Effect of solution treatment on the microstructural evolution and mechanical properties of an aged Mg–4Zn–0.3Ca alloy

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A B S T R A C T

The effect of solution treatment on the microstructure, mechanical properties, and creep resistance of cast Mg–4Zn–0.3Ca (wt%) alloy was investigated. Creep behavior was assessed by the impression creep testing at 175 and 225 °C, while shear yield stress (SYS) and ultimate shear strength (USS) values were measured by the shear punch testing (SPT) at room temperature and 175 °C. A semi-continuous network of Ca2Mg6Zn3 phase was found to form at grain boundaries after a single-step (SS) solution treatment (500 °C/4 h). This phase was, however, completely dissolved into the matrix after a double-step (DS) solution treatment (350 °C/20 h+510 °C/3 h). The SS treated samples exhibited better mechanical properties and creep resistances, due to the presence of the thermally stable Ca2Mg6Zn3 phase, mainly at grain boundaries. This phase, however, made the SS treated samples more susceptible to brittle fracture by acting as preferred sites for initiation of micro-cracks that could easily propagate through the intergranular phase network. On the other hand, DS treated samples had inferior mechanical properties and creep resistances, as compared to the SS treated condition, due to the elimination of the intergranular phases and activation of twinning during deformation.

A R T I C L E   B U I L D E R

1. Introduction

During the last decade, a great deal of interest has been shown to magnesium alloys by the automobile, aerospace and electronic industries. This has been stemmed from their superior properties such as low density, high specific strength, and good castability. Unfortunately, some disadvantages like limited cold workability, poor creep resistance, and low strength at elevated temperatures have restricted the use of Mg alloys in these applications [1]. Among different Mg alloys, those based on the Mg–Zn–Ca system have a great potential for development of low-cost magnesium alloys with good elevated temperature mechanical properties, caused by their age hardening capability [2]. Formation of the thermally stable phases such as Ca2Mg6Zn3 and Mg2Ca (at higher levels of Ca) further improves high-temperature mechanical properties of these alloys [3,4]. These alloys are considered as heat-treatable wrought Mg alloys, the mechanical properties of which can benefit from aging treatment after deformation processing [5].

Most of the existing investigations on the aging behavior of Mg–Zn–Ca alloys involve detailed characterization of the precipitates and the precipitation sequences [6–8]. Different solution treatment regimes have been applied in this regard; some at high temperatures in a single step [6,7], and some via double-step solution treatments [2,3]. In some studies, a long-term homogenization step before solution treatment has been reported [8,9]. It is concluded that different solution treatment regimes result in different microstructures, which could affect the final mechanical properties of the aged material. The solutionizing parameters of a ZA84 magnesium alloy were optimized and the parameters required for maximum dissolution of precipitates were determined [10]. It was also found that, heating of this material to temperatures higher than the formation temperature of the second phase, might lead to the phase melting. The effects of heat treatment on the microstructure and mechanical properties of a ZW21 magnesium alloy were investigated. A proper heat treatment technique was found which corresponded to the highest strength, elongation and hardness values [11]. In another study on the age-strengthening in an Mg–Zn–Al–Er alloy, it was found that a two-step progressive solution treatment could enhance the age-hardening response, due to the dissolution of the ternary eutectic phases in the Mg–Zn–Al system without the formation of microstructural overheating defects [12]. Solution treatment can also affect the final mechanical properties by modification of the second phase particles, as reported for an AZ61–0.7Si magnesium alloy with Mg5Si phases having undesirable Chinese script morphology [13].

The above findings emphasize the influence of solution treatment on mechanical properties of the age-hardenable Mg alloys. However, none of the above-mentioned studies on the aging behavior of the Mg–Zn–Ca alloys has taken into account the
influence of the solution-treated microstructure on the final mechanical properties. Therefore, the aim of the current work is to study the effect of solution treatment on the microstructural evolution and mechanical properties of the Mg–4Zn–0.3Ca alloy.

