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# Ultrasound-assisted casting of AZ91D-1.5%Ca – Shifting T4 paradigm for downstream processing

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## Highlights

- Mg<sub>17</sub>Al<sub>12</sub> phase is refined using ultrasound during AZ91D-1.5%Ca cooling.
- Dissolution rate during T4 is higher for fine and divorced morphologies of Mg<sub>17</sub>Al<sub>12</sub>.
- T4 optimization of samples treated by acoustic energy helps downstream processing.

## Abstract

The effect of the as-cast microstructure on solution treatment of AZ91D-1.5%Ca was investigated. Ultrasound treatment was applied during the casted alloy's cooling, promoting the refinement of  $\alpha$ -Mg and  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phases. Fine and divorced  $\beta$ -phase was found in the ultrasound-treated sample, resulting in a superior dissolution rate of this intermetallic during subsequent solution treatment. The results indicate that tailoring the as-cast microstructure may be a route for optimizing the solution treatment necessary for downstream plastic deformation processes. The solution treatment's duration and temperature may be decreased, making the process economically and ecologically sustainable.

## Introduction

Magnesium alloys are the green structural material of the 21st century [1], given their high specific strength and great recyclability. However, casting these alloys is challenging due to their flammability, demanding a protective atmosphere of SF<sub>6</sub>, a powerful greenhouse gas [2]. Growing environmental awareness has prompted researchers and industries to develop innovative alternatives to SF<sub>6</sub>. Adding Ca considerably raises the ignition temperature of magnesium alloys by 200 to 300 °C [3], reducing their flammability and making their manufacturing less harmful to the

environment [4]. However, Ca-containing magnesium alloys exhibit a high fraction of intermetallic phases, namely  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>, which is detrimental to its formability and, therefore, to downstream plastic processing. Homogenization treatment before the deformation process for  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> dissolution has been suggested as a route for producing wrought alloys with improved mechanical properties [5]. Despite the promising results, the temperature and duration required due to the coarse intermetallic morphology make the process commercially undesirable and promote surface oxidation and grain growth [6]. The solution treatment (ST) optimization relies thus on the chemical or physical modification of the microstructure of the as-cast material. The addition of nanoparticles [7] in aluminium alloys has shown remarkable results in enhancing the dissolution of secondary phases, highlighting the potential of nano-treating approaches to control interfacial energy. Rare Earth (RE) elements can be used to refine  $\alpha$ -Mg, but their high cost makes them impractical for industrial uses, and increasing density reduces specific strength [8], [9]. Conversely, Ultrasound Treatment (UST) is a simple and cost-effective method for refining the primary and intermetallic phases, promoting a uniform distribution of the latter [10]. Some work has been published, however, there is a lack of research on the impact of UST on Ca-containing Mg alloys, especially on the subsequent processing routes.

Herein, we studied the effect of UST during the cooling of AZ91D-1.5% Ca alloy in its as-cast microstructure and assessed its impact on the kinetics dissolution of the intermetallic phase by performing ST under various conditions. This work discloses an opportunity of tailoring the as-cast microstructure to ST optimization of Ca-containing magnesium alloys, making it economically feasible and improving the properties of wrought material.

### **Experimental Procedure**

300 g of AZ91D-1.5%Ca (Mg-9.7Al-0.5Zn-0.2Mn, wt.%) was melted in a SiAlON crucible under an Ar protective atmosphere. The melt was held at  $620\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  for 20 min allowing the formation of the CaO protective layer, following which it was heated to  $660\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ , held for homogenization, and poured into a pre-heated metallic mold ( $350\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ ) coupled to an ultrasonic (US) device. US vibration was applied until the solidus temperature  $525\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ . Casted samples were solution treated at different

temperatures (385 °C and 415 °C) and times (2 h, 5 h, 12 h and 24 h), then quenched in water at room temperature. Samples for hardness testing and microstructural characterization were prepared according to standard metallographic procedures and etched with a 4% solution of HNO<sub>3</sub> in ethanol. Detailed analysis concerning the phase's morphology and chemical composition was performed using a Scanning Electron Microscope (SEM) equipped with an energy dispersive spectroscope (EDS).

Hardness tests were performed using an Officine Galileo under a load of 50 gf with a dwelling time of 15 s.

