

Low Density Multi-principal Element Alloy from Al-Mg-Ca-Si-B System

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The scientific paper presents a numerical modeling of the chemical composition for the optimization of the multicomponent light alloys in the Al-Mg-Ca-Si-B system. The effects of the proportion of each chemical element on the main characteristics of the alloy based on the mixture rule and the correlation between the melting temperature and the modulus of elasticity were analyzed numerically. The model results has reveals that even other factors must be taken into account, i.e. the mechanical characteristics which varied significantly with changing of chemical compositions. A compromise was set, by slightly increasing the density to acquire better mechanical characteristics. The selected chemical composition was then used to obtain the new low density alloy. In current research stage we conclude that the as cast alloy comprises an inhomogeneous solid solution and complex oxides. Further studies are ongoing on the experimental alloy in various states (homogenization annealed and processed by plastic deformation).

Keywords: multi-component alloy, chemical composition, low density, microstructure

Light weight alloys are attractive for transport and energy industry where titanium alloys are the heaviest of this class used in engineering applications. Common structural alloys where weight is of main concern are based on a single principal element like Al, Mg or Ti. These conventional alloys have shown their limits and starting 2004 [1 - 3] a new class of alloys with excellent and customizable characteristics given by their unique composition and microstructure, named high entropy alloys (HEA) is developed.

Although 15 years have passed since their emergence, these alloys are loosely defined by Yeh [4] as composed of five or more principal elements in equimolar ratios. The definition expands the range by specifying that the principal elements concentration can range between 35 at% and 5 at%. Minor element additions for properties customization are also accepted [5, 6]. Along high entropy alloys the concept of *multi-principal element alloys* (MPEA) is introduced by Cantor [1]. In literature the terms are used interchangeably, Miracle [7] uses the term *HEA* when configurationally entropy or single-phase solid solution are the intent.

Since the aim of this research was not to obtain a Single-phase solid solution or the entropy, the terminology *multi-component principal element* is more adequate for the alloy analyzed in this study.

The difficulty in raw material melting and procedural costs make HEA's currently inaccessible for large structural components therefore, using a similar approach, has been studied the possibility to obtain a low density MPEA from the Al-Mg-Ca-Si-B system, using Al as the base chemical element. There are know many aluminum alloys, but only several chemical elements are important as alloying elements in commercial alloys.

The choice of alloying elements is based on the mutual chemical compatibility and the possibility of obtaining the best technological properties [8 - 29]. For the Al-Mg-Ca-Si-B system, the solubility of the alloying elements is shown in table 1.

From the classical metallurgy point of view key aspects from binary and ternary systems are presented along the influence of each alloying element. The Al-Mg binary alloy

Table 1

THE VALUES OF SOLUBILITY IN SOLID AND LIQUID STATE FOR ALLOYING ELEMENTS IN ALUMINUM [8, 11, 15, 30]

Element	Liquid solubility, %wt	Solid solubility, %wt
Mg	35.0	14.9
Ca	7.6	<0.1
Si	12.6	1.65
B	0.022	<0.001

system is complex: a eutectic appears at 35 wt% Mg at 450°C, a temperature at which Mg reaches its maximum solubility in Al at 14.9wt%. At room temperature Mg solubility in Al reaches roughly 1.7 wt%. The addition of Mg in Al has an effect in decreasing alloy density by 0.5% for each 1 wt% of Mg [7, 30].

In Mg-Ca binary alloys the microstructure is altered by Ca content: in as cast condition the dendritic cell size appears finer as Ca content increases (up to 10%) and MgCa₂ phase appears on grain boundaries [8 - 11, 24].

The Al-Si binary systems and Al-Mg-Si, Al-Si-Mg ternary systems are overviews together. In binary Al-Si systems, Si forms coherent clusters in solid solution [12 - 14], Al-Si clusters in hypoeutectic alloys and primary silicon crystals in hypereutectic alloys [15]. In Al-Si alloys Mg is added for strengthening since the formation of Mg₂Si precipitates occurs. From the Al-Mg-Si system the majority of the commercial alloys are intended for extrusion. Usually Mg and Si content is somewhat equal, 0.75wt% to 1.2wt%, but, by adding excess Si an additional response to age hardening by Mg₂Si precipitates refining [16] is gained. High silicon content, 5 to 20wt% Si in Al-Si-Mg alloys creates best casting properties. In the Al-B system a eutectic appears at 660°C at 0.022 wt% B between Al and B₂Al. Boron is mainly added to refine grain size or increase the electrical conductivity.

