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MANUFACTURE AND CHARACTERIZATION OF AN AL-MG-RE ALLOY APPLIED TO AN ALUMINUM A-356

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Abstract: We present a study of cerium (Ce) recovery in a liquid aluminium (Al) bath through the metallothermic reduction of cerium oxide (CeO_2), using the mechanical agitation technique with inert gas protection. The conditions were as follows: 80 g of CeO_2 added every 10 min; a flow of 6 L Ar/min; a pressure of 1 atm; and a treatment time of 1 h. The variables were the temperature of the liquid (750, 800 and 850 °C) and the magnesium content (0.5, 3.0 and 4.0 wt %). The induction power of the oven ranged from 8 to 10 kW. The results indicate that the cerium oxide (RE) was reduced through a metallothermic mechanism because the amount of cerium present in the liquid bath increased with agitation time. Phases were identified by XRD and scanning electron microscopy (SEM) and by the complementary energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD) techniques. The results of these tests allowed the products and stages of the reaction to be determined. In the end, the addition of CeO_2 led to a 3.90% increase in the amount of cerium after 60 min of stirring. Therefore, this technique offers an alternative method for the fabrication of Al-Mg-Ce master alloys. Which was used in an A-356 aluminum as a modifier, obtaining better mechanical properties when performing its characterization.
Keywords: Cerium incorporation; Metallothermic reduction; Mechanical properties.

INTRODUCTION

During the last 50 years, the science and technology of aluminium and its alloys have undergone important changes. This has led to a considerable increase in the consumption of this metal in industrialised countries. Aluminium has properties that make it suitable for a number of applications. One important example is its use in Al-Si master alloys, which are now widely used in the automotive industry. These applications have specific requirements in terms of the mechanical properties of the alloy, which demand an ever-increasing level of control over the introduction of refiners and modifiers in the metallic bath [1]. The use of rare earths has been a subject of intense research because rare earths such as cerium change the morphology of the eutectic Si in aluminium alloys, generating better physical and mechanical properties [2].

This article presents a method to obtain an Al-Mg-Ce master alloy, starting from the metallothermic reduction of CeO_2 to Ce by means of mechanical agitation in liquid Al-Mg [3]. The method represents an alternative way to make a product that can be used as a modifier agent in conventional Al-Si alloys. This alloy was added to an A-356 aluminum, later it was characterized obtaining favorable results.

EXPERIMENTAL PROCEDURE

The experiments were carried out using an *inductotherm* brand 70 kW *PowerTrack 75-30* electromagnetic induction oven in a silicon carbide crucible with a capacity for 13 kg of liquid aluminium.

To maintain a controlled inflow of CeO_2 to the fusion unit, an agitation system with speed control was integrated, and a graphite agitator was used. The atmosphere was inert, composed of 99.99% argon.

To obtain 3.9 wt% Ce in the alloy, stoichiometry calculations were carried out, which established the necessary amount of CeO_2 to be added. The chemical composition of the alloy in the experimental stage was 98 wt% aluminium and 99 wt% magnesium.

The experiments used to evaluate the chemical behaviour of CeO_2 in the liquid bath had the following parameters:

- Temperature: 3 levels; 750, 800, 850 °C
- Initial magnesium concentration: 3

levels; 0.5, 3.0, 4.0 wt%

- Reagent grain size distribution: 1 level; -140 to +200

Throughout the experiments, the following conditions were kept constant:

- Initial amount of alloy: 10,000 g.
- CeO_2 added: 80 g every 10 min and 6 L of Ar per min.
- Added amount of reagent: 480 g.
- Stirring rate: 320 rpm
- Treatment time: 60 min.
- Sampling time: 10 min intervals
- The form factor and dimensions of the agitator

CHARACTERISATION

The Ce and Mg contents in the aluminium alloy were analyzed chemically by means of atomic absorption spectroscopy and spark emission spectroscopy, respectively. Phases were identified by X-ray diffraction (XRD).

The samples were also analyzed in a SEM using energy dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD). To assess the crystallographic features of the phases of interest by EBSD, the software TSL Delphi 2 was incorporated into the computer of the SEM.

When obtaining the master alloy Al-Mg-Ce, it was used by adding it in a liquid aluminum bath of an A-356 alloy and the samples obtained were subjected to the following characterizations: metallographic analysis, hardness test, and tension test to assess the efficiency of the master alloy as a modifying agent.

RESULTS AND DISCUSSION

CHEMICAL ANALYSES

Figure 1 shows the results of the chemical analysis of samples obtained by means of metallothermic reduction, with different magnesium concentrations at constant temperature and stirring rate. The figure demonstrates the incorporation of Ce into the Al-Mg alloy. The cerium oxide was reduced by the liquid alloy because the cerium content increases with both time and temperature of the liquid bath. The maximum cerium concentration of the alloy was 3.90 wt% at a temperature of 850 °C, with an initial magnesium concentration of 4.0 wt%. The treatment time was 60 minutes, and the mesh-particle size was -140 to +200.

Figure 2 shows the concentrations of both Mg and Ce in the Al-Mg alloy bath as functions of time at 850 °C with constant stirring. Figure 2 shows that the Ce concentration increases with time as the Mg concentration decreases.

