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Composites and Alloys Based on the Al-Ce System

David Weiss

Abstract

Aluminum alloys containing small amounts of cerium have been investigated to improve the grain refining, casting characteristics, and mechanical properties of aluminum alloys. These additions were usually made at levels of 1% or less but did not produce appreciable improvements. Recent work has shown that additions between 4% and the approximate eutectic composition of 10% improve the high-temperature performance of aluminum alloys. Corrosion performance of aluminum alloys can also be improved through the addition of Ce. Traditional aluminum alloying elements such as magnesium and silicon can be used to control casting characteristics and thermal and physical properties. Cerium oxide is the predominate oxide in rare earth mining. Much of it is discarded after separation from the heavy rare earth oxides containing Nd and Dy. The beneficial use of Ce should reduce the cost of the more desirable rare earths. Results of using Ce as an addition to aluminum in multiple manufacturing methods such as additive manufacturing, extrusion, and casting are explored. The results show significant strengthening and improved mechanical property retention at higher temperatures than in other aluminum alloys and, in some compositions, show complete recovery of mechanical properties at room temperature when exposed to elevated temperatures as high as 500°C for 1000 hours.

Keywords: aluminum-cerium alloys, aluminum-cerium composites, casting, extrusion, additive manufacturing

1. Introduction

Auto manufacturers are under commercial and regulatory pressure to improve engine efficiency. Potential solutions include direct fuel injection, higher compression ratios, and turbochargers. All these solutions can cause higher operating temperatures and pressures. Al-Si-Mg or Al-Si-Cu-Mg alloys, typically solution treated and aged, are used for automotive products because of their good mechanical properties at room temperature and easy processing. However, these alloys rapidly lose strength above their aging temperature, typically around 155°C. For engines to be able to operate between 180 and 300°C, a different paradigm for alloy design is needed. The requirement for high-temperature lightweight alloys is not restricted to automobile components. Aerospace and military sectors, as well as commercial sectors such as trucking and industrial equipment, all require alloys that meet the increased demands of new fuel-efficient designs.

Several strategies have been employed to improve the performance characteristics of aluminum alloys. The addition of Cu generally improves both room temperature and high-temperature strength, although there can be an impact on corrosion

because of a greater change in electrode potential with variations in the amount of copper in solid solution and the presence of nonuniformities in solid solution concentration [1]. The addition of transition metals such as Zr, Mn, and V is being used to stabilize the precipitates in alloys of the Al-Cu-Mg and Al-Si-Mg system. Many types of metal matrix composites have been developed that will generally improve modulus, yield strength, and elevated temperature properties although the composites are generally less ductile and are more difficult to process.

Cerium addition can improve the performance characteristics of both solid-solution-strengthened and precipitation-strengthened aluminum alloys, particularly at elevated temperatures.

2. Background and history

Mondolfo [2] reviewed the aluminum-cerium and the aluminum-cerium-iron system and reported that small additions of Ce do not produce appreciable improvements and that the alloys did not have a wide application. He reported that a eutectic is formed with 13% Ce at 638°C. In a later work [3], he reported that an increase of strength without loss of conductivity and improved machinability had been claimed for cerium additions to aluminum alloys. He referenced sources that claimed an Al-CeAl₄ eutectic at approximately 12% Ce.

An analysis of the Al-Ce-Fe system produced via powder metallurgy showed extraordinary strengths in an Al-8Fe-4Ce alloy at temperatures up to 343°C [4]. There was no documented attempt to cast these materials.

There has been some experimental work to use Ce as a component of cast aluminum alloys. Shikun [5, 6] reviewed the effect of cerium additions on the cast microstructure and solidification range of an Al-4.5Cu alloy. He concluded that the addition of cerium improved castability but the mechanical properties were not studied. Belov [7] explored Ce for the development of creep-resistant aluminum alloys in combination with transition metals such as Zr, Mn, Cr, Fe, and Ni. Later [8], Belov focused on the Al-Ce-Ni system. He concluded that alloys of the Al-Ce-Ni ternary eutectic system had high mechanical properties at room and elevated temperatures along with good casting characteristics.

Al-Si alloys are the most important Al-based foundry alloys. They have good mechanical properties, narrow solidification ranges, and good fluidity. Gröbner [9] considered aluminum alloys containing up to 25 at.% Ce and 45 at.% Si and studied several Al-Ce-Si systems where the aluminum was held at a constant 90 at.% and the concentrations of Ce and Si varied between 0 and 10%. He showed that small Ce additions could provide high-temperature stable AlCeSi phases in equilibrium with Al-Si-rich melt. He concluded that Ce between 1 and 5 at.% could be used as a grain refiner.

