Effect of microalloying with Ca and Al on the microstructure, mechanical and corrosion properties of the ZM60 alloy

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Abstract
The microstructure, mechanical and corrosion properties of the ZM60 alloy with different contents of Al and Ca were investigated by optical microscopy (OM), x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and tensile tests. The results show that the as-cast ZM60 alloy consisted of \( \alpha \)-Mg and \( \text{Mg}_{51}\text{Zn}_{20} \) phases. There is no obvious change of microstructure when adding 1 wt% of Al to the ZM60 alloy. With the increasing addition of Al, \( \text{Mg}_{51} \text{Al}_{90} \text{Zn}_{10} \) phase presented in the alloy replacing the \( \text{Mg}_{51}\text{Zn}_{20} \) phase. The microstructure of the as-cast alloy in which Ca and Al were simultaneously added was composed of \( \alpha \)-Mg, \( \text{Al}_{8}\text{Mn}_{5} \) and \( \text{Mg}_{52} \text{Al}_{90} \text{Zn}_{10} \) phases. The grain size of the extruded alloys were well refined with the addition of Al or a mixture of Al and Ca. The grain refining effect of adding Al and Ca is better than adding Al alone, leading to the smallest grain size of 2.2 \( \mu \)m. The strengthening mechanism of the alloys were mainly fine-grain strengthening with the addition of Al and Ca. Compared with the ZK60A alloy, the tensile strength of the ZAMX6100 alloy increased by about 20MPa, the yield strength increased by about 30MPa, and the elongation was similar. The corrosion resistance of Mg-6Zn alloy was also improved significantly through adding Al and Ca.

As the lightest structure metal material, the research and application of Mg alloy have received large attention from researchers and the industry [1]. Wrought Mg alloys have high specific strength and can be used in transportation and aerospace industries. The ZK60A alloy is one of the most successful wrought commercial magnesium alloys. However, its application is restricted due to the high production cost and poor corrosion resistance. Currently, the amount of the wrought magnesium alloys is less than 5% of the total amount of Mg products [2].

It is known that microalloying is an effective way to improve the mechanical properties of magnesium alloys. Studies have shown that the strength of the Mg–4.9Zn–0.2Ce wt%, as follows) [3], Mg–1Zn–0.12Sr [4], Mg–5Zn–0.9Y–0.16Zr [5], Mg–2Zn–0.3Zr–0.9Y [6], Mg–4Zn–0.3Ca–0.1Ce [7], Mg–5.25Zn–0.6Ca–0.3Mn [8], Mg–6Zn–0.2Ca–0.8Zr [9] and Mg–3Zn–0.25Ca–0.5Zr–0.15Mn [10] alloys are much higher than their Mg–Zn counterparts.

Al has a great strengthening effect on Mg alloys [8]. Park et al [11] concluded that the addition of Al could refine the microstructure of the Mg–6Zn–1Mn alloy (ZM61). The amount of the MgZn2 phase decreased with the presence of the Al3Mn5 phase in the alloy. In this study, the Mg–6Zn–1Al alloy had good comprehensive properties with tensile strength of 330MPa, yield strength of 307MPa and an elongation of 16.2%. However, adding too much Al is detrimental to the toughness of the alloy due to the precipitation of coarse \( \Phi \)-\( \text{Mg}_{52}\text{(Al, Zn)}_{17} \) phase. The grain refining effect of Ca in magnesium alloys comes from two parts. On one hand, the diffusion rate of Ca in magnesium alloys is very low, which restricts the growth of the grains. On the
other hand, the Ca atoms have a strong tendency to precipitate leading to a constitutional super cooling inside the diffusion layer at the front of the solid-liquid interface of Mg solidification. More nucleation sites are activated inside this super cooling area and lead to a significant grain refinement. In addition, the grain refinement can also occur during deformation as well as the weakening of deformation texture [12, 13].

Compared with the addition of single element, adding multi-elements can refine microstructure and improve the mechanical properties of Mg-Zn alloy [8, 9, 14, 15] more effectively. For example, the extruded microstructure of the Mg-6Zn–0.2Ca–0.8Zr alloy has a smaller grain size than the Mg-6Zn–0.2Ca alloy, and the size of the precipitates in the Mg-6Zn–0.2Ca–0.8Zr alloy is also smaller and more dispersively distributed [9]. K Oh-ishi et al [16–18] studied the effect of Ca and Ag addition on the ZK60A alloy. The results show that with the addition of a small amount of Ca and Ag, the density of the precipitated MgZn2 phase (rod shape) was significantly increased. At the same time, the length-width ratio of this phase was also raised. The distribution and aggregation condition of the Ca, Ag and Zn atoms was studied by three dimensional atom probe, and they concluded that the increased density of the precipitates was closely related with the aggregation of the Ca atoms.

