Chapter 4

Castability and Characteristics of High Cerium Aluminum Alloys

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Abstract

This chapter describes the development and the castability of near eutectic aluminum-cerium (Al-Ce) alloy systems. These alloys have good mechanical properties at high temperatures and are very castable. The castability of the binary systems is as good or better than the aluminum-silicon system with some deterioration as additional alloying elements are added. In alloy systems that use cerium in combination with common aluminum alloying elements such as silicon, magnesium, and/or copper, the casting characteristics are generally better than the aluminum-copper system. Alloying with magnesium increases room temperature strength considerably.

Keywords: aluminum, high-temperature alloys, intermetallic, cerium, casting alloys

1. Introduction

Recent research and development work has shown that cerium containing binary Al-Ce and ternary Al-Ce-Mg alloys have the potential to be used for high-temperature use in a number of automotive components [1–3]. In the 1980s, it was shown that powder metallurgy (hot pressing and forging) can be used to produce an Al-4 wt% Ce alloy component that had high-temperature mechanical properties (300 MPa at 230°C) that exceeded the best aluminum commercial aluminum casting alloys [4]. Microstructure and mechanical properties of Al-Ce-Ni alloys containing up to 16 wt% Ce and 8 wt% Ni had been studied by Belov et al. [5]. Shikun et al. reviewed the effect of Ce additions up to 4 wt% on the solidification range, solidification volume change, and cast microstructure [6]. New development work has taken place since 2010 in the Al-Ce system because of a potentially large impact on the economics of rare earth mining if large amounts of cerium could be consumed. A significant amount of data on solidification characteristics and mechanical properties of Al-Ce alloys followed by prototyping to demonstrate the castability of the alloys has been completed [1–3]. While some investigation of thermal treatments is described here, the alloys generally do not require thermal treatment. The alloys are primarily solid solution and intermetallic strengthened and do not require heat treatment to develop properties. Homogenization has proved to be beneficial in some alloys.

2. Casting characteristics

Figure 1 shows a Thermo-Calc calculated Al-Ce phase diagram [2]. It has a eutectic composition at about 10 wt% Ce with a eutectic temperature of 640°C. Hypo- and hyper-eutectic alloys contain the intermetallic compound Al_{11} Ce_3. Sims et al. focused on Al-12Ce, Al-12Ce-0.4 Mg, and Al-12Ce-4Si-0.4 Mg alloys and evaluated their castability, microstructure, and mechanical and physical properties [1]. Test bars were given the T6 heat treatment (8 h at 537°C, water quenched and then artificially aged at 155°C for 3 h). Castability of the Al-12Ce alloy met or exceeded the castability of commercial Al-Si casting alloys. Addition of 0.4% Mg had no adverse effect on casting castability. However, addition of 4 wt% silicon greatly inhibits the fluidity of the alloy. Influence of lower amount of Si on castability has not been evaluated. No hot tearing was observed when cast into a 6-arm hot tear mold. SEM images of the three alloys are shown in **Figure 2** in both as-cast and heat-treated conditions together with XRD data for phase analysis. **Figure 2a** shows the FCC aluminum (gray) and the intermetallic Al_{11} Ce_3 (white), which has an orthorhombic crystal structure. Although this is a hyper-eutectic alloy, no primary crystallization is observed. Heat treatment modified the cast microstructure containing interconnected lath-like structure to particle-like structure. Microstructure of the Al-12Ce-0.4 Mg alloy shows additional primary crystals of cubic Al_3Mg_2 phase in the as-cast condition, as shown in **Figure 2b**. Microstructural modification of the ternary alloy is similar to that of the binary alloy after heat treatment. The as-cast microstructure of the quaternary Al-12Ce-4Si-0.4 Mg alloy is characterized by the FCC aluminum and the intermetallic Al_{11} Ce_3