2. Experimental procedure

2.1. Materials and processing

Pure Mg (99.8 wt%), Zn (99.9 wt%), and an Mg–10 wt% Ca master alloy were used to prepare the alloy with nominal composition of Mg–4Zn–0.3Ca (wt%), corresponding to Mg–1.5Zn–0.2Ca (at%). Melting was carried out in a graphite crucible placed in an electrical furnace under protection of a covering flux. The detailed description of the melting procedure has been provided elsewhere [14]. Casting bars had the dimensions of 12 mm × 30 mm × 180 mm, from which samples were cut by electrodischarge machining for heat treatment, impression creep, SPT, and microstructural characterizations. Two solution treatment regimes were used, namely single step (SS) and double step (DS). The SS route involved solutionizing at 500 °C for 4 h, followed by water quenching (WQ). The DS treatment consisted of solutionizing at 350 °C for 20 h, heating up to 510 °C in 2 h, holding at 510 °C for 3 h, and then WQ. Samples were coated with a thin layer of MgO in order to avoid the oxidation during solution treatment. Several specimens from each conditions were then aged at 210 °C for different times in the range of 2–60 h, to obtain the peak aging condition. This aging time was selected for processing of the samples for the impression creep test and SPT.

2.2. Microstructural characterization

Microstructural examinations were conducted using optical microscopy, scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS), and X-ray diffraction (XRD). XRD measurement was performed using CuKα radiation at 40 kV and tube current of 30 mA over the 2θ ranging from 20° to 80°, using a step size of 0.02° with a counting time of 0.5 s at each step. An 8 vol% Nital solution and an acetic picral solution (100 cc ethanol, 10 cc acetic acid, 5 cc distilled water and 4.2 g picric acid) were used to reveal the microstructural features of the SS and DS samples, respectively, in the solution-treated and peak-aged conditions.

2.3. Mechanical tests

Hardness measurements were performed on the aged specimens, using Vickers harness test under 100 N load, to determine the aging time corresponding to the peak hardness. At least five indentations were made on each sample and the average lengths of the diagonals were used to estimate the hardness values. A universal tensile testing machine equipped with a three-zone split furnace was used to perform shear punch and impression creep tests in the air atmosphere. The details of testing arrangement of these tests are explained elsewhere [15,16] and will only be briefly described here. 10 mm × 10 mm × 1 mm slices, cut from the as-cast as well as the peak-aged conditions, were ground to a thickness of about 0.7 mm for the shear punch test (SPT). These tests were conducted at room temperature and 175 °C using a fixture with a 3.175 mm diameter flat-ended cylindrical punch and 3.225 mm diameter receiving-hole at a constant cross-head speed of 0.25 mm min⁻¹. In impression creep tests, a flat-ended cylindrical punch 2 mm in diameter was mounted in a holder positioned in the center of the vertical loading bar. The 3-mm-thick specimens were located on an anvil below the loading bar; the assembly of the specimen and the indenter was accommodated by the split furnace. Measurements were made on each sample at 175 and 225 °C and under the respective punch stresses of 450 and 350 MPa, for dwell times up to 3600 s. After application of the load, the impression depth was measured automatically as a function of time by the machine; the data were acquired by a computer.

3. Results and discussion

3.1. Microstructure of the as-cast alloy

The optical and SEM micrographs of the as-cast Mg–4Zn–0.3Ca alloy are shown in Fig. 1a and b, respectively. It can be observed that, there exists a dendritic microstructure with some second phases that are located in the interdendritic regions. These interdendritic particles
are eutectic phases that form in the final stages of solidification. The irregular morphology and the distribution of these eutectic phases in the matrix are demonstrated in the SEM micrograph of the alloy in Fig. 1b. X-ray diffraction pattern, exhibited in Fig. 1c, indicates that the microstructure consists of α-Mg phase and the MgZn and Ca₂Mg₆Zn₃ phases. The eutectic phase in the Zn-rich binary Mg–Zn alloys is Mg₅₁Zn₂₀, which forms at 340 °C [17]. This phase transforms to MgZn through an eutectoid decomposition at 320–316 °C [18]. Depending on the alloy chemical composition, the Ca₂Mg₆Zn₃ phase that is the most common ternary compound in Mg–Zn–Ca alloys, also forms through a eutectic reaction in the temperature range of 370–400 °C [19,20]. Formation of such a phase has been frequently reported in the Mg–Zn–Ca alloys containing 4–6 wt% Zn and 0.3–0.6 wt% Ca [19–21].

