Aluminum Cast Alloys Based on the Al–Ce–Si–Mg System: An Influence of Silicon on Crystallization, Phase Composition, and Tensile Properties

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An attempt at strengthening the aluminum-cerium-based alloys through additions of silicon was assessed using the experimental Al5Ce3Si0.5Mg (wt. pct) cast hypo-eutectic composition, designed based on the commercial A356 (Al–7Si–0.3Mg, wt. pct) grade by substituting a portion of Si with Ce. To determine a role of Si, the Al5Ce0.5Mg (wt. pct) reference was cast and tested under identical conditions. An addition of 3 wt. pct Si to the Al5Ce0.5Mg base increased the room temperature yield stress almost three times, from 47 to 135 MPa, but reduced its elongation by an order of magnitude from 8 pct to that below 1 pct. A presence of Si led also to essential changes in the alloy crystallization with the melting range widened substantially from 10 °C to 91 °C mainly due to a reduction in the solidus level. As-cast microstructure of the Al5Ce0.5Mg base consisting the primary α-Al along with 44 pct of the α-Al + Al11Ce3 eutectic was replaced in the Al5Ce3Si0.5Mg alloy with the α-Al + AlCeSi2 coarse lamellae ternary eutectic, bulky compounds having the Ce-rich core of AlCe2Si with external shell of Al2CeSi2 along with the quaternary eutectic of fine α-Al, Si, Al2MgSi/Al2Mg2Si, and Al–Si–Mg–Ce phases. The fractographic analysis revealed that additions of Si caused a transition from largely ductile fracture to the predominantly brittle mode with crack paths propagating mainly along the interface between the coarse AlCeSi2 lamellae and Al(Si, Mg) solid solution, which explains the measured drastic reduction in the alloy elongation.

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I. INTRODUCTION

To overcome the present barrier in development of cast aluminum alloys with high temperature capabilities, a novel eutectic with a superior thermal stability to the conventional Al–Si base is needed. Among alternatives, the Al–Ce system, containing the technologically important Al–Al\textsubscript{11}Ce\textsubscript{3} eutectic, is considered with anticipated advantages mainly due to very low solid-state diffusivity of cerium in aluminum\textsuperscript{[1]}. However, the cast Al–Ce binary alloys with a yield stress around 50 MPa, offer a limited strengthening that is insufficient for engineering applications\textsuperscript{[2]}.

A number of directions have been explored to improve the Al–Ce strengthening. Due to a negligible solid-state solubility of cerium in aluminum, alloying to generate precipitation hardening was exercised using highly effective Sc\textsuperscript{[3]}. Then, combined additions of Sc and Zr, e.g. 0.2 wt. pct Zr and 0.2 wt. pct Sc in the Al5Ce (wt. pct) matrix helped to reach the tensile strength of 211.5 MPa, yield stress of 156.5 MPa along with high elongation of 11 pct\textsuperscript{[4]}. As another attempt, refining the coarse eutectic and generating the nano- and sub-microcrystalline structures through liquid metal engineering in molten state\textsuperscript{[5]} or through high pressure torsion-deformation in solid state\textsuperscript{[6]} were used. In case of the latter, the Al9Ce (wt. pct) alloy deformed under high-pressure torsion increased the yield stress from 75 to 456 MPa and the ultimate tensile strength from 135 to 495 MPa, with an elongation remaining unchanged at about 18 pct\textsuperscript{[6]}. As a separate direction, the high solubility of Mg in Al, reaching 17.35 wt. pct, is explored through alloying with large contents of magnesium to generate the solid-solution strengthening. As an example, the near-eutectic Al11Ce7Mg (wt. pct) alloy produced via additive manufacturing reached at room temperature an average yield stress of 374 MPa and tensile strength of 384 MPa with elongation of about 1 pct\textsuperscript{[7]}.

A unique option was proposed through alloying of the Al–Ce binary system towards creating ternary or higher-order eutectics, containing high volumes of fine phases, which would lead to an increased strength. For instance, published examples of Al–Ce–Ni\textsuperscript{[8]} and Al–Ce–Cu\textsuperscript{[9]} are promising. This strengthening concept was investigated in this study through alloying the Al–Ce system with silicon. Although being the fast diffuser at increased temperatures, silicon is also very effective strengthenner of aluminum. Minor additions of magnesium were used to mainly promote solid solution strengthening although in a combination with silicon.
they produce a precipitation hardening effect and could potentially react with cerium. The experimental Al5Ce3Si0.5Mg (wt. pct) alloy was designed based on the commercial high-temperature A356 (Al–7Si–0.3Mg, wt pct) grade by substituting a portion of silicon with cerium. To determine the influence of silicon on microstructure, tensile properties and solidification characteristics, the silicon-free Al5Ce0.5Mg base was cast and tested under identical conditions.

