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Influence of Ce and Mn addition on α-Fe morphology in recycled Al-Si alloy ingots

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Abstract: The influence of Ce or Ce and Mn combined additions on the morphology of α-Fe phases in recycled Al-Si alloys was experimentally investigated by microstructure observation and room temperature tensile testing. It is found that Ce modifies the morphology of α-Fe phase from the large Chinese script-like into the individual and fine nodular shape. A combined addition of Ce and Mn results in the promotion of primary α-Fe formation, and their size increases considerably with the increase in Ce content. The mechanism of the above morphological changes was discussed in accordance with the nucleation and growth of α-Fe phase during solidification.

Keywords: aluminum-silicon alloys; cerium; manganese; modification; morphology

1. Introduction

Along with the increase of the amount of scrap aluminium alloys year by year, the proportion of recycled aluminium alloys used in aluminium alloys keeps rising. However, the iron content in recycled aluminium alloys is notably higher than that in primary aluminium alloys, and the mechanical properties of aluminium alloys are highly sensitive to the iron content, especially to the morphology of Fe-rich phases. Therefore, understanding the morphology of Fe-rich phases and their morphological changes plays a significant role in scientifically utilizing recycled aluminium alloys and has remarkable meaning in science, technology, and economy.

The solid-state solubility of Fe in Al is very low, most Fe present forms intermetallic compounds, and the nature of which depends mainly on the other alloying elements present [1-2]. The most common intermetallic compounds are polyhedral primary α-Fe, Chinese script-like α-Fe, and needle-like β-Fe [3]. Many studies have been focused on modifying β-Fe with the addition of neutralization element, such as Mn, Co, Cr, Be, Sr, etc. [4-6]. However, few literatures reported the modification of α-Fe. The present study was performed to investigate the individual and combined roles of Ce and Mn on the modification of α-Fe in recycled Al-Si alloys. The reactions and phases obtained have been analyzed using optical microscopy and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) analysis. The room temperature tensile properties of the samples were tested.

2. Experimental procedure

The commercial ingots of recycled Al-Si alloys were employed, and the chemical composition is given in Table 1. The ingots were cut into smaller pieces, cleaned, dried, and melted in a 3-kg-capacity graphite crucible, which was heated by an electric resistance furnace. The melting temperature was kept at (750±5)°C. Measured quantities of Ce or Mn additions (as seen in Table 2) were made at this temperature, using a perforated graphite bell. Ce and Mn were added in the form of Al-20wt%Ce master alloy and Al-30wt%Mn master alloy, respectively. The melt was stirred for 15 min to ensure homogeneous mixing of the added material. Then, the melt was held at 750°C for 30 min before being adjusted to the required temperature and then cast.

The samples were cast for each alloy in a small metallic mould (inner dimensions: 50 mm in height; 40 mm in diameter) preheated at 250°C to investigate the microstr-

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Table 1. Chemical composition of Al-Si commercial alloy wt%

Si	Fe	Cu	Zn	Mn	Cr	Mg	Ca	Al
3.5181	1.22214	0.8207	0.5504	0.5024	0.15555	0.121	0.0357	Balance

Table 2. Details of Mn and Ce additions

Sample No.	Mn / wt%	Ce / wt%
1	—	—
2	0.75	—
3	1.0	—
4	—	0.05
5	—	0.1
6	1.0	0.05
7	1.0	0.1

ucture. Test bars were cast in a permanent mould at the pouring and mould temperatures of (730±5)°C and (200±10)°C, respectively. The bars were fabricated to a gauge length of 60 mm and a gauge diameter of 12 mm for the ambient temperature tensile test.

The metallographic samples were prepared by mechanical grinding and polished. The polished samples were etched with a water solution of 0.5vol% HF [7]. Microstructure observation (or optical microscopy) was conducted on a Axiovert 40MAT optical microscope (OM) and a TESCAN VEGA LMU scanning electron microscope equipped with an Oxford Inca Energy 200 dispersive energy spectrometer (EDS). The chemistry of the intermetallic compounds was semiquantitatively analyzed with EDS at a beam size of ∼50 nm. The room temperature tensile properties of the samples were tested on an AG-X10KN universal tensile testing machine at a strain rate of 1 mm·min^{-1}.