## Results and Discussion

Figures 1 (a) and (b) show the microstructure of non-treated and US-treated samples in the as-cast condition, respectively. Both microstructures are characterized by the presence of the same phases, identified through EDS analyses as primary  $\alpha$ -Mg,  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>, and Al<sub>2</sub>Ca. The application of US vibration during the solidification is suggested to have modified the morphology of the intermetallic phases, especially of the eutectic  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>. An increased tendency of small and homogeneously distributed divorced  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> was noticed, which may be justified by the higher cooling rate promoted by the acoustic streaming [11]. The refinement of primary  $\alpha$ -Mg may have led to the refinement of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase once the intermetallic is formed in the gaps left between the grains [10]. Conversely, in the absence of the US vibration, the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase was significantly coarser and presented mostly a partially divorced morphology typical of low cooling rates.

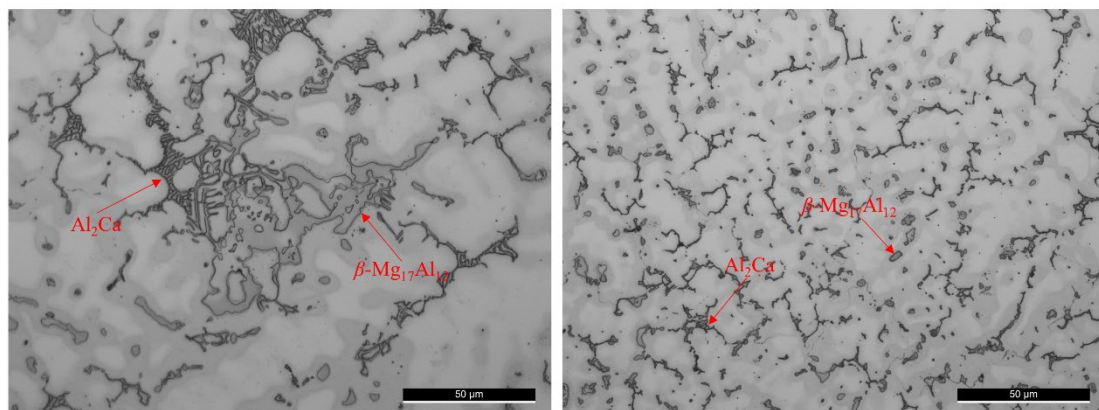


Figure 1 Microstructure of (a) non-treated and (b) US-treated samples in the as-cast condition.

In addition to the modification of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase morphology, remarkable changes could be observed regarding the shape and distribution of the Al<sub>2</sub>Ca phase. In the non-treated sample, a combination of reticular intermetallic distributed along the grain boundaries and coarse skeleton-like particles could be observed. When US vibration was applied, the network formed by the intermetallic became discontinuous and fragmented, showing a more uniform dispersion. The application of US vibration in a temperature range close to Al<sub>2</sub>Ca formation [12] may have restricted the intermetallic growth, resulting in its modification and homogeneous distribution. This modification of the intermetallic morphology has been reported to increase both strength and ductility of the alloy, stressing the potentiality of US treatment to enhance its performance in the as-cast condition [13].

The microstructure evolution of the non-treated and US-treated samples solutionized at 385 °C is presented in Figure 2 for solution treatment duration from 2 h to 24 h.