The development of Al-Ce casting alloys is driven by the increasing demands for high-temperature-tolerant aluminum alloys and the use for the excess cerium that was available as a by-product of the production of the heavy rare earths.

3. Metallurgical aspects of the Al-Ce system

The equilibrium diagram, Ce-Al crystal structure data, and Ce-Al lattice parameter data were reviewed in 1988 [10], and a eutectic composition of Al and Al₁₁Ce₃ was shown at 4 at.% Ce at 640°C. This reference confirms the Al-rich compound had previously been incorrectly identified as Al-CeAl₄. Recently calculated Thermo-Calc data predicted a eutectic of Al₁₁Ce₃ at 580°C at 10 wt.% [2.09 at.%] [11].

Typical microstructures of the Al-Ce binary composition are shown in **Figure 1** [12]. The as-cast microstructures show a very fine interconnected $\text{Al}_{11}\text{Ce}_3$ eutectic microstructure in a pure aluminum phase. The intermetallic can be as small as 50 nm wide at permanent mold cooling rates. These structures are stable up to the melting point of the aluminum phase. The intermetallics cannot dissolve since Ce has extremely low solubility in the aluminum matrix. A solubility diagram for the binary Al-Ce system is shown in **Figure 2**. Yield strength retention is about three times conventional alloys when tested at 300°C. When Ce is used with solid solution strengthening elements such as Mg or Zn, room temperature properties remain stable regardless of exposure times with exposure temperatures up to 400°C. The data in **Figure 3** shows an actual increase in room temperature properties after exposure at 400°C. This is due to the homogenization of magnesium that is not uniformly distributed because of low and variable cooling rates in the cast structure. In solid-solution-strengthened alloys, there are no phases that dissolve or coarsen such as the Mg_2Si in 300 series alloys or the Al_2Cu in 200 series.

Load partitioning studies in compression conducted by Oak Ridge National Laboratory at their Vulcan Beam Line show unusual load sharing behavior between the matrix and the $\text{Al}_{11}\text{Ce}_3$ intermetallic. As illustrated in **Figure 4**, as the compressive stress increases, a higher proportion of that stress is transferred to the intermetallic. An extensive analysis of the strengthening mechanisms and microstructural analysis of the Al-Ce system can be found in Ref. [11].

Figure 1.
(A) As-cast microstructure of Al-Ce8 binary alloy. (B) Al-Ce8 binary showing sub-micron width laths.

Figure 2.
Ce solubility in aluminum.

Figure 3. Long-term exposure data of Al-Ce alloys measured at room temperature compared to some standard casting alloys.

Figure 4. Phase load sharing for Al-12Ce-0.4 Mg under compressive load. Shaded region denotes differences between binary and ternary alloy composition's mechanical response from Ref. [4].

4. Alloying element interactions

At room temperature, the $\text{Al}_{11}\text{Ce}_3$ intermetallic is not an effective strengthening mechanism. Mechanical properties for pure binary compositions are shown in **Table 1**. To develop reasonable room temperature strengths, other alloying elements such as Mg, Zn, Cu, Si, or others can be added along with Ce to strengthen the aluminum matrix. Sun [13] reported on a comprehensive study of 19 binary systems of Ce and 4d or 5d transition metals using high-throughput first-principles calculations. Understanding the reaction mechanics between Ce and other alloying

elements can be used to identify elements that could independently strengthen the aluminum matrix without interference from the Ce as well as those that form compounds with the Ce that can synergistically increase the strength or potentially immobilize elements required for strengthening during heat treatment.

In commercially pure aluminum, magnesium in solid solution gives a near-linear concentration dependence of strength at a given strain. The solid solution hardening is a result of an interaction between the mobile dislocations and the solute atoms [14]. In an Al-8Ce alloy, the addition of 10% magnesium increases the yield strength by over 300% from about 50 MPa to about 162 MPa. There is no evidence that the formation of some CeMg intermetallic is a significant factor in the strength increase, with the primary mechanism being the matrix strengthening by the magnesium.

The addition of copper to the alloy forms immobile Cu-Ce phases. This is illustrated in **Figure 5** using a 4.5% Cu alloy with the addition of 1 and 8% Ce. Most of the Cu is not free to strengthen the alloy since it is tied up with the Ce phase. On the other hand, the modification of the traditional grain boundary phases improves the hot tear resistance of the alloy and reduces intergranular corrosion. Additional Cu needs to be added to create “free Cu” that can participate in heat treat response. For copper-containing alloy such as A206 (**Figure 6**), the cerium acts as a diffusion barrier, preventing the formation of copper-depleted zones. In all alloys tested, the addition of small amounts of cerium increases their resistance to intergranular corrosion, as shown in **Figure 7**.