3. Results and discussion

3.1. Effect of Mn addition

Fig. 1 shows the microstructures of the Ce-free samples. Fig. 1(a) shows a typical cast microstructure of the reference alloy sample. The microstructure consists of primary aluminum and Chinese script-like Fe-bearing intermetallic particles. The convoluted eutectic structure named 'script α-Fe' occurs after the aluminium dendrites have begun to solidify. However, the needle-like β-Fe was not found in the reference sample, because the Mn and Cr contents in it are 0.5024wt% and 0.15555wt%, respectively. Their amounts are nearly half of the iron content so that they can substitute iron in the same crystal structure that is body centered cubic and similar to the Chinese script-like α-Al_{15}(Fe, Mn, Cr)$_3Si_2$ phase observed by Lu and Dahle [8] and Couture [9]. Additions of Mn do change the phase portrait of the alloy noticeably. When the addition of Mn reaches 0.75wt%, as shown in Fig. 1(b), the eutectic α-Fe phase formed as large Chinese script. An interesting change in the nature of intermetallics is observed for the alloys with 1wt% Mn, as shown in Fig. 1(c), in which particles with the polyhedral morphology exist at the center of the Chinese script particles. As the Mn content increases, the size of the Chinese script-like α-Fe enlarges. However, a coarser variation of the α-phase in the form of polyhedral shaped particles can also appear, which occurs when α-Fe forms as a primary phase before the α-Al begins to grow. The particle grows in a faceted manner bonded by the (111) faces, giving an approximately hexagonal shape in cross-section [8]. The examination of polyhedral and Chinese script-like Fe-bearing intermetallics in Fig. 1(c) using EDS is summarized in Table. 3. According to the outcome of EDS analysis, the chemical composition and the stoichiometry of the Chinese script-like α-Fe and sludge are approximately the same and corresponds to α-Al_{15}(Fe,Mn,Cr)$_3Si_2$, which is called the primary α-phase.

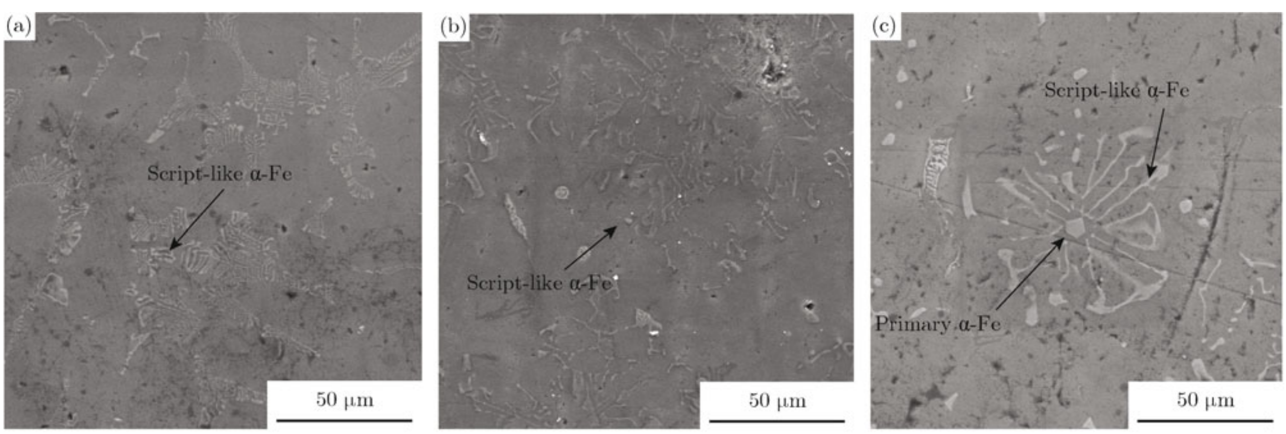

Fig. 1. SEM images showing the effect of Mn addition on the microstructure of the secondary Al-Si alloys: (a) sample 1 without Mn addition; (b) sample 2 with 0.75wt% Mn addition; (c) sample 3 with 1wt% Mn addition.