Recent studies have shown that a liquid Al-Mg alloy can be kept at a temperature of 800 °C for up to 2 hours without significant Mg loss due to evaporation or oxidisation by the environment [4, 5]. This allows us to assume that the Mg loss is due to the reduction of CeO_2.

X-RAY DIFFRACTION.

Figure 3 represents an X-ray diffraction pattern obtained from a slag generated during the stirring process. The percentage of cerium reached during the formation of the afore mentioned slag was of the order of 3.90% e.p. The peaks captured in PDRX identify MgO, $MgAl_2O_4$, Al_2O_3,CeO_2 as the main compounds. The presence of the oxides MgO and $MgAl_2O_4$ in the slag indicates that both aluminum and magnesium are reducing cerium oxide through a metallothermic mechanism [6], where the oxygen of CeO_2 joins the magnesium and aluminum forming a spinel and an alumina during the reaction and the metallic cerium deposits interstitially in the liquid aluminum bath. The conditions for obtaining the slag were; temperature

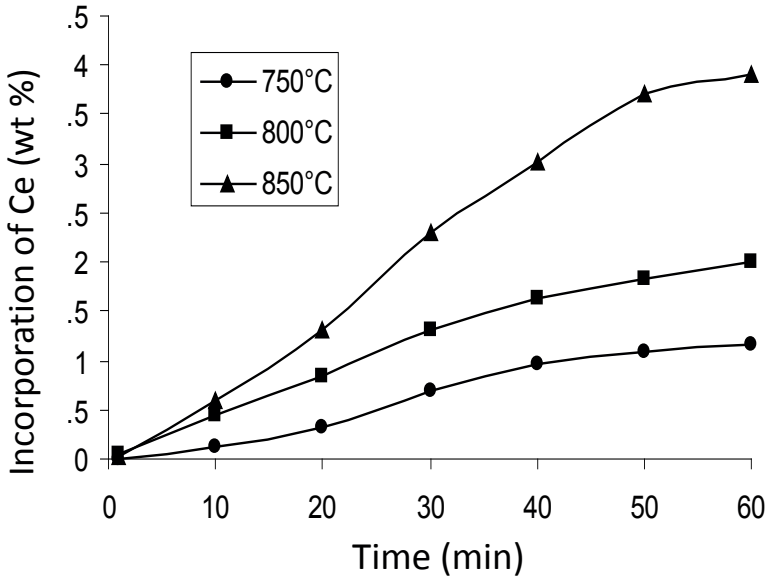


Figure 1. Addition of Ce to an Al-Mg alloy with 4 wt% Mg as a function of time at different temperatures.

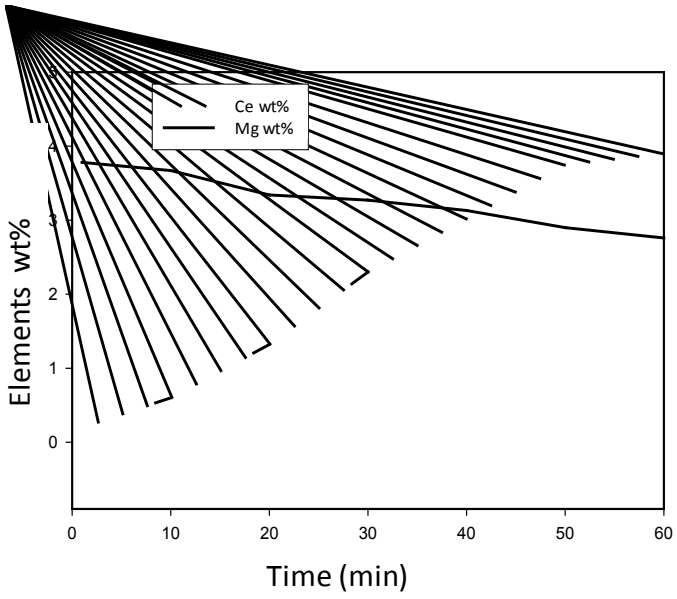


Figure 2. Mg and Ce concentrations in the liquid Al-Mg alloy as a function of time.

850°C, initial content of Mg 4%, CeO_2 powder size -140 + 200 mesh adding 80g CeO_2 every 10 minutes / 6l Ar / min, for a time of 1 hour, with agitation in the 320 rpm bath.

Figure 4 shows a schematic representation in which the impermeable aluminum oxide layer was reduced by magnesium in the molten reducer and the cerium oxide was reduced by Magnesium and Al_2O_3 in the molten reducer and dissolved "freely". Since metallic cerium has a great affinity for both oxygen and nitrogen, this element is hardly ever used naturally as a modifying agent. For this reason, cerium is added to the metallic bath in the form of a master alloy.

Figure 5 shows the XRD pattern of the Al-Mg alloy sample with 4.0 wt% Mg, 60 min stirring at 850 °C and the addition of 80 g of CeO_2 every 10 min. The spectrum indicates the presence of Al, Al_3Ce and AlCe [7]. This shows that part of the CeO_2 added to the bath underwent a chemical reaction with the alloy to yield Al_3Ce and AlCe. This matches the results of the chemical analysis (Figure 1), which indicated that during the process, 3.90% Ce was added to the alloy.

