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Modification of Mg_2Si in Mg−Si alloys with neodymium

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Abstract: The modification effect of neodymium (Nd) on Mg_2Si in the hypereutectic Mg−3%Si (mass fraction) alloy was investigated by optical microcopy, scanning electron microscopy and X-ray diffraction. The results indicate that the morphology of the primary Mg_2Si transforms from coarse dendrite into fine polygon with increasing Nd content. The average size of the primary Mg_2Si significantly decreases to about 10 μm with increasing Nd content up to 1.0%, and then becomes coarser again. The modification and refinement of the primary Mg_2Si are mainly attributed to the poisoning effect. The $NdMg_2$ phase in the primary Mg_2Si transforms into NdSi and $NdSi_2$ compounds as the Nd content exceeds 3.0%. Therefore, it is reasonable to conclude that the proper Nd (1.0%) addition can effectively modify and refine the primary Mg_2Si.
Key words: Mg−Si alloy; modification; Mg_2Si; Nd

1 Introduction

Recently, Mg alloys have a great potential application to the lightweight components of transportation vehicles due to their low density and high specific strength. Among them, Mg-high Si alloys are Mg matrix composites (MMCs) containing in-situ synthesized Mg_2Si particles [1]. According to the Mg−Si phase diagram, the solubility of Si in Mg matrix is only 0.003% (mole fraction), extra Si atoms react with magnesium and are precipitated as an intermetallic compound of Mg_2Si. Many researchers [1−3] reported that Mg alloys containing Mg_2Si particles have high potential because Mg_2Si exhibits a low density (1.99×10^3 kg/m^3) , high melting point (1085 °C), high hardness (4.5×10^9 Pa), reasonably high elastic modulus (120 GPa), and a low coefficient of thermal expansion (7.5×10^{-6} K^{-1}). However, the large and brittle Mg_2Si particles will greatly deteriorate the mechanical properties of Si-containing magnesium alloys, which is a principal obstacle for their application [2,4]. Therefore, how to modify and refine the coarse Mg_2Si particles in Mg-high Si alloys has attracted considerable attention. It has been reported that some processing techniques (rapid solidification, hot extrusion) [2,5,6], heat treatment [4,7] and alloying addition (Ba, Sb, Bi, Sr or Y) [1,3,8−10] were able to produce positive modification effect on the morphology of Mg_2Si in Mg−Si alloys. Up to date, only XU et al [11] proposed that Nd element can effectively modify the primary and eutectic silicon in hypereutectic Al−Si alloy. Rather limited information is available regarding the modification effect of Nd on the primary Mg_2Si in hypereutectic Mg−Si alloys.

Considering the similarity between Si modification in Al−Si alloy and Mg_2Si modification in Mg−Si alloy [3], we attempt to apply the Nd element to modifying the primary Mg_2Si in the hypereutectic Mg−Si alloys. The aim of this work is to develop an effective modifier on the primary Mg_2Si for hypereutectic Mg−Si alloys and explore the modification mechanism. It is also expected that the preliminary results can be significant in promoting the fabrication of high quality Mg−Gd−Y−Nd−Si system alloys as demonstrated [12].

2 Experimental

Mg−3%Si (mass fraction, the same below if not

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mentioned) alloy was prepared by melting pure Mg (>99.93%) and Si (>99.95%) in a steel crucible placed in an electrical resistance furnace at 760 °C under the protection of Ar atmosphere. After about 20 min, the desired amounts of Mg−30.15%Nd master alloys with 0.5%, 1.0%, 2.0% and 3.0% Nd were added into the Mg−Si melts, respectively. The melts were stirred for about 90 s at a speed of 300 r/min, then poured into a preheated (250 °C) permanent low-carbon steel mold (*d*55 mm×150 mm).