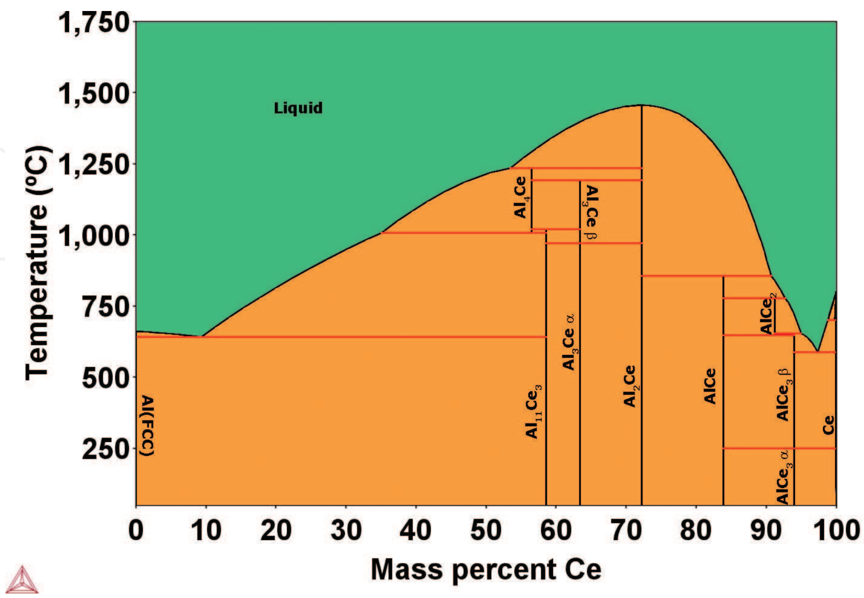

Figure 1. Thermo-Calc calculated Al-Ce phase diagram.

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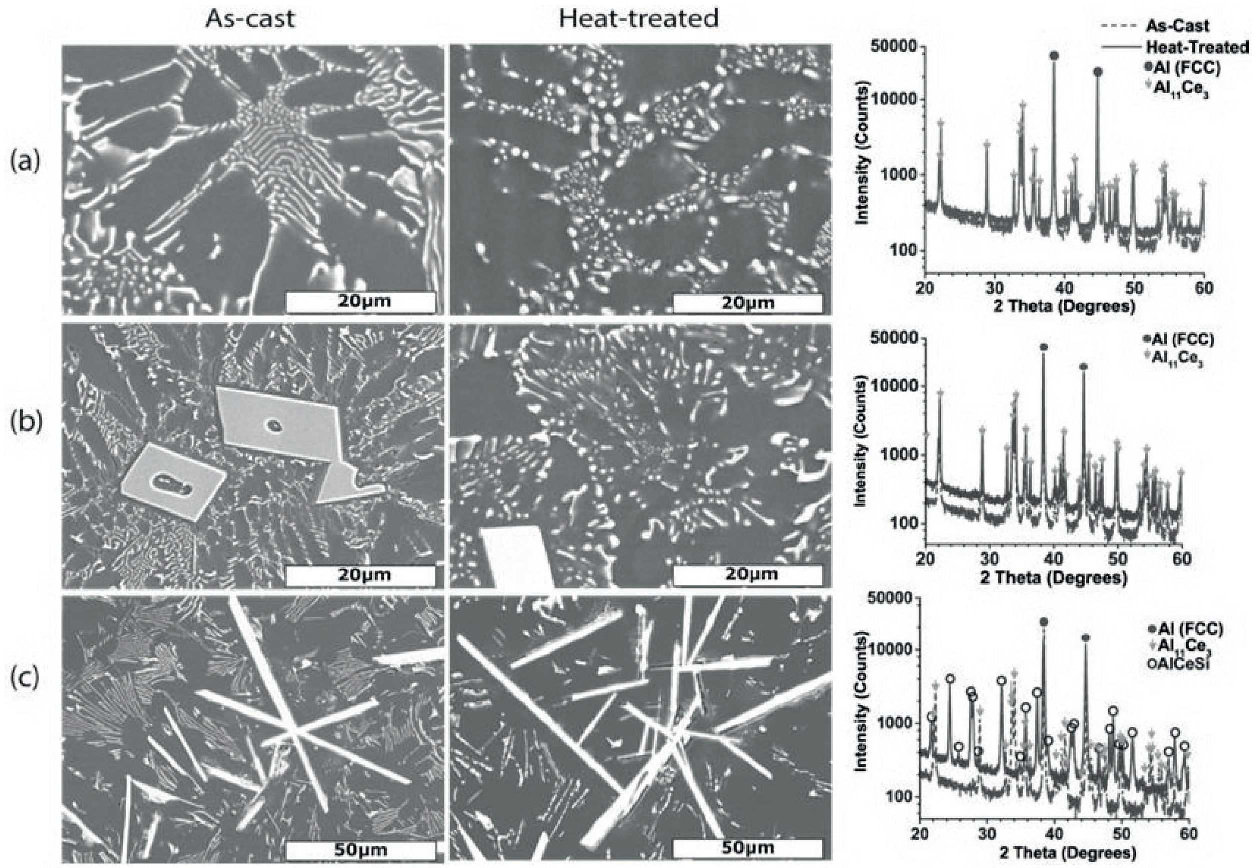