Table 3. EDS analysis results of the composition of the script-like α-Fe and primary α-Fe at%

Phase	Al	Si	Cr	Mn	Fe
Script α-Fe	79.69	6.72	0.85	5.10	7.64
Primary α-Fe	75.18	7.66	1.29	6.38	9.50

3.2. Effect of Ce addition

The morphology, size, and distribution of Fe-containing intermetallic compounds in the Ce-modified secondary Al-Si alloys are shown in Fig. 2. It can be found that these Fe-containing intermetallic compounds are only Chinese script-like α-Fe. It means that the addition of Ce could not contribute to the formation of polyhedral primary α-Fe if the Mn content is not high enough. As the Ce addition increases from 0 to 0.1wt%, the relative size of the Chinese script-like α-Fe decreases. Fig. 2(a) gives the morphology of the Chinese script-like α-Fe of the reference alloy sample; the α-Fe ranging from 10 μm × 50 μm to 50 μm × 150 μm distributes randomly along the interdendritic regions. The Ce additive produces metamorphism and the efficiency depends on the addition level of Ce. As can be seen in Fig. 2(b), when the Ce addition is 0.05wt%, the sizes of Chinese script-like α-Fe are reduced obviously, ranging from 5 μm × 20 μm to 30 μm × 100 μm. As the addition level of Ce increases to 0.1wt%, the sizes of Chinese script-like α-Fe are further reduced, ranging from 3 μm × 10 μm to 20 μm × 50 μm (Fig. 2(c)).

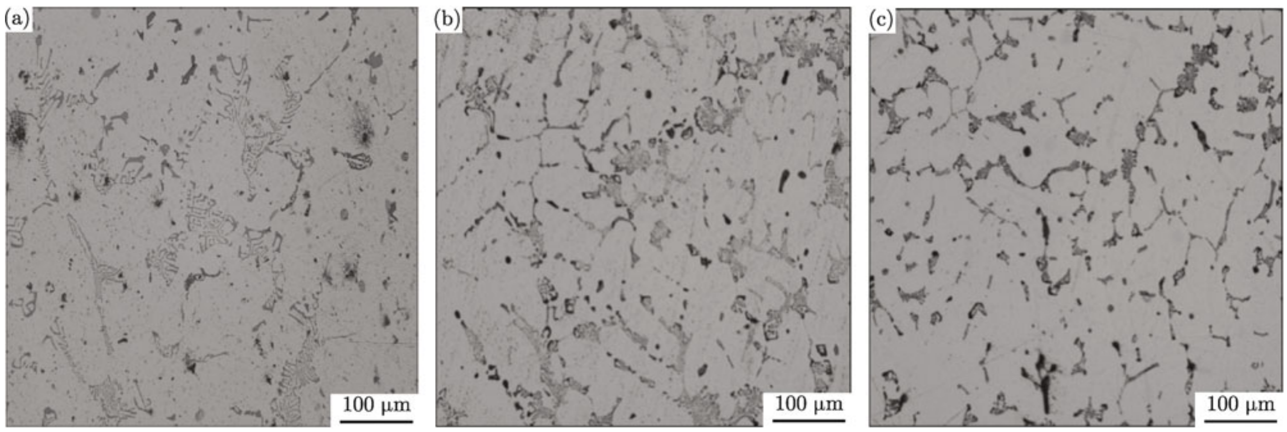

Fig. 2. Microstructures of the secondary Al-Si alloys showing the effect of Ce addition: (a) sample 1 without Ce addition; (b) sample 4 with 0.05wt% Ce addition; (c) sample 5 with 0.1wt% Ce addition.