II. EXPERIMENTAL DETAILS

A. Alloy Synthesis

The Al5Ce3Si0.5Mg and Al5Ce0.5Mg (wt. pct) alloys were cast in a pilot scale in-house foundry using a resistance furnace with a steel crucible coated with a mica wash under argon cover gas. The charge makeup with a weight of 15 kg comprised of 99.9 wt pct purity elemental ingredients. After melting, a liquid alloy was held at 780 °C to 800 °C for 0.5 h under intense mixing, followed by measurements and adjustments of the chemical composition. Next, the dross/oxide was removed from the melt surface and the crucible content was poured at 730 °C into a water cooled steel mold with internal dimensions of approximately 25 × 152 × 305 mm (1 × 6 × 12 inch), having an internal surface covered with boron nitride. Following solidification, the cerium concentration was determined by the Inductively Coupled Plasma (ICP) method in accordance with MCLM F-23C and BAERDG-GEN-018E specifications. The contents of remaining elements were measured by the Optical Emission Spectroscopy (OES). Detailed chemical compositions are listed in Table I.

B. Alloy Examination

The solidification characteristics of alloys were assessed using the Computer-Aided Cooling Curves Thermal Analysis (CCTA) associated with measurements by a Universal Metallurgical Simulator and Analyzer (UMSA).[10] During thermal analysis, controlled heating to 780 °C was performed at a rate of 0.4 °C/s, followed by isothermal holding at 780 °C for 5 min and natural cooling to 50 °C at a rate of 0.2 °C/s. Metallographic samples were prepared using the conventional procedures, starting from grinding to polishing. No etching was applied and as-polished surfaces were examined with an optical microscope Olympus BX534 and scanning electron microscope FEI Nova NanoSEM650. The transmission electron microscopy was conducted using FEI’s Tecnai Osiris TEM equipped with X-FEG gun at 200 keV. Specimens for TEM were prepared by grinding to a thickness of 100 μm, cutting discs with a diameter of 3 mm and ion milling. The STEM mode with bright field (BF) and high angle annular dark field (HAADF) detectors were employed in a combination with energy dispersive spectrometry (EDS). The EDS with the ESPRIT software, applying a deconvolution of overlapping peaks was used for mapping the elemental distribution. EDS acquisition was performed with all spectrum images having a size of 256 × 256 pixels and 2048 energy channels. Each spectrum image used a pixel size of 34 pm and a 0.01 keV/channel energy dispersion. A single frame spectrum image was acquired with a per pixel dwell time of 5 ms. The computational thermodynamic analysis of phase composition under equilibrium and non-equilibrium (Scheil) cooling conditions was conducted using the FactSage software with the FTlite database. The phase composition was measured using PANalytical X’Pert Pro X-ray diffractometer in the powder diffraction mode, equipped with copper sealed tube source radiation, λCuKα = 1.5418 Å. The data were collected with the PANalytical Data Collector software. The analysis was performed in Match! software using the crystallography open database (COD). The room temperature uniaxial tensile test was conducted in accordance to the ASTM E8 standard using rectangular samples machined from as-cast plates using the Instron tensile test machine (Model 5969, 50 KN) at the strain rate of 0.4 mm/min.

III. RESULTS

A. Al–Ce–Si Ternary Phase Diagram, FactSage Calculation of Alloy Phase Composition

A thermodynamic description of the ternary Al–Ce–Si phase diagram available in the literature[11,12] was developed using the CALPHAD method incorporating the limited experimental data. The computed isothermal section at 500 °C is shown in Figure I(a). According to this diagram, two three-phase equilibria exist in the Al-rich corner: (1) (Al) + Al11Ce3 + τ1 and (2) (Al) + τ1 + τ2, where τ1 is Ce(Si1-xAlx)2 being an extension of the binary phase CeSi2 into the ternary region with x = 0 to about 1 at high temperatures and x = 0.1–0.9 at 500 °C, and τ2 is AlCeSi2.