In this work, the alloys were prepared with squeeze casting and extrusion. Al and Ca were added to the Mg-6Zn alloy instead of the commonly used Zr. The effect of microalloying with Al and Ca on microstructure, mechanical and corrosion properties were studied systematically. The results of this work will provide a theoretical basis for developing low-cost high-strength corrosion-resistant Mg alloys.

1. Experiments

1.1. Alloy preparation

Four kinds of Mg–6Zn–0.5Mn–xAl(–0.5Ca) alloys were prepared using an electric resistance furnace melting high purity Mg, Al, Zn billets and Mg–10%Mn, Mg–20%Ca alloys in a steel crucible under the mixed gas atmosphere of CO2 and SF6 (mix ratio 100:1). The ZK60A alloy was prepared according to the ASTM standard B107/B107M-17. The molten alloy was squeeze-cast after the refining process. The pressure of squeeze casting was held 30s at 100MPa. The mold temperature was 250 °C and the size of the cylindrical casting ingots was Ø150 mm x 100 mm. The chemical composition of the alloys is summarized in table 1. The ingots were homogenized at 335 °C for 8h and then extruded at 360 °C with the extrusion ratio of 16:1 and an extrusion rate of 1.0 mm s–1.

1.2. Experimental methods

All samples were cut from the billets along the extrusion direction, cleaned and polished. The samples for microstructure observation were etched in a solution of 10 ml deionized water, 6 g picric acid, 5 ml acetic acid and 100 ml of ethanol. Thin foil specimens for the transmission electron microscopy (TEM) observation were prepared using a standard mechanical grinding followed by the ion-beam milling techniques. The TEM observation was carried out at 5.0 kV. Electron back-scatter diffraction (EBSD) samples were electro-polished in a solution of 37.5% phosphoric acid and 62.5% ethanol under the electric current of 0.1–0.5 A for 10–60 s at a temperature of lower than 20 °C.

Through inductively coupled plasma (ICAP6300) analysis, the chemical composition of the tested alloys were determined according to the standard GB/T13748.20–2009. Optical microscopy (OM, Olympus) was used to observe the microstructure of the extruded alloys. Scanning electron microscopy (SEM, Quanta Feg250) and transmission electron microscopy (TEM, FEI 5022/22 Tecnai G2 20 S-TWIN) were used to observe the refined microstructure and the distribution of second phases in detail. The second phases in the as-cast alloys were characterized by a x-ray diffractometer (XRD, Rigaku D/max-2500/PC). Tensile tests were performed at ambient temperature following the ASTM standard A370–03a at a crosshead speed of 1 mm min–1. Cylindrical tensile samples of 36 mm in gauge length and 6 mm in gauge diameter were machined from as-extruded bars. The electrochemical corrosion behavior of the alloys was evaluated by the traditional three-electrode system
using an electrochemical workstation (EC500) at the room temperature. The working electrode, the counter electrode and the reference electrode were the specimen, a platinum electrode and a saturated calomel electrode (SCE), respectively. All samples were immersed in the 3.5% NaCl solution for 5 h to achieve stable OCP values, and the potentiodynamic polarization tests were performed at a scanning rate of 1.0 mV s\(^{-1}\). The exposed area of each sample was 1.0 cm\(^2\).

2. Experimental results

2.1. Microstructure of the as-cast alloys

Figure 1 shows the XRD patterns of the four as-cast alloys. The data shows that the ZM60 and the ZAM610 alloys were consisted of \(\alpha\)-Mg and Mg\(_{51}\)Zn\(_{20}\) phases; while \(\alpha\)-Mg and Mg\(_{32}\)(Al,Zn)\(_{49}\) phases were detected in ZAM620 and ZAMX6100.

The SEM images of the four as-cast alloys are shown in figure 2. In the ZM60 alloy, there was a small amount of second phases, which were mainly distributed at the grain boundaries. Since the Zn content in these alloys was close to the solution limit, the second phases presented a typical dissociated eutectic structure. EDS analysis shows that the second phases of ZM60 was composed of Mg and Zn elements, which later were identified as Mg\(_{51}\)Zn\(_{20}\) phase through XRD results. This phase is identical with the solidified equilibrium phase of the Mg–Zn alloy [19].