A possible mechanism proposed for Ce addition considers the solidification sequence leading to the metamorphism of the Chinese script-like α-Fe. The solid-state solubility of Ce in aluminum is very low. Cerium is reported [10] to have only 0.05wt% solid solubility in aluminum. Only a very small fraction of Ce goes into the solution. A greater part concentrates ahead of the interface during solidification. Since they are surface active elements, they can adsorb elements such as Si, Fe, and Mn that also exist ahead of the interface and prevent them from penetrating into α-Al. The increase in concentrations of elements Si, Fe, Mn, etc. in the interface leads to producing constitutional supercooling, and hence, the dendritic structure of the alloy is refined. During the solidification, Ce accumulates in the melt and may affect the formation of iron-containing intermetallics. When Ce is added to the alloy, it combines with Si, Fe, Mn, and Cr to form intermetallic compounds in fine and particle shape. It can be seen in Fig. 3 marked with P1, P2, P3, and P4. They prevent these elements available in the alloy from the formation of Chinese script-like α-Fe, thereby reducing the size and number of the latter. The composition of such a particle phase is given in Table 4. On the other hand, these Ce bearing intermetallic compounds grow around the Chinese script-like α-Fe, as illustrated in Fig. 3, and they can hinder and lower the growth of script-like α-Fe. As a result, the Fe-rich precipitates are thinner and smaller.

3.3. Effect of Ce and Mn combined additions

Fig. 4 shows the microstructures of the samples with Ce and Mn combined additions. The Chinese script-like α-Fe and the polyhedral primary α-Fe directed at arrows are indicated in Fig. 4(a) for the 0.05wt% Ce and 1wt% Mn addition alloy. Compared with Fig. 1(c) for the Ce free alloy (only 1wt% Mn addition), the number and the size of the Chinese script α-Fe do not change, but the number of the primary α-Fe increases obviously. The addition of Ce

Table 4. Composition of particles P1-P4 shown in Fig. 3 at%

Particle	Al	Si	Cr	Mn	Fe	Ce
P1	96.19	1.14	—	—	—	2.67
P2	89.21	3.53	—	1.01	5.04	1.21
P3	88.06	10.52	—	—	—	1.43
P4	74.12	9.19	0.5	1.86	12.86	1.74

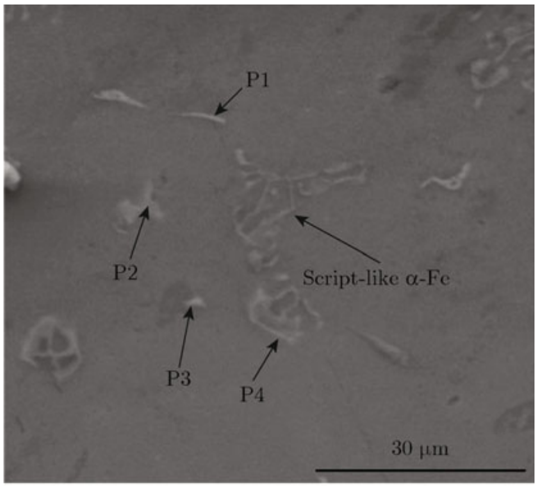

Fig. 3. SEM image depicting the presence of Ce-bearing intermetallic compounds in sample 5 by adding 0.1wt% Ce.

up to 0.1wt% results in not only increasing the number of the primary α-Fe but also enlarging their size from 5 to 10 μm as indicated in Fig. 4(b). This can be clearly observed in the SEM images of the deep-etched samples (Fig. 5). SEM images also show that the Chinese script-like α-Fe phase is well modified into small structure, and its number decreases evidently.

The mechanisms of the modification of α-Fe by Ce can be explained with regards to the nucleation and growth of α-Fe.

The increase in number of the primary α-Fe correlates with the nucleation mechanism. A change in the interfacial surface energy by the addition of an impurity element (e.g. Ce) may affect the nucleation process. It can be suggested that Ce may reduce the interfacial surface energy between α-Al and the primary α-Fe, influencing the nucleation process of the primary α-Fe. The nucleation of primary α-Fe takes place above the liquidus temperature of α-Al in the

