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# Segregation Behavior and Evolution Mechanism of Iron-Rich Phases in Molten Magnesium Alloys

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A new method has been proposed to prepare Mg–Al–Si master alloys by utilizing scrap Al–Si–Fe alloys with higher Fe levels, which aims to segregate Fe from Al–Si–Fe alloys by Mg melt. The segregation behaviors, microstructure morphology and evolution mechanism of iron-rich phases in Mg–Al–Si alloy melts were studied, after Al–14Si–4Fe (wt%) alloys were added and dissolved completely. In the Mg–Al–Si alloys, iron has very little solubility and tends to combine with other elements to form intermetallic phases, which grow into a deposition layer due to the higher density. During the cooling and solidifying process of Mg–Al–Si melts, the needle-like $Al_5SiFe$ phase in Al–14Si–4Fe alloy evolved into blocky $Al_5Fe_2$ and $Al_{0.7}Fe_3Si_{0.3}$ phases. Besides, the Fe levels of the Mg–Al–Si master alloys were reduced to 0.017 wt% from nominal content of 0.164 wt%. Based on the above results, this work carried out a semi-quantitative phase-compositions analysis for the deposition layer by relative intensity ratio (RIR) method, and evolution mechanism of the iron-rich phases had also been discussed. This study has paved a new way to regenerate the scrap Al–Si–Fe alloys, which has a great significance of promoting the recycling of aluminum resources.



## 1. Introduction

Recycling of scrap aluminums has great potential and advantages in energy conservation and environmental protection[1,2]. Compared to primary aluminums, scrap aluminums are characterized by complex components and more impurities[3], which to a large extent restrict the recycling of aluminum resources. Moreover, the impurity element Fe is very easily excessive and usually considered detrimental in Al alloys, especially for Al–Si based alloys[4–6]. Unfortunately, iron is a natural impurity that cannot be completely avoided during the manufacture of aluminum alloys[7,8]. In fact, iron can enter aluminum melts through two basic approaches[8,9], unprotected ferrous tools, crucible or furnace equipment, and low-purity alloying materials, i.e. silicon, secondary aluminums containing higher iron levels. It is implicated that Fe levels in Al alloys will constantly increase with each remelt cycle, and the iron levels can even end up to 5.0 wt% in the Al–Si alloys destined for aluminized materials[10]. A large number of studies[7,11–13] have shown that iron-rich phases prefer to form with a platelet or needle-like morphology in Al–Si alloys, tending to generate micro cracks as a result of stress concentration, which is responsible for the impact on castability and mechanical properties. Thus, decreasing the detrimental effects of iron impurity is a highly effective way to promote the recycling of scrap aluminums.

Generally, eliminating or reducing the impact of Fe-containing intermetallics is mainly based on the following two classes of approaches[14–16]: reducing the Fe levels in Al–Si alloys and transforming the platelet iron-containing phases into Chinese script or blocky morphology. The former is usually accomplished by the methods of precipitation, centrifugation, gravity filtration, magnetic separation, etc., while the latter is implemented throughout adding specific alloying elements[17], i.e. Mn, Sr, B, Mg, RE and so on. However, these two traditional approaches have practical disadvantages, such as high cost and complex technology or increasing the whole amount of iron-rich phases containing modified elements. So it is hard to economically or commercially remove high Fe levels in the foundry aluminum industry[18]. Currently, the common method to recycle scrap Al–Si–Fe alloys needs a lot of primary aluminum for dilution, resulting in the addition amount of scrap aluminums only limited to ~20%–30%, assuring the iron values around 0.4–0.7 wt%. In addition, sometimes scrap Al–Si alloys are forbidden to serve as raw materials in high-quality cast aluminum products. Therefore, the current common method is too simple to develop the values and economic benefits of the scrap aluminums.

This work propounded a new method to recycle scrap Al–Si–Fe alloys via preparing Mg–Al–Si master alloys, in which impurity Fe

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**Table 1**
Chemical composition of Al–14Si–4Fe alloys (wt%)

| Fe | Si | Mn | Zn | Al |
|---|---|---|---|---|
| 4.1 | 13.9 | <0.1 | <0.1 | Bal. |

can be easily removed, and then the Mg–Al–Si master alloys containing little Fe levels can be used to produce Al–Si–Mg alloys. Or if the Fe levels are low enough, with values less than 0.005 wt%, the Mg–Al–Si master alloys can be directly served as raw material of Mg alloys. In a sum, this method can fundamentally remove the impurity Fe levels from scrap Al–Si–Fe alloys.

## 2. Experimental

Commercial pure Mg ingots (99.8%, all compositions quoted in this paper are in wt% unless otherwise stated) and Al–14Si–4Fe alloys were used as raw materials to prepare Mg–Al–Si alloys. The Al–14Si–4Fe alloys were fabricated by remelting aluminized materials provided by Kinkong Piston, and the chemical composition is listed in Table 1.

The preparation methods were presented as follows. First, Mg ingots were melted and heated up to 750 °C in a ceramic crucible (Ø50 mm × 70 mm) in an electrical resistance furnace under the protection of flux (mixture of $MgCl_2$, KCl, $CaF_2$, etc.). Second, the liquid Mg melts were added with 4 wt% Al–14Si–4Fe alloys, which were preheated, and then held for 15 min with stirring adequately. Third, the newly prepared Mg–Al–Si melts were kept still for 30 min at 750 °C, and at last the melts maintaining in the crucible were transferred into the air and cooled to room temperature.

