Rare Metal Materials and Engineering
Volume 45, Issue 2, February 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(2): 0287-0291.

ARTICLE

Microstructure and Mechanical Properties of Extruded Mg-Sm-Ca Alloys

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Abstract: Microstructure, age hardening response and mechanical properties of Mg-4.0Sm-*x*Ca (*x*=0.5, 1.0, 1.5, wt%) alloys extruded followed by isothermal aging at 200 °C were investigated. The results indicate that with the addition of Ca, the bulk and particle-like $Mg_{41}Sm_5$ phase containing Ca and the needle/rod-like Mg_2Ca phase are formed in the Mg matrix, grains of the alloy are refined and tensile mechanical properties are improved remarkably. Under T5 (peak-aging) condition, the Mg-4.0Sm-1.0Ca alloy shows the smallest grain size of 5.1 μm. With the increase of Ca content the amount of Mg_2Ca phase increases gradually, but that of the bulk Ca-containing $Mg_{41}Sm_5$ phase, which is mainly distributed at the grain boundaries, decreases obviously when Ca content reaches 1.5 wt%. The peak-aged Mg-4.0Sm-1.0Ca alloy exhibits the highest hardness HV (820 MPa) and the optimal ultimate tensile strength, yield tensile strength and elongation of 267 MPa, 189 MPa and 24%, respectively. The improved mechanical properties of the alloy are attributed to the grain refinement, the solution strengthening and the precipitation strengthening of Mg_2Ca phase and $Mg_{41}Sm_5$ phase.

Key words: Mg-Sm-Ca alloy; extruding-aging; microstructure; mechanical property

Magnesium alloys, as the lightest structural materials, have great potential applications in aircraft, automotive industry and transportable equipment due to their excellent properties [1]. However, the use of magnesium alloys was restricted in the past owing to their poor mechanical properties and low formability[2-4]. Extruded magnesium alloys exhibit superior mechanical properties to as-cast one, due to the refinement of the grains, the elimination of casting defects and the homogenization of microstructure during the plastic deformation processes[5].

It is reported that the addition of rare earth elements (RE) can remarkably improve the mechanical properties of magnesium alloys by a solid solution strengthening and a precipitation strengthening[6,7]. It has been found that the Mg-Nd alloys exhibit promising mechanical properties[8]. Samarium (Sm) belongs to the same subgroup as Nd, and the maximum solid solubility of Sm in Mg is 5.7 wt% at 803 K, which is higher than that of Nd (3.6 wt%) in Mg. Therefore, it is reasonable to assume that the Mg-Sm alloys also exhibit good mechanical properties.

The alkaline earth element Ca is often added to magnesium alloys to improve the mechanical properties by the grain refinement and precipitation strengthening of the Mg_2Ca phase[9,10]. In addition, Jun et al.[11] investigated that Ca addition can not only refine the primary α-Mg grains but also increase the thermal stability of the Mg-RE phases in the Mg-Nd-RE-Ca alloys. Accordingly, it can be concluded that Ca may play a beneficial role in the improvement of mechanical properties of Mg-Sm based alloys.

Although some Sm containing magnesium alloys have been developed, the investigation on the effect of Ca addition on the microstructure and the mechanical properties of Mg-Sm alloys has not been reported yet until now. In the present work, the microstructure and the mechanical properties of Mg-4.0Sm-*x*Ca (*x*=0.5, 1.0, 1.5, wt%) alloys extruded followed by isothermal aging at 200

Received date: February 14, 2015
Foundation item: Doctoral Fund of Taiyuan University of Science and Technology (20122011)
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°C were investigated, and the corresponding strengthening mechanism was discussed.

1 Experiment

The alloy ingots with nominal compositions shown in Table 1 were prepared from high purity Mg (>99.95%) and master alloys of Mg-25% Ca (wt%) and Mg-25% Sm (wt%) by melting in an electric resistance furnace at about 730 °C under the mixed gas of CO_2 and SF_6 with the ratio of 99:1. As-cast ingots with 80 mm in diameter and 110 mm in length were homogenized at 500 °C for 24 h followed by quenching in water of 70~80 °C, and then were hot extruded at 460 °C into rods of 16 mm in diameter with an extrusion ratio of 25:1. The aging treatment was carried out at 200 °C for 170 h in an electric furnace. In the present experiment, the aging treatment was immediately carried out after extrusion, and the T5 condition means the peak-aged state. Vickers hardness (HV) was measured at the loading force of 100 g and the holding time of 20 s.

The microstructures of the alloys were examined by an optical microscope (OM, Nikon) and a scanning electron microscope (SEM, S4800) equipped with an energy dispersive X-ray spectrometer (EDS). The metallographic specimens were mechanically polished and etched by immersing for 3~5 s in a solution of 10 mL acetic acid, 5 g picric acid, 10 mL distilled water, and 85 mL ethanol. The grain sizes were measured using a linear intercept method in the OM micrographs. The overall phase constitution analyses were identified by X-ray diffractometer (XRD, Y-2000) with Cu-Kα radiation. The flat dog-boned specimens for tensile tests had 14 mm in gauge length and 3 mm×2 mm in a cross section. The tensile axis was aligned parallel to the extrusion direction. The tests were conducted on a universal testing machine (Instron1121) at ambient temperature with an initial strain rate of 1.0×10^{-3} s^{-1}. The ultimate tensile strength (UTS), 0.2% yield strength (YS) and elongation to fracture were obtained based on the average value of three tests.