Samples for microstructure observation were initially polished using different grades of polishing papers and finally polished with 0.25 μm diamond paste. Polished samples were chemically etched in a solution of 4% (volume fraction) nital for 10 s. Microstructure observation was performed on an optical microscope (OM) and scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). The size of primary Mg_2Si particles was measured by a mean linear intercept method. X-ray diffraction (XRD) analyses were carried out using a Rigaku D/max 2500 diffractometer (Cu K_α radiation) with a scanning angle from 10° to 80° and a scanning speed of 2 (°)/min. The phases were identified by the ICDD PDF2—2004 database in the Jade 6 software.

3 Results

3.1 Microstructure of Mg−3%Si alloy

According to the Mg−Si binary phase diagram, the composition of Mg−3%Si alloy is a hypereutectic alloy with a solidified microstructure of primary Mg_2Si and eutectic α-Mg+Mg_2Si phases. The SEM microstructure of the unmodified Mg−3%Si alloy is shown in Fig. 1(a). It should be mentioned that the coarse dendritic phases are primary Mg_2Si (as shown by arrow *A*), while the rod-like shaped phases are eutectic Mg_2Si (as shown by arrow *B*), and the gray areas are Mg matrix (as shown by arrow *C*). The average size of the primary Mg_2Si particles is about 65 μm. Moreover, the primary Mg_2Si dendritic phases are surrounded by Mg dendritic halos, around which the eutectic α-Mg+Mg_2Si phases are formed, which is similar to the microstructure feature that was observed in other hypereutectic systems, such as Al−Si and Mg−Si alloys [1,13]. Figure 1(b) shows the XRD pattern of the Mg−3%Si alloy. It is evident to note that the components of the alloy are only α-Mg and Mg_2Si phases, which agrees fairly well with the results of SEM observation.

3.2 Microstructures of Mg−3%Si alloys with Nd addition

Figure 2 shows the OM images of Mg−3%Si alloys with 0, 0.5%, 1.0%, 2.0% and 3.0% Nd, respectively.

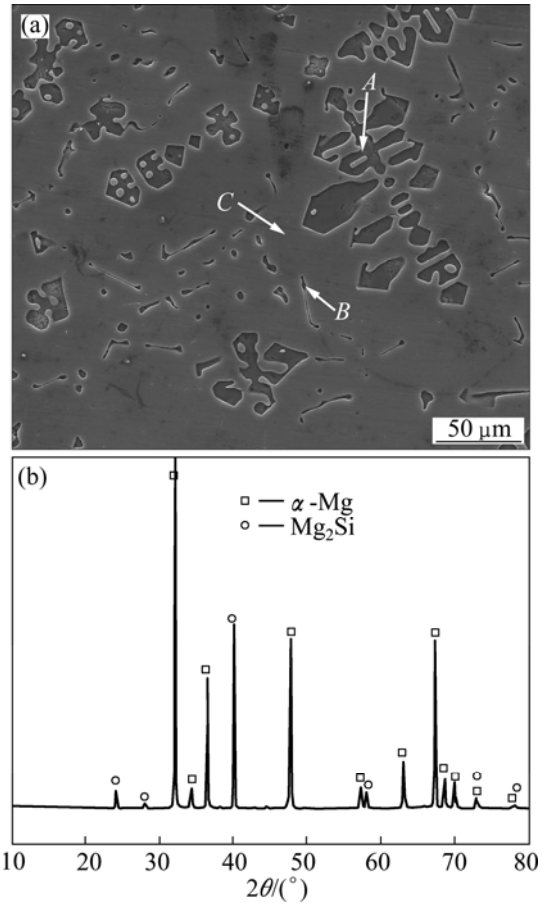

Fig. 1 SEM image (a) and XRD pattern (b) of as-cast Mg−3%Si alloy

When the Nd content is 0.5%, the primary Mg_2Si is only slightly refined to about 50 μm and its morphology is changed from coarse dendrite to polygon (Fig. 2(b)), which can be named sub-modified alloy. When the Nd content is 1.0%, the average size of the primary Mg_2Si is the smallest, which is about 10 μm, and its morphology still keeps the irregular and fine polygon (Fig. 2(c)). It can be named a fully modified alloy. However, when the Nd content is further increased to 2.0% and 3.0%, the primary Mg_2Si becomes coarser again, although there is no obvious change in its morphology (Figs. 2(d) and (e)), which means that the modification effect of Nd is weakened, and consequently it can be named an over modified alloy. Compared with the primary Mg_2Si, it should be noted that the Nd addition has little effect on the morphology of the eutectic Mg_2Si.