With the addition of Al or Al+Ca, the amount of second phases increased obviously. When the content of Al is small, the morphology and the amount of the eutectic microstructure was similar to the ZM60 alloy. The second phases in the alloy was mainly Mg\(_{51}\)Zn\(_{20}\) phase determined by EDS and XRD. With the increase of Al content, the lamellar eutectic microstructure at the grain boundaries became thick and large. At the same time, some second phases grew into half-net shape, which was the Mg\(_{32}\)(Al,Zn)\(_{49}\) phase according to the EDS results. Meanwhile, there was some fine bright particles in the matrix which was determined as Al\(_6\)Mn\(_3\) by EDS.

After adding Al+Ca, lamellar microstructure formed at the grain boundaries of the ZAMX6100 alloy. This lamellar phase was not in net-shape and obviously thinner than that in the ZAM620 alloy. It was determined as the Mg\(_{52}\)(Al,Zn)\(_{49}\) phase by EDS. In the ZAMX6100 alloy, there were two types of granular second phases: the large grey granules, which were Mg\(_{52}\)(Al,Zn)\(_{49}\) and the small white granules, which were Al\(_6\)Mn\(_3\).

The determination of the second phases in the ZAMX6100 alloy can be found in detail in the related research about Mg–6Zn–0.5Ca–0.5Mn [20].
2.2. Microstructure of the as-extruded alloys

Figure 3 shows the optical microstructure of the homogenized alloys. As shown in the figure, there were also some undissolved second phases in the alloys due to the same homogenized temperature and time. Those particles broke in extrusion and were largely distributed on the recrystallized grain boundary.

Figure 4 shows the optical microstructure of the extruded alloys. A completely recrystallized microstructure could be found in these alloys. The grain size of the ZM60 alloy was large. After adding 1 wt% of Al, the recrystallized microstructure of the alloy was refined obviously. There was no obvious further refinement of the microstructure when the addition of Al was increased to 2 wt%. However, with the addition of Al+Ca, the microstructure in the ZAMX6100 alloy was refined further compared with the ZAM610 and the ZAM620 alloys. The average grain size was measured using the intercept method. The average grain size of the ZM60, ZAM610, ZAM620 and ZAMX6100 alloys were 19.8 μm, 5.6 μm, 5.4 μm and 2.2 μm, respectively. The results show that, adding of Al or Al+Ca has a significant refining effect on the Mg–Zn alloy, and the refining effect of Al+Ca is better.

Since the cast ingots were homogenized before being extruded, most second phases in the microstructure were resolved in the matrix. Only few residual second phases could be observed in the extruded alloys. These were broken into micro-meter irregular shape particles, distributed along the extrusion direction. Figure 5 shows the SEM microstructure of the as-extruded alloys. The EDS results show that the residual second phases in the extruded ZAMX6100 alloy was Al_{6}Mn_{5} phase.

Figure 6 shows the TEM images of the extruded alloys. As can be seen from the figure, there are many dislocation entanglements in the grains of the ZM60 alloy. In the ZAM610 and ZAM620 alloys, there are some phases in submicron size, as shown in figures 6(b) and (c). The amount of particles in ZAM620 is more than that
in ZAM610 due to the increase of Al content. According to the previous EDS analysis results, these submicron particles were Al₈Mn₅ phases. In the ZAMX6100 alloy with the addition of Al⁺Ca, as shown in Figure 5(d), the amount of the precipitates was obviously more than the ZM60, ZAM610 and ZAM620 alloys. These particles can be divided into two types according to their sizes: the larger particles were Al₈Mn₅ phases in several hundred nanometers or several micrometers; the smaller particles were in the size of several tens of nanometer. Figure 7 shows the high resolution TEM image of the dynamically precipitated phases in the extruded ZAMX6100 alloy.
The smaller particles were in very large amount and they were precipitated during the extrusion process. According to the SEAD results, these were MgZn2 phases. Extrusion texture of the ZAM610, ZAM620 and ZAMX6100 alloys were analyzed by EBSD with the extrusion direction vertically placed. Figure 8 is the EBSD map of the (0001) pole chart of the as-extruded alloy. According to figures 8(a) and (b), complete dynamic recrystallization occurred in the extruded ZAM610 and ZAM620 alloys. An obvious grain growth can also be observed due to the high temperature of extrusion of these two alloys. ZAM610 and ZAM620 demonstrated typical fiber texture of extrusion with the basal planes of most grains parallel to the extrusion direction.