Results of EDS analysis and elemental maps of Mg, Zn and Ca obtained for the as-cast material are presented in Fig. 2. It is evident in Fig. 2b–d that the second phase particles have higher concentrations of Zn and Ca atoms rather than α-Mg matrix. EDS results indicate that the α-Mg matrix contains 1 at% Zn with no dissolved Ca. Two types of second phase particles with different morphologies and chemical compositions are also detected. The gray particles, denoted as B and C in Fig. 2a, are rich in Zn and Ca. The typical chemical composition of these particles is Mg₆₀Zn₂₄Ca₁₅, which corresponds to the Ca₂Mg₆Zn₃ compound. Other particles with bright contrast, denoted as D and E in Fig. 2a, are rich in Zn and contain small amounts of Ca. The typical Mg₅₄Zn₄₃Ca₂.₃ composition of these particles is close to that of the MgZn phase.

3.2. Microstructure after solution treatment

The optical images of the solution-treated samples are presented in Fig. 3. The microstructure of the SS solution-treated
sample shown in Fig. 3a consists of equiaxed grains with a grain size of $65 \pm 8 \mu m$. As can be seen, second phase particles are mostly distributed along grain boundaries and triple points. Some spherical particles are also observed in the grain interiors. After the DS treatment, however, the network of the grain boundary particles vanishes, due to the dissolution at the lower solutionizing temperature of 350 °C (Fig. 3b). It is further revealed that some fine particles are distributed at the grain boundaries as well as within the grains. The grain size of the DS solution-treated sample is 140 ± 20 μm.

A higher magnification SEM image and EDS results of the SS sample are shown in Fig. 4a. The α-Mg matrix, denoted as A, in this case contains 1.5 at% Zn and 0.1 at% Ca in the form of solid solution. The maximum solid solubility of Zn in Mg is 2.4 at% at 340 °C [17]. With regards to the chemical composition of the studied alloy, the maximum amount of Zn has been dissolved in the α-Mg matrix during SS regime. However, EDS analysis of second phase particles demonstrates that these particles also contain high levels of Zn. Points B and C in Fig. 4a correspond to the grain boundary phase and spherical second phase particles, respectively. Although these phases have different morphologies, they seem to possess similar compositions containing 22.7–24.4 at% Zn and 12.7–13.4 at% Ca. Both the grain boundary phase with semi-continuous network morphology and the isolated spherical particles inside the grains are identified as Ca$_2$Mg$_6$Zn$_3$. Formation of the Ca$_2$Mg$_6$Zn$_3$ phase with a similar morphology has been previously reported in an Mg–5.12Zn–0.32Ca alloy after solution treatment at 500 °C for 3 h [22].

As mentioned in the previous section, Ca$_2$Mg$_6$Zn$_3$ phase is formed through a eutectic transformation from liquid at about 400 °C [19]. Therefore, the temperature of the SS solution treatment, i.e. 500 °C, is higher than the formation temperature of this phase. In other words, solution treatment at 500 °C is believed to cause the melting of the Ca$_2$Mg$_6$Zn$_3$ phase which re-solidifies during the subsequent water quenching at room temperature. According to the isothermal section of the ternary Mg–Zn–Ca phase diagram at 465 °C [23], a liquid phase is formed in a region close to the Zn-rich corner of the diagram at this temperature. The chemical composition of the alloy in the present study lies in this region. Therefore, it is reasonable to expect that melting of Ca$_2$Mg$_6$Zn$_3$ phase occurs during the SS solution treatment at 500 °C. Those Ca$_2$Mg$_6$Zn$_3$ particles that are close to dendrite boundaries are located along the newly-formed grain boundaries, while others that are trapped in the grain interiors, form the spherical particles. Formation of such a continuous network of Ca$_2$Mg$_6$Zn$_3$ second phase at grain boundaries has a great influence on the mechanical behavior of the aged sample. This effect will be discussed in the next section.