The selection of the chemical composition of this MPEA proves difficult given the contradictory and various effects

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of the alloying elements, but using a HEA approach we were able to establish and use the proportions to manufacture an alloy. In the current stage of the research microstructure investigations using scanning electron microscopy and chemical compositions using the energy dispersive X-ray spectrometer were performed.

Experimental part

Materials and methods

The paper presents the compositional analysis of an Al-Mg-Ca-Si-B alloy system with low density. Lack of information regarding this alloying system has required a comparative study, based on a numerical analyze model, in order to determine optimal chemical composition for low density alloy. The study was performed by estimating of some alloy characteristics and investigating the influence of each alloying element on the density, melting temperature and elastic modulus of the resulting alloy.

Based on the results of calculations, an experimental chemical composition was chosen and then the alloy was obtained in a CTC50K15 induction heating furnace under argon protective atmosphere, using zirconia crucibles. The obtained alloy was studied, in as cast state, using a FEI Quanta Inspect Scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) installation to determine its microstructure and local chemical composition.

Experimental alloy planning

Using the data presented in table 1 a full factorial design of experiments with 4 factors (B, Mg, Si, Ca expressed in at% concentrations) was developed to observe the influence of each alloying element on the density and melting temperature which were estimated using a weighted mean method, based on the rule of mixtures [17, 18]. Although deviation from the linearity of the rule is

to be expected [19, 20], a rough property estimate is useful since no experimental data was available.

The elastic modulus was estimated via correlation using equation (1) proposed by M. F. Ashby [21]. Young's modulus value depends upon the alloy composition and the rule of mixture is limited when more phases appear, due to the fact that each phase exerts its own influence:

$$C_L < \frac{E V_m}{R T_m} < C_U \quad (1)$$

In equation (1) E stands for elastic modulus in GPa, V_m the average volume per kmol in the structure, R the gas constant in $\text{kJ kmol}^{-1} \text{K}^{-1}$, T_m the melting temperature in K and C_L and C_U are dimensionless limits for various properties groups. In Ashby's study non-ferrous metals and alloys have limits values for the elastic modulus from 4.6 GPa to 570 GPa. In this study the limits for the elastic modulus were set according to those of some possible binary phases which were determined by Wang [22] in a similar system, as follows: $\text{Mg}_{17}\text{Al}_{12}$ of 70.12GPa, Mg_2Ca of 43.71GPa, Al_2Ca of 103.59GPa while the elastic modulus of aluminum is roughly 70GPa, thus setting the lower limit at roughly 43GPa and the higher one at 103GPa.

The uncertainty of this rule, estimated according to Ashby's work is 1.54. To increase the safety factor for our estimations, the lower value as reference for all computations has been used (table 2).

In the designed experiment boron influence was studied on a 1 (low) to 5 (high) at% while Mg, Si and Ca were studied on a 10 (low) to 20 (high) at% composition interval.

Aluminum content was varied as necessary to balance the composition, while its main characteristics (density, melting temperature and elastic modulus) were established as constants in the response equations for each characteristic. By performing the computations on a randomized order shown in table 3, results were estimated on model imposed theoretical chemical compositions.

Characteristics	Chemical elements				
	B	Mg	Al	Si	Ca
Atomic weight	10.811	24.305	26.98154	28.0855	40.078
Density, g/cm^3	2.46	1.738	2.66	2.33	1.55
Melting temperature, $^{\circ}\text{C}$	2075	650	660.32	1414	842
Atomic radius, pm	506.00	320.94	404.95	543.09	558.84
Valence electron concentration	2.04	1.31	1.61	1.9	1

Table 2
PHYSICAL DATA USED FOR
COMPUTATIONS [22]

Table 3
RUN ORDER AND INFLUENCE FACTOR VALUES USED IN THE DESIGN OF EXPERIMENT

Standard order	Run order	at% B	at% Mg	at% Si	at% Ca
10	1	High	Low	Low	High
1	2	Low	Low	Low	Low
7	3	Low	High	High	Low
13	4	Low	Low	High	High
14	5	High	Low	High	High
8	6	High	High	High	Low
12	7	High	High	Low	High
15	8	Low	High	High	High
5	9	Low	Low	High	Low
4	10	High	High	Low	Low
9	11	Low	Low	Low	High
11	12	Low	High	Low	High
2	13	High	Low	Low	Low
6	14	High	Low	High	Low
3	15	Low	High	Low	Low
16	16	High	High	High	High

The models generated from this runs order were applied for the study of the influence of the alloying elements concentrations on the density, melting temperature and elastic modulus of the alloy.