The SEM image, EDS line scans of Mg, Si and Nd, XRD pattern and EDS results of points *A* and *B* of the Mg−3%Si alloy with 1.0% Nd are shown in Fig. 3. In Fig. 3(a), some tiny white particles are found in the primary Mg_2Si. It can be seen from Fig. 3(b) that the white particle (as shown by arrow *A*) is a Mg−Nd compound. However, it is hard to identify this phase by the XRD pattern (Fig. 3(c)) due to its low intensity.

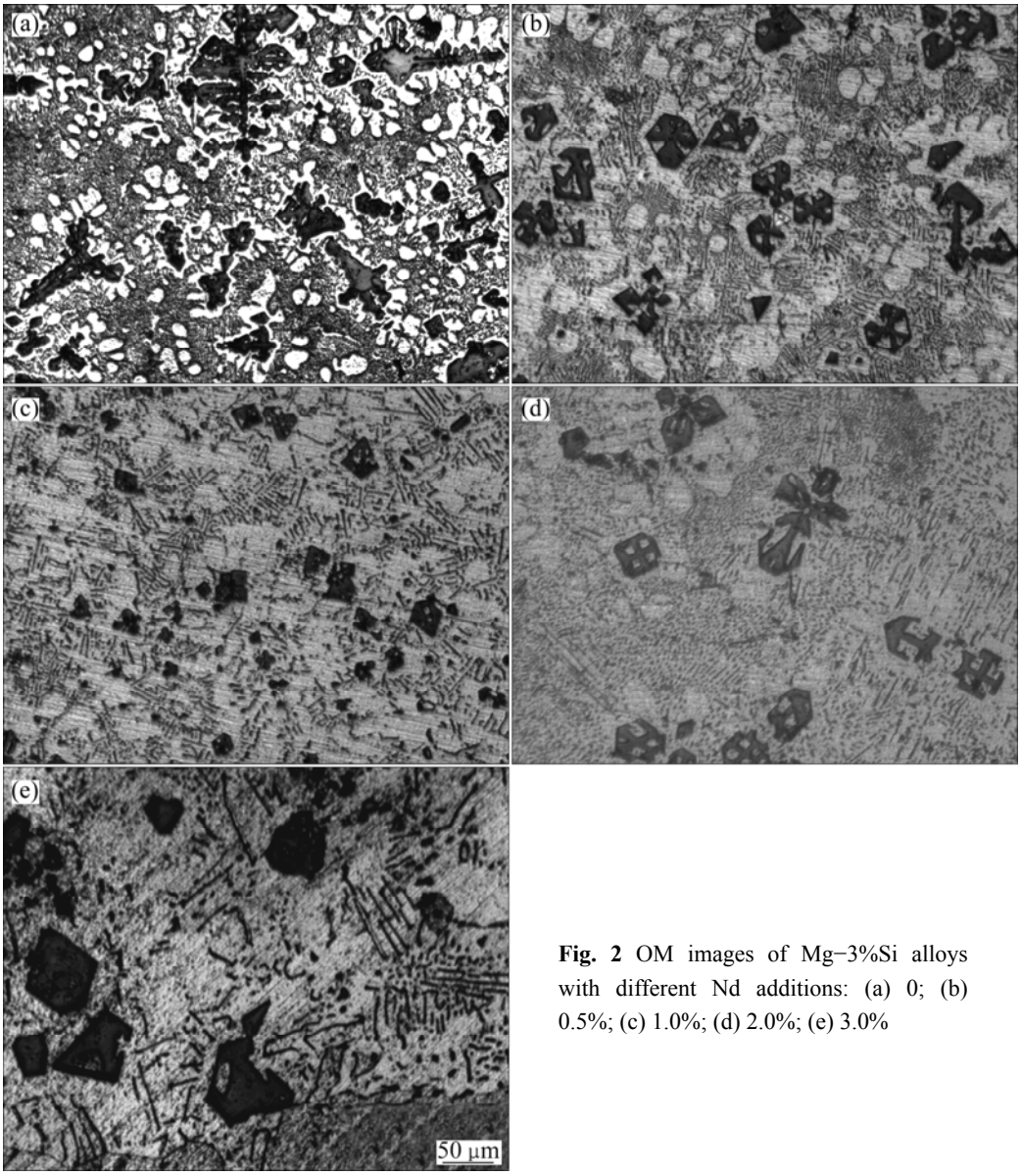

Fig. 2 OM images of Mg−3%Si alloys with different Nd additions: (a) 0; (b) 0.5%; (c) 1.0%; (d) 2.0%; (e) 3.0%

According to the EDS result (Fig. 3(d)), the chemical composition of the white particle in the primary Mg_2Si is Mg−28.75%Si−4.12%Nd (mole fraction), which indicates that its stoichiometry is near $(Mg_2Si)(NdMg_2)$. Therefore, it is reasonable to conclude that the Mg−Nd compound is $NdMg_2$ phase. Furthermore, it is also observed that there are some tiny white particles (as shown by arrow *B*) located in the matrix, and the chemical composition is Mg−10.87%Si−10.23%Nd (mole fraction) according to the EDS result (Fig. 3(e)). This indicates that its stoichiometry is near NdSi, which is different from that in the primary Mg_2Si.

Figure 4 shows the SEM image and XRD spectrum of the Mg−3%Si alloys with 3.0%Nd. Compared with Fig. 3(a) and Fig. 4(a), it is evident that the white particles (as shown by arrow *A*) in the primary Mg_2Si are obviously coarsened from 0.5 μm to 5.0 μm and agglomerate. According to the EDS result (Fig. 4(c)), it can be seen that its chemical composition is Mg−34.10%Si−29.14%Nd (mole fraction). This indicates that its stoichiometry is near $NdSi_{2-x}$. While the chemical composition of the white particle (as shown by arrow *B*) in the matrix is Mg−39.91%Si−35.27%Nd (mole fraction) according to the EDS result (Fig. 4(d)), which is also near $NdSi_{2-x}$. It is also evident that more diffraction peaks of NdSi and $NdSi_2$ appear in the alloy according to the XRD spectrum (Fig. 4(b)), which means that the white $NdSi_{2-x}$ particles are NdSi and $NdSi_2$ compounds. Therefore, it is concluded that the white particles in the primary Mg_2Si transform from $NdMg_2$ phase into the NdSi and $NdSi_2$ compounds as Nd content increases.