To determine the phase composition for the specific alloy chemistry used in this work, including small quantities of minor phases formed after solidification, the FactSage commercial software was used. Additional purpose of using the FactSage calculations was to estimate melting temperatures required during the alloy synthesis. FactSage uses the thermodynamics calculations to predict the solidification behavior of the alloys under equilibrium and Scheil cooling conditions. Since during casting and solidification experiments the cooling rate is high so that the diffusion does not happen uniformly in the solid material, which results in segregation what is an equivalent to the Scheil cooling condition in FactSage calculations. Under Scheil cooling conditions that assumes no diffusion in the solid but complete mixing in the liquid, as a result of solute rejection to the remaining liquid, the liquid metal saturates, causing decreasing the solidus temperature. Therefore, the solidification ends at lower temperature in comparison to the equilibrium condition. The
resulting microsegregation profiles and some phases predicted under Scheil cooling condition may not exist under equilibrium assumptions.

The FactSage calculated projection of the Al–Ce–Si diagram in Al rich corner at 500 °C is shown in Figure 1(b) and projection of the liquidus temperatures is shown in Figure 1(c). According to the FactSage calculations, the Al5Ce3Si0.5Mg alloy with the specific chemistry listed in Table I should reach the solidus at 547.75 °C. Phases predicted in the Al5Ce3Si0.5Mg alloy by FactSage from a Scheil solidification calculation with all available solution phases and pure solid phases enabled are listed in Table II. It is seen that the vast majority of alloy volume of 93.4 vol. pct represents aluminum solid solution with 0.51 at. pct (0.53 wt. pct) Si and 0.30 at. pct (0.27 wt. pct) Mg. A content of 0.0019 at. pct Ce indicates practically a lack of solid-state solubility of Ce in Al. The minority phases represent 5.59 vol. pct of AlCeSi along with 0.73 vol. pct Mg2Si and 0.25 vol. pct of Si.

B. X-Ray Diffraction Measurement of Phase Composition

The objective of X-ray diffraction was to determine the bulk phase composition of alloys, to verify a possible presence of metastable phases and to determine the eventual change in Al lattice parameter due to alloying. The X-ray diffraction pattern of the Al5Ce0.5Mg alloy, measured using a Cu radiation with λCuKα = 1.5418 Å, is shown in Figure 2(a), where Al and Al11Ce3 phases are marked according to 96-431-3218 and 04-002-7472.
Additions of Si led to a replacement of the Al$_2$Ce$_3$ phase by aluminum cerium silicate AlCeSi$_2$ with peaks marked according to the 99-900-001 card in Figure 2(b). The diffraction peaks seem also to indicate the Al$_2$CeSi$_2$ phase. A presence of expected Mg$_2$Si phase is difficult to definitely confirm since according to the 96-153-7741 card, key Mg$_2$Si peaks coincide with AlCeSi$_2$ peaks and peaks at 2-theta 47.433 deg and 72.901 deg are the only unique indicators. The change in the Al peak intensity at 2-theta of 65.17 and 77.50 deg, corresponding accordingly to (220) and (311) Al in both alloys is most likely caused by the preferred grain orientation (crystallographic texture) formed during solidification, and different orientation of samples used for X-ray diffraction.

A comparison of X-ray diffraction patterns from both alloys examined revealed a shift of Al peaks in Al5Ce3Si0.5Mg towards lower 2-theta values than in Al5Ce0.5Mg. The key observation is that a presence of 0.5 wt. pct Mg in the Al5Ce0.5Mg alloy led to an increase in lattice constant as compared to pure Al. An addition of Si in the Al5Ce3Si0.5Mg alloy, however, reduced the lattice constant back to the level similar to pure Al.

C. Effect of Si on Solidification Characteristics

Thermal events taking place during alloys solidification were recorded using the computer-aided cooling curves thermal analysis. For a cooling curve that represents the balance between evolution of heat in the sample and the heat flow away from the sample, solidification start-up is determined by the latent heat changed by a liquid–solid transformation. The cooling curve for the Al5Ce0.5Mg alloy, plotted along with the first derivative dT/dt as a function of time, is shown in Figure 3(a) where proeutectic solidification of primary Al and the eutectic solidification Al + Al11Ce3 are the major thermal events. The similar plot for the Al5Ce3Si0.5Mg alloy is shown in Figure 3(b). The first peak of dT/dt, aligned with a change of the slope on cooling curve, is associated with beginning of solidification of the proeutectic a-Al (solid solution) phase. The change in slope of the cooling curve around 1900s is associated with the start of univariant eutectic reaction L \(\rightarrow\) a-Al + AlCeSi$_2$ + L. The second large peak of derivative dT/dt, aligned with a beginning of the short plateau on cooling curve, around time of 2270 s, indicates the invariant quaternary eutectic reaction of L \(\rightarrow\) a-Al + Si + Al$_2$MgSi/Al$_2$MgSi$_2$ + Al–Si–Mg–Ce.