Figure 6(a) shows a low-magnification micrograph, in which a dark phase is observed that corresponds to the Al matrix. A clear phase is homogeneously distributed throughout the matrix, showing the flake-like morphology typical of Ce. The EDS spectrum of Figure 6(b) indicates the presence of mainly Al and Ce. The presence of Ce in this qualitative analysis confirms the metallothermic reduction of CeO_2 by Mg in the alloy, in agreement with the results shown in Figures 1 and 4.

Figure 6(c) presents a micrograph of a particle trapped in the matrix. Point analysis by EDS [Figure 6(d)] indicates the presence of Al, Mg and O, suggesting the formation of the product Al_2MgO_4 (spinel) [8].

Finally, the micrograph of another particle trapped in the matrix is shown in Figure 6(e). Point analysis by EDS [Figure 6(f)] indicates the presence of Al and O typical elements of the Al_2O_3 (alumina) phase.

EVOLUTION OF THE AL-MG-CE ALLOY.

Figure 7 shows the different concentrations of cerium in a representative sample of the different experimental tests carried out using the stirring technique, where it is reflected that the increase in magnesium in the bath and high temperatures of the order of 850°C are beneficial for the incorporation of the cerium in the aluminum liquid bath

According to the results obtained (AQ, SEM) it is established that the cerium oxide is being reduced by the liquid alloy through a metallothermic mechanism, since the cerium content in the bath increases as the stirring time passes.

ELECTRON BACKSCATTERING DIFFRACTION (EBSD)

Figure 8 presents the results from the SEM, EDS and EBSD analyses of the Al-Mg-Ce master alloy, which were conducted after 60 min of treatment at 850 °C. Figure 8(a) shows a micrograph in which a clear particle with flake-like morphology is visible. Figure 8(b) presents an EDS point analysis of the particle (the arrow indicates the point of analysis), and the spectrum indicates the presence of Al and Ce.

Figure 8 [(c) and (d)] shows the results of the EBSD analysis of the particle. In Figure 8(c), the characteristic pattern is presented. Figure 8(d) shows the indexation of said pattern by Kikuchi lines, indicating that the particle corresponds to the intermetallic phase Al_3Ce. According to the crystallographic chart of this compound, the indexing was obtained with a confidence of 1.0 (Crystallographic chart 29-0012) [9].

The experimental characterisations of

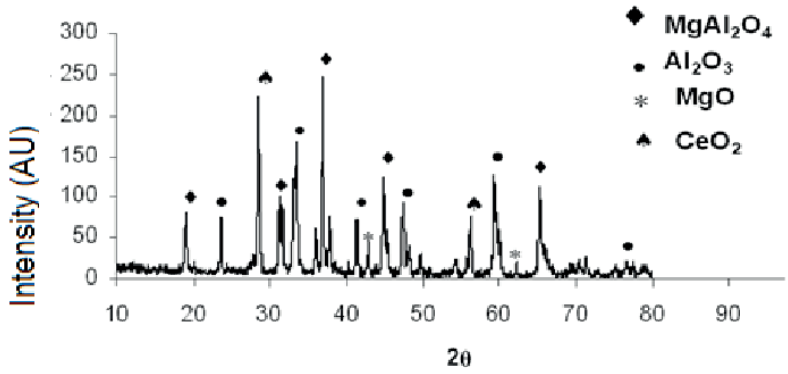


Figure 3. XRD pattern of slag samples obtained from the liquid Al-Mg alloy.

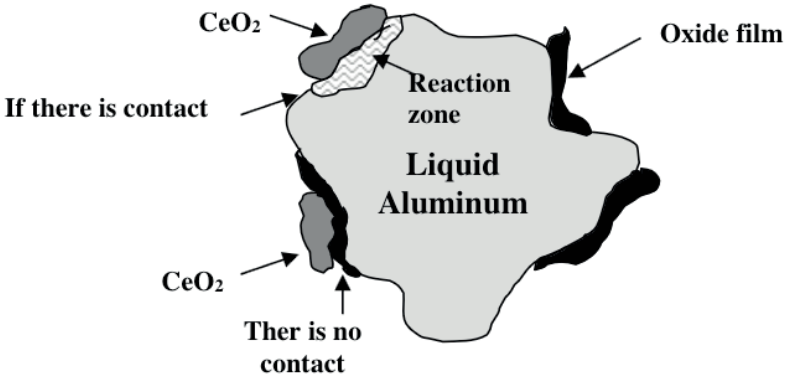


Figure 4. Scheme of the reaction mechanism in the metallothermic process with the presence of magnesium and CeO2 in the liquid aluminum bath.

