Materials Research Express

**PAPER**

**Effects of Sr addition on microstructures and mechanical properties of Mg-1Zn-1Ca-xSr alloys**

Dong Geng-Yi, Sha Gui-Ying, Liu Teng and Zhang Chong

School of Materials Science and Engineering, Shenyang Aerospace University, Shenyang 110136, People’s Republic of China

1. Authors to whom any correspondence should be addressed

E-mail: guiysha@sina.com and tliu7@foxmail.com

Keywords: Mg alloy, Sr, microstructure, mechanical properties

**Abstract**

The Sr-containing magnesium alloys have unique characteristics and demonstrate potentials to broaden the application of magnesium alloys. The microstructures and room temperature tensile properties of the as-cast Mg-1Zn-1Ca-xSr (x = 0.1, 0.5, 1.5, 2.5 weight%) alloys were investigated in this study. The results indicated that the grains of the Sr-containing alloys were gradually refined and the quantity of second phases was obviously increased with increasing the Sr content. In addition, the phase constituents of the alloys were found to be α-Mg, Mg2Ca, Mg6Ca2Zn3 and Mg17Sr2. The tensile results at room temperature showed that the tensile strength and elongation increased for low Sr-content alloys, but didn’t change or even decreased a little for high Sr-content alloys. The yield strength changed little with increasing Sr content. The alloy with 0.1% Sr exhibited the best comprehensive properties, with yield strength of 65.69 MPa, tensile strength of 118.23 MPa and elongation of 2.45%. Fracture analysis showed that the fracture mode of the alloys was mainly quasi-cleavage mechanism.

1. **Introduction**

Magnesium alloys have wide application in the fields of transportation, aerospace and biomedical applications due to their advantages of light-weight, high specific stiffness, electromagnetic shielding, damping and shock absorption, electrical and thermal conductivity, easy recycling, and excellent bio-compatibility[1, 2]. However, due to the lattice structure of hexagonal close-packed (HCP), the plasticity and formability of magnesium alloys cannot meet the requirements of practical applications[3].

Grain refinement is one of the effective ways to improve the mechanical properties of magnesium alloys. It can be achieved by appropriate alloying in magnesium alloys[4]. Sr is proved to be effective in refining grain structures of magnesium alloys[5, 6]. In recent years, the Sr-containing magnesium alloys have raised attention from magnesium researchers. The effects of Sr content (0–1 weight%) on microstructures and mechanical properties of magnesium alloys, such as AZ91[7], AZ91–0.5RE[8], ZA84[9] and Mg-5Zn[10], have been studied. The results indicate that the addition of Sr can refine grain size and re-distribute second phases, thus improving strength, elongation and other mechanical properties of magnesium alloys. Lina et al[11] investigated the effects of Sr (0–1.2 weight%) on the microstructures and mechanical properties of Mg-3.5Zn-2.0Ca alloy in as-cast and solution-treated states. The results demonstrate that the addition of Sr can refine the as-cast and solution-treated microstructures of Mg-Zn-Ca alloy and improve the tensile properties at room temperature and 150 °C. Meng[12] studied the effects of Sr (0–1 weight%) on the microstructures and mechanical properties of as-cast Mg-2Zn-0.25Ca alloy. The results present that, with the content of Sr increasing, the grain size is gradually refined, the quantity of second phase is increased, and the strength and plasticity first increase and then decrease.

In summary, magnesium alloys with addition of Sr have not been systematically reported, and the phase constituent of Sr-containing magnesium alloys is still unclear. This paper mainly studied the effects of Sr addition on the microstructures and mechanical properties of Mg-Zn-Ca-Sr alloy, aiming to provide experimental support for the development of Sr-containing magnesium alloys.
2. Experimental materials and methods

The alloys with different Sr contents were made of pure magnesium (purity 99.95%), pure zinc (purity 99.95%), Mg-20%Ca and Mg-20%Sr master alloys. Under the protection of the mixed SF6 and CO2 gas, the melting was carried out in a crucible furnace at 750 °C, followed by casting at 720 °C. The carbon steel crucible and graphite mold were used for casting. The diameter of the ingots was 70 mm. The chemical compositions of the alloys were analysed by atomic absorption spectroscopy, with the results shown in Table 1.

The samples for microstructural observation, with the size of 10 mm × 10 mm × 10 mm, were cut by the DK7790 EDM wire cutting machine. The targeted surfaces were ground with SiC paper from 600 grit up to 2000 grit, followed by polishing by 0.05 μm colloidal silica. The samples then were etched by a 4% nitric acid solution, and the optical morphologies were observed by an OLYMPUS GX71 inverted metallographic microscope. Grain sizes were measured by linear interception method (GB/T 6394-2017). The phase constituent of the alloy was determined by Ultima IV x-ray diffractometer. The microstructures and element distribution were analysed by XSM-6700 scanning electron microscopy (SEM) equipped with EDS. The tensile properties of the alloy were measured using an AL-7000-LA20 electronic universal testing machine with a tensile speed of 1 mm min⁻¹. The shape and size of tensile specimen are shown in Figure 1 (Non-standard specimen). The tensile fractures were observed and analysed using a JSM-6700 SEM.