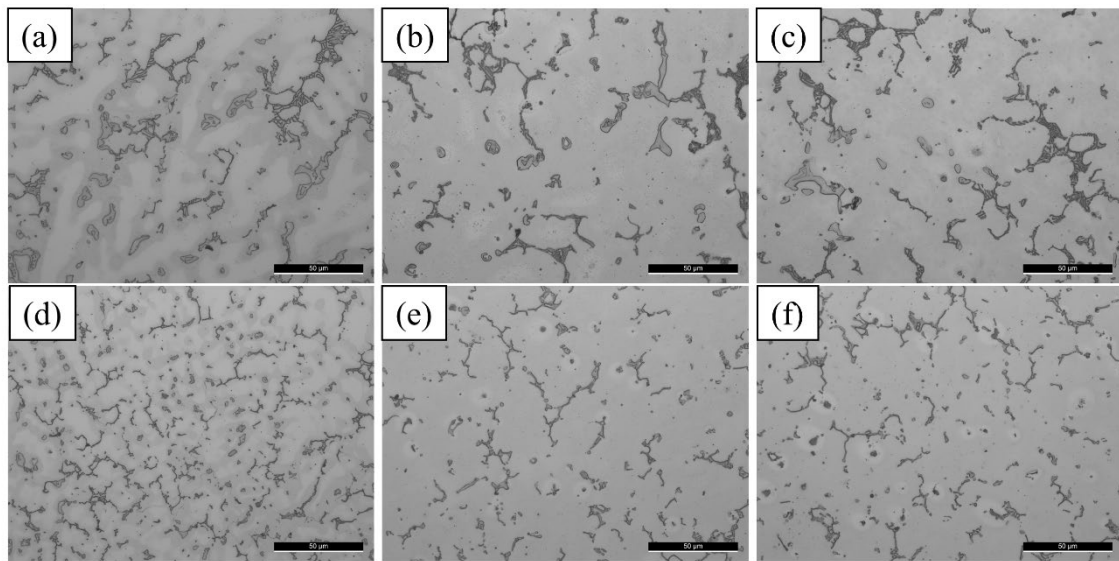


Figure 2 Evolution of the microstructure of non-treated (a, b, c) and US-treated (d, e, f) samples during solution treatment at 385 °C for 2 h, 5 h, and 24 h, respectively.

As can be observed, no significant difference in the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> morphology was noticed in the non-treated sample, regardless of the holding time. Indeed, coarse particles could be found even after 24 h of treatment, suggesting that no considerable dissolution occurred under these conditions. However, the US-treated sample showed a decrease of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase within the first treatment hours (see Figure 2 (e)); only a few particles could be observed after ST for 2 h. The difference observed in response to ST at 385 °C of the non-treated and US-treated samples is suggested to lay essentially in two

factors: (i) coarser particles require more time and/or higher temperature to dissolve [14] and (ii) according to EDS results, the concentration of aluminum in the matrix surrounding the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase in the non-treated sample is higher than the observed in the US-treated sample, making the diffusion process more difficult due to the lower aluminum gradient. Therefore, a longer time may be needed to allow the homogenization of the aluminum distribution throughout the matrix, so the dissolution of the intermetallic may occur.

As depicted in Figure 3, microstructural changes could be observed in both non-treated and US-treated samples by increasing the ST temperature to 415 °C, being noticeable a more significant evolution in the latter.

