Research on the Degassing Behavior and Purification Mechanism of Rare Earth Elements on the Melt of Al-Si Series Cast Heat-resistant Aluminum Alloys

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Abstract: This study investigates Al-Si based cast heat-resistant aluminum alloys to enhance melt degassing efficiency and improve casting quality/serviceability through rare earth element (Ce, Er) additions. Experimental results demonstrate the significant influence of rare earth additions on degassing performance in these alloys. The introduction of 0.3 wt.% Er achieves optimal degassing effectiveness, reducing the density index of ingots to a minimum value of 0.1072. Further increasing rare earth content beyond this threshold fails to sustain degassing improvement, as evidenced by stagnated density index reduction and limited melt purification efficiency. Significantly, rare earth element incorporation in Al-Si cast heat-resistant alloys effectively diminishes casting porosity while enhancing material compactness. This improvement in structural integrity directly correlates with enhanced service reliability of cast components under thermal stress conditions.

Keywords: Heat-resistant Aluminum Alloy; Rare Earth Elements; Degassing.

1 Introduction

Cast aluminum alloys, recognized as pivotal lightweight high-strength materials, are extensively utilized in aerospace, transportation, and mechanical manufacturing sectors due to their advantageous combination of low density, high specific strength, superior corrosion resistance, excellent machinability, and exceptional castability. Among these, Al-Si series casting alloys dominate the field, constituting over 90% of total aluminum alloy castings production, making them the most diversified and widely implemented alloy system[1]. With the escalating demands for high power density and lightweighting in advanced equipment industries, conventional cast aluminum alloys have shown increasing limitations in their elevated-temperature performance. During the melting and pouring processes, aluminum alloy castings are highly prone to absorbing gases (primarily hydrogen) [2], leading to porosity defects that reduce the material density, severely compromise service performance, and diminish fatigue life.

Conventional degassing techniques—including rotary argon injection, vacuum degassing, and flux agent addition[3]—can reduce hydrogen content to some extent, yet suffer from inherent limitations such as complex equipment configurations, elevated installation/maintenance costs, and hazardous gaseous emissions.

Rare earth elements (REEs) exhibit high chemical reactivity, readily combining with oxygen, hydrogen, sulfur, and nitrogen to form stable compounds[2]. The addition of rare earth elements to aluminum alloys also refines grain structure[4-5]. This study investigates the effects of gradient Ce and Er additions on the degassing efficiency of M174 cast heat-resistant aluminum alloy and analyzes the underlying mechanism of rare earth element-induced degassing. The results provide theoretical support for the design and engineering applications of high-performance heat-resistant aluminum alloys.

2 Experimental section

The experimental material comprised M174 aluminum alloy from the Al-Si-Cu-Ni-Mg system, with chemical composition detailed in **Table 1**[1]. The alloy was prepared by melting 99.7% commercial purity aluminum ingots with master alloy additions in an SG-2 low-frequency resistance furnace, following a controlled melting protocol. Thorough melt homogenization was achieved through mechanical stirring during the smelting process. Al-10Ce master alloy, Al-10Er master alloy, C_2Cl_6, and A-700R refining agent (Japan) were respectively added to the heat-resistant aluminum alloy.

The addition amounts of both rare earth elements and both refining agents were set at 0.1%, 0.3%, and 0.5% (mass percentage, hereafter).

Following complete alloy melting, the temperature was elevated to 750°C ± 10°C for homogenization, stir thoroughly and keep this temperature for a period of time to ensure chemical uniformity. Subsequently, predetermined quantities of Al-10Ce master alloy, Al-10Er master alloy, C_2Cl_6 (hexachloroethane), and A-700R refining agent (Japan) were sequentially introduced into the melt according to the specified mass ratios. After thorough stirring and slag removal, the melt was poured into two identical pure titanium crucibles (A, B) preheated above 200°C, with a pouring temperature of 700°C. Crucible A underwent natural solidification under ambient atmospheric conditions, while Crucible B was solidified using reduced pressure treatment (RPT). After complete solidification and cooling of both ingot groups, the density values were measured separately for each group using Archimedes' principle with a density balance. Based on the density variation characteristics induced by the two distinct solidification processes, this study introduces the Density Index (*Di*) as an evaluation metric. The *Di* can be calculated from the atmospheric-solidified ingot density (D_{atm}) and the RPT ingot density (D_v) using the following formula [6]:

$$D_i = \frac{D_{atm} - D_v}{D_{atm}} \times 100\% \qquad (1)$$

In the formula:

Di: Density Index of the ingot (%);

D_{atm}: Density of the atmospheric-solidified ingot (g/cm³);

D_v: Density of the ingot solidified under Reduced Pressure Treatment (RPT) (g/cm³).