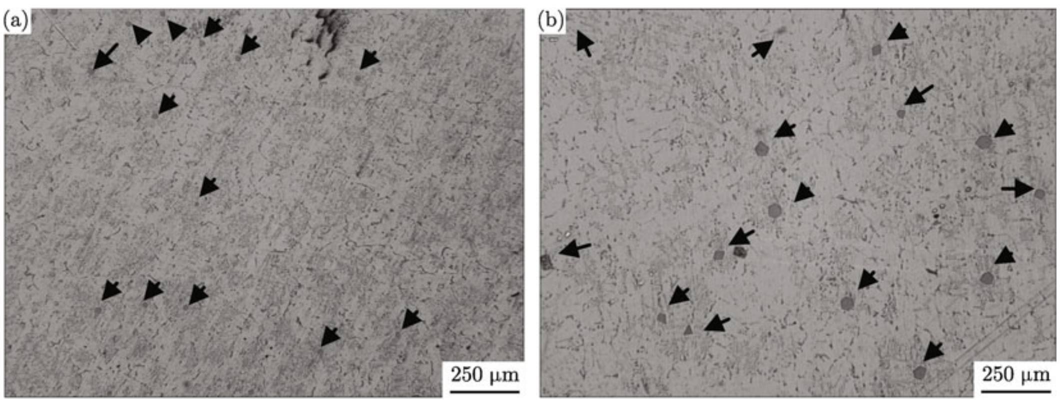

Fig. 4. Microstructures of the secondary Al-Si alloys showing the effect of Ce and Mn combined addition: (a) sample 6 with 1wt% Mn and 0.05wt% Ce addition; (b) sample 7 with 1wt% Mn and 0.1wt% Ce addition.

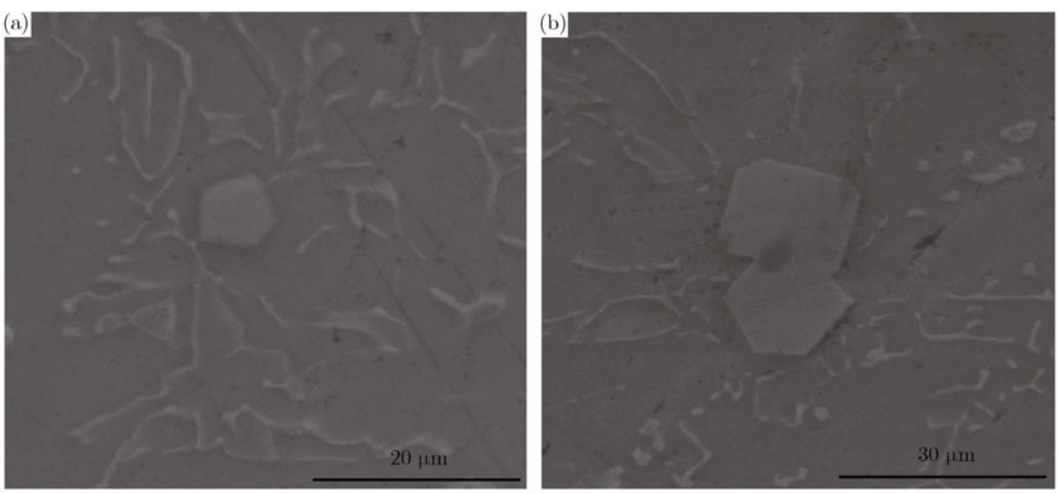

Fig. 5. SEM images showing the effect of Ce and Mn combined addition on the microstructure of the secondary Al-Si alloys: (a) sample 6 with 1wt% Mn and 0.05wt% Ce addition; (b) sample 7 with 1wt% Mn and 0.1wt% Ce addition.