Starting with the estimated density of the alloy (ρ_{alloy}), the resulting response is described by equation (2) in uncoded units, where B, Mg, Si and Ca are the concentration of the element in atomic percent.

$$2.66 - 0.0015B - 0.012Mg - 0.004Si - 0.021Ca = \rho_{\text{alloy}} \quad (2)$$

In equation (2) second, third and fourth order interactions were neglected given their low coefficient values (10^{-5} - 10^{-9}) when compared to ones of main factors. The higher order interactions have such low values because the rule of mixture generates a linear variation.

Using equation (2) response surfaces were constructed and shown in figure 1. Because four factors can be varied, the surface construction required that 2 factors have fixed values (these are specified in the legend below), while the others have been varied. In figure 1a the concentrations of Si and Ca were fixed at 10, 15 and 20 at% while the concentration of B and Mg was varied from low to high values. In Figure 1b same procedure was applied, but this time B and Mg concentrations were fixed at values shown in the legend, while Si and Ca concentrations were varied from low to high.

The results show that a major influence in density decrease is played by Ca concentration, while Mg is second as importance. Boron and Silicon have a lower impact on density decrease when compared to Ca and Mg. Regarding the melting temperature (T_{melt}) of the alloy, the influence of

each of the alloying elements can be described using equation (3).

$$660.320 + 14.15B - 0.10Mg + 7.54Si + 1.81Ca = T_{\text{melt}} \quad (3)$$

Also, in equation (3) the second, third and fourth order interactions are neglected given their low coefficient values (10^{-15} - 10^{-18}). The response surfaces constructed in the same manner as described previously are shown in figure 2.

According to the variations of the response surface it appears that B has the largest role in increasing melting temperature, second being Si and third Ca. Magnesium has an opposite effect, because it lowers (almost insignificantly) the melting temperature of the alloy.

Studying the elastic modulus evolution of the alloy (E_{alloy}), its variation can be described by equation (4):

$$70.00 - 0.70B - 0.25Mg - 0.23Si - 0.50Ca = E_{\text{alloy}} \quad (4)$$

Again, second, third and fourth order interactions are omitted given their low coefficient values (10^{-16} - 10^{-19}). The response surfaces obtained by alloying element concentration variation are shown in figure 3.

Alloying element concentration increase tends to lower the elastic modulus of the alloy; most significant influences are shown by B followed by Si while Mg and Si are on par. These results combined allowed an alloy composition to be established for the experimental research. The goal of achieving a lower density alloy was slightly altered since

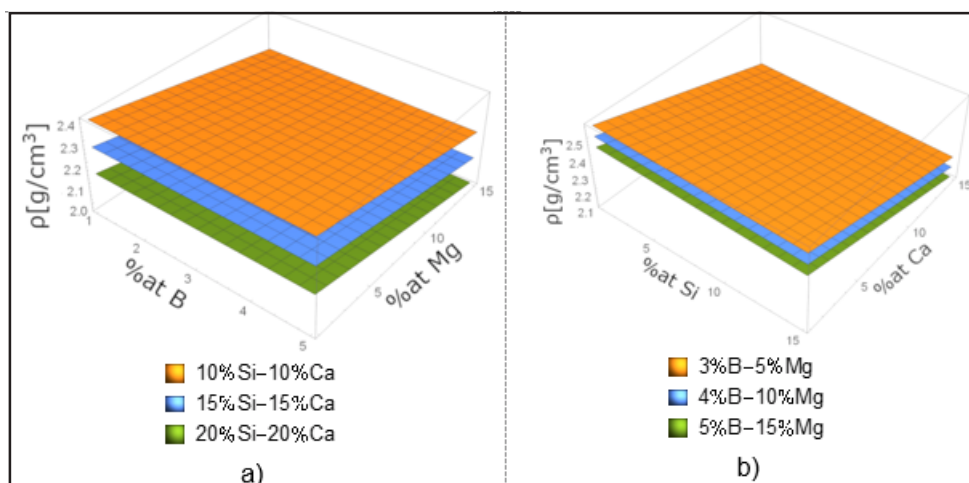


Fig. 1. Response surface showing factor influence on the density of the alloy.