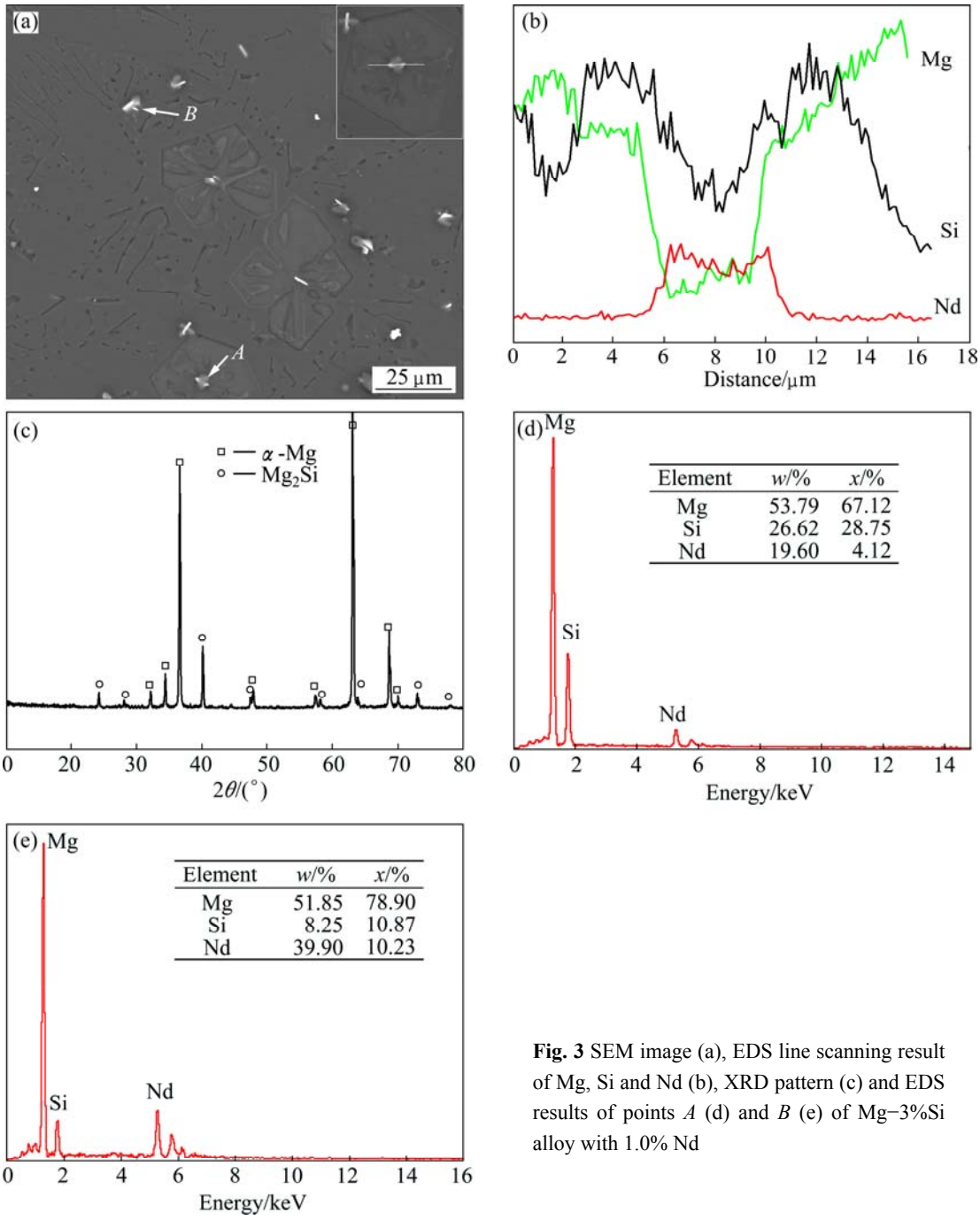

Fig. 3 SEM image (a), EDS line scanning result of Mg, Si and Nd (b), XRD pattern (c) and EDS results of points *A* (d) and *B* (e) of Mg−3%Si alloy with 1.0% Nd

4 Discussion

CHEN et al [3] reported that there are two major mechanisms of modification and refinement of the Mg_2Si particles. One is the increase of nucleation, which is the simplest and most effective. The formation of large amount of nuclei in the melts leads to the refinement of the Mg_2Si particles [14]. The other is inhibition of crystal growth through changing the solidification condition and the modification is attributed to the poisoning effect. Rare earth (RE) elements, which are surface-active elements, are prone to adsorbing into the crystal growth front to changing the surface energy of the crystal, effectively poison the growth steps, resulting in the isotropic growth of the crystals. JIANG et al [1] reported that the adsorption of Y atoms on the Mg_2Si growing surface front can change the solidification condition and modify the primary Mg_2Si particles.