The DS solution treatment regime was attempted in order to avoid the local melting of the Ca$_2$Mg$_6$Zn$_3$ phase that occurred during the SS solution treatment, and to prevent the formation of semi-continuous network of second phase at grain boundaries. According to the isothermal section of the ternary Mg–Zn–Ca phase diagram at 335 °C [24], no melting occurs at this temperature and Ca$_2$Mg$_6$Zn$_3$ phase is expected to dissolve during the long-term heat treatment in the first step of the DS solution treatment. The second step of the DS solution treatment at 510 °C provides higher concentration of vacancies which are expected to remain in the microstructure supersaturated during the subsequent quenching and provide more inhomogeneous nucleation sites during the aging treatment [25]. The corresponding microstructure of the DS condition is exhibited in Fig. 3b. As can be seen, most of the interdendritic phases have been dissolved during the solution treatment. The 350 °C temperature is well below the formation temperature of the Ca$_2$Mg$_6$Zn$_3$ phase. Therefore, during holding at this temperature for prolonged periods, Ca$_2$Mg$_6$Zn$_3$ particles are dissolved. The microstructure in this case is composed of equiaxed grains with well-defined boundaries together with very fine particles distributed mostly in the grain interiors. The grain size of 140 ± 20 μm, which is higher than that of the SS condition, has been achieved by a long time exposure to high temperature during the double-step solution treatment. Furthermore, restricted grain boundary movement due to the grain boundary phases leads to smaller grain sizes in the SS condition. As demonstrated in Fig. 4b, the matrix contains about 1.6 at% Zn and trace amount of Ca. EDS analysis shows that there are two types of second phase particles; namely, Zn-containing particles with 8.2 at% Zn and 0.9 at% Ca, and Ca-containing particles with 0.4 at% Zn and 7.1 at% Ca. These compositions are not close to those of the well-known second phases in the Mg–Zn–Ca alloys. More investigations are thus required for accurate identification of these particles.

### Table 1. Chemical composition (at%) of the studied alloy.

<table>
<thead>
<tr>
<th>Point</th>
<th>Chemical composition (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
</tr>
<tr>
<td>A</td>
<td>98.3</td>
</tr>
<tr>
<td>B</td>
<td>90.9</td>
</tr>
<tr>
<td>C</td>
<td>92.5</td>
</tr>
</tbody>
</table>

Fig. 4. SEM micrographs after (a) single-step (SS) and (b) double-step (DS) solution treatments. Results of EDS analysis from indicated points are also presented for each condition.
3.3. Microstructure and mechanical behavior after aging treatment

Variations of hardness value as a function of aging time for the SS and DS treatments are shown in Fig. 5. It is evident from this figure that SS sample has higher hardness than DS sample in the as-solutionized condition. This may be due to the presence of \( \text{Ca}_2\text{Mg}_6\text{Zn}_3 \) particles in a high volume fraction after the SS solution treatment. These particles are present in all aged SS samples, and therefore, the strength of these samples comes partly from such particles. The DS sample has a lower hardness in the as-solutionized condition, as expected, since most of the second phase particles have been dissolved during the double-step solution treatment. Both SS and DS solution-treated samples show good response to aging treatment. This response is more pronounced for the DS samples with lower hardness in the solution-treated condition. In other words, aging treatment in this route leads to a more increase in hardness due to the formation of precipitates from supersaturated matrix. At all aging times, DS samples possess higher hardness values, as compared to the SS samples. The peak hardness values in the SS and DS conditions during aging at 210 °C are 57.7 and 57.1 Vickers, which are achieved after 8 and 14 h aging, respectively.

The optical microstructures of the peak-aged SS and DS samples are shown in Fig. 6. During the aging treatment, grain growth occurs in both of the samples. The grain size of the peak-aged SS sample is \( 70 \pm 15 \text{ μm} \), while DS sample experiences a significant grain growth during aging, such that the grain size in this case increases to \( 220 \pm 20 \text{ μm} \). Some abnormally large grains also exist in the peak-aged DS samples. In the SS solution treated sample (Fig. 6a), two kinds of secondary phases are detectable; a grain boundary network of \( \text{Ca}_2\text{Mg}_6\text{Zn}_3 \) particles with a nominal thickness of about 4–6 μm, and some spherical particles of the same composition with an average size of 5 μm, located in the grain interior. Again, grain boundary phases in the SS sample have a considerable pinning effect that confines grain growth during the aging treatment in this condition. In the DS solution treated sample (Fig. 6b), however, a rather uniform distribution of spherical particles with an average size of 4 μm is achieved.