The specimens for spectrometric analysis were taken from the central section of each sample of Mg–Al–Si alloys, cut into a cuboid with a size of 30 mm × 30 mm × 20 mm, and then investigated by X-ray fluorescence spectrometry (XRFS) (ARL3460, Germany). Metallographic specimens were taken from the bottom of each sample, and then mechanically ground and polished by standard preparation procedures. The microstructure analysis was conducted by field emission scanning electron microscopy (FESEM) (SU-70, Japan) and electron probe micro-analysis (EPMA) (JXA-8840, Japan). The quantitative phase analysis was performed with X-ray diffraction (XRD) (Rigaku D/max-rB, Japan) using Cu*K*α radiation. The diffraction pattern was recorded for 2θ from 10° to 90° with 2° per minute. The voltage and current of the generator were set at 50 kV and 100 mA, respectively. Besides, in order to acquire the melting temperature of the Al–14Si–4Fe alloy, thermal analysis using a NETZSCG 404C differential calorimeter (DSC) was also performed.

## 3. Results and Discussion

### 3.1. Formation and segregation of iron-rich phases during solidification

The diffraction patterns and microstructures of Al–14Si–4Fe alloy are presented in Fig. 1. As indicated in Fig. 1(a), the diffraction peaks which correspond to α-Al, Si, β-$Al_5SiFe$ are identified. Fig. 1(b) shows the β-$Al_5SiFe$ phase forms with a typical needle-like morphology, with the average length of several micrometers.

With the purpose of segregating iron from Al–14Si–4Fe alloy, a certain amount of the alloy was added into pure Mg melt. After solidification, a thin deposition layer was formed at the bottom of the Mg–Al–Si alloy sample, as seen in Fig. 2. It shows in Fig. 2(a) that the height of the deposition layer is close to 1 mm, which fills with small particles. Fig. 2(b) shows a sketch of the deposition layer and its relative position in the Mg–Al–Si alloy sample. Since the heights

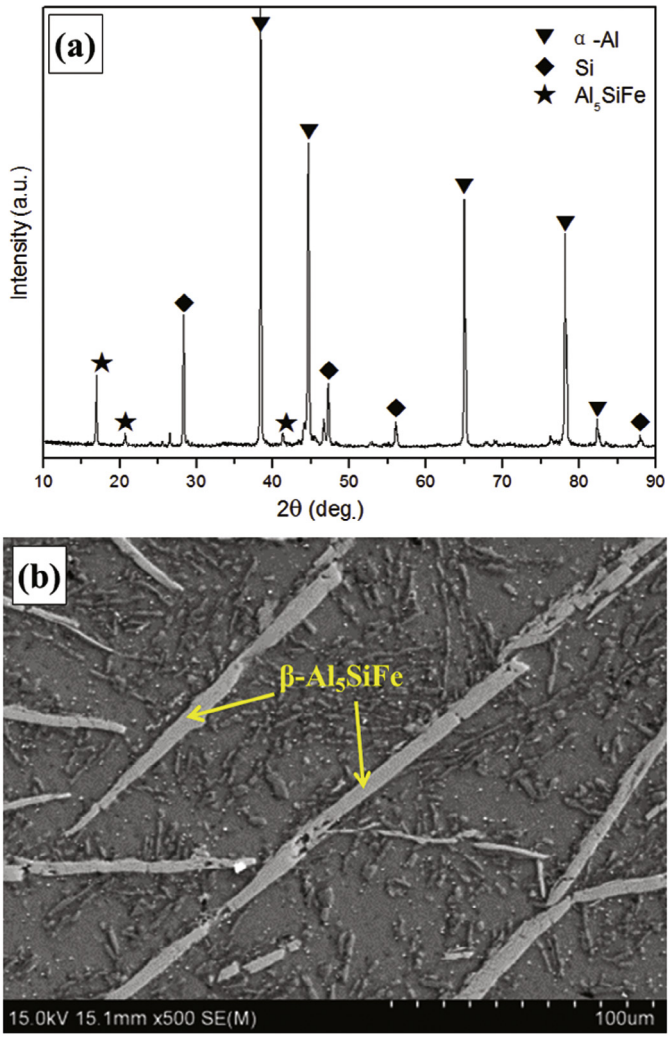


**Fig. 1.** XRD patterns (a) and microstructure (b) of Al–14Si–4Fe alloy.

of the deposition layer and the whole sample are ~1 and 50 mm, respectively, it is easily calculated that the volume fraction of the deposition layer is only about 2%.

Detailed FESEM and EDS analyses of the deposition layer are shown in Fig. 3. As indicated in Fig. 3(a), the diffraction peaks which correspond to Mg matrix, $Mg_2Si$, $Al_5Fe_2$, $Al_{0.7}Fe_3Si_{0.3}$ are identified. Besides, Fig. 3(b) shows that the sporadic dark gray phases in polygonal shape are $Mg_2Si$ and other dense light gray phases are Fe-rich phases. Moreover, $Mg_2Si$ phases are approximately of random distribution in the deposition layer, as marked by yellow circles in Fig. 2(a). It is shown in Fig. 3(c) that both of the Fe-rich phases form with a granular and blocky morphology, which are obviously distinguished from the needle-like β-$Al_5SiFe$ phase in the Al–14Si–4Fe alloy. In order to confirm the exact composition of the both Fe-rich phases, EDS results are shown in Fig. 3(d and e), which correspond to spectrum 1 and 2, respectively. Therefore, it is revealed that the dark phase located outside is proven to be $Al_5Fe_2$ phase, while the light gray phase located inside is $Al_{0.7}Fe_3Si_{0.3}$ phase, as shown in Fig. 3(c). It is noted in Fig. 3(e) that the Fe content of the $Al_{0.7}Fe_3Si_{0.3}$ phase is up to ~60 wt%, which is greatly beneficial to segregating iron.

In order to acquire rough Fe levels in the deposition layer, EDS area scanning was performed on a selected section, as shown in Fig. 4. The result is presented in Table 2, and it shows that the Fe