The post-experiment metal ingots were longitudinally sectioned, with specimens undergoing coarse grinding with abrasive paper followed by mechanical polishing. Subsequent etching with Keller's reagent (comprising 2.5 mL HNO_3, 1.5 mL HCl, 1 mL HF, and 95 mL H_2O) enabled concurrent observation of macrography and microstructural features.

Table 1. The chemical composition ratio of M174 cast heat-resistant aluminum alloy

Alloy grade	Chemical composition (wt.%), with a margin of Al					
	Si	Cu	Mg	Ni	Fe	Mn
M174	12	4.0	0.6	2.0	0.7	0.3

3 Results and discussion

3.1 The influence of rare earth element addition amount on degassing

Table 2 presents the ingot densities and corresponding density indices under gradient additions of Ce, Er, C_2Cl_6, and A-700R refiners, processed using conventional solidification and Reduced Pressure Treatment (RPT) techniques.

As shown in Figure. 1 , he relationship between addition levels and density index is presented under gradient additions of two rare earth elements, C_2Cl_6, and A-700R refiners. As indicated by Equation (1), increased gas content in the ingot leads to greater density differentials between atmospherically solidified ingots (D_{atm}) and those processed via Reduced Pressure Treatment (D_v), thereby elevating the density index. Conversely, reduced gas content corresponds to lower density index values. The addition of rare earth elements demonstrates superior effectiveness in reducing the density index compared with refining methods using C_2Cl_6 and A-700R refiners, confirming that rare earth additions effectively decrease porosity while enhancing casting quality in heat-resistant aluminum alloys.

Table 2. The density and density index of ingots under different refining methods

Refining Methods	Density &density index	Addition Level (wt.%)		
		0.1	0.3	0.5
Ce	Atmospheric solidification (g/cm³)	2.6850	2.7345	2.7090
	RPT (g/cm³)	2.3745	2.3753	2.2125
	D_i	0.1156	0.1314	0.1833
Er	Atmospheric solidification (g/cm³)	2.6713	2.6667	2.6421
	RPT (g/cm³)	2.2831	2.3809	2.3519
	D_i	0.1453	0.1072	0.1099
C_2Cl_6	Atmospheric solidification (g/cm³)	2.6989	2.6906	2.7014
	RPT (g/cm³)	1.9843	2.2491	2.2624
	D_i	0.2648	0.1641	0.1625
A-700R refiners	Atmospheric solidification (g/cm³)	2.6707	2.6709	2.7086
	RPT (g/cm³)	2.1271	1.8003	2.1603
	D_i	0.2035	0.3260	0.2024

The density index of the ingot reached its minimum value of 10.72% when 0.3% Er was added. Compared with ingots refined with 0.5% C_2Cl_6, the degassing efficiency increased by 34.03%, and compared with those treated with 0.5% A-700R refiner, the improvement was 47.04%. Further increasing the Er content resulted in only a marginal rise in the density index, indicating that no additional enhancement in degassing efficiency was achieved. In contrast, when Ce was introduced into the heat-resistant aluminum alloy melt, the density index increased with higher Ce additions. The lowest density index (11.56%) was observed at 0.1% Ce, corresponding to a 28.86% improvement over 0.5% C_2Cl_6 and a 42.89% improvement over 0.5% A-700R refiner. However, further increases in Ce content led to a gradual decline in degassing efficiency.