To determine precisely temperatures of thermal events, dT/dt curves for the Al5Ce3Si0.5Mg alloy and the Al5Ce0.5Mg alloy were plotted as a function of temperature (Figure 3(c)). For the Al5Ce3Si0.5Mg alloy the distinct peak at 648 ºC (liquidus) marks the start of primary Al solidification and the second peak at 638 ºC is associated with the binary eutectic transformation L \(\rightarrow\) a-Al + Al$_2$MgSi/Al$_2$MgSi$_2$ + Al–Si–Mg–Ce. The broad peak at 573 ºC is related to solidification of the AlCe$_2$Si/Al$_2$CeSi$_2$ bulky
compound. The summary of thermal analysis is listed in Table III.

### Table III. Solidification Characteristics of Al5Ce0.5Mg and Al5Ce3Si0.5Mg (wt. pct) Alloys Determined by Computer-Aided Cooling Curves Thermal Analysis (CCTA)

| Alloy               | Liquidus °C | Eutectic °C | Solidus (Non-equilibrium) °C | Solidification Range (equilibrium) °C | Eutectic Content Pct |
|---------------------|-------------|-------------|------------------------------|---------------------------------------|----------------------|
| Al5Ce0.5Mg          | 648         | 638         | 612                          | 10                                    | 44                   |
| Al5Ce3Si0.5Mg       | 630         | 618         | 535                          | 91                                    | 35 total (7 invariant) |
| A356                | 615         | 535         | 80                           | approx 50                              |

1Univariant start.  
2Invariant.

![Diagram](image)

Fig. 3—Thermal analysis showing thermal events during alloy solidification: (a) cooling curve and first derivative dT/dt for Al5Ce0.5Mg alloy plotted as a function of time; (b) cooling curve and first derivative dT/dt for Al5Ce3Si0.5Mg alloy plotted as a function of time; (c) first derivatives dT/dt for Al5Ce0.5Mg and Al5Ce3Si0.5Mg alloys plotted as a function of temperature.

D. General Solidification Microstructure

At a magnification of optical microscope the Al5Ce0.5Mg alloy shows hypoeutectic features, where the proeutectic aluminum is arranged into a dendritic morphology while the eutectic fills interdendritic regions (Figure 4(a)). At higher magnifications, the morphology of the eutectic intermetallic phase is revealed. In contrast to uniform lamellae developed for the binary Al–Ce alloys,[13] the eutectic phase in the Al5Ce0.5Mg alloy resembles rather a Chinese script with a portion representing plates or rods (Figure 4(b)). For larger contents of Mg and rapid solidification Ce-rich precipitates having near-equiaxed and cellular shapes were reported.[14]
A presence of Si led to substantial changes in the alloy microstructure. First, there is no dominant morphology of proeutectic aluminum, which was replaced by smaller dendritic islands (Figure 4(c)). The intermetallic compounds exhibit three dark-contrast morphologies; plate-like marked as ternary T eutectic, blocky phases as well as areas with dark and white contrast located in interdendritic regions marked as quaternary Q eutectic (Figure 4(d)). The volume fraction of the latter is small, as revealed earlier through thermal analysis, reaching just 7 pct.

Fig. 4—General view of as-solidified microstructure of Al5Ce0.5Mg alloy (a, b); Al5Ce3Si0.5Mg alloy (c, d). B binary, T ternary, Q quaternary eutectic.

Fig. 5—STEM bright field image of as solidified microstructure of Al5Ce0.5Mg alloy: (a) general morphology of primary aluminum dendrites; (b) eutectic islands with Al11Ce3 phase with mixed morphology; (c) Al11Ce3 phase morphology within interdendritic regions.