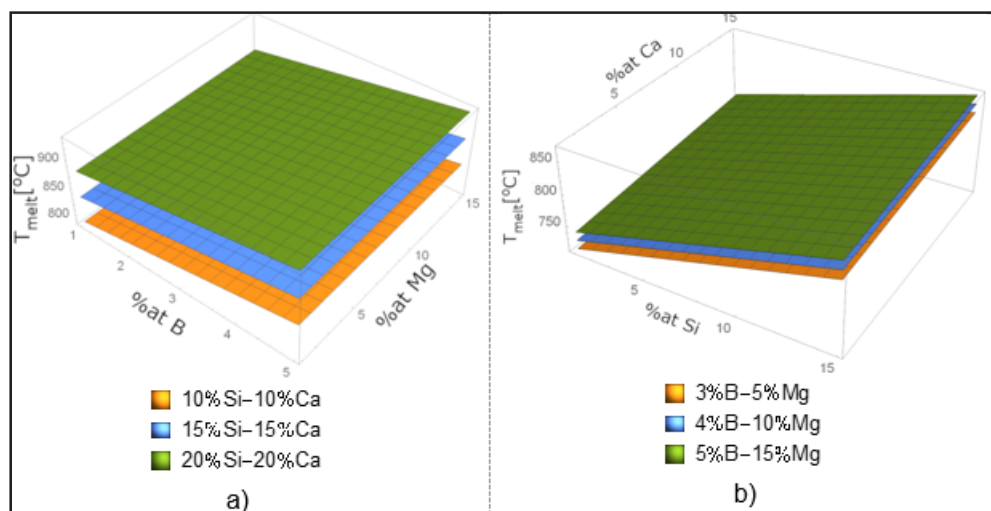


Fig. 2. Response surface showing factor influence on the melting temperature of the alloy.

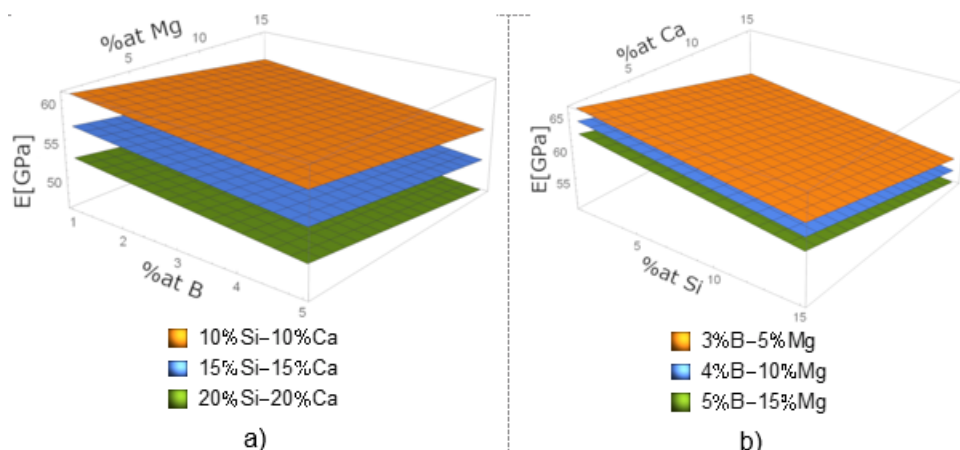


Fig. 3. Response surface showing factor influence on the elastic modulus of the alloy.

rigidity was also desired. The melting temperature was considered as an optional requirement.

A compromise was inevitable: a sacrifice on density was necessary in order to achieve higher mechanical characteristics, thus the alloy chosen for experimental elaboration was not the lightest in this system. Boron lowers the elastic modulus and density, but increases melting temperature – a concentration of around 5-7 wt% at was considered as optimum. Magnesium decrease all the parameters above, but its presence in aluminum alloys is proven beneficial for cold working, 15-20 wt% was taken into account and 15-20 wt% for silicon and 10-15wt% calcium. Aluminum concentration should balance to 100w%.

Alloy preparation

To obtain the alloy with the chemical composition within proposed ranges alloying elements and pre-alloys were used, as presented in table 4. Experimentally 30g batches can be made in available installations. Weighing individual

alloying elements, 5g of Mg, Ca and Si were added as pellets and an Al-B with 7 %wt B alloy was added, thus resulting 0.8g B and 14.2g Al. The experimental alloy expected chemical composition would comprise 47.33 wt% Al, 16.66 wt% Mg, 16.66 wt% Si, 16.66 wt% Ca and 2.69 wt% B as weight.