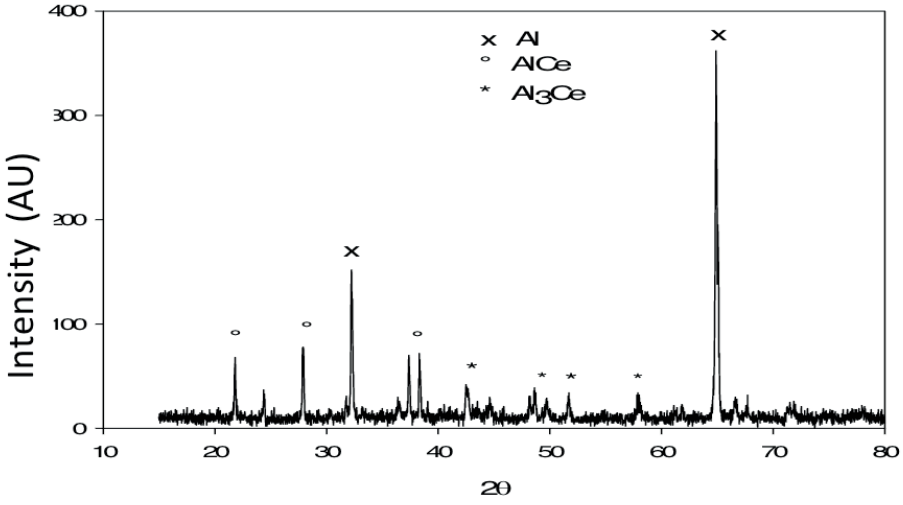


Figure 5. XRD pattern of the Al-Mg alloy with 4 wt% Mg, 60 min stirring at 850 °C and the addition of 80 g of CeO_2 every 10 min.

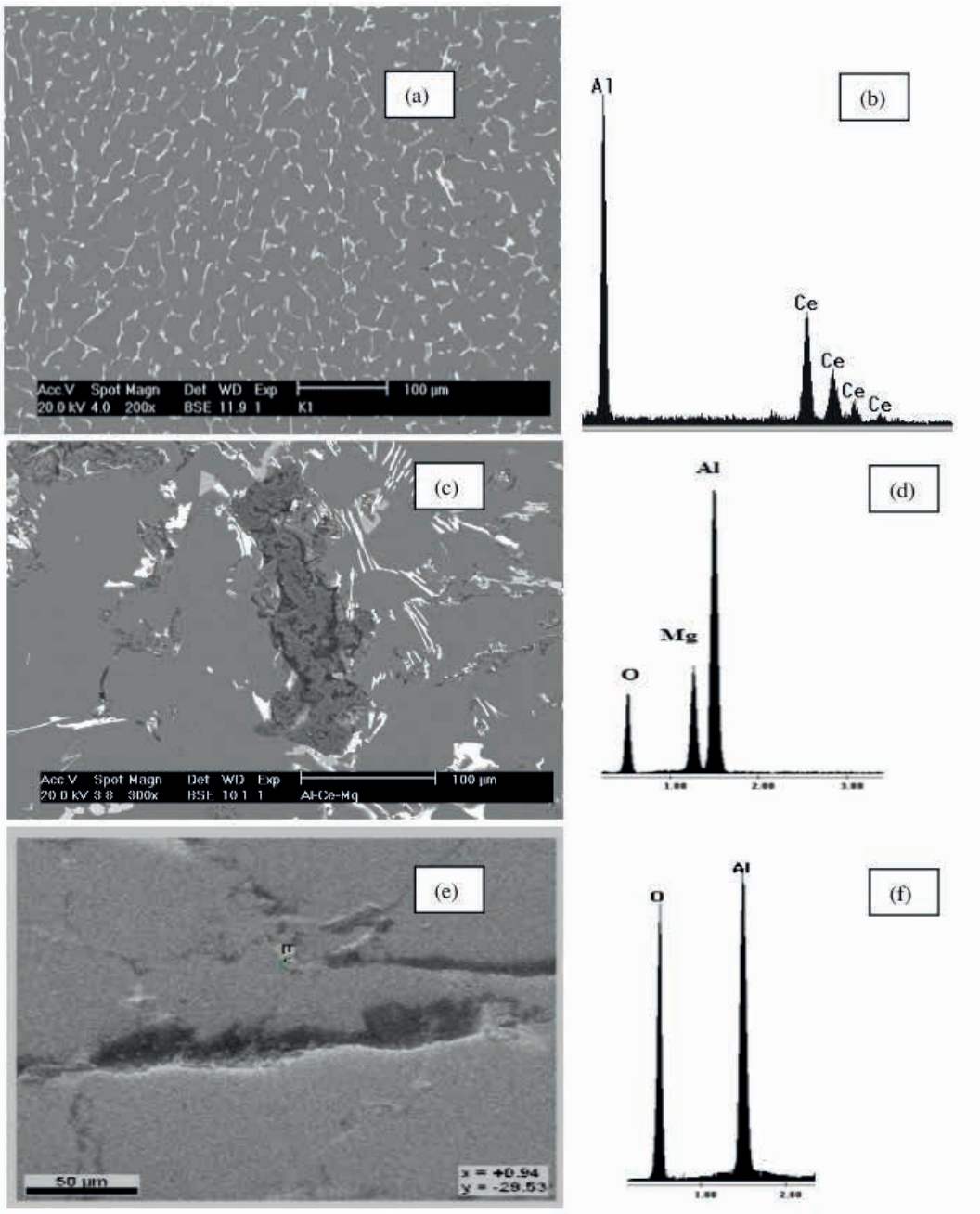
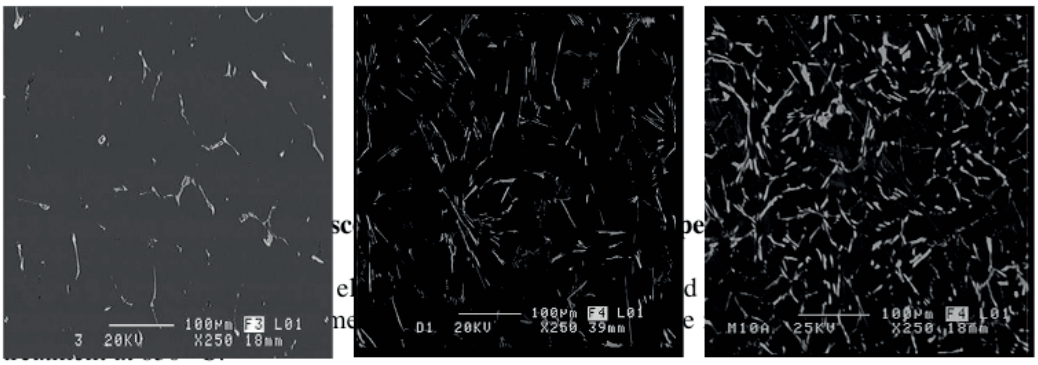