Figure 2. (a) As-cast and heat-treated SEM images of Al-12Ce with accompanying XRD spectra and phase information. (b) As-cast and heat-treated SEM images of Al-12Ce-0.4 Mg with accompanying XRD spectra and phase information. (c) As-cast and heat-treated SEM images of Al-12Ce-4Si-0.4 Mg with accompanying XRD spectra and phase information.

since Si remains in solid solution, **Figure 2c**. However, the $Al_{11}Ce_3$ shows both primary and eutectic solidification in the as-cast state. A new phase, intermetallic AlCeSi phase appears after T6 heat treatment.

3. Mechanical properties

Room temperature mechanical properties of these binary, ternary, and quaternary alloys are summarized in **Table 1** for the as-cast and heat-treated conditions. The ductility of the binary Al12Ce alloy is high despite the presence of the intermetallic phase $Al_{11}Ce_{3.}$ UTS and yield strengths are decreased after heat treatment; but the ductility has doubled. There is marked

	As-Cast				T6 Heat Treated		
Alloy	UTS (MPa)	Yield (MPa)	Yield (4 point flexural testing)	Elongation(%)	UTS (Mpa)	Yield (Mpa)	Elongation (%)
Al-12Ce	161	57	82	13.5	131	47	26.5
Al-12Ce-0.4Mg	200	78	106	6	224	62	8.5
Al-12Ce-4Si-0.4Mg	141	75	155	2	252	128	8.5

Table 1. Room temperature mechanical properties (MPa) for Al-Ce alloys.

increase in UTS and yield strength of the ternary Al12Ce-0.4 Mg alloy over the binary alloy due to the dispersion of the Al_3Mg_2 particles in the aluminum matrix. However, the elongation is reduced by more than 50%. The decrease in elongation may be due to the presence of the large primary Al_3Mg_2crystals. Heat treatment reduces the yield strength, although there is some increase in the ductility. The quaternary Al-12Ce-4Si-0.4 Mg alloy has relatively low UTS and elongation in comparison with the binary and ternary alloys. However, its response to T6 heat treatment is similar to AlSiMg alloys, which are strengthened by the formation and precipitation of Mg_2Si. In the heat-treated condition, this alloy had the best tensile strength of the initial group of alloys tested.

Weiss and Rios determined the mechanical properties of five binary Al-Ce alloys containing 6, 8, 10, 12, and 16% Ce by using the ASTM B108 test bar mold for permanent mold casting [2]. Among these five alloys, the first two belong to the hypoeutectic group, the last two to the hypereutectic group, and the 10% Ce alloy has the eutectic composition. Mold filling was influenced by the Ce content. The hypoeutectic and eutectic alloys filled the mold cavity completely at 750°C pouring temperature and 400°C mold temperature. Mold filling became difficult with further increases in Ce content. At 12% Ce, metal temperature was increased by 25°C to fill the mold cavity. This mold filling behavior is similar to binary Al-Si alloys. At 16% Ce, the mold did not fill completely. Optical micrographs for hypoeutectic Al-6Ce and hypereutectic Al-16Ce are given in **Figures 3** and **4**. The presence of large crystals of the intermetallic $Al_{11}Ce_3$ phase is evident in the Al-16Ce alloy microstructure. By contrast, a very fine interconnected eutectic microstructure is evident for the hypo-eutectic Al-6 alloy.