Since Nd element has a high solubility (3.6%) in magnesium matrix, it is unlikely to form any Nd-containing compounds in Mg–Si melts at the early solidification stage. And the primary Mg_2Si becomes coarser again (Fig. 2(d) and Fig. 4(a)) as more Nd-

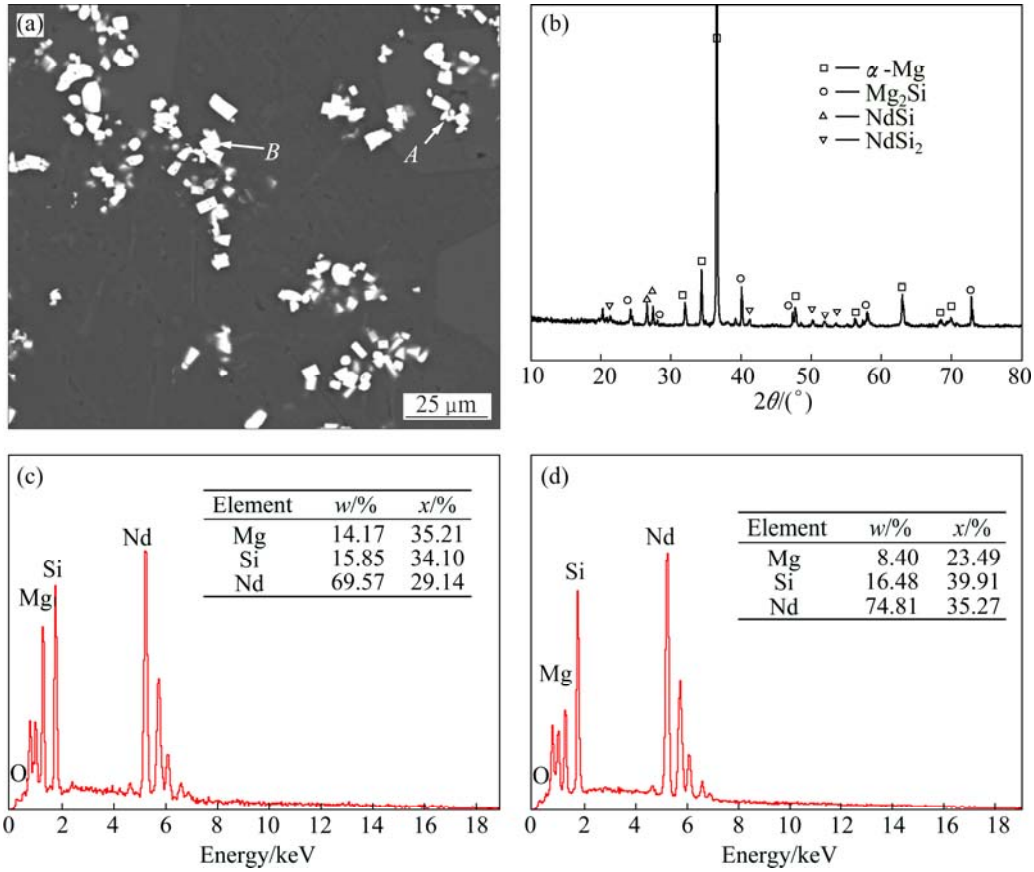

Fig. 4 SEM image (a), XRD spectrum (b) and EDS results of points *A* (c) and *B* (d) of Mg−3%Si alloy with 3.0% Nd

containing compounds form, which rules out the possibility of the Nd-containing compounds acting as heterogeneous nucleation sites for the primary Mg_2Si. Meanwhile, the faceted growth of Mg_2Si crystals is very sensitive to the solidification conditions [15]. LU and HELLAWELL [16] proposed the impurity-induced twinning mechanism in which atoms of the modifier are absorbed onto the growth steps of the silicon surface. A growth twin will be created at the interface when the ratio (the atomic radius ratio of the modification elements relative to silicon) is close to 1.6457 (1.54−1.85). The radius ratio of Nd atom (r_{Nd}=0.18214 nm) to Si atom (r_{Si}=0.11720 nm) is 1.55 [16]. Therefore, it is reasonable to deduce that the modification effect of Nd on Mg_2Si is attributed to the poisoning effect.