3. Results and discussion

3.1. As-cast microstructures

The optical microstructures of the as-cast Mg-1Zn-1Ca-xSr alloys are shown in Figure 2. All the Sr-containing alloys had typical eutectic characteristics. The addition of Sr had a significant effect on grain size of the alloys and the distribution of the second phases. It can be seen from figures 2(a)–(c) that the average grain sizes of the Mg-1Zn-1Ca-xSr alloys (x = 0.1, 0.5, 1.5) were 134 μm, 120 μm, and 111 μm, respectively. Figure 2(d) shows that the average grain size of the Mg-1Zn-1Ca-2.5 Sr alloy was 77 μm. The grain size of the Mg-1Zn-1Ca-2.5 Sr alloy was 42.5% smaller than that of the Mg-1Zn-1Ca-0.1 Sr alloy. It was obvious that higher Sr content could effectively refine the grain size of the Mg-1Zn-1Ca-xSr alloys. At the same time, the eutectic structures along grain boundary were gradually increased and coarsened. Furthermore, the morphology of the eutectic structures evolved from a semi-continuous shape to a continuously distributed network structure. There might be two reasons for the grain refinement. On the one hand, the addition of Sr increased the degree of subcooling of the alloys and elevated the nucleation rate of the primary α-Mg phase, and refined the grain structures [13, 14]. On the other hand, an increase of the Sr content increased the growth limiting factor (GRF). In other words, Sr alloying hindered grain growth.

Table 1. Chemical compositions of the Mg-Zn-Ca-Sr alloys (weight%).

| Alloy            | Zn  | Ca  | Sr  | Mg  |
|------------------|-----|-----|-----|-----|
| Mg-1Zn-1.0Ca-0.1Sr | 1.010 | 1.100 | 0.084 | Bal |
| Mg-1Zn-1.0Ca-0.5Sr | 0.990 | 0.910 | 0.410 | Bal |
| Mg-1Zn-1.0Ca-1.5Sr | 0.940 | 1.020 | 1.420 | Bal |
| Mg-1Zn-1.0Ca-2.5Sr | 0.930 | 0.960 | 2.470 | Bal |

Figure 1. Schematic diagram for tensile testing samples (Unit: mm).
In formula (1), \( m_i \) is the slope of the liquidus line in the binary phase diagram, \( c_{0,i} \) is the initial concentration of the \( i \) element in the alloy, and \( k_i \) is the solute equilibrium partition coefficient. It can be deduced from the formula (1) that, when the concentration of Zn and Ca does not change, as the content of Sr increases, the GRF value increases, indicating that the ability of the Sr alloying to inhibit the grain growth of the alloy becomes stronger, resulting in finer grain size [15, 16].

Figure 3 gives the XRD profiles of the as-cast Mg-1Zn-1Ca-xSr alloys. It shows that all alloys were composed of \( \alpha\)-Mg, \( \alpha\)-MgCa, \( \alpha\)-Mg$_6$Ca$_2$Zn$_3$, and \( \alpha\)-Mg$_{17}$Sr$_2$ phases. When the Sr content was less than 0.5%, the peaks of second phases did not change evidently. When the Sr content exceeded 0.5%, the diffraction peak intensities of the two phases \( \alpha\)-Mg$_6$Ca$_2$Zn$_3$ and \( \alpha\)-Mg$_{17}$Sr$_2$ were obviously enhanced. The change of the Sr content from 1.5% to 2.5% did

\[
GRF = \sum_i m_i c_{0,i} (k_i - 1)
\]
not lead to obvious increase in the same peaks. It was proved that the Sr addition increased the quantities of 
$\text{Mg}_6\text{Ca}_2\text{Zn}_3$ and $\text{Mg}_{17}\text{Sr}_2$ phases, with no apparent change for $\text{Mg}_2\text{Ca}$ phase.

The SEM image and EDS element mapping of the as-cast Mg-1Zn-1Ca-2.5 Sr alloy are illustrated in figure 4. It verifies that Zn was mainly distributed in the eutectic area along grain boundaries, and Ca and Sr were also distributed along grain boundaries. Combined with the results of XRD (figure 3), the Zn-rich and Ca-rich areas should be $\text{Mg}_6\text{Ca}_2\text{Zn}_3$ phase, and the remaining Ca-rich and Sr-rich domains are $\text{Mg}_2\text{Ca}$ phase and $\text{Mg}_{17}\text{Sr}_2$ phase.