As-cast mechanical properties of the five binary Al-Ce alloys (hypoeutectic, eutectic, and hypereutectic) are reported in **Table 2**, together with those for the Al-5Si type alloy 443. The room temperature mechanical properties were not high enough for many commercial applications. They also did not have a positive response to the T6 heat treatment. In order to evaluate the effect of other alloying elements on the mechanical properties of binary Al-8Ce alloys,

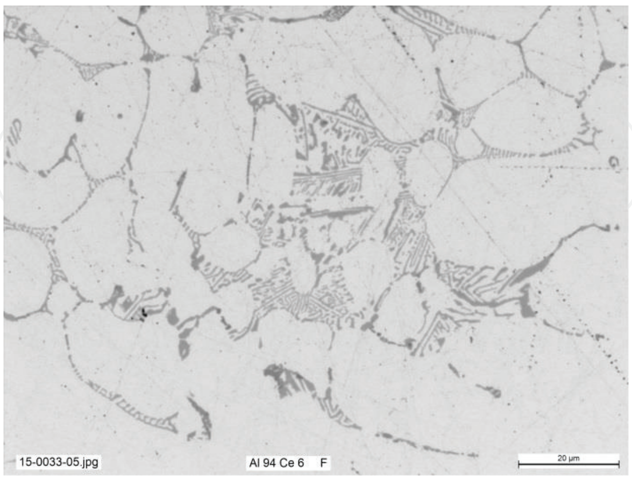

Figure 3. As-cast microstructure of Al-6Ce.

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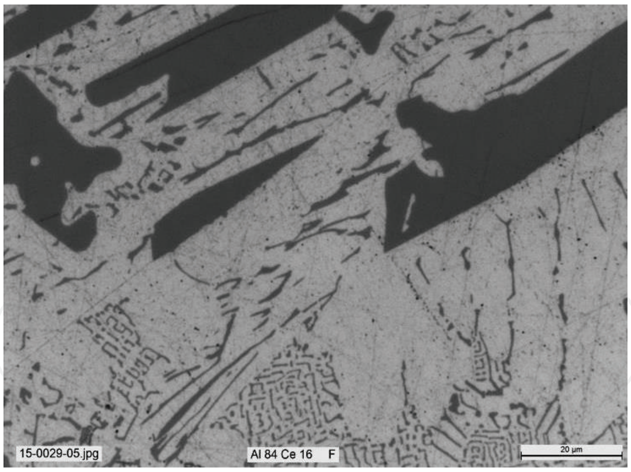

Figure 4. As-cast microstructure of Al-16Ce.

	Tensile, as Cast	Yield, as Cast	% E, as Cast
Al-16Ce	144	68	2.5
Al-12Ce	163	58	13.5
Al-10Ce	152	Test Error	8
Al-8Ce	148	Test Error	19
Al-6Ce	103	30	25
443 (Al-5Si)	145	40	2.5

Table 2. As-cast mechanical properties (MPa) of binary compositions in the Al-Ce system.

	Tensile	Yield	% E
Al-8Ce-4 Mg	189	107	3
Al-8Ce-7 Mg	195	151	2
Al-8Ce-10 Mg	227	186	1

Table 3. As-cast mechanical properties (MPa) of ternary compositions in the Al-Ce system.