Fig. 7 shows the shear punch curves of the peak-aged SS and DS samples in the peak-aged condition at (a) room temperature and (b) 175 °C. For comparison, SPT curves of the as-cast material are also presented.

\[
\tau = \frac{P}{\pi d t}
\]
where $P$ is the punch load, $t$ is the specimen thickness, and $d$ is the average of the punch and die diameters. Similar to the conventional tensile stress–strain curves, the shear punch curves consist of three stages. The first stage is an elastic region in which the shear stress varies linearly with normalized displacement. At the end of this region, shear stress deviates from linear behavior at a point which is taken as the shear yield stress (SYS). The material is then plastically deformed till the shear stress reaches a maximum value. The stress corresponding to this maximum point is referred to as the ultimate shear strength (USS). The material finally goes through necking and fracture.

Values of SYS and USS for the peak-aged SS and DS samples, derived from SPT curves in Fig. 7, are summarized in Table 1. SYS and USS data in the as-cast condition are also included in Table 1. It is observed that the SS condition has higher SYS and USS values than the DS condition at room temperature and 175\degree C. It is worth noting that the drop in the SYS and USS values with increasing temperature is more pronounced for the DS condition.

Typical impression creep curves at 175 and 225\degree C for the peak-aged SS and DS materials together with the as-cast alloy are presented in Fig. 8. Similar to the conventional creep curves, in the first stage of the creep curves impression depth increases with dwell time with a decreasing rate. A steady-state is then reached in which the impression depth increases linearly with time. Impression velocity ($V_{imp} = dh/dt$) in this region is taken as a parameter for comparing the creep resistance of different materials. Values of the minimum creep rate ($\dot{\epsilon}_{\text{min}} = V_{imp}/2$) for the as-cast and peak-aged SS and DS samples are included in Table 1. Since the impression test is compressive in nature, the third stage of the conventional tensile creep curves is not recorded. It is clear in Fig. 8 and Table 1 that the SS condition shows lower impression depth and also lower minimum creep rate, as compared to the DS condition.

It is well-known that the room- and high-temperature mechanical properties of the materials are affected by their microstructural features. Peak-aged SS sample has a smaller grain size which could be effective in the enhancement of its mechanical properties by the Hall–Petch strengthening mechanism. Moreover, the presence of the thermally-stable Ca$_2$Mg$_6$Zn$_3$ phase, in the form of semi-continuous grain boundary networks and isolated spherical particles, in the SS condition is also responsible for its better mechanical properties at room and high temperatures. However, it has been reported that the Ca$_2$Mg$_6$Zn$_3$ phase is the main strengthening agent of the aged Mg–Zn–Ca alloys [3]. Therefore, the inferior mechanical properties of the peak-aged DS samples may be due to different deformation modes which are activated under the applied load in the peak-aged samples. Accordingly, microstructural examination of the tested conditions after shear punch

<table>
<thead>
<tr>
<th>Condition</th>
<th>SYS (MPa)</th>
<th>USS (MPa)</th>
<th>$\dot{\epsilon}_{\text{min}}$ ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT 175\degree C</td>
<td>43</td>
<td>22</td>
<td>$6.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>SS</td>
<td>96</td>
<td>71</td>
<td>$4.8 \times 10^{-6}$</td>
</tr>
<tr>
<td>DS</td>
<td>67</td>
<td>44</td>
<td>$9.8 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Fig. 8. Impression creep curves of the single-step (SS) and double-step (DS) samples in the peak-aged condition, (a) at 175\degree C under impression stress of 450 MPa and (b) at 225\degree C under impression stress of 350 MPa. For comparison, creep curves of the as-cast material are also presented.

Fig. 9. Optical microstructures of the deformed area under shear punch for (a) single-step (SS) and (b) double-step (DS) solution treatments.
and impression creep deformations could be clarifying in this regard.