According to figure 8(c), the extrusion microstructure of the ZAMX6100 alloy is finer with some deformed part remained, shown as blue grains in the figure of microstructure. Low angle grain boundaries can be detected in these deformed part as shown with white lines. Compared with the extruded ZAM610 and ZAM620 alloys, the component of basal texture in the ZAMX6100 alloy is weaker due to the addition of Ca and Al. The randomized extrusion texture is beneficial to the improvement of ductility of the alloy.

2.3. Mechanical properties of the extruded alloys
Table 2 shows the mechanical properties of extruded alloys. The extruded ZM60 alloy has very poor mechanical properties. With a small addition of Al, the toughness of the ZAM610 alloy was raised significantly. Compared with the ZM60 alloy, the average tensile strength, yield strength and elongation were raised about 78MPa, 78MPa and 9.3%, respectively. With an increasing amount of Al content, the strength of the ZAM620 alloy was...
further improved, while the elongation decreased. With the addition of Al+Ca, the tensile and yield strength of the ZAMX6100 alloy were higher than that of the ZAM 620 alloy, and its elongation was similar to ZAM610. Compared with the ZK60A alloy, the tensile strength of the ZAMX6100 alloy increased by about 20MPa, the yield strength increased by about 30MPa, and the elongation was similar.

Table 2. Tensile properties of the as-extruded Mg–Zn–Mn–Al–Ca alloys.

| Alloy    | Tensile strength /MPa | Yield strength /MPa | Elongation /% |
|----------|-----------------------|---------------------|---------------|
| ZM60     | 205/231/238           | 133/134/147         | 7.5/11.5/12.0 |
| ZAM610   | 304/302/302           | 216/215/217         | 19.0/21.5/18.5|
| ZAM620   | 324/332/317           | 246/262/235         | 7.5/7.5/9.5   |
| ZAMX6100 | 358/355/350           | 317/316/307         | 16.5/17.5/18.0|
| ZK60A    | 329/330/330           | 279/282/279         | 18.5/15.5/18.5|

Figure 8. The EBSD maps and corresponding pole figures of the as-extruded alloys. (a) ZAM610 alloy; (b) ZAM620 alloy; (c) ZAMX6100 alloy.
2.4. Corrosion properties of the as-extruded alloy

Figure 9 shows the polarization curves of the as-extruded ZAM610, ZAMX6100 and ZK60A alloys. The corrosion electric potential ($E_{corr}$) and the electric current density ($i_{corr}$) value were deduced from the Tafel curves, as shown in Table 3. Compared with the ZK60A alloy, the $E_{corr}$ of the ZAM610 alloy was 57mV higher while the $i_{corr}$ was 1.633mA higher. The $E_{corr}$ of the ZAMX6100 alloy was comparable with the ZK60A alloy, however its $i_{corr}$ was smaller by one order of magnitude. Generally, the more positive the $E_{corr}$, the smaller the $i_{corr}$, and the better the corrosion-resistant properties. Therefore, the corrosion-resistant properties of the experimental alloys almost remained the same after adding Al. While it was improved significantly with the addition of Al+Ca.

Figure 10 shows the morphology of the alloys after the corrosion experiments. It can be seen that the corrosion product of the ZK60A alloy was short-rod-shape particulates loosely cumulated with many micro-cracks (width < 1 μm) on the surface. The corrosion product of the ZAM610 alloy was plate-shape particulates cumulated more loosely and there was more micro-cracks on the sample surface. The surface of ZAMX6100 is similar to that of ZK60A with more fine particulates cumulated.