Figure 6. SEM and EDS of the Al alloy sample with 4 wt% Mg, obtained after 60 min of treatment at 850°C. a) Low-magnification micrograph; c) particle micrograph (spinel); e) particle micrograph (alumina); and b), d) and f) corresponding EDS spectra.



(a) **(b)** **(c)**

Figure 7 presents three micrographs of the experimentation. The CeO_2 addition conditions were constant (80g / 10min.) as well as the temperature at 850ºC. The initial magnesium content was: for sample (a) 0.5% Mg, sample (b) 3% Mg and sample (c) 4% Mg. The incorporation of cerium for these alloys were: (a) 0.77% Ce, (b) 1.74% Ce and for (c) 3.90% Ce.

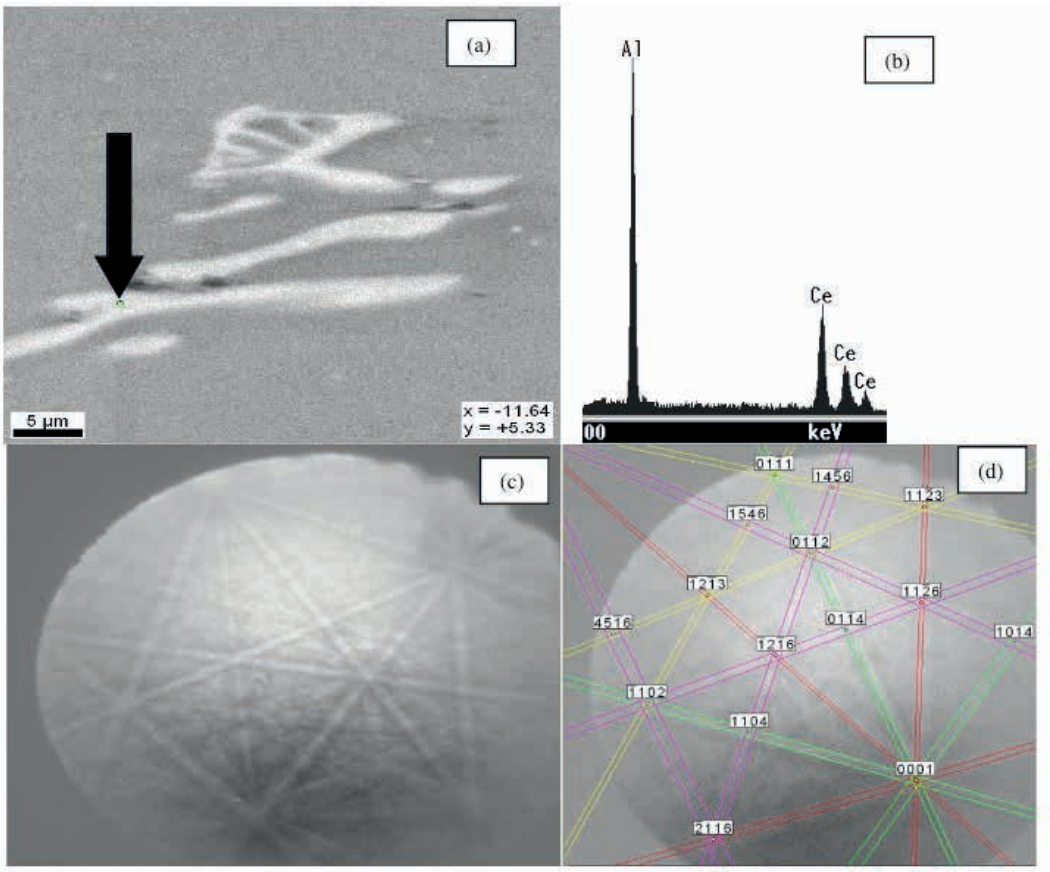


Figure 8. SEM, EDS and EBSD of an Al alloy sample with 4 wt% Mg, obtained after 60 min of treatment at 850 °C. a) Micrograph; b) EDS spectrum of the clear particle; d) EBSD pattern; and d) indexation by Kikuchi lines.