Converting the values alloy characteristics were determined by direct computations and using the models. The results are shown, for comparison, in table 5.

A good agreement between direct computations and the models has been observed. The alloy was prepared in a CTC50K15 induction heating furnace under argon protective atmosphere using zirconia crucibles (fig. 4). The raw materials were homogenized and placed simultaneously in the zirconia crucible.

After a preheating stage at 450°C, the materials were melted at 650 - 680°C followed by slow cooling, all the processes being performed under inert protective atmosphere. Losses by oxidation were estimated at 2%, despite the protective argon atmosphere.

Alloying element	Materials details	Average purity, %
Aluminum	2 – 5 mm pellets	99.5
Magnesium	2 – 5 mm pellets	99.5
Calcium	2 – 6 mm pellets	98.5
Silicon	technical silicon powder	99.5
Boron	Al – B pre-alloy containing 7% Boron	-

Table 4
MATERIALS USED FOR EXPERIMENTAL ALLOY

	Density, g/cm ³	Melting temperature, °C	Elastic Modulus, GPa
Direct computation	2.17	894.86	51.44
Model computation	2.13	894.98	51.34

Table 5
COMPARISON OF PREDICTED ALLOY CHARACTERISTICS

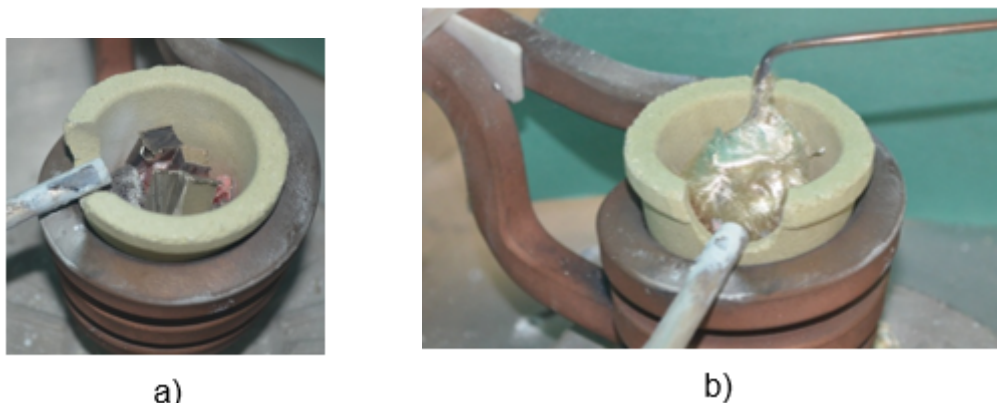


Fig. 4. Raw materials (a) and alloy melted by induction in the ceramic crucible (b).

Table 6
CHEMICAL COMPOSITION ON THE AREA OF INTEREST IN FIGURE 5b AND FIGURE 5c

Element	% wt		% at		Error %	
	b)	c)	b)	c)	b)	c)
Mg	8.55	4.79	9.62	5.31	3.36	5.58
Al	72.17	77.26	73.17	77.13	3.39	3.81
Si	13.54	3.95	13.19	3.79	8.93	11.13
Ca	5.67	-	3.87	-	4.84	-
Fe	1.14	8.16	0.57	3.93	12.11	3.18