Fig. 9 exhibits the optical micrographs of the cross-sections adjacent to and beneath the punch in the peak-aged SS and DS samples after the room-temperature shear punch test. The tests corresponding to these micrographs were interrupted immediately after the maximum point, when a load drop was detected in the curves. As can be seen in Fig. 9a, grains surrounded by the Ca$_2$Mg$_6$Zn$_3$ phase in the SS sample have been deformed along shear direction. In the microstructure of the DS sample, shown in Fig. 9b, on the other hand, activation of twinning in the sheared region is evident. In contrast to the SS condition, there is a ductile deformation pattern with no visible cracks in the sheared region. Twinning is a prevalent deformation mode during room-temperature loading of Mg alloys with hcp crystal structures, because the basal slip provides only two independent slip systems, far fewer than the necessary five independent systems for a homogeneous deformation. Single crystal studies have shown that the basal slip and (10T2) twinning are relatively easily activated under only a few MPa of stress [27].

The after-creep microstructure of the peak-aged SS sample in the vicinity of the impression edge after creep testing at 175 °C under the applied stress of 650 MPa is depicted in Fig. 10. Three zones can be distinguished which are labeled as regions 1, 2, and 3. Region 1 is a hemispherical dead zone underneath the indenter, in which the material undergoes no considerable deformation because the stresses are hydrostatic. This situation is similar to region 3, far from the indenter, in which there is no detectable flow pattern. In region 2, however, an extensive shear deformation takes place in a narrow region under the indenter. It can be seen in Fig. 10a that grains surrounded by Ca$_2$Mg$_6$Zn$_3$ network in region 2 are elongated along the deformation path. A higher magnification view of this region shown in Fig. 10b indicates that the grains tend to align in the flow direction of the material. The presence of thermally stable Ca$_2$Mg$_6$Zn$_3$ network around the grains can hinder the dislocation movement and grain boundary sliding in the deformation zone. The after-creep microstructure of the peak-aged DS sample, presented in Fig. 11, shows that the specimen has experienced an intensive twinning in region 2 during creep deformation. This observation could explain the weaker creep resistance of the peak-aged DS condition, as compared to the SS treated samples.

There is a distinct difference between microstructures of the peak-aged SS and DS samples, in terms of average grain size and presence of coarse second phase particles. Therefore, it is worth considering the effect of these two microstructural parameters on the twinning. It is well known that a reduction in grain size serves to reduce the tendency for twinning because small grain size suppresses twinning nucleation. The stress to activate twinning has been reported to follow a linear Hall–Petch relationship [28,29]. With the decrease in the grain size, higher stress is required to activate twinning. Thus, twinning is more easily activated in the alloy with a large grain size. The Hall–Petch coefficient is larger for twinning than for slip [28], meaning that twinning activation is more sensitive to the grain size than slip. On
the other hand, many experimental studies have shown that particles can strongly affect the twinning in magnesium [30,31]. Twins can interact with particles in various ways, depending on the particle size and shape. However, the effect of coarse particles, especially those located along grain boundaries on the twin nucleation is not clear. Generally, in the competition between twinning and slip, the presence of more mobile dislocations in the microstructure leads to the occurrence of slip [32]. The coarse precipitates are expected to suppress twinning because the high strains in the particle/matrix interface are accommodated by the formation of dislocations which could facilitate slip. Furthermore, in the absence of any grain boundary phases, stresses can be transmitted from one grain to another, activating twinning or slip. Therefore, in the peak-aged SS sample containing grain boundary phases, activation of twinning requires more stress.

The higher tendency of the peak-aged DS samples for twinning can now be explained with regards to their larger grain size, resulted from the long time exposure to high temperatures during solution treatment, and grain boundaries that are free of second phase particle, exhibiting no resistance to grain growth during solutionizing and subsequent aging treatment (Fig. 3b). Very large grain size and the activation of twinning under the applied load lead to poor mechanical properties in this condition. This is in contrast to the SS samples, with smaller average grain sizes and Ca$_2$Mg$_6$Zn$_3$ second phase particles at the grain boundaries. The role of twinning in deterioration of mechanical properties of the peak-aged DS condition will be clearer when the shear punch data of the DS samples are compared with those of the as-cast material in Fig. 7 and Table 1. It is interesting that no significant enhancement is observed in the mechanical properties of the DS sample, as compared to the as-cast material at room temperature, even though it possesses higher hardness value. At 175 °C, the SYS and USS values of the DS sample are lower than that of the as-cast material. This is because small dendrites and interdendritic particles in the as-cast condition can efficiently inhibit the formation of twins in this case. As can be seen in Fig. 8 and Table 1, creep resistance of the as-cast material is better than that of the peak-aged DS condition.