	Tensile MPa	Yield MPa	%E
Al-16Ce	144	68	2.5
Al-12Ce	163	58	13.5
Al-10Ce	152	50	8
Al-8Ce	148	40	19
Al-6Ce	103	30	25

Table 1.
Mechanical properties of Al-Ce binary alloys.

Figure 5.
As cerium addition moves from 0 to 8%, the cerium phase dominates grain boundary phases and restricts Cu diffusion.

The addition of scandium to Al-Ce alloys has been investigated [15]. At levels of 0.4% Sc, room temperature hardness levels increased by 20%, and room temperature hardness values after 300°C exposure for 100 hours increased by 60%. While the ternary Al-Ce-Sc had good thermal stability, the room temperature hardness values are not sufficient for structural castings. The addition of Mg at levels of up to 12.15% resulted in significant improvement in hardness at room and elevated temperatures.

Silicon as an alloying element in the Al-Ce system can be used to control the coefficient of thermal expansion, but the additions at higher levels cause several processing issues. While increasing the silicon in a binary composition with aluminum will reduce the solidification range up to the eutectic composition, the addition of Ce will increase that range which may make the alloy more difficult to feed in traditional casting applications. The solidification range of a standard Al7Si alloy is approximately 70°C. It was experimentally determined using thermal analysis that as the ratio of Ce to Si in an alloy is increased, the solidification range increases as

Figure 6.
The addition of Ce to Al-Cu alloys acts as a diffusion barrier by blocking grain boundary motion.

Figure 7.
ASTM G110-92(15) intergranular attack test; submerged in hydrogen peroxide with NaCl.

well. At a Ce/Si ratio of 3.16, the solidification range increases to 120°C. At a Ce/Si ratio of 0.46, that solidification range is reduced to 82°C. Generally, maintaining a Ce/Si ratio of about 0.5 results in an alloy with excellent castability. The Ce will also form CeSi phases making some of the Si unavailable for combining with Mg when added to form Mg₂Si strengthening precipitates. However, Si-rich alloys contain enough excess Si that the response to heat treatment is not affected.

5. Composite potential in Al-Ce alloys

In conventional hard particle-reinforced aluminum alloys, failure at elevated temperature can occur when the matrix softens and causes particle decoherence. Secondly, the aluminum loses stiffness at high temperature, minimizing the modulus improvement attempted by the introduction of high modulus particles. Alloys containing Ce retain a higher percentage of modulus at elevated temperatures. **Figure 8** shows the modulus retention of an Al₁₀Mg₈Ce-F alloy compared with 7075-T6.

Preliminary work has been completed using SiC and carbon nanotubes as reinforcement in AlCe and AlCeSi alloys as well as Al₂O₃ in AlCeMg alloys. The addition of 50 nm Al₂O₃ at reinforcement levels of about 0.1% results in a tensile strength improvement of 12%. As shown in **Figure 9**, a substantial number of particles are in the grain and are not exclusively pushed into the grain boundaries. Particles in the grain enhance Orowan strengthening by resisting dislocation passing in the presence of closely spaced hard particles. Whether this is directly due to the cerium content of the alloy or other processing techniques is unknown. More data and functional testing is required to fully understand the use of Al-Ce alloys as a composite matrix material.

6. Product forms

Much of the early work in the Al-Ce system concentrated on casting alloys. The casting characteristics of the binary Al-Ce systems are as good as the aluminum-silicon system but can change as additional alloying elements are added [16]. When other alloying elements are used such as silicon, magnesium,

Figure 8.
Comparison of room temperature and 350C modulus between Al₁₀Mg₈Ce-F and 7075-T6.

Figure 9.

Fifty nm alumina particles in a matrix of AlMg10Ce8 alloy. Large white particles are aluminum oxide formed during melt processing.

or copper, the solidification range is determined primarily by the secondary alloying elements. Standard systems for melting, degassing, and alloy cleaning of cast alloys can be used without modification for the conventional casting of aluminum-cerium alloys.

At solidification rates typical of castings in Ce alloys that contain more than 7% Mg, a homogenization heat treatment can be used to improve mechanical properties [17]. This treatment reduces the size and volume fraction of magnesium pools that can segregate in high magnesium alloys. The amount of cerium does not affect the segregation behavior. The alloys have been cast successfully in most traditional casting processes, such as sand, permanent mold, low pressure permanent, and die casting. **Figure 10** shows a cylinder head poured as a gravity casting showing the good fluidity of the alloy system.

