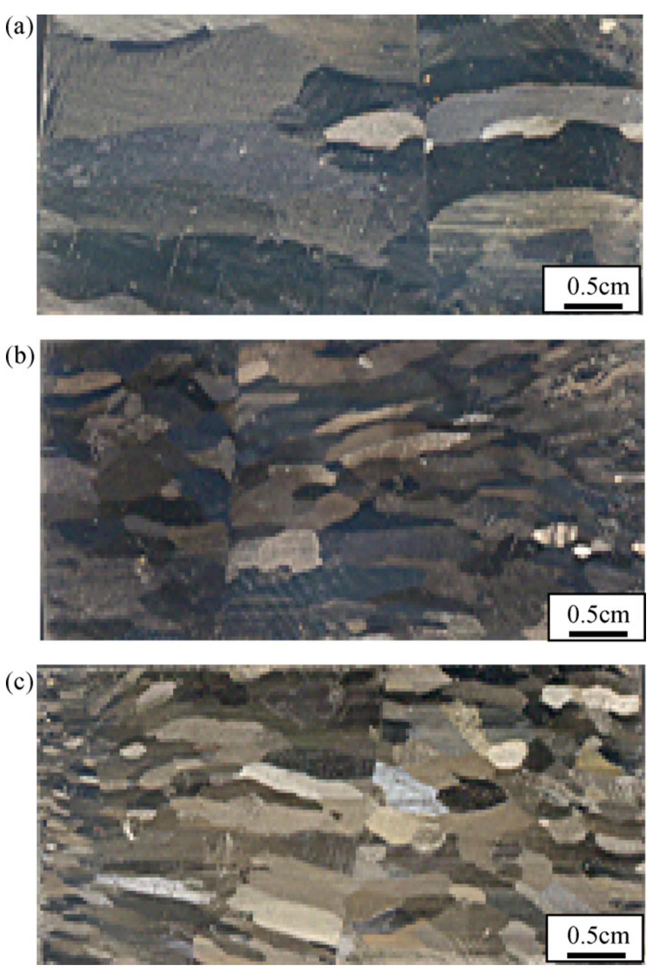

Fig. 2. Macrostructure of pure Mg-*x* wt.% HfC. (a) *x* = 0.2; (b) *x* = 0.7; (c) *x* = 1.2.

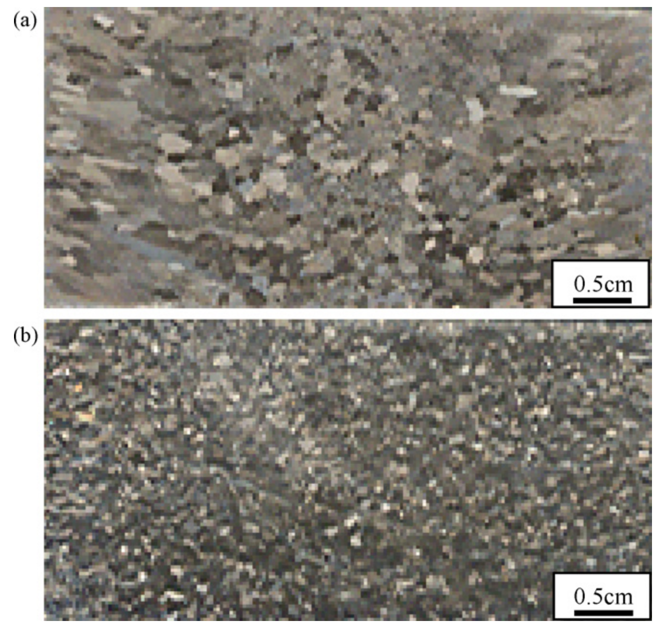

Fig. 3. Macrostructure of Mg-3 wt.% Al-*x* wt.% HfC. (a) *x* = 0; (b) *x* = 0.7.

In order to elucidate the effect of HfC addition on grain refinement, the refined microstructure under a scanning electron microscope was examined. Besides $Mg_{17}Al_{12}$ and Al–Fe phases (not shown in Fig. 6 but commonly observed at the alloys with the same alloy compositions), the particle with high content of Fe, Al and Hf formed in the Mg-3 wt.% Al alloy with the addition of HfC, indicating that the new particle in Fig. 6 formed after the HfC powder was added to Mg-3 wt.% Al alloy.

According to the classical theory of grain nucleation and growth, the final grain structure of as-cast polycrystalline materials is determined by the nucleation and growth conditions that prevail during phase transformations. The growth restriction factor (Q) is often used to quantify the role of solutes in controlling grain growth. The quantification is based on the segregation behavior of the solutes at the advancing solid-liquid interface. Thus,

$$Q = mC_0(k - 1) \tag{1}$$

where m is the gradient of the liquidus line of the Mg–X binary system, C_0 is the bulk concentration of the solute of interest (X), and k is the equilibrium partition coefficient of the solute (X) between the solid and liquid [16]. A solute with a higher value of Q is expected to have a stronger impact on grain restriction. However, the bulk concentration of HfC or its components (C and Hf), which are almost insoluble in molten magnesium, is close to zero. Thus, from the viewpoint of growth restriction, the addition of HfC appears to have poor grain refining efficiency.