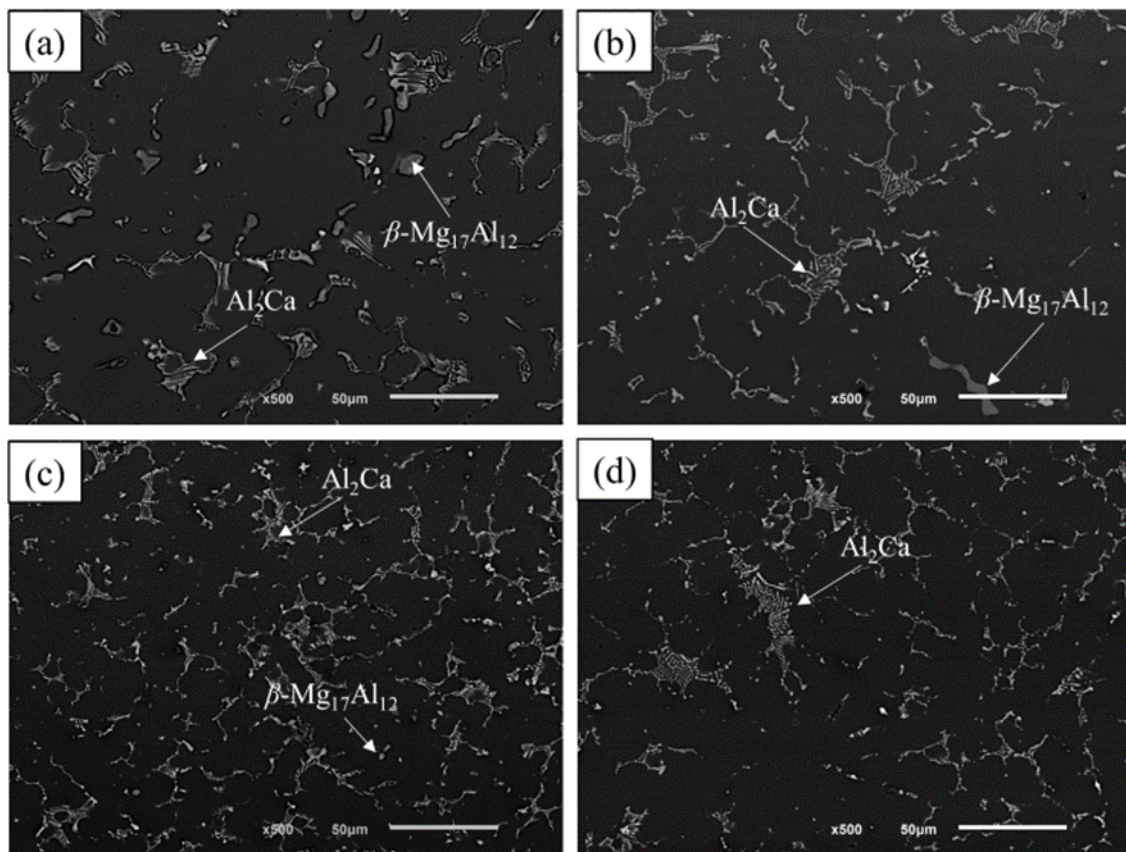


Figure 3 Microstructure of non-treated (a, b) and US-treated (c, d) samples solutionized at 415 °C for 2h and 24h, respectively.

In the non-treated sample, although a reduction of the presence of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> was evident even after only 2 h (Figure 3 (a)), some coarse particles remained regardless of the heat treatment duration (Figure 3 (b), indicating that longer ST could be required to dissolve them further. Conversely, after ST for 2 h (Figure 3 (c)), only small  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> particles

could be found in the US-treated sample, suggesting that it had been nearly completely dissolved after 24 h (Figure 3 (d)).

The hardness curves for the non-treated and US-treated samples are presented in Figure 4. The evolution of both samples' hardness agrees with the microstructural changes described above.