The above-mentioned results indicate that; (i) a long time annealing at temperatures lower than the formation temperature of Ca$_2$Mg$_6$Zn$_3$ phase during solution treatment of the Mg–4Zn–0.3Ca alloy will result in the loss of mechanical properties of the aged alloy, and (ii) the presence of the thermally stable Ca$_2$Mg$_6$Zn$_3$ phase which forms during the single-step solution treatment is more beneficial to improvement of mechanical properties of the aged alloy. However, the semi-continuous network of the Ca$_2$Mg$_6$Zn$_3$ particles at grain boundaries has a detrimental effect on the ductility of the material. The peak-aged SS treated sample is susceptible to brittle fracture under high stresses. The reason is that the presence of such a network of second phase particles may favor micro-crack initiation, especially during quenching from high temperature. Actually, the difference between the thermal expansion coefficients of the matrix and coarse Ca$_2$Mg$_6$Zn$_3$ particles may cause tensile stresses in the second phase particles and/or along the matrix/particle interfaces. Therefore, micro-cracks could initiate in the hard Ca$_2$Mg$_6$Zn$_3$ particles. In Fig. 12a a network of grain boundary Ca$_2$Mg$_6$Zn$_3$ particles in the peak-aged SS sample is shown at a high magnification, clearly exhibiting such micro-cracks. Moreover, the initiated micro-cracks can easily propagate through grain boundary networks which may lead to fracture of the whole sample cross section by development of the macro-cracks. Examples of these macro-cracks are exhibited in Figs. 9a and 10a in the shear zone and near the impression edge, respectively. A possible solution to avoid the early failure of the peak-aged SS samples caused by the propagation of such macro-cracks could be decreasing the ΔT of quenching by increasing the temperature of the quenching media, of course not to an extent that largely affects the super-saturation capacity and subsequent age-hardenability of the resultant material.

4. Conclusions

Two kinds of single-step and double-step solution treatments were applied to an Mg–4Zn–0.3Ca alloy and the effect of microstructure on the room- and high-temperature mechanical properties was studied. The obtained conclusions are summarized as follows:

1. After single-step solution treatment, the microstructure consists of equiaxed α-Mg grains with a semi-continuous network of Ca$_2$Mg$_6$Zn$_3$ phase at grain boundaries, and some isolated spherical particles of the same intermetallic compound inside the grains. After double-step solution treatment, Ca$_2$Mg$_6$Zn$_3$ phase is completely dissolved and there exist two types of Zn-rich and Ca-rich particles mostly inside the grains. The grain sizes of the single- and double-step solution-treated samples were 65 ± 8 and 140 ± 20 μm, respectively.

2. Both single-step and double-step solution-treated samples were hardened during subsequent aging at 210 °C, reaching the hardness values of 57.7 and 57.1 Vickers at peak-aged condition, respectively. Grain sizes of the peak-aged SS and DS samples were 70 ± 15 and 220 ± 20 μm, respectively.

3. The peak-aged single-step solution-treated samples exhibited higher SYS and USS values and better creep resistances than the peak-aged double-step solution-treated samples. This is because of the smaller grain size, and formation of hard and thermally stable Ca$_2$Mg$_6$Zn$_3$ phase in high volume fractions during the single-step solution treatment.

4. The peak-aged single-step solution-treated samples were susceptible to developing micro-cracks. Ca$_2$Mg$_6$Zn$_3$ is a brittle phase which is easily being cracked during quenching or under the applied load. The initiated cracks in the Ca$_2$Mg$_6$Zn$_3$ phase or its interface with the matrix could easily propagate through the grain boundary semi-continuous network and lead to failure of the sample before it could undergo a considerable plastic deformation.

References