Besides the growth restriction mechanism, heterogeneous nucleation is another important mechanism for refining the

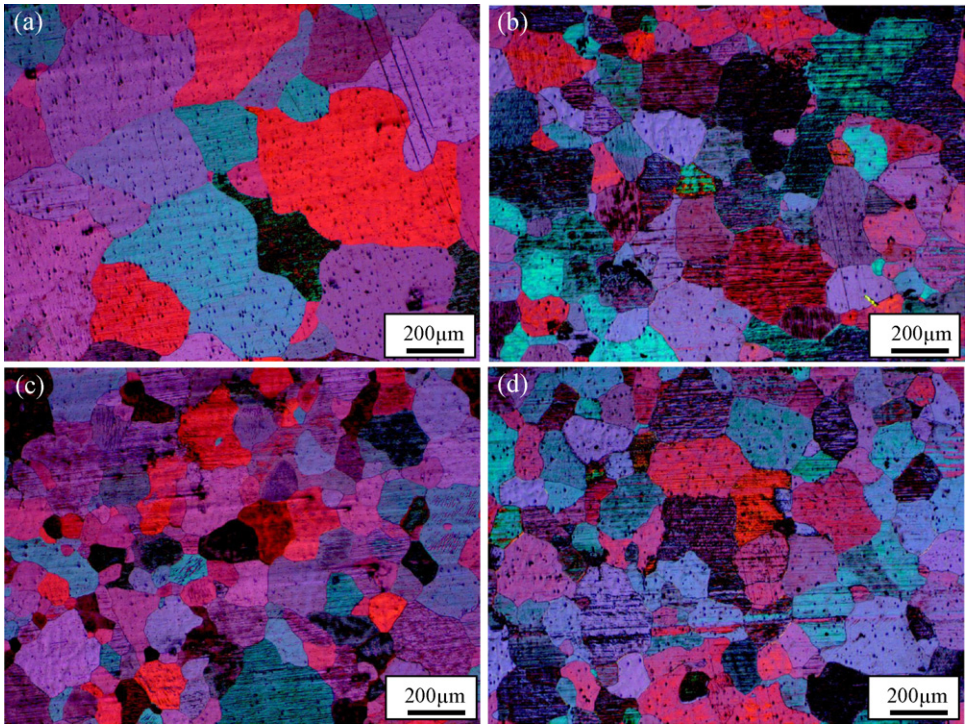

Fig. 4. Microstructure of Mg-3 wt.% Al-*x* wt.% HfC after pouring at 740 °C and heat treatment at 380 °C for 8 h. (a) $x=0$; (b) $x=0.2$; (c) $x=0.7$; (d) $x=1.2$.

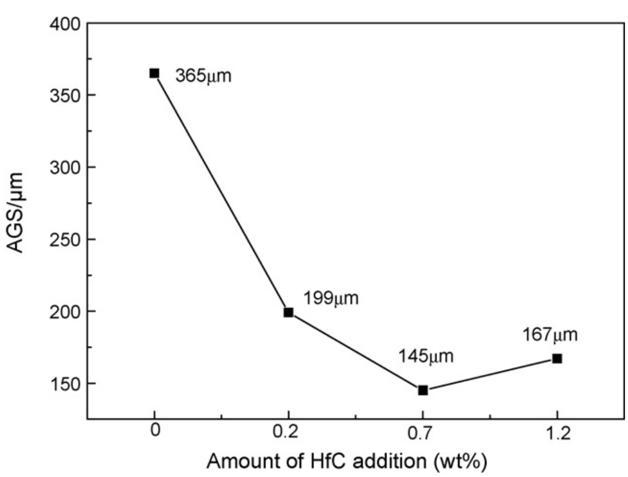

Fig. 5. AGS of Mg-3 wt.% Al-*x* wt.% HfC ($x=0.20$, 0.70 and 1.20).

Table 1
Inter-atomic spacing misfit (%) along possible directions between Mg and HfC.

$\langle 0\,1\,1\rangle_{HfC}/\langle 1\,1\text{–}2\,0\rangle_{Mg}$	$\langle 1\,1\,2\rangle_{HfC}/\langle 1\,1\text{–}2\,0\rangle_{Mg}$	$\langle 0\,0\,1\rangle_{HfC}/\langle 1\,1\text{–}2\,0\rangle_{Mg}$
2.4	43.7	31.0

grain size of magnesium alloy. A specified orientation relationship between two phases is defined by the minimization of interfacial energy, which requires minimum atomic mismatch across the interface. Table 1 lists the possible matching directions of magnesium and HfC and Table 2 lists the possible matching planes of magnesium and HfC. According to the edge-to-edge matching crystallographic model, the potential matching directions and matching planes are $(0\,0\,1)_{HfC}||(1\,0\text{–}1\,1)_{Mg}$ and $[0\,1\,1]_{HfC}||[1\,1\text{–}2\,0]_{Mg.}$ However, from the experimental finding that the addition of HfC fails to refine pure magnesium as effectively as expected, the similarity of crystallography is not the only factor that affects the grain refinement efficiency. Nonetheless, in the absence of any other impurities or grain refiner, HfC is expected to inevitably cause some increase in the number of heterogeneous nucleation sites, and those sites in turn are expected to yield some grain refinement and reduce the length of the columnar grains (Fig. 2). Research on other factors that affect the grain refinement efficiency of HfC is in progress.