Figure 5 exhibits the SEM structures and EDS checking points of the Mg-1Zn-1Ca-xSr alloys. The EDS results are shown in table 2. The width of the second phase at grain boundary was larger in the Mg-1Zn-1Ca-2.5 Sr alloy than that in the Mg-1Zn-1Ca-0.1 Sr alloy. According to EDS, the ratio of Zn and Ca in points A and B of the Mg-1Zn-1Ca-0.1 Sr alloy was about 3:2, proving that the $\text{Mg}_6\text{Ca}_2\text{Zn}_3$ phase was in bulk shape. At C point, the Sr content was higher than that in other areas, supporting that the $\text{Mg}_{17}\text{Sr}_2$ phase was distributed in grain boundaries. At D point, the Ca content was higher than that from other areas, indicating that the dark second phase in the concave was $\text{Mg}_2\text{Ca}$ phase. Similarly, in the Mg-1Zn-1Ca-2.5 Sr alloy, the Sr content was relatively high at E point, so the $\text{Mg}_{17}\text{Sr}_2$ phase should have a strip shape. At F point, the Ca content was high, indicating the dark second phase in the recess was the $\text{Mg}_2\text{Ca}$ phase. The G point was obviously the magnesium matrix. The Zn and Ca ratio at H point was about 3:2, meaning that the $\text{Mg}_6\text{Ca}_2\text{Zn}_3$ phase was distributed in bulk shape. It could be seen that the phase of the alloy in the grain boundary was mainly of the $\text{Mg}_{17}\text{Sr}_2$ phase, and the dark second phase in the grain boundary was the $\text{Mg}_2\text{Ca}$ phase. The bulk phase within the matrix grains was the $\text{Mg}_6\text{Ca}_2\text{Zn}_3$ phase.
3.2. Mechanical properties of the alloys

Figure 6 exhibits the stress-strain curves of the Mg-1Zn-1Ca and Mg-1Zn-1Ca-xSr alloys. The mechanical parameters are shown in Table 3. Compared with Mg-1Zn-1Ca alloy, the alloys with low Sr-content demonstrated higher tensile strength and elongation, while the alloys with high Sr-content demonstrated these mechanical parameters with no obvious increase. The yield strength had no obvious change with changing the Sr content. Combined with alloy microstructure analysis and phase analysis, it could be seen that when the Sr content was lower than 1.0%, with increasing Sr content, the grain refinement effect was smaller than that of high Sr content alloys. But the second phase at grain boundary gradually increased, which led to the inhibition of grain refinement strengthening. Meanwhile the second phase accumulated at grain boundaries. When tensioned, the second phase was subject to tensile stress, which readily generated microcracks, and the second phase fell off from the accumulated sites, resulting in the weakening of the strength and elongation of the alloy [12]. On the other hand, Mg₆Ca₂Zn₃ and Mg₉Sr₂ are brittle phases, and such phases increased with increasing Sr content, which led to the decrease of strength and elongation [10].

When the Sr content reached 2.5%, fine grain strengthening mechanism played an important role because the grain size was greatly reduced as compared to the negative effect caused by second phase in grain boundaries. Due to grain refinement, adjacent grains were affected by the stress field of the dislocation group at grain boundaries.

### Table 2. The EDS analysis results in Mg-1Zn-1Ca-0.1 Sr and Mg-1Zn-1Ca-2.5 Sr alloys.

| Alloy         | Point | Mg (at%) | Zn (at%) | Ca (at%) | Sr (at%) |
|--------------|-------|----------|----------|----------|----------|
| Mg-1Zn-1Ca-0.1 Sr | A  | 74.98    | 14.01    | 9.90     | 1.11     |
|               | B  | 69.38    | 17.81    | 11.79    | 1.02     |
|               | C  | 88.92    | 1.82     | 1.65     | 7.61     |
|               | D  | 75.07    | 2.18     | 21.97    | 0.78     |
| Mg-1Zn-1Ca-2.5 Sr | E  | 88.77    | 2.01     | 1.06     | 8.16     |
|               | F  | 66.48    | 2.07     | 30.22    | 1.23     |
|               | G  | 99.56    | 0.29     | 0.15     | 0.00     |
|               | H  | 73.31    | 16.02    | 9.62     | 1.05     |