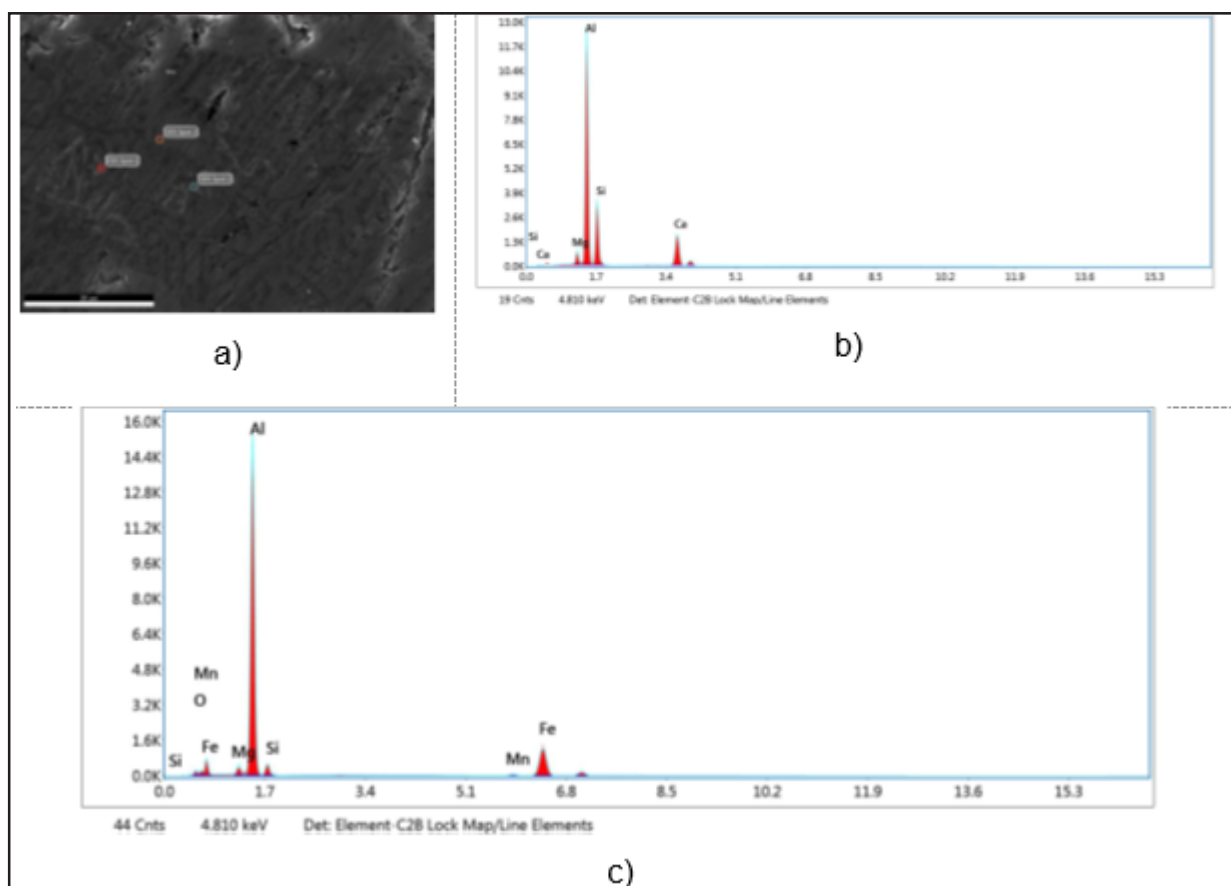


Fig. 5. Experimental alloy microstructure (a) and EDS spectra of micro-zones (b and c)

Results and discussions

Using the scanning electron microscope FEI-Quanta Inspect S equipped with an EDAX Z2e analyzer the microstructure and local chemical composition were studied on metallographic prepared specimens. In Figure 5 the microstructure can be observed with EDS spectra on a region of interest.

The microstructure presented in figure 5a reveals a typical as cast dendritic microstructure and chemical compounds. The material is inhomogeneous with obvious segregation, pores and microcavities. The quantification of the spectra shown in Figure 5b and Figure 5c revealed the chemical composition presented in table 6 for micro-zones of interest.

The presence, in small amounts, of Fe was observed and can be traced, most likely, to the Al-B pre-alloy used. Boron could not be quantified via EDS because of method limitation when dealing with elements with low atomic number Z. The element repartition suggests that inter-

dendrite regions are richer in magnesium, while inside the dendrite higher silicon and calcium contents are present. In the compound iron, silicon, magnesium and oxygen were found, similar to a natural occurrence reported by Neumann [23]. More electronegative elements (Al and Mg) are rejected in the interdendritic regions [1], while boron, the element with highest electronegativity, unfortunately could not be accurately detected by EDS. Based upon these results an inhomogeneous solid solution and inter-metallic compounds can be inferred to be present in the experimental as-cast alloy.

Conclusions

According to the aim of the research an alloy from the multi elements Al-Mg-Ca-Si-B system was manufactured, despite difficulties given by the oxidation tendencies of alloying elements. The alloy was studied by SEM and EDS and the results showed a multi-phase alloy with an

inhomogeneous solid solution and complex inter-metallic compounds.

The current results are satisfactory since the production method yields goods results. Based on these results, HEA with Al, Mg, Ca and Si in equimolar ratios can be obtained, by varying B content. In this situation the results predict a lower density, ranging, depending on composition, from 1.7 to 1.9 g/cm³ with the value of elastic modulus in the 45±3GPa range. The current experimental alloy will be gone through various processing routes and studied to establish the optimal processing route -microstructure - properties relation.

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