the alloy indicate that certain products were formed, which can be verified from the following reactions [10]:

$2Mg + CeO_2 \rightarrow 2MgO + Ce$ --------- $\Delta G°$ at 850 °C = - **24.225Kcal** ……..……. (1)

$4Al + 3CeO_2 \rightarrow 2Al_2O_3 + 3Ce$ ------$\Delta G°$ at 850 °C= - **16.418kcal** …….. (2)

$2MgO + 2Al_2O_3 \rightarrow 2MgAl_2O_4$ ------- $\Delta G°$ at 850 °C = - **27.549Kcal** …….. (3)

According to the phase diagram, under the temperature conditions used throughout this work (850 °C), reduction of cerium oxide by Al and [Mg]Al occurs, which generates MgO, Al_2O_3 and $MgAl_2O_4$. The cerium released from the CeO_2 during the reactions tends to dissolve in the aluminium matrix and subsequently form the compound Al_3Ce during solidification [11].

According to the reactions (1, 2 and 3) determined by characterisation of the alloy, the global solid-liquid reaction that takes place during the metallothermic reduction of the CeO_2 is as follows:

$2Mg + 4Al + 4CeO_2 \rightarrow 2MgAl_2O_4 + 4Ce$ --- $\Delta G°$ at 850 °C = - **20.451 kcal** ..... (4)

APPLICATION OF AL-MG-CE MASTER ALLOY ON AN A-356 ALUMINUM.

The modification test consisted of using an ingot of 600 grams of Al-Mg-Ce master alloy obtained in the previous experimental test with the composition of 3.90% ep of Ce To carry out the test, first 10Kg of A-356 alloy were melted at a temperature of 850°C. The Al-Mg-Ce master alloy ingot was subsequently added and kept for a time of 20 minutes with a protective atmosphere of argon conducted through the cover of the induction furnace used. Samples were obtained to be characterized. The main objective of this test was to add the ingot with 3.90% ep of cerium to the liquid Aluminum bath to see the feasibility of carrying out the modification of the eutectic silicon contained in the A-356 alloy to achieve better mechanical properties. The equipment used is represented in Figure 9.

Figure 10 shows the effect of cerium on the microstructure of an A-356 alloy. The unmodified structure Figure 10 (a) consists mainly of alpha aluminum, the eutectic silicon is in fibrous form and laminated flakes, typical of a microstructure free of modification. The silicon present in the microstructure begins its modification under cerium contents of the order of 0.02% ep, obtained after 20 minutes of treatment, as can be seen in Figure 10 (b). They show a structure of eutectic silicon in acicular form, representing a good degree of modification, presenting a structure required in Al-Si alloys to provide good mechanical properties. Similar structures, showing the refinement of eutectic silicon, have recently been reported in previous investigations using other modifiers such as strontium [7].

Figure 11 (a). It shows the precipitation of the intermetallic cerium in the modification treatment carried out by dissolving the Al-Mg-Ce master alloy in an A-356 alloy. The quantification of elements of the EDS spectrum figure 11 (b), obtained by micro-point analysis, shows that these precipitates are mainly composed of Al, Si and Ce. The atomic ratios recorded by the EDS spectrum and shown in Table II indicate the presence of a compound with the following Al_2Si_2 stoichiometry. The Ce intermetallic is commonly identified when an overmodification occurs in Al-Si alloys. That is, when the maximum content of cerium in solution is exceeded with the aluminum matrix

Figure 12 shows the graphs of the tension tests carried out on an Instrom machine with a capacity of 10,000kgf, where the graph (a) is the result of a test piece for tension of an

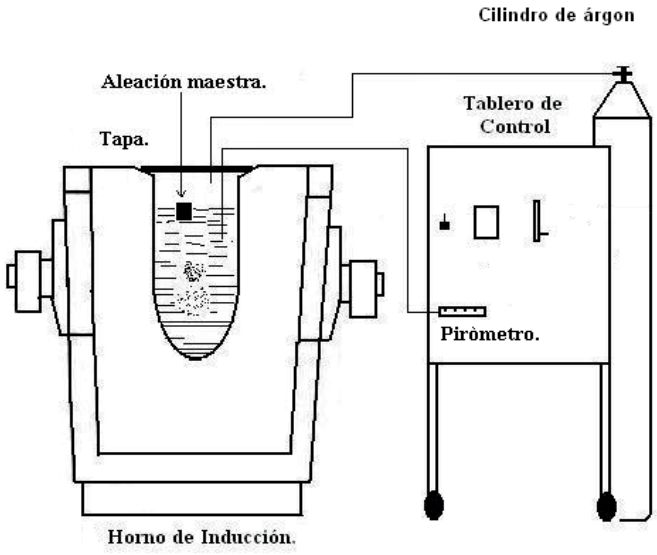


Figure 9. Schematic representation of the equipment used in modification tests. The results of the chemical analysis before and after the modification test are shown in Table I.