E. Microstructural Details and Microchemical Analysis of Phase Composition

1. Al5Ce0.5Mg alloy

Detailed morphology of the Si-free alloy is shown in Figure 5. The majority of shapes resembles plates with evident colonies and within a single colony the plates are parallel to each other (Figure 5(a)). An image contrast in Figure 5(b) indicates an increased dislocation density within proeutectic dendrites of aluminum that could be generated as a result of stresses during solid-state
Fig. 6—STEM EDS microchemical analysis of the eutectic phase with lamellae morphology in Al5Ce0.5Mg alloy: (a) STEM-HAADF image; (b) EDS area quantification with individual elements displayed and spot results listed in the accompanied table.

| Area | wt.% | at.% |
|------|------|------|
| 1    | Al   | 31.92| 70.89|
|      | Ce   | 68.08| 29.11|
| 2    | Al   | 69.45| 82.17|
|      | Fe   | 30.06| 17.18|
|      | Mg   | 0.5  | 0.65 |
| 3    | Al   | 98.81| 98.68|
|      | Mg   | 1.19 | 1.32 |

Fig. 7—STEM EDS microchemical analysis of the eutectic phase with Chinese script morphology in Al5Ce0.5Mg alloy: (a) STEM-HAADF image; (b) STEM-BF image; (c) EDS area quantification with individual elements displayed and spot results listed in the accompanied table.

| Area | wt.% | at.% |
|------|------|------|
| 1    | Al   | 31.15| 71.77|
|      | Ce   | 66.67| 27.80|
|      | Mg   | 0.18 | 0.44 |
| 2    | Al   | 98.86| 98.74|
|      | Mg   | 1.14 | 1.26 |
cooling from solidification temperatures, caused by differences in expansion coefficients between the intermetallics and aluminum. A Chinese script morphology is often located at triple junctions between solidifying aluminum dendrites, so it is the last portion that became solid (Figure 5(c)).

The microchemical analysis of plate-rod like morphology is shown in Figure 6. All cerium is located in plates with measured Al\textsubscript{70.9}Ce\textsubscript{29.1} (at. pct) composition. Magnesium in a content of 1.3 at. pct is in the aluminum matrix forming the solid solution. The iron as the most common impurity, due to its low solubility in Al, exists in the form of Fe-containing intermetallic compounds (Fe-IMCs), including the primary \(\theta\)-Al\textsubscript{13}Fe\textsubscript{4}\textsuperscript{15}. According to EDS, Fe is bound almost exclusively with Al in the form of Al\textsubscript{82.1}Fe\textsubscript{17.2} compounds, being close to the \(\Theta\) phase. Some traces of Mg were also detected in Fe-IMCs.

An example of the Chinese script morphology located at a triple junction between dendrites is shown in Figure 7. The EDS results, listed in the accompanying table, show good agreement with previous microchemical measurements of plate-like compounds and the matrix in Figure 6. In both cases, there is a higher content of Ce in Al\textsubscript{11}Ce\textsubscript{3} compounds than in the Al\textsubscript{11}Ce\textsubscript{3} stoichiometry; Al\textsubscript{2.5}Ce versus Al\textsubscript{3.6}Ce corresponding to the Al\textsubscript{11}Ce\textsubscript{3} formula. The difference is of the opposite nature than it could be caused by the analysis error due to a thin precipitate and collecting a signal portion from the underlying Al matrix. A difference is the presence of Mg traces in Al–Ce intermetallic phase, although in this case it could be caused by the signal collected from the underlying Al matrix that is a solid solution of Mg in Al.

2. \(\text{Al5Ce3Si0.5Mg}\) alloy
The Al\textsubscript{5}Ce\textsubscript{3}Si\textsubscript{2} eutectic plates with a thickness well below 1 \(\mu\)m and a length around 50 \(\mu\)m are arranged in colonies, where in a single colony plates are roughly parallel to each other (Figure 8(a)). The aluminum matrix around them contains areas with varying densities of dislocations. A higher dislocation density around plates of as-cast state suggests a stress generated during alloy solidification and cooling from the solidification
temperature as a result of difference in thermal expansion coefficients of the plate and Al matrix (Figure 8(b)). In contrast, the bulky morphologies were located along boundaries of dendritic regions and at triple junctions (Figures 8(c) and (d)). The inhomogeneous image contrast suggests differences in chemical composition what has been proven by EDS measurements. Namely, an analysis summarized in Figure 9 shows two distinct compositions with different Ce content. The regions marked as 1 and 3 are Al_{22-25}Ce_{47-45}Si_{29}. The adjacent regions marked as 2 are Al_{36}Ce_{24}Si_{36}Mg_{2}. Impurities like iron, which is the most deleterious impurity for AlSiMg alloys, form various intermetallic compounds with Si and Mg such as α(Fe_{2}Si_{Al_{8}}), β(FeSi_{Al_{3}}) and π(Fe_{Mg_{3}}Si_{6}Al_{8}).