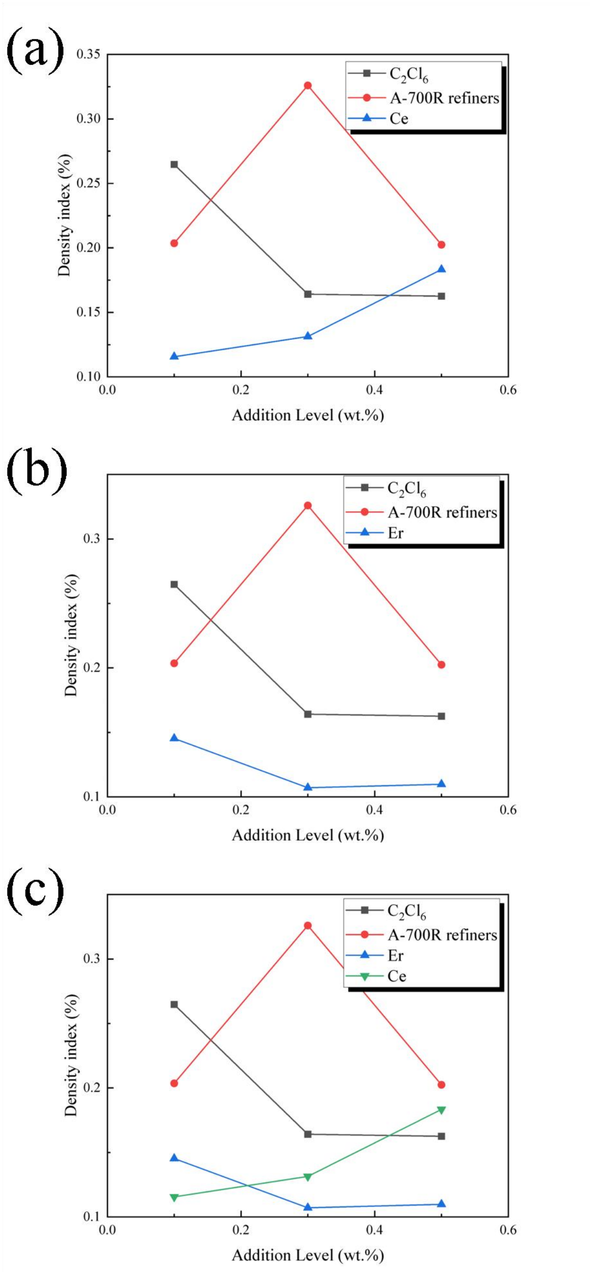

Fig. 1 Variation of density index in ingots under different refining methods

3.2 Macroscopic pore morphology and microstructural analysis

Figure 2 presents the macroscopic pore morphology of heat-resistant aluminum alloy ingots obtained under different refining methods. It can be seen that both pores and shrinkage cavities exist simultaneously inside the ingot. The gas pores are primarily concentrated in the upper region near the solidification interface； pores located closer to the melt surface exhibit larger dimensions, more spherical morphology, and smoother internal surfaces. Shrinkage porosity primarily concentrates in the ingot core region, exhibiting finer dimensions, rough internal surfaces, and highly irregular morphology. The wide solidification range of heat-resistant aluminum alloys promotes hydrogen enrichment at the solid-liquid interface, facilitating bubble nucleation. Under slow solidification rates, bubbles have sufficient time for growth and entrapment. As shown in Figures 2(a) and 2(b), the large, spherical pores near the solidification interface represent entrapped gas bubbles. The pure titanium crucible employed in experiments provided rapid cooling rates, resulting in typical shrinkage porosity as demonstrated in Figure 2(d). Figure 2(c) reveals composite pores characterized by: Elongated elliptical cross-sections, Larger dimensions, Irregular geometry, Rough internal surfaces. These features indicate combined hydrogen-induced and shrinkage-type porosity.

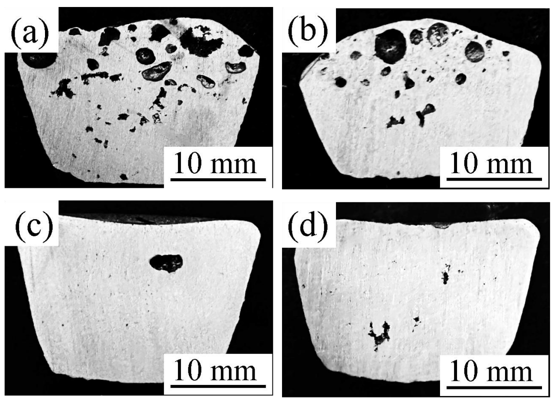

Fig. 2 Macroscopic pore morphology in heat-resistant aluminum alloy ingots:(a) Macroscopic pore morphology of ingot with 0.3% A-700R refiner addition; (b) Macroscopic pore morphology of ingot with 0.1% C_2Cl_6 addition; (c) Macroscopic pore morphology of ingot with 0.1% rare earth Ce addition; (d) Macroscopic pore morphology of ingot with 0.3% rare earth Er addition.

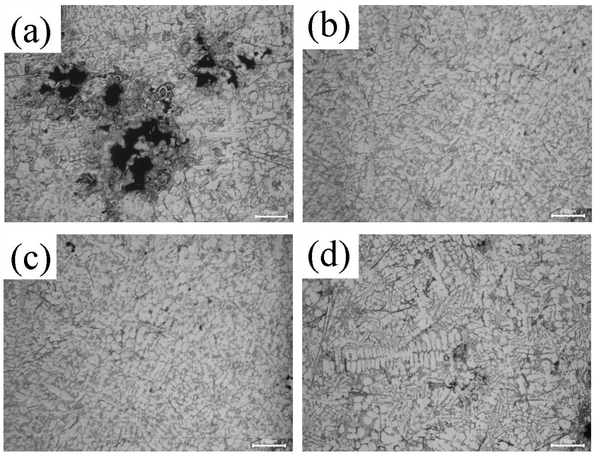

Fig. 3 Microstructure of heat-resistant aluminum alloy ingots :(a) Microstructure near pores in ingot with 0.1% Ce addition; (b) Microstructure of ingot with 0.3% Er addition; (c) Microstructure of ingot with 0.1% Ce addition; (d) Microstructure of ingot with 0.5% A-700R refiner addition.