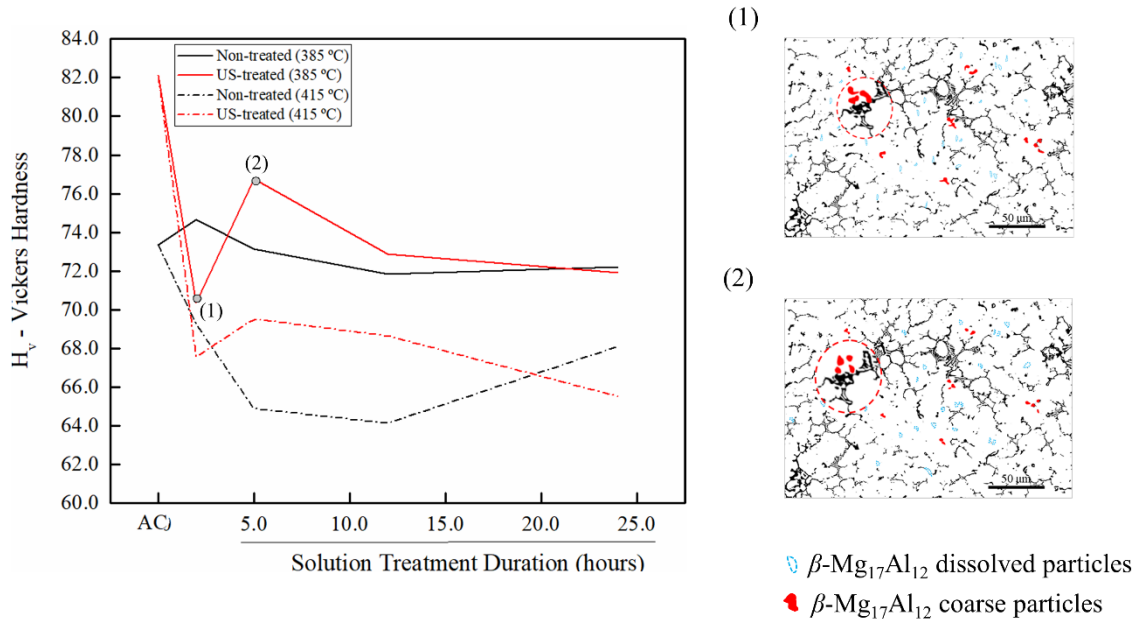


Figure 4 (a) Hardness curves for the non-treated and US-treated samples solutionized at 385 °C and 415 °C for different periods; (1) and (2) representation of the dissolution process of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> particles in the US-treated samples after 2 h and 5 h.

In the as-cast state, the hardness of both non-treated and US-treated samples was higher. In this condition, the US-treated sample exhibited a significantly higher hardness, which is the result of the refined microstructure. The difference in the hardness of the non- and US-treated samples showed a tendency to decrease as the ST proceeded. While for the non-treated sample solution-treated at 385 °C, the hardness value remained nearly constant throughout the treatment due to the lack of microstructural evolution, a sharp decrease in the hardness of the US-treated one was observed during the first 2 h of ST, followed by its increasing. The inversion in the hardness decreasing tendency of the US-treated sample is suggested to be resultant of the balance between two mechanisms that act contrarily: (i) within the first hours of the ST, the smallest  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> particles dissolved into the matrix (see Figure 4 (1)), leading to the softening of the material once this is the hardest phase of the material [15]; (ii) as ST proceeded to 5 h, the coarser  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> particles continued dissolving, decreasing their size (see Figure 4 (2)) and becoming more evenly distributed, which led to an increase in the hardness [16]. For

longer ST, the dissolution of most of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> occurs, and the particles' barrier effect fades out, causing the hardness value to decrease and stabilize.

When the ST is performed at 415 °C, the hardness of both non- and US-treated samples decreases due to the dissolution of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase. The dissolution of the intermetallic phase is mediated by the diffusion process, which is favored by the temperature increase, occurring faster. This way, despite the remarkable differences observed between the as-cast microstructures of non- and US-treated samples,  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> dissolution occurred in both. The increase in the ST temperature also contributed to the enhancement of aluminum diffusivity in magnesium, shortening the time required for achieving a homogenous aluminum concentration in the matrix and, thereby, a suitable concentration gradient to promote intermetallic dissolution. However, given the coarse and partially divorced morphology of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> in the non-treated sample, this process is suggested to take longer than in the US-treated sample, and a continuous decrease in the material's hardness could be observed until after 12h. The hardness of the sample increased after 24 h, which may have been promoted by the presence of smaller and rounder intermetallic particles resulting from the dissolution of coarser ones. As previously suggested, such smaller and rounder particles of the intermetallic phase can offer an enhanced combination of strength and elongation [17]. Nevertheless, a continuous decrease in the US-treated sample hardness was observed. Grain growth promoted by prolonged exposure to high temperature may explain this tendency as the average grain size increases, and the reduced  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> fraction has been reported to lead to the alloy softening [18].

Considering the results obtained, it is possible to conclude that the significant difference in the dissolution rate of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> during ST between the non- and US-treated specimens may be justified mainly through the particles' morphology, composition, and distribution in the as-cast state along with the aluminum concentration in the matrix. In the non-treated sample,  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> appears mainly as non-uniformly distributed partially divorced coarse lumps characterized by a small interfacial area for Al atoms diffusion, hindering their dissolution [17]. The concentration gradient in the partially divorced eutectic found in the non-treated sample is not uniform, which, together with the high aluminum concentration in their surroundings, leads to the dissolution of the intermetallic to be slowed down [19]. Moreover, part of the added Ca is dissolved in the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>,



which is known to increase the thermal stability of this phase. According to the EDS results shown in Figure 5, the amount of Ca dissolved in the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> is higher in the non-treated sample than in the US-treated one. This difference, allied to the larger intermetallic particles and higher aluminum concentration in their surroundings, can explain the lower dissolution rates of the non-treated sample. Also, the US-treated sample exhibited smaller and evenly distributed  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> throughout the alloy, reducing the diffusion distance and, therefore, shortening the time required for the dissolution process.