The eutectic regions are located at interfaces between Al dendrites and at triple junctions between them (Figure 10(a)–(c)). As indicted by EDX area elemental

|   | Area | wt.% | at.% | Area | wt.% | at.% |
|---|------|------|------|------|------|------|
| 1 | Ce   | 80.78| 45.28| Al   | 97.16| 97.72|
|   | Al   | 8.59 | 25.92| Si   | 0.75 | 0.73 |
|   | Si   | 10.62| 29.71| Mg   | 0.84 | 0.94 |
| 2 | Al   | 17.56| 36.11| Fe   | 0.89 | 0.43 |
|   | Si   | 18.64| 36.81| Mg   | 0.97 | 2.21 |
|   | Ce   | 62.83| 24.87| Al   | 42.54| 42.54|
| 3 | Al   | 7.16 | 22.91| Mg   | 17.88| 19.85|
|   | Si   | 10.13| 29.33| Fe   | 0.87 | 0.42 |
distribution below Figure 10(a), while plates and bulk morphologies show dominant Ce content, the quaternary eutectic shows evidently dominant Si content. According to a detailed analysis, which will be described separately, the eutectic contained Si, Al$_2$MgSi, Al$_2$Mg$_2$Si, and Al–Si–Mg–Ce phases in the Al matrix.

F. Tensile Properties

The engineering stress–strain plots, recorded during tensile test at room temperature, are shown in Figure 11 with the sample geometry detailed in the figure inset. The assessment and comparison of the results is summarized in Figure 12. Additions of Si, caused an almost 3 times increase in the yield stress from 47.5 MPa to 136.5 MPa along with a raise in the ultimate tensile strength from 113.5 to 142 MPa (Figure 12(a)). At the same time, however, there was a significant lowering in alloy ductility with 10 times reduction of elongation from 7.7 pct to 0.9 pct, and area reduction from 11.5 to 1.5 pct (Figure 12(b)).

G. Fractography

The rupture surfaces of tensile samples were imaged with SEM to determine the mechanisms of failure that operated at a local, i.e. microscopic scale and to correlate them with the microstructural features. In the Al5Ce0.5Mg alloy, the fracture surface exhibits mixed regions; those failed due to void coalescence but also those failed by mechanical instability of the alloy itself (Figure 13(a)). In general, in dimpled regions characteristic of ductile fracture, relatively large amount of plastic deformation is seen that took place before failure, apparently associated with the pre-eutectic aluminum dendrites. Two types of fracture can be distinguished at higher magnifications where regions of brittle fracture resemble the Al$_{11}$Ce$_3$ plates or laths arrangement in the eutectic with a separation at the Al$_{11}$Ce$_3$/Al interface, as marked in Figure 13(b).

The fracture surface of the Al5Ce3Si0.5Mg alloy exhibits highly brittle nature with very little deformation of the alloy around the fracture (Figure 13(c)). Brittle fracture includes both cleavage and intergranular fracture, where energy is absorbed through regions of small plastic deformation. Since there is the prevalence of the flat plateau regions, they likely are responsible for the relatively low elongation at fracture of 0.9 pct during tensile testing at room temperature (Figure 13(d)). For both alloy compositions, an occasional casting shrinkage porosity was seen with pores promoting failure by instability through acting as crack nucleation sites.

IV. DISCUSSION

The results of this study show that in a search for the strengthening solution of the Al–Ce alloys, containing the Al–Al$_{11}$Ce$_3$ eutectic, a concept of alloying towards formation of the Al–Ce–X or higher order eutectics...
represents a viable option. At the same time, however, the results revealed that alloying with silicon, the most common ingredient of Al cast alloys, provides more complex picture than that predicted from numerical analysis, with Si causing essential changes in crystallization characteristics, phase composition, eutectic transformation temperature, its contribution to the alloy volume and eutectic morphology. The changes reported for Al–Ce–Si–Mg alloys are much more complex than the pathway of the eutectic refining, documented through the ternary Al–Ce–Ni system, where the eutectic phases were much finer than in the corresponding binary systems; the strength of three-phase eutectic (Al) + Al$_4$Ce + Al$_3$Ni was higher than that of individual two-phase eutectics (Al) + Al$_3$Ni and (Al) + Al$_4$Ce.\[8\]

The Al–Ce based alloys containing Si were recently considered mainly numerically in different configurations. Using a Thermo-Calc software package (TCAI4.0 database), unexplored data concerning the phase composition and crystallization behavior of Al–Mg–Si–Ce alloys have been obtained in the range of two-phase cast Al–Mg alloys such as (Al) + Mg$_2$Si.\[16\] In another study the CALPHAD method was used to explore an alloy within the quinary Al–Ce–Cu–Mg–Si system by developing a thermodynamic database with self-consistent parameters.\[17\] However, there is no systematic experimental assessment of the Al–Ce–Si system and the common literature approach is where Al–Si alloys are modified by small additions of Ce, typically below 1 wt. pct.\[18\] To link this research with engineering practice, the experimental Al5Ce3Si0.5Mg cast hypoeutectic composition used in this study was designed based on the commercial A356 (Al–7Si–0.3Mg, wt. pct) grade by substituting a portion of Si with Ce. An addition of magnesium was intended to promote solid solution strengthening as it dissolves in Al and reacts with both Ce and Si.