According to the impurity-induced twinning mechanism, the Nd atoms may be adsorbed onto the growth steps of the Mg_2Si crystal and change the surface energy of the Mg_2Si crystal by lattice distortion during solidification. Then, this will effectively poison the growth steps of Mg_2Si and promote multiple twinning to cause structural modification. Consequently, the preferred growth manner of the primary Mg_2Si is suppressed, while another type of growth, isotropic growth type, is accelerated [1,11,16].

When the content of Nd is 0.5%, the concentration of Nd atoms is comparatively low in melts, so the Nd atoms absorbed upon the growth steps of the Mg_2Si crystal are less. Therefore, the morphology and size of the primary Mg_2Si are only slightly modified. When the content of Nd is up to 1.0%, more Nd atoms can be adsorbed onto the growth steps of the Mg_2Si crystal. In this case, the enriched Nd layer encloses the growing primary Mg_2Si and changes its surface energy, which makes the external Mg and Si atoms difficult to diffuse into the internal Mg_2Si, and further effectively depress the preferred growth manner of the primary Mg_2Si. Consequently, the coarse primary Mg_2Si is fully modified.

It is well known that the possibility of the compound formation among elements generally depends on the electronegativity difference. The larger the electronegativity difference, the higher the binding force between elements and the easier the formation possibility. The electronegativities of Mg, Nd and Si are 1.31, 1.14 and 1.80, respectively. The electronegativity difference between Nd and Si (0.66) is larger than that between Mg and Si (0.49) or Mg and Nd (0.17), which means that the tendency of Nd atom reacting with Si is greater than Mg atom. Therefore, when the Nd content is increased to 2.0%, especially 3.0%, large Nd atoms are absorbed onto the growth steps of the Mg_2Si crystal, which provides

more Nd atoms to form NdSi and $NdSi_2$ compounds. Nd atoms cannot effectively depress the diffusion of Mg and Si atoms into the growing front of the primary Mg_2Si any more, which finally makes the primary Mg_2Si coarser again. This is also the major reason for the white particles ($NdMg_2$ phase) in the primary Mg_2Si transforming into NdSi and $NdSi_2$ compounds.

5 Conclusions

1) Nd can effectively modify and refine the primary Mg_2Si particles in the Mg−3%Si alloy. The average size of the primary Mg_2Si particles significantly decreases to 10 μm with increasing Nd content up to 1.0% and then becomes coarser again. And its morphology changes from coarse dendrite to fine polygon.

2) The optimal modification effect is obtained when the content of Nd is 1.0%, which is mainly attributed to the poisoning effect. The $NdMg_2$ phase in the primary Mg_2Si transforms into NdSi and $NdSi_2$ compounds as the Nd content increases to 3.0%.

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稀土元素 Nd 对过共晶 Mg–Si 合金中 Mg_2Si 粒子的变质作用

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摘 要：利用光学显微镜、扫描电镜及 XRD 物相分析研究稀土元素 Nd 对过共晶 Mg−3%Si 合金中 Mg_2Si 粒子的变质作用与机理。结果表明：随着 Nd 含量的增加，初生 Mg_2Si 粒子的形貌由粗大的树枝状转变为细小的多面体状。当 Nd 含量增至 1.0%时，初生 Mg_2Si 粒子被完全细化，尺寸约为 10 μm。然而，随着 Nd 含量的进一步增加，初生 Mg_2Si 粒子反而又出现了粗化的现象。其变质机理主要是 Nd 元素富集于初生 Mg_2Si 相的生长表面并抑制其优先生长晶向的生长，即中毒效应。当 Nd 含量超过 3.0%时，初生 Mg_2Si 粒子中的白色粒子由 $NdMg_2$ 相转变为 NdSi 和 $NdSi_2$ 化合物。因此，适量的 Nd 元素可以有效地细化初生 Mg_2Si 粒子。

关键词：Mg−Si 合金；变质；Mg_2Si；Nd

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