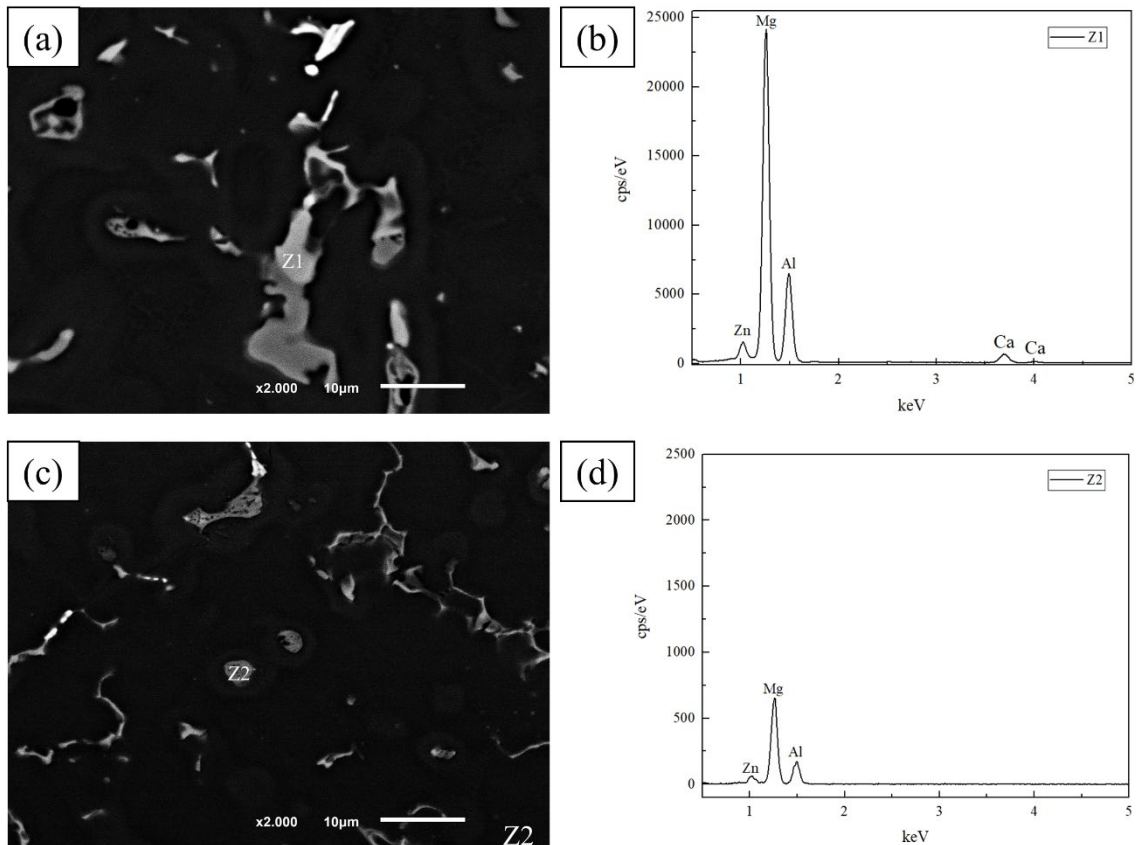


Figure 5 SEM image of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> particle in the (a) non-treated and (b) US-treated samples; (c) and (d) composition of Z1 and Z2, respectively.

## Conclusions

Applying US treatment during AZ91D-1.5%Ca alloy cooling has significantly changed its microstructure, promoting the refinement of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> and Al<sub>2</sub>Ca intermetallic phases. In the as-cast state, the US-treated sample exhibited higher hardness which is suggested to be explained by the finer microstructure. A faster dissolution rate was observed for the US-treated sample, which is explained by the presence of a divorced and uniformly distributed small  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> eutectic phase with a lower Ca content. It has been demonstrated that tailoring the as-cast microstructure through US treatment is a

promising route for optimizing the ST, enabling a reduction in the temperature and time needed. By increasing productivity and reducing energy consumption, ST required for downstream plastic deformation processes becomes more economically and environmentally sustainable.

### **CRedit authorship contribution statement**

**I.V.Gomes; F. D’Errico; J.L. Alves; H. Puga**

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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