The results revealed the essential influence of silicon on crystallization paths, phase composition, and tensile properties of aluminum cast alloys based on the Al–Ce–Si–Mg system. The presence of Si caused changes in the alloy solidification characteristics where the invariant eutectic temperature reduced from 638 °C to 539 °C with the latter located below 577 °C, the binary Al–Si eutectic temperature and very close to 535 °C known as the eutectic temperature in the A356 alloy.\[19\] The substantial reduction of the

Fig. 13—Fracture cross-sections of alloys ruptured during tensile test at room temperature: (a, b) Al5Ce0.5Mg alloy; (c, d) Al5Ce3Si0.5Mg alloy.
non-equilibrium solidus temperature after Si addition, reported in this study confirms the trend of Thermo-Calc modeling, where additions of 0.7 wt. pct Si, to the Al4Mg (wt. pct) alloy, slightly reduced the liquidus temperature to 636 °C and substantially lowered the non-equilibrium solidus temperature by about 30 °C to 421 °C. A reduction in the eutectic temperature is seen as a factor negatively affecting the thermal stability of the Al5Ce3Si0.5Mg alloy. Observed at the same time, an almost ten-fold widening of the melting range from 10 °C to 91 °C may affect the alloy casting behavior and its susceptibility to solidification cracking. Still, the melting range of the Al5Ce3Si0.5Mg alloy is slightly higher than 80 °C gap seen for the A356 alloy, known of good casting behavior. There is also a possibility that some reduction in the alloy fluidity occurs due to a reduction in the eutectic volume from 44 pct to about 35 pct, which is less than the eutectic volume of about 50 pct seen in the A356 (Table III).

The low strengthening of Al–Ce binary alloys is related, in part, to a lack of solid-state solubility of Ce in Al, resulting in the eutectic phase being practically pure Al. Additions of Si and Mg aimed at improving the solid solution strengthening. An increase in lattice parameter of Al in the Al5Ce0.5Mg alloy as compared to pure Al is caused by larger atomic radii of Mg being 0.160 nm, as compared to pure Al 0.143 nm. The range of increase in Al lattice constant from 4.0366 nm to 4.0348 nm of 0.0029 nm is slightly higher than the increase of 0.0018 nm calculated based on the Nelson–Riley extrapolation function during changing the Mg content from 0 wt. pct to 0.75 wt. pct. Due to the solid solution strengthening effect of Mg atoms, the yield strength of Al–8Ce–yMg alloys and the hardness of z-Al matrix in the Al–8Ce–yMg alloys showed a parabolically increasing tendency, from 92 to 115 MPa and 0.502 GPa–0.575 GPa, respectively. Alloying with Si aimed at improving this factor in addition to an influence of Mg. According to Thermo-Calc calculations the maximum amount of magnesium, which can be dissolved in z-Al at simultaneous presence of Si and MgSi is between 0.45 wt. pct and 0.75 wt. pct at 555 °C. An excess of magnesium, which cannot be dissolved in the matrix, is available for the formation of intermetallic compounds. A potentially positive influence of Ce on Al matrix strengthening was revealed while studying the phase composition of Al–Ce–Si–Mg system after annealing at 400 and 550 °C. It is argued that the (Al) solid solution became supersaturated as a result of the Al3Mg2 phase dissolution, where each 0.1 pct Ce increased the Mg content in the (Al) solid solution by 0.005 pct in the first case (400 °C) and by 0.01 pct in the second one (550 °C). According to EDX measurement, 1.15 wt. pct of Mg in Al matrix of the Al5Ce0.5Mg alloy reduced to 0.84 wt. pct in matrix of the Al5Ce3Si0.5Mg alloy, where the Al matrix contained additionally 0.75 wt. pct of Si. Thus, apparently a presence of Si reduced the content of Mg in Al solid solution.