	Temp	Time (h)	Tensile	Yield	% E	
Al-8Ce-10 Mg	260°C	0.5	137	130	4	
	260°C	336	137	97	5	
	315°C	0.5	97	55	20	
	315°C	216	172	159	1	Tested at 25°C
	260°C	336	159	138	1	Tested at 25°C

Table 4. Elevated temperature properties (MPa) of Al-8Ce-10 Mg.

another 20 alloys containing Si, Mg, Cu, Zn, Ni, Ti, Mn, or Fe were prepared. However, the mold filling capability was reduced for all alloys when added in excess of 1 wt%, except with Mg, even though many of the alloys had improved mechanical properties. The yield strength increased and percentage of elongation decreased with increasing Mg contents for the ternary Al-Ce-Mg alloys (**Table 3**). Mold filling ability remained unaffected. Extensive high-temperature mechanical testing has been carried out. The data shown in **Table 4** are the average of six test bars.

It was noted that room temperature properties were better after long-term exposure at 315°C than at 260°C. This indicates some positive effects from long-term exposure at high temperatures. Thermal treatments have been investigated to improve room temperature mechanical properties.

4. Thermal treatment

Generally, the Al-Ce-Mg alloys are not heat treated. However, at high levels of Mg, there was microstructural evidence of magnesium pools that were not fully dissolved in the matrix (**Figure 5**). Depending on the amount of segregation present, traditional heat treatments were either not effective or resulted in incipient melting of magnesium aluminum phases. A stepped thermal treatment has been developed that homogenizes the alloy through the dissolution of these segregated aluminum pools (**Figure 6**). For the Al-8Ce-10 Mg, this results in a significant increase in elongation with a 10% increase in tensile and yield strength (**Table 5**).

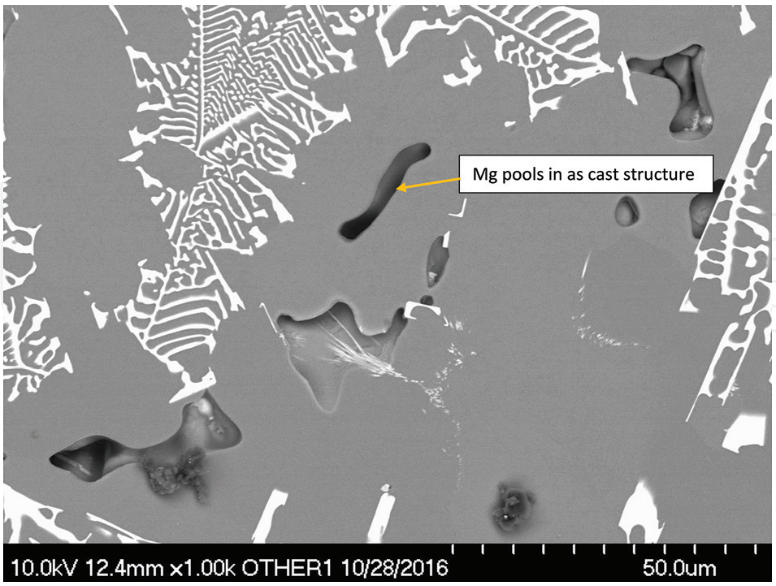

Figure 5. Undissolved magnesium pools in Al-8Ce-10 Mg.

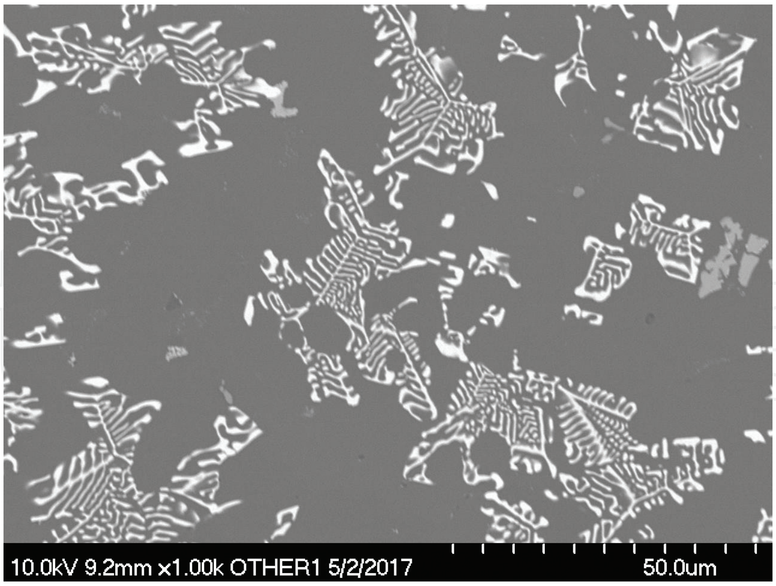

Figure 6. Same sample as shown in **Figure 5** after stepped homogenization treatment.