sample with 1wt% Mn. Adding Ce to the melt, they can enrich in the interfacial surface between α-Al and the primary α-Fe because of their tiny solid solubility in aluminum. Due to their property of surface active elements, they may reduce the interfacial tension between α-Al and the primary α-Fe. Accordingly, the interfacial surface energy between them and the nucleation resistance of the primary α-Fe are reduced. More primary α-Fe can nucleate in the melt, as seen in Figs. 4 and 5. Another factor that possibly influences the nucleation behavior is the nucleation site for the formation of the primary α-Fe during solidification. Cao and Campbell [11-12] found that the primary α-Fe phase nucleated on the wetted external side of double oxide films. Different oxide films may have different potentials for the nucleation and growth of Fe-rich phases. The surface nature of oxide films, including their interfacial energy (which certainly has strong influence on the nature of their interatomic bonding) and the modification of their interfacial composition by trace impurities, may influence the nucleation and growth of such Fe-rich phases. When Ce present in the melt reaches a certain quantity, cerium aluminates ($Ce_2O_3 \cdot Al_2O_3$) may form. These cerium aluminates may have a good lattice matching with primary α-Fe and can act as an effective nucleation site for the primary α-Fe. The cubic structure primary α-Fe has lattice parameters of 1.25-1.27 nm; however, in the absence of correlative data for cerium aluminates, it needs further work to prove this hypothesis.

The increase in size of primary α-Fe and the decrease in size of Chinese script-like α-Fe correlate with the growth mechanism. Primary α-Fe can nucleate the Chinese script-like α-Fe as shown in Figs. 1(c) and 5. This conclusion is in agreement with previous reports [13-14]. As the Ce addition increases, the growth of the Chinese script-like α-Fe on the primary α-Fe is likely to be affected. Growth takes place in certain crystallographic lattice planes of the Chinese script-like α-Fe phases, and the adsorption of Ce on the lattice planes will suppress the growth. On the other hand, it can be suggested that Ce poisons the preferential nucleation sites on the primary α-Fe. As a result, the modification (less structure and decrease in number) of the Chinese script-like α-Fe can take place. This modification decreases the growth resistance of the primary α-Fe so that they can absorb more elements (Si, Fe, Mn, Cr, etc.) and become bigger.

3.4. Mechanical properties

The effect of Mn and Ce addition on the ultimate tensile strength (UTS) and the elongation (EL) of the secondary Al-Si alloys are shown in Table 5. It can be observed that the addition of small amount of Mn (0.75wt%) decreases the UTS from 111.7 to 109.2 MPa, while the EL decreases from 7.709% to 5.625%. The decrease in UTS and EL of the as cast alloy can be attributed to the change of the Chinese script-like α-Fe into larger shape, as shown in Fig. 1. Further, it can be noticed that adding 1wt% Mn to the alloy, the UTS and EL are reduced to 108.1 MPa and 4.855%, respectively. Further reduction in properties might be due to the presence of polyhedral shaped primary α-Fe, as shown in Fig. 1(c).

Table 5. Tensile properties of the samples

Sample	UTS / MPa	EL / %
1	111.7	7.709
2	109.2	5.625
3	108.1	4.855
4	114.0	8.261
5	115.2	10.306
6	107.1	4.623
7	103.3	4.437

These phases will act as harmful inclusions in the alloy and go against mechanical properties [15]. It can also be noted that Ce addition produced higher ultimate tensile strength and ductility compared to the reference alloy; this is due to the refining of grain and the metamorphism of the Chinese script-like α-Fe as shown in Fig. 2. The effect of Ce and Mn combined additions on the mechanical properties is also shown in Table 5. It can be observed that the mechanical properties reduce in sample 6 due to the increase of number of primary α-Fe, and reduce further in sample 7 due to the increase of size of these phases.

4. Conclusions

(1) The addition of 0.75wt% Mn to the secondary Al-Si alloys leads to enlarging the size of the Chinese script-like α-Fe phase. Adding 1.0wt% Mn, primary α-Fe phases can appear in the alloys.

(2) Apart from grain refinement, the addition of Ce from 0.05wt% to 0.1wt% to the alloy leads to the metamorphism of the Chinese script-like α-Fe. Their size decreases with the increase in Ce content. There will be no primary α-Fe formation in the absence of Mn in the alloys.

(3) The addition of Ce and Mn to the alloy promotes the nucleation of primary α-Fe, and their size increases with the increase in Ce content.

(4) An optimum addition of Ce to the alloy results in significant increase in tensile strength and ductility, which is due to grain refinement and Chinese script-like α-Fe metamorphism.

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