Figure 3 presents the microstructures of heat-resistant aluminum alloy ingots processed with different refining methods. As shown in Figure 3(d), the gray continuous matrix corresponds to the α-Al phase, exhibiting typical dendritic casting morphology. The eutectic silicon phase appears as lamellar or needle-like structures, forming a network within the α-Al matrix. Dark intergranular regions represent porosity defects, potentially consisting of interdendritic shrinkage or reactive gas pores (resulting from reactions between rare earth elements and oxygen/sulfur in the melt). Figures 3(b) and 3(c) display the microstructures of alloys with rare earth elements Er and Ce addition, respectively. Compared with the A-700R-refined ingot, rare earth-addition alloys demonstrate: Finer α -Al grains; Eutectic silicon appearing as short fibers or particles rather than the characteristic coarse plates/needles of Al-Si alloys[5]; Uniform dispersion of secondary phases and intermetallic compounds. Figure 3(a) reveals clustered dark regions of porosity defects. The adjacent microstructure shows: Relatively refined grain structure; Fine eutectic silicon phases distributed in the α-Al matrix.

Rare earth elements adsorb hydrogen and impurity elements[2], forming finely dispersed composite phases distributed along grain boundaries and eutectic silicon surfaces. This reduces the growth anisotropy of eutectic silicon, decreases grain growth rates, inhibits coarse phase formation, and refines the as-cast microstructure.

3.3 Discussion on influencing mechanisms

Aluminum melts readily absorb hydrogen from the environment at elevated temperatures. However, as the melt temperature decreases, hydrogen solubility in aluminum declines rapidly[2]. During cooling to lower temperatures, the dissolved hydrogen precipitates, forming hydrogen pores within the casting.

Rare earth elements, as typical metals, exhibit chemical reactivity second only to alkali and alkaline earth metals, demonstrating significantly higher activity than other metallic elements[2]. These rare earth metals react with hydrogen dissolved in the melt to form stable rare earth hydrides[2], as represented by the following reaction:

$$2RE+3H_2 \xrightarrow{\Delta} 2REH_3 \qquad (2)$$

The formed rare earth hydrides immobilize hydrogen within the alloy, reducing hydrogen precipitation and suppressing hydrogen pore formation.

Rare earth elements can also modify aluminum melt oxide inclusions (primarily Al_2O_3) into more stable rare earth oxides or complexes through reduction and displacement reactions. The typical reaction between rare earth elements and Al_2O_3 is as follows[2]:

$$2Ce+Al_2O_3 \rightarrow 2CeAl0_3 \qquad (3)$$

$$CeAlO_3+O_2 \rightarrow 2Ce_2O_2S \cdot Al_2O_3 \qquad (4)$$

Rare earth Ce directly reacts with oxide inclusions to form cerium aluminate, disrupting the dense structure of Al_2O_3 and reducing oxide film size. The cerium aluminate further oxidizes to generate Ce_2O_3-Al_2O_3 complexes, which combine with impurity sulfur (S) in the aluminum melt to form $Ce_2O_2S \cdot Al_2O_3$ composite inclusions. With the refinement of oxide inclusion structures, their hydrogen adsorption capacity decreases, the hydrogen lens structure[7] is disrupted, further reducing porosity and improving the density of the ingot.

The addition of rare earth elements to cast heat-resistant aluminum alloys leads to their adsorption on the surface of eutectic silicon[4-5], reducing its growth anisotropy. This promotes the transformation of coarse plate-like eutectic silicon into fine spherical or fibrous morphologies, while significantly decreasing the size of primary silicon particles. Concurrently, the typical dendritic α-Al phase transitions into finer rod-like structures. The alloy microstructure is effectively refined, melt viscosity is reduced, facilitating bubble movement within the melt, promoting gas escape, decreasing porosity defects, and improving the uniformity of the as-cast structure.

4 Conclusions

- T The experimental results demonstrate that the addition of rare earth elements (Ce, Er) effectively enhances degassing. When 0.3% Er is introduced into the heat-resistant aluminum alloy melt, the density index of the ingot reaches its minimum value of 0.1072 , indicating optimal degassing efficiency .
- Rare earth elements (Ce, Er) react with impurity elements such as hydrogen and oxygen entrained in the alloy, forming stable rare earth compounds. The hydrogen content and oxide inclusions are significantly reduced, the density of the microstructure is increased, and superior casting quality is obtained.
- The addition of rare earth elements to cast heat-resistant aluminum alloys effectively refines the grain structure. In the refined microstructure, hydrogen bubbles exhibit enhanced mobility and are more readily released from the melt, thereby reducing the formation of gas porosity defects.

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Conflicts of interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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