### Table 3. Corrosion potential and corrosion current density deduced from Potentio dynamic polarization curves.

| Sample     | ZK60A | ZAM610 | ZAMX6100 |
|------------|-------|--------|----------|
| $E_{corr}$ / V | -1.535 | -1.478 | -1.536    |
| $i_{corr}$ / mA·cm$^{-2}$ | 8.592  | 10.225 | 0.908     |
Table 4. Weightlessness of the samples after immersion in a 3.5% NaCl solution for 5h.

| Sample   | ZK60A | ZAM610 | ZAMX6100 |
|----------|-------|--------|-----------|
| Initial mass/g | 1.1975 | 1.4117 | 1.2571    |
| Mass after immersion/g | 1.1985 | 1.4125 | 1.2569    |
| Mass without corrosion product/g | 1.1501 | 1.4047 | 1.2522    |
| Corrosion velocity/mg cm$^{-2}$·h | 9.68 | 1.40 | 0.98 |

Table 4 shows the weightless of the corrosion samples after immersion in the solution. According to this table, the corrosion velocity of the ZK60A alloy was highest and its weight loss after corrosion was also maximum. The weight loss of the ZAMX6100 alloy after corrosion is minimum indicating the best corrosion-resistant properties. The corrosion velocity of the ZAMX6100 alloy was approximately one-tenth of the ZK60A alloy. The corrosion resistance of the ZAM610 alloy was slightly lower than that of the ZAMX6100 alloy.

3. Discussion

3.1. Effect of microalloying with Al on microstructure and mechanical properties

According to the Mg–Zn binary phase diagram, eutectic reaction occurs at 613K (340 °C), the liquid phase solidifies and forms $\alpha$-Mg and primary eutectic compounds. Currently, there is no conclusion about whether the primary eutectic phase is $\text{Mg}_5\text{Zn}_2$ or $\text{Mg}_7\text{Zn}_3$ determined [21, 22]. Both the $\text{Mg}_5\text{Zn}_2$ and the $\text{Mg}_7\text{Zn}_3$ phases have the same body centered orthogonal crystal structure, in space group of $I_{mmm}$, with lattice parameters of $a = 1.4083$ nm, $b = 1.4486$ nm and $c = 1.4025$ nm. According to the results of this work, the primary eutectic phase in the as-cast ZM60 alloy is $\text{Mg}_5\text{Zn}_2$. Figure 11 shows the ternary phase diagram of Mg–Zn–Al at 335 °C [23]. Since Al has a high solubility in Mg (12.9wt% at eutectic temperature), most Al in the ZAM610 alloy was in the solution and only few $\text{Al}_8\text{Mn}_5$ phases formed. When the Al content increased, $\text{Mg}_3\text{Zn}_2$ formed in the ZAM620 alloy, and the amount of the $\text{Al}_8\text{Mn}_5$ phases also increased. WAN et al [24] studied the microstructure of the Mg–(8%–12%)Zn–(2%–6%)Al alloys. The results showed that when the mass ratio of Zn/Al was high (about 4–6), the microstructure is mainly composed of $\alpha$-Mg phase, plate-shape $\varepsilon$-$\text{Mg}_5\text{Zn}_2$ phase and bulk shape $\tau$-$\text{Mg}_5\text{Zn}_2$ phase. When the mass ratio of Zn/Al is medium (2–3), $\varepsilon$-$\text{Mg}_5\text{Zn}_2$ phase disappeared, only $\tau$-$\text{Mg}_5\text{Zn}_2$ phase remained distributed half-continuously or continuously along the grain boundaries.

After the homogenization treatment at 335 °C, most second phases in the as-cast alloys dissolved in the matrix and only $\text{Al}_8\text{Mn}_5$ phase remained due to its high melting point. According to the Mg-rich corner of the Mg–Zn–Al ternary phase diagram at 335 °C, it can be found that the alloy was composed of $\alpha$-Mg, $\text{Al}_3\text{Mg}_1\text{Zn}_4$...
and MgZn phases. Therefore, $\text{Mg}_{32}(\text{Al},\text{Zn})_{49}$ is a metastable phase [23]. Thus, during the homogenization process, with the diffusion of Al atoms, $\text{Mg}_{32}(\text{Al},\text{Zn})_{49}$ phase decomposed into the matrix. Dynamic recrystallization occurred in the four alloys during the extrusion process. The critical resolved shear stress (CRSS) value of the $(c + a)$ prismatic slip system at elevated temperatures deformation is quite low. Therefore, the $(c + a)$ slip system could be easily activated [25]. There is very few second phases in the ZM60 alloy, which hinder the movement of dislocations and the grain boundaries. Therefore, the grain size of the ZM60 alloy was large. The addition of Al lowers the stacking fault energy of the Mg alloy [26, 27], and promotes the occurrence of dynamic recrystallization, which is beneficial to the grain refinement. In addition, the broken $\text{Al}_6\text{Mn}_5$ phases have a pinning effect on dislocations. Thus, the grain sizes of ZAM610 and ZAM620 were smaller than ZM60.