	Tensile	Yield	% E
As Cast	227 MPa	186 MPa	1%
-T4	248 MPa	199 MPa	2%

Table 5. Comparison of properties in as-cast with T4 condition (Al-8Ce-10 Mg).

5. Prototyping and production

Considering the good castability and good mechanical properties of the Al-Ce and Al-Ce-Mg alloys, commercial castings such as air-cooled cylinder heads (**Figure 7**) and cylinder heads and rotary engine rotors (**Figure 8**) were prototyped. Extensive work has been done by Oak Ridge National Laboratory by using neutron scattering to measure microstructural changes in an Al-Ce cylinder head in an operating engine. **Figure 9** shows the operating setup. SNS pulsed neutron diffraction of alloy showed that load was borne mainly by the Ce_3Al_{11} intermetallic phase. Parts currently in production in Al-Ce alloys include high performance impeller blades and pistons (**Figure 10**).

6. Applications of high cerium aluminum alloys

Early applications of AlCe alloys have focused on two different areas. The first has been complicated thin wall castings and airfoils that require moderate room temperature properties without heat treating. Most heat-treating processes for aluminum require a water

Figure 7. An air-cooled cylinder head cast in Al-8Ce alloy.

Figure 8. Experimental rotary engine rotor produced in chemically bonded sand with an Al-Ce-Mg alloy.

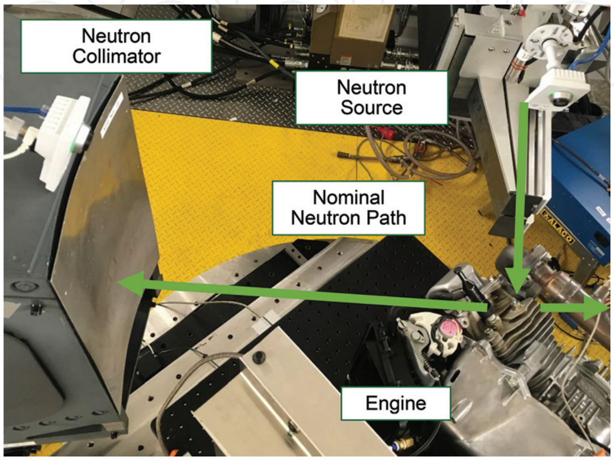

Figure 9. Setup for operating engine neutron scattering experiment.

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Figure 10. High performance pistons produced from various formulations of Al-Ce alloys.

quench where significant distortion can occur. This distortion then needs to be corrected by a straightening operation, which can be time consuming and risks damage to the casting. The rapid quench can also induce residual stress into the casting, which reduces its performance or causes difficulty for machining. The second group of applications focuses on high temperature products that operate above the aging temperatures of standard aluminum alloys of about 150°C. These applications include turbocharger components, cylinder heads and pistons.

7. Future prospects of Al-Ce alloys

The basic Al-Ce binary system is a new template for alloy development that is similar in many respects to the Al-Si system. The castability is comparable, and like Si, Ce can form many varieties of potentially useful strengthening structures. Other alloying elements can be used to enhance the performance for specific applications. The roll of transition metals in the improvement of the Al-Ce system is being actively investigated. The impact of other elements, such as Zn, for solid solution strengthening is under development. The lack of solubility, diffusion, or coarsening of the $Al_{11}Ce_3$ intermetallic up to the melting point of the alloy suggests the possibility of a large family of lightweight alloys that demonstrates superior mechanical properties from room temperature up to 500°C.

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