Mechanical properties for the ternary Al-Ce-Mg system have been studied at both room and elevated temperatures (**Table 2**). The room temperature properties can be improved by both homogenization and hot isostatic pressing. One of the key attributes in the Al-Ce-Mg system is the recovery of mechanical properties at room temperature when exposed to elevated temperatures for prolonged periods of time. This alloy system does not contain any precipitates that become unstable after prolonged high-temperature exposure.

Extrusions have been produced for applications where improved high-temperature performance or resistance to corrosion is desired. In these alloys, extrusion improves the properties through a combination of work hardening and alignment of the intermetallic. Extrusions have been produced at 300°C billet temperature and at extrusion ratios of 5.75–1 and 52–1 from an Al10Mg8Ce alloy. A comparison of average permanent mold properties to extruded properties is shown in **Table 3**. As the extrusion ratio increases, tensile strength remains constant, with the elongation increasing and yield strength decreasing. The mechanical properties can be affected by the starting microstructure of the billet. Structural extrusions have also been produced as shown in **Figure 11**.

Figure 10.
Air cooled cylinder head poured from Al-Ce binary alloy.

	Temp	Time Hours		At Temp			At RT After Heating		
				Tensile	Yield	%E	Tensile	Yield	%E
Al-10Mg-8Ce	260C	0.5		137	131	4			
Al-10Mg-8Ce	260C	336		137	97	5	159	137	1
2618-T61	260C	0.5		90	62	50			
4032-T6	200C	0.5		90	62	30			
Al-10Mg-8Ce	315C	0.5		97	55	20			
2618-T61	315C	0.5		52	31	80			
4032-T6	300C	0.5		38	24	70			
Al-10Mg-8Ce	315C	216		94	56	13.8	172	159	1
Al-10Mg-8Ce	400C	120					218	191	1.5
Al-10Mg-8Ce	500C	500					252	185	3
Baseline Room Temperature Properties Al-10Mg-8Ce-F						Cast	228	186	1
						T4	248	200	2
						HIP	262	207	2
				2618-T61		Forged	380	290	4
				4032-T6		Forged	380	315	9
Tensile and Yield (Mpa)									
All Al-Ce properties as cast unless otherwise noted									

Table 2.
Room and elevated temperature properties of Al-10Mg-8Ce compared to common piston alloys.

	Tensile (Mpa)	Yield (Mpa)	%E
Extrusion 5:1	375	342	6
Extrusion 52:1	364	274	12
Permanent Mold	228	186	1

Table 3.
Comparison of extruded data at different extrusion ratios with cast Al₁₀Mg₈Ce.

Figure 11.
Structural extrusion produced for the marine industry.

The alloy system has been used for both the direct write and powder bed fusion. Manca [18] has reported high mechanical properties of Al-3Ce-7Cu in both high-temperature tension and compression testing via selective laser melting. Fine eutectic phases of $\text{Al}_{11}\text{Ce}_3$ and $\text{Al}_{6.5}\text{CeCu}_{6.5}$ were found in the microstructure. High hardness values were noted after annealing at 400°C due to the precipitation of nanosized particles. Kessler [19] used induction heated Al-Ce wire to take advantage of the inherent rheology of molten Al-Ce and the high enthalpy of fusion for the reactive Ce-containing intermetallic. This intermetallic phase enhances the surface energy and stabilizes the extruded filament, imparting shape stability and facilitating layer-to-layer joining.

7. Economics of Al-Ce alloys

As an alloying element used typically in the 1–10% weight range, cerium is relatively inexpensive. Its cost is in the range of \$4–5/lb. and is widely available. The as-alloyed cost of Al-Ce material is competitive with other high-performance aluminum alloy systems. Further cost reduction in Ce is enabled by direct metal-thermic reduction of cerium oxide. Luna [20] directly reduced the oxide on a laboratory scale in aluminum alloys containing between 0.5 and 4.0 wt.% Mg. This technique is now being developed on a commercial scale.

8. Conclusions

Aluminum-cerium alloys are being rapidly developed as alternatives to Al-Si and Al-Cu alloys. These alloys have good fabrication characteristics and excellent corrosion performance. The alloys have superior performance at elevated temperatures and long exposure times. The use of the least expensive of the rare earth elements and standard processing methods makes the transition to use Al-Ce alloys available for lightweight high-performance applications in the automotive, trucking, aerospace, and other industrial sectors.

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