Microalloying with Al also improved the mechanical properties of the alloys significantly. The grain sizes of ZAM620 and ZAM610 were 27% and 29% of ZM60. According to the Hall-Petch relationship, the smaller the alloy grain size, the higher its strength. Because of its HCP crystal structure, Mg alloys have few slip systems and large Taylor factor (Magnesium is 6.5, Aluminum is 3.1) [25]. Therefore, grain size refinement of Mg alloys has a prominent effect on the increase of its strength. There was only a small amount of $\text{Al}_6\text{Mn}_5$ phases in the ZAM610 and ZAM620 alloys. During the extrusion process, they were broken and distributed along the extrusion direction and thus increased the yield strength of the alloy. The amount of the $\text{Al}_6\text{Mn}_5$ phases in ZAM620 was significantly larger than in ZAM610. As a result, the yield strength of ZAM620 was higher than ZAM610.

Alloying affects corrosion properties of Mg alloys mainly in two ways: on one side, alloy elements dissolve into the matrix and change the electric potential of the matrix, and affect corrosion properties in this way; on the other side, second phases form and affect the corrosion behavior by controlling the amount and the distribution characteristics [28, 29].

The corrosion electric potential of the four alloys in this study is between $-1.60$ and $-1.40$V. Compared with the standard electric potential of Mg of $2.37$V [30], the corrosion electric potential of these alloys were more negative. After adding Al, the corrosion electric potential of ZAM610 became larger compared with ZK60A. Since the as-extruded microstructure of ZAM610 was composed of $\alpha$-Mg and a small amount of $\text{Al}_6\text{Mn}_5$ phase, the Al mostly dissolved into the $\alpha$-Mg matrix. Thus, Al is beneficial to the improvement of the corrosion electric potential of the matrix. This is identical with the present research results [31].

3.2. Effect of microalloying with Al+Ca on microstructure and mechanical properties

After adding 0.5%Ca, $\text{Mg}_{32}(\text{Al},\text{Zn})_{49}$ appeared in the ZAM610 alloy, replacing the $\text{Mg}_{32}\text{Zn}_{20}$ phase. The study of ANYANWU et al shows that, the solubility of Al and Zn decreased after the addition of a small amount of Ca, leading to the precipitation of MgZn and $\text{Mg}_{32}(\text{Al},\text{Zn})_{49}$ phases. Since the melting point and the high-temperature stability of $\text{Mg}_{32}(\text{Al},\text{Zn})_{49}$ were higher than that of the $\text{Mg}_{32}\text{Zn}_{20}$ phase, the $\text{Mg}_{32}\text{Zn}_{20}$ phase was substituted [32]. Moreover, adding Al in the Mg–Zn alloys can enhance the Zn solubility in Mg matrix [23], and the Ca atoms can aggregate at the solid-liquid interface. It can promote the precipitation of $\text{Mg}_{32}(\text{Al},\text{Zn})_{49}$ phase, as was observed in the ZAMX6100 alloy. In addition, Al atoms and Mn atoms have a strong tendency to form the $\text{Al}_6\text{Mn}_5$ phase, which was observed in the twin-roll cast Mg–6Zn–1Al and Mg–6Zn–1Mn–3Al alloys [11].

Since the entropy of mixing between Ca–Zn is larger than Mg–Zn and Mg–Ca, Ca atoms easily aggregate with Zn atoms and provide nucleation sites for the dynamic precipitation of the MgZn$_2$ phase [33, 34]. During the extrusion, large amount of MgZn$_2$ phase precipitated dynamically in the ZAMX6100 alloy were in the size of nanometers. These dynamically precipitated MgZn phases together with the undissolved phases in the alloy can effectively hinder the movement of dislocations. Therefore, the deformation band formed during the extrusion retained [7]. In addition, there were small amount of micrometer-size $\text{Al}_6\text{Mn}_5$ phases in the matrix. The combination of large and small particulates has a very strong pinning effect on dislocations, leading to the smallest grain size in the ZAMX6100 alloy after dynamic recrystallization compared with the ZAM610 and ZAM620 alloys.