### Table 3. Mechanical parameters of the Mg-1Zn-1Ca-xSr alloys.

| Alloy           | Yield strength σ_{y,0.2} (MPa) | Tensile strength σ_{b} (MPa) | Elongation δ (%) |
|-----------------|---------------------------------|------------------------------|-----------------|
| Mg-1Zn-1Ca      | 68.61                           | 99.08                        | 0.92            |
| Mg-1Zn-1Ca-0.1 Sr| 65.69                           | 118.23                       | 2.45            |
| Mg-1Zn-1Ca-0.5 Sr| 64.88                           | 105.17                       | 1.67            |
| Mg-1Zn-1Ca-1.5 Sr| 65.03                           | 91.35                        | 0.78            |
| Mg-1Zn-1Ca-2.5 Sr| 63.91                           | 99.72                        | 1.16            |
boundaries, and the dislocation source was activated to make the grains deform co-ordinately, reducing the unevenness of deformation in grain scale, consequently improving the elongation of the material [17]. Therefore, we could break the hard and brittle phases at grain boundaries by some specific thermal-mechanical treatments, such as forging, hot extrusion, etc, so that they could be evenly distributed inside grains and at grain boundaries, which would significantly improve the performance of the corresponding Sr-containing magnesium alloys.

3.3. Fracture mechanism

SEM images of the tensile fractures are shown in figure 7. There were a large number of quasi-cleavage steps and a very limited amount of shallow dimples in the fracture morphology of the as-cast Mg-1Zn-1Ca-xSr alloys. In alloys with relatively low Sr-content, facets of the quasi-cleavage plates were relatively small. Additionally, height drop between different cleavage plates in low Sr-content alloys was also smaller than that in high Sr-content alloys. These features of the quasi-cleavage plates in low Sr-content alloys might contribute to the improved elongation shown in figure 6. It could be concluded that the micro-fracture mechanism was mainly characterized by quasi-cleavage fracture, and the Sr content did not alter the fracture mechanism fundamentally.

4. Conclusions

(1) The microstructures of the as-cast Mg-1Zn-1Ca-xSr alloys consisted of α-Mg, Mg2Ca, Mg6Ca2Zn3 and Mg17Sr2 phases. The Mg17Sr2 phase was mainly distributed in stripe shape at grain boundaries. The Mg2Ca phase was mainly distributed in the concave matrix at grain boundaries. The Mg6Ca2Zn3 phase was mainly distributed in form of bulk shape within matrix grains.

(2) With increasing Sr content, the grain size of the Mg-1Zn-1Ca-xSr alloys was gradually refined, decreasing from 134 μm in Mg-1Zn-1Ca-0.1%Sr to 77 μm in Mg-1Zn-1Ca-2.5%Sr, with reduction of 42.5%.

(3) With increasing Sr content, the tensile strength and elongation of the Mg-1Zn-1Ca-xSr alloys increased first and then decreased. The Mg-1Zn-1Ca-0.1%Sr alloy possessed the best overall mechanical properties.

(4) The fracture of the as-cast Mg-1Zn-1Ca-xSr alloys was dominated mainly by quasi-cleavage fracture mechanism.
References

[1] Zhao C Y, Pan F S and Zhang L 2016 Materials Science and Engineering (Chinese Journal) C70 1081–88
[2] Cui X M, Yu Z L and Zhang X T 2018 Rare Metal Materials and Engineering (Chinese Journal) 47 3112–19
[3] Jiang H T, Liu P and Kang Q 2017 Rare Metal Materials and Engineering (Chinese Journal) 12 3897–902
[4] Zhang N, Cheng R J and Dong H W 2019 Materials Reports (Chinese Journal) 33 2565–71
[5] Feng Z X, Pan F S and Shi Q N 2014 Journal of Functional Materials (Chinese Journal) 45 7061–65
[6] Zeng X Q, Wang Y X and Ding W J 2006 Metallurgical & Materials Transactions A 37 1333–41
[7] Bai X, Hu W J and Zhang L Q 2008 Transactions of Nonferrous Metals Society of China (Chinese Journal) 18 1596–601
[8] Zhang D D, Zhang D P and Bu F Q 2017 Materials Science and Engineering: A 693 51–9
[9] Yang M B, Zhu Y and Pan F S 2010 Transactions of Nonferrous Metals Society of China 20 506–10
[10] Cheng M X, Chen J H and Yan H G 2017 Journal of Alloys & Compounds 691 95–102
[11] Lu W U, Pan F S and Yang M B 2011 Transactions of Nonferrous Metals Society of China 21 784–9
[12] Lin N and Lu Z J 2014 Foundry Technology (Chinese Journal) 11 2561–3
[13] Xun C X, Ju H and Zhang Z W 2013 Transactions of Nonferrous Metals Society of China (Chinese Journal) 2 349–55
[14] Li Y M 2016 Research on the effect of Sr on Microstructure and Properties of Mg-Zn-Y Alloys Master’s Dissertation Chongqing University
[15] He J G, Zheng L G and Wen J B 2018 Transactions of Materials and Heat Treatment (Chinese Journal) 6 35–41