HfC can be thermally reduced by Al due to high thermal reduction ability of Al. The reduced reaction is likely to occur in Mg-3 wt.% Al melts in accordance with the following thermal dynamic calculation:

$$4Al + 3HfC = 3Hf + Al_4C_3 \quad \Delta G = -1837.72\ \text{kJ/mol at } 740\,^{\circ}\text{C} \qquad (2)$$

In the literature, Al_4C_3 is commonly accepted as an effective grain refiner [7,8,11,16] due to its thermodynamic stability at melting temperature and its crystallographic similarity with the magnesium matrix. Unfortunately, it is impossible to observe Al_4C_3 particle probably because of the following reaction: $Al_4C_3(s) + 12H_2O(l) = 4Al(OH)_3(s) + 3CH_4$ [6,16]. Nevertheless, the presence of particles that are rich in Hf, Al and Fe (as shown in Fig. 4) provides the indirect evidence of the occurrence of (2); that is, the Hf from the dissolution of HfC forms an Hf–Al–Fe phase later in the solidification stage. According to thermodynamic calculations and energy dispersive X-ray results, the in situ formation of Al_4C_3 is considered the most likely mechanism of grain refinement when HfC is added to Mg-3 wt.% Al alloy.

Table 2
d-value mismatch (%) between potential matching planes for Mg and HfC.

$\{0\,1\,1\}_{HfC}/\{1\,0\text{–}1\,1\}_{Mg}$	$\{0\,0\,1\}_{HfC}/\{1\,0\text{–}1\,1\}_{Mg}$	$\{0\,1\,1\}_{HfC}/\{1\,0\text{–}1\,0\}_{Mg}$	$\{0\,0\,1\}_{HfC}/\{1\,0\text{–}1\,0\}_{Mg}$
30.9	5.1	39.1	16.3

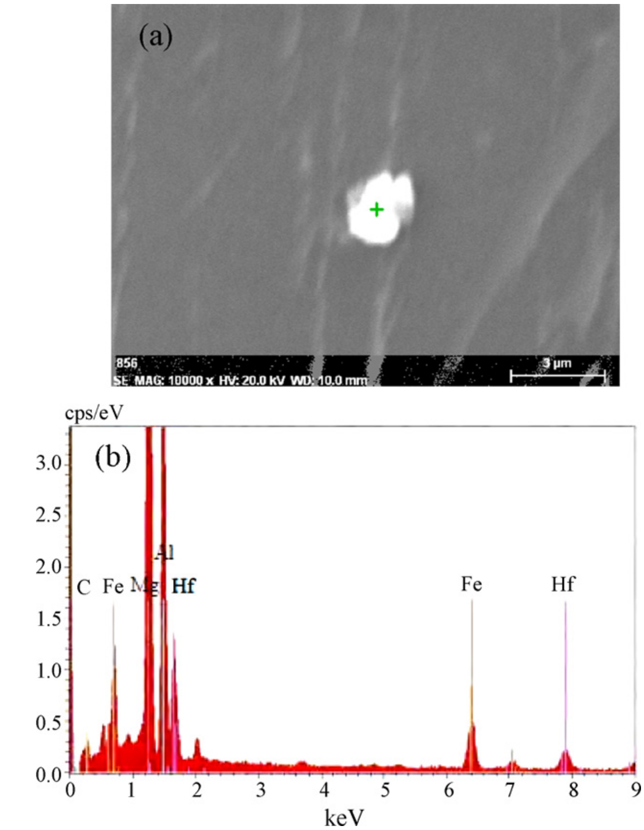

Fig. 6. The back-scattered electron micrograph of particles in Mg-3 wt.% Al-0.7 wt.% HfC alloy. (a) particle; (b) EDX spectrum from the particle

4. Conclusions

While the use of HfC powders cannot directly lead to the grain refinement of pure magnesium with typical columnar grains, a fine grained structure can be obtained by adding HfC powders to Mg-3 wt.% Al alloy. The optimal grain refinement efficiency can be obtained by adding 0.7 wt.% HfC powder to Mg-3 wt.% Al alloy. According to thermal dynamic calculations and energy dispersive X-ray results, the in situ formation of Al_4C_3 is considered the main mechanism of grain refinement for Mg-3 wt.% Al alloys.

Acknowledgements

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