Microalloying with Al and Ca can significantly enhance the mechanical properties of the Mg–Zn alloy. The strength and toughness of the ZAMX6100 alloy in this study were higher than the ZK60A alloy. After dynamic recrystallization during the extrusion, the grain size of the ZAMX6100 alloy was 10.9% of ZM60. The yield strength of the ZAMX6100 alloy was one time higher than the ZM60 alloy, and the fine grain strengthening effect was predominant. At the same time, the amount of grain boundaries also increased after the refinement, which makes it easier for grain boundary sliding under outside uploaded stress. This allows the ZAMX6100 alloy to bear more deformation and it’s the toughness was improved greatly.

Precipitation strengthening is another important reason for the improvement of the strength. The ZAMX6100 alloy hadn’t only broken $\text{Al}_6\text{Mn}_5$ particles from the extrusion process, but also large amount of fine dispersed MgZn$_2$ particles, which could hinder movement of dislocation effectively. Thus, the yield strength of the ZAMX6100 alloy was higher than the other three alloys. Generally, the larger the precipitates, the stronger the pinning effect on moving dislocations. These precipitates were beneficial to the increase of yield strength, but
detrimental to the toughness, because large precipitates could work as the nucleation sites of cracks [35]. Therefore, the elongation of the ZAMX6100 alloy was smaller than ZAM610, but higher than ZAM620. It indicates that grain size has a larger effect on the ductility than the precipitation. In this study, the high strength and elongation of ZAMX6100 alloy were mainly attributed to the fine grain sizes.

Texture is also an affecting factor on Mg alloy toughness. The peak texture intensities of the four Mg–Zn alloys after microalloying were as follows: ZM60 alloy > ZAM610 alloy > ZAMX6100 alloy > ZAM620 alloy. The weakening of texture lowers the activation stress level of the basal slip and prismatic slip [36]. A weak recrystallization texture is beneficial to the ductility of Mg alloys.

After adding Al and Ca, the corrosion electric potential of the ZAMX6100 alloy was lower than ZAM610 and similar to the ZK60A alloy. The as-extruded ZAMX6100 alloy was composed of $\alpha$-Mg, MgZn2 and Al6Mn5 phases. Due to the precipitation of MgZn2, the concentration of Zn decreased in the matrix, which may be the main reason for the decrease of the corrosion electric potential. Previous research shows that large amount of fine precipitates in alloy is beneficial to improvement of the corrosion resistance [37]. Although the fine second phase particles cannot prevent the corrosion, they work as the cathode of the micro-corrosion electric couple. Thus, large amount of second phases can transform the local corrosion to more uniform micro-corrosion and prevent the further corrosion. It can be verified by the phenomena of the very small corrosion electric current of ZAMX6100 alloy in this study. In addition, a layer of membrane was also produced by corrosion on the surface of the sample, which can protect the alloy from further corrosion. According to figure 9, the surface membrane of the ZAMX6100 alloy is the densest, while that of the ZAM610 alloy is the loosest. Therefore, the ZAMX6100 alloy has the best corrosion resistant properties due to the reason discussed above.

4. Conclusions

(1) The microstructure of the as-casted ZM60 alloy was composed of $\alpha$-Mg and Mg51Zn20 phases. After adding Al, the morphology of eutectic phase in the ZAM610 alloy changed little, while its amount increased. With the increase of Al content, Mg52(Al,Zn)49 phase formed in the ZAM620 alloy and substituted Mg51Zn20. The as-cast microstructure of the ZAMX6100 alloy was composed of $\alpha$-Mg, Al6Mn5 and Mg32(Al,Zn)49 phases.

(2) Extrusion promotes the occurrence of dynamic recrystallization. The average grain size of ZAMX6100 after the recrystallization was the smallest, about 2.2 $\mu$m. Adding Al or Al+Ca had a grain refining effect on the Mg–Zn alloys. Adding Al+Ca addition was more effective than adding Al alone.

(3) Fine-grained strengthening is the main reason for the improvement of mechanical properties of the Mg–Zn alloys in this work. Al6Mn5 phase formed with the addition of Al, which is beneficial to the increase of the strength. However, its strengthening effect was less than the MgZn2 phases dynamically precipitated with the addition of Al+Ca. Compared with ZK60A, the tensile strength of the ZAMX6100 alloy increased by about 20MPa, yield strength increased by about 30MPa, and elongation was similar.

(4) The corrosion electric current of the ZAMX6100 alloy decreased sharply after the addition of Al+Ca compared to the ZM60 alloy and the corrosion resistance was also greatly improved. It was attributed to the large amount of dynamically precipitated MgZn2 phases, which transformed the local corrosion to micro-corrosion and prevented the continuous corrosion of the alloy.

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