Element	Al	Fe	Cu	Mn	Si	Mg	Zn	Ti	Ce
Alloy A-356	88.06	0.385	0.16	0.23	10.1	0.268	0.12	0.16	0
Alloy Modified	88.55	0.42	0.19	0.22	9.33	0.39	0.12	0.13	0.26

Table I. Chemical analysis of aluminum A-356 before and after the modification test.

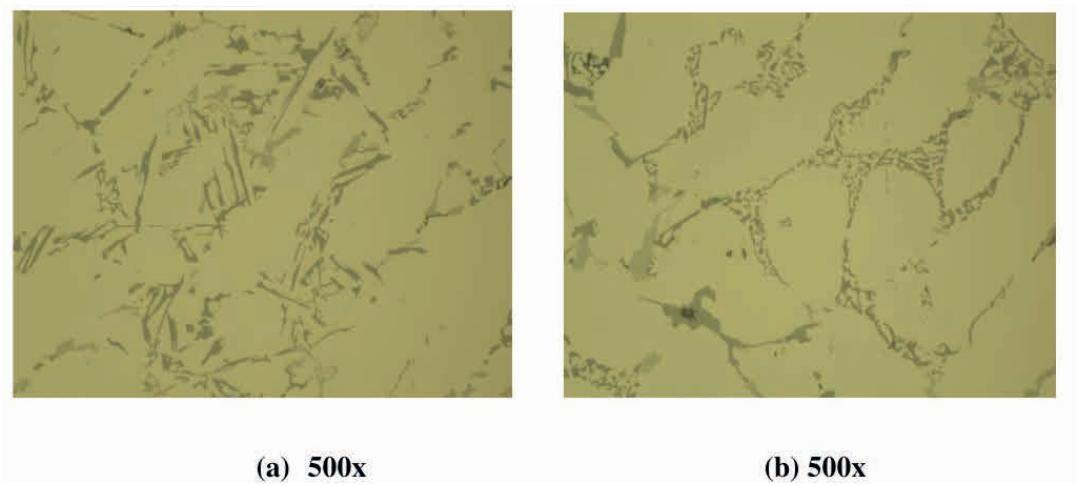


Figure 10. Modification of the structure of the eutectic silicon present in an A-356 alloy as a function of the cerium concentration.

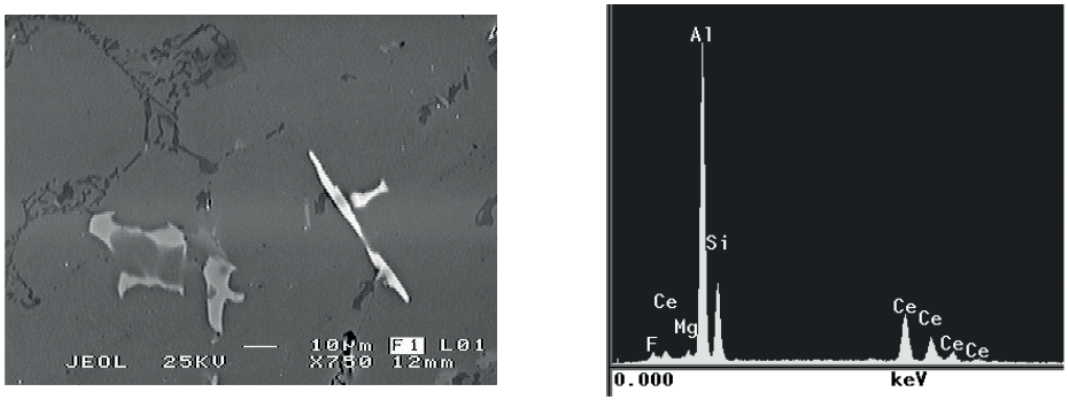
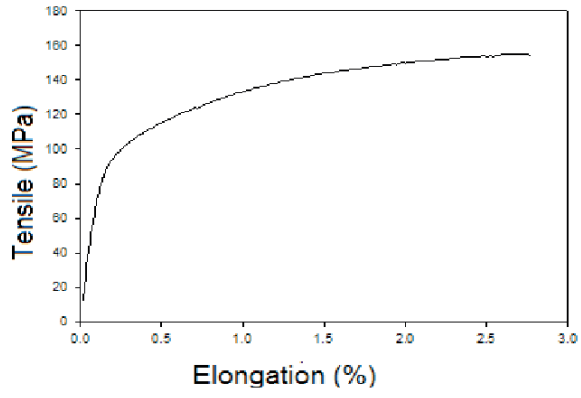


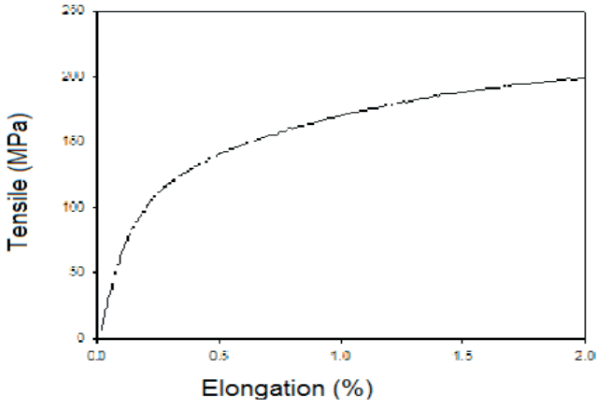
Figure 11 shows the precipitate of the intermetallic in the matrix of aluminum A-356.