An essential improvement in the Al5Ce3Si0.5Mg alloy strengthening observed in this study with the room temperature yield stress increasing almost three fold, was caused by changes in the alloy phase composition after additions of 3 wt. pct Si. As a result of Ce reaction with elements forming solid solutions such as Mg and Si, a number of cerium aluminum silicides were created. It is reported that small additions of Si lead to the tetragonal intermetallic Ce(Si1-xAlx), with x = 0.1–0.9, which extends across the central portion of the phase diagram. According to the low solubility of Ce in Al and Si along with the tight bonding of vacancies to Ce and the formation enthalpy of the 1 phase, which reaches a minimum of 67 kJ/mol near x = 0.5, all contribute to the stability of this phase.

In contrast to the FactSage calculations, revealing the cerium aluminum silicide AlCeSi2 as the major compound in addition to traces of Si (Table II), this experiment identified more intermetallic phases. As shown by both the X-ray and EDX (EDS) analysis the as-cast microstructure of the Al5Ce0.5Mg alloy consisting of the primary Al along with 44 pct of the Al(Mg) + Al11Ce3 eutectic, having a mixed lamellar and Chinese script morphology was replaced in the Al5Ce3Si0.5Mg alloy with the primary z-Al, AlCeSi2 lamellae and bulk compounds, having the Ce rich AlCe2Si core with Al2CeSi3 external shell. A lack of Al11Ce3 after Si additions is in contrast to Thermo-Calc calculations, which for much lower content of Ce, namely Al4Mg0.5Si0.7Ce (wt. pct) alloy, still predicted Al1Ce of 1.19 pct, the [Mg2Si/Al4Ce] ratio of 0.89, Al5Mg5 fraction of 7.92 pct at 20 °C, along with Mg concentrations in the (Al) solid solution of 3.22 pct and 3.36 pct at 400 °C and 550 °C, respectively (note that Al1Ce is used by some authors instead of generally accepted Al11Ce3). Although at least 6 different cerium aluminum silicates are reported, the Ce rich AlCe2Si identified in this study is not present in the X-ray database. However, an equivalent to Al3Si2Ce identified in this study, Al3Si2Sr was formed in the Al7Si0.04Sr (wt. pct) alloy after modification with Sr where the compound precipitates acted as sites for porosity nucleation.

The lastly solidified structural component of the new alloy is the quaternary eutectic of z-Al, Si, Al5MgSi2/ Al2Mg2Si, and Al–Si–Mg – Ce intermetallic. The results show that the minor addition of 0.5 wt. pct Mg in the alloy led to a presence of Mg as the major ingredient of the quaternary eutectic phases. It appears that this phenomenon where the minority Mg element left solid solution in Al and formed phases the ternary and quaternary phases within the eutectic, was caused by the presence of Si in the alloy, which limited the content of Mg in Al(Si, Mg) solid solution as confirmed through both the reduction in Al lattice parameter and EDX (EDS) microchemical measurement. The mechanism of Mg redistribution within the liquid alloy and the role of Si in this process requires further examination.

V. CONCLUSIONS

This study revealed the essential influence of silicon on crystallization paths, phase composition, and tensile properties of aluminum cast alloys based on the Al–Ce–Si–Mg system. An addition of 3 wt. pct Si to
the Al5Ce0.5Mg base increased the room temperature yield stress almost three times, from 47 to 135 MPa, but reduced its elongation by an order of magnitude from 8 pct to that below 1 pct. A presence of Si led to essential changes in the alloy solidification characteristics with the melting range widened substantially from 10 °C to 91 °C mainly due to a reduction in the solidus level.

As-cast microstructure of the Al5Ce0.5Mg base consisting the primary Al along with 44 pct of the Al(Si, Mg) + Al11Ce3 eutectic was replaced in the Al5Ce3-Si0.5Mg alloy with the primary Al and AlCeSi2 coarse lamellae/plates formed through the ternary eutectic reaction along with bulk compounds having the Ce-rich core of AlCe2Si with external shell of Al2CeSi2. A small alloy portion was occupied by the quaternary eutectic of zAl, Si, Al12MgSi/Al2Mg2Si, and Al–Si–Mg–Ce phases with ultra-fine globular morphology.

The fractographic analysis revealed that additions of Si caused a transition from a morphology having a large contribution of ductile fracture to the predominantly brittle one with crack paths propagating mainly along the interface between AlCeSi2 lamellae and zAl(Si, Mg) solid solution, apparently contributing to the measured drastic reduction in the alloy elongation.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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