	Elemento	% e.p.	% atm
Al_2Si_2Ce	Al	26,78	40,97
	Si	24,57	36,11
	Ce	48,65	22,92
	Total	100,00	100,00

Table II. Atomic ratio recorded by the EDS spectrum shown in Figure 11



(a)



(b)

Figure 12. Tensile test of an A-356 alloy by adding Al-Mg-Ce master alloy

alloy A-356, and the graph (b) is the A-356 alloy with addition of Al-Mg-Ce master alloy with a content of 3.90% ep of Ce. The values obtained for alloy A356 were: Maximum stress 153 Mpa with a hardness of 50HB. For alloy

A-356 with Al-Mg-Ce master alloy additions were: Maximum stress 199 Mpa with a hardness of 75HB. Therefore, this Al-Mg-Ce master alloy can be used as a modifying alloy in conventional aluminum alloys. For this study, an increase of 30% was achieved with respect to the maximum stress of aluminum A-356 and with respect to hardness it was 50% with respect to the original sample, this being significant since this aluminum is used for manufacturing of engine heads and monoblocks in the automotive industry.

CONCLUSIONS

The method presented in this work allows for the metallothermic reduction of Al-Mg alloys through the addition of CeO_2 by mechanical agitation in a molten bath. Using this procedure, 3.90% incorporation of cerium was achieved at 850 °C, with an initial magnesium concentration of 4 wt % and the addition of 80 g of CeO_2 every 10 min with a flow of 6 L Ar per min. Characterization by XRD, SEM, EDS and EBSD allowed for the identification of the phases involved in the process and made it possible to determine the reaction mechanism. In addition, the presence of Mg influenced the reduction of CeO_2 in the liquid alloy bath.

Based on the experimentation carried out, the incorporation of metallic cerium in the liquid bath of aluminum can be improved, by modifying the addition of magnesium, cerium oxide, particle size, temperature and protective atmosphere.

The addition of Al-Mg-Ce master alloy with 3.90% ep of metallic cerium, in an A-356 aluminum served as a modifying agent of the eutectic of silicon, observing the morphological change of fibrous needles and laminated flakes to an eutectic silicon structure in acicular shape, in terms of its brinell hardness properties (HB) an increase of 50% was obtained, therefore in the tension test the increase was 30%, being something very significant since the elongation values were better achieving a value above 3%. With these favorable results they can be useful to improve a conventional aluminum used mainly in the automotive or aerospace industry.

REFERENCES

[1].- YANG M B, HOU M D, ZHANG J, PAN F S. Effects of Ce, Y and Gd additions on as-cast microstructure and mechanical properties of Mg-3Sn-2Sr magnesium alloy [J]. Transactions of Nonferrous Metals Society of china, 2014, 24: 2497-2506.

[2].- DUAN R, BAI P, YANG J, ZHANG W, DING H. Influence of Rare Earth Modification and Homogenization on the Microstructure and Mechanical Properties of Recycled Can 3004 Aluminum [J]. The Journal of Wuhan University of Technology-Materials Sciense, 2014, 29(2): 264-268.

[3].- ESCOBEDO J, HERNANDEZ J, FLORES A. Estudio Cinético de la Eliminación de Mg en las Aleaciones de Aluminio Mediante la Inyección de Polvos de Sílice [J]. Revista de Metalurgia (Madrid), 2003, 9:171-182.

[4].- FLORES A, MARTINEZ C, ESCOBEDO J, TOSCANO J.A Kinetic of Demagging of Molten Aluminium by the Use of SiO2 Submerged Powder Injection [C]. Light Metals, 1999. Aluminum Committee at the 128th Tms Annual Meeting

[5].- LANGLAIS J. Strontium Extraction by Aluminiumthermic Reduction [T], Thesis degree of master engineering, McGill University, Montreal Canada, 1991.

[6].- LUNA J. FLORES A, MUÑIZ R, FUENTES A, TORRES J, RODRIGUEZ N, ORTIZ J, OROZCO P. Cerium extraction by metallothermic reduction using cerium oxide powder injection [J]. Journal of Rare Earths, 2011, 29 (1): 74-79.

[7].- WU L, LIU X, WU R, CUI CH, ZHANG J, ZHANG M. Microstructure and tensile properties of Mg-Li-Al-Zn based alloys with Ce addition [J]. Transactions of Nonferrous Metals Society of china, 2012, (22): 779-785.

[8].- McLEOD A, GABRYEL C. Kinetics of Growth of Spinel, $MgAl_2O_4$, on Alumina Particulate in Aluminium Alloys Containing Magnesium [J]. Metallurgical and Materials Transactions A, 1992, (23): 1279-1283.

[9].- Adam J.Schawartz, Mukul Kumar and Brent L. Adams "Electron Backscatter Diffraction in Materials Science"2000 New York.

[10].- HSC Chemistry for Windows 3.0 Abril 30, 1997.

[11].- O. Levenspiel, Ingeniería de las Reacciones Químicas, Editorial Reverté, 2a. Edición Barcelona, España, 2002, pp. 406–415