2 Results and Discussion

2.1 Effects of Ca on microstructure

Fig.1 shows the optical micrographs of alloys as the extruded state and the peak-aged state. The alloys are mainly composed of equiaxial grains. Compared with the extruded alloy, the average grain size of the peak-aged one increases slightly. The average grain sizes of the alloys as the two states are listed in Table 2.

Fig.2 shows the XRD patterns of the peak-aged alloys. As shown in Fig.2, the alloys are mainly composed of α-Mg, $Mg_{41}Sm_5$ and Mg_2Ca phases. Furthermore, it is found that the diffraction peaks of the Mg_2Ca phase are not observed in S1 alloy. The absence of the Mg_2Ca phase is ascribed to the relatively small amount of Ca in S1 alloy.

As shown in Fig.1, the Ca content has a great effect on grain size of alloys. Under T5 condition, the average grain sizes of the S1, S2 and S3 alloys are about 10.2, 5.1 and 11.0 μm, respectively. When the content of Ca increases to

Table 1 Nominal chemical composition of alloys (wt%)

Alloy	Sm	Ca	Mg
S1	4.0	0.5	Bal.
S2	4.0	1.0	Bal.
S3	4.0	1.5	Bal.

Table 2 Average grain sizes of the alloys for different states (μm)

Alloy	Extruded state	Peak ageing state
S1	8.6	10.2
S2	4.2	5.1
S3	9.1	11.0

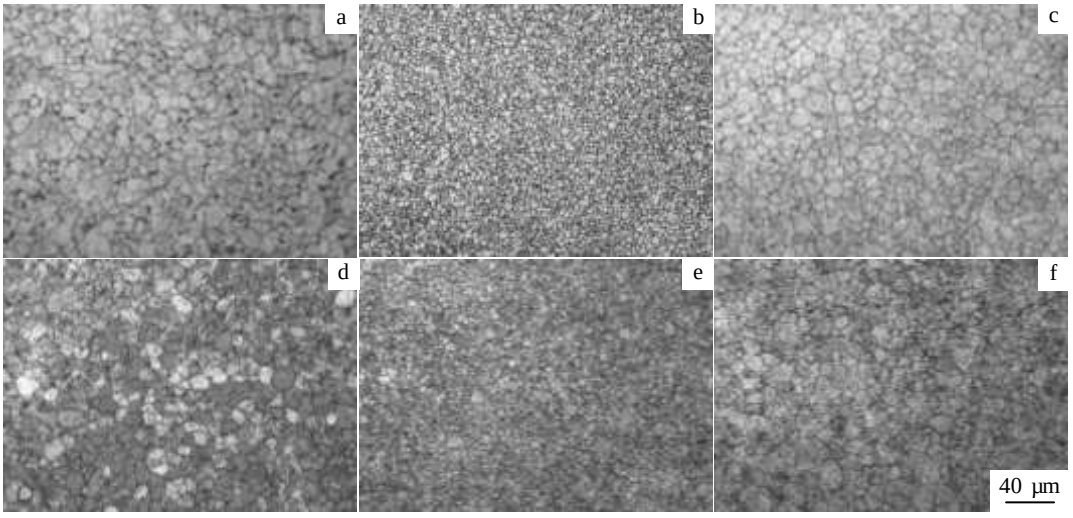

Fig.1 Optical micrographs of Mg-Sm-Ca alloys: (a) S1 alloy as extruded state, (b) S2 alloy as extruded state, (c) S3 alloy as extruded state, (d) S1 alloy as peak aged state, (e) S2 alloy as peak aged state, and (f) S3 alloy as peak aged state

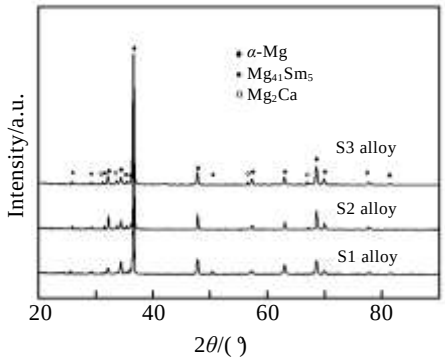

Fig.2 XRD patterns of Mg-Sm-Ca alloys as peak aged state

1.0 wt%, the alloy shows the smallest grain size (Fig.1e). According to the classic solidification theory, the relationship between the critical nucleus radius and the undercooling degree are given as follows [12]:

$$r^* = \frac{2\sigma}{\Delta G_r} = \frac{2\sigma T_m}{L_m \Delta T} \quad (1)$$

where r^* is the critical nucleus radius, ΔG_r is the variation of volume free energy, σ is the interfacial energy of unit surface area, T_m is the equilibrium crystallizing temperature, L_m is the crystallizing latent heat and ΔT is the undercooling degree.

According to Eq.(1), the critical nucleus radius decreases with the increasing of ΔT, then the nucleation energy of crystal nucleus reduces and the probability of nucleation increases, which results in the grain refinement. As a surface active element, Ca tends to segregate in the melt alloy to form intensive constitutional undercooling ahead of solid/liquid interface in diffusion layer, which promotes nucleation and restrains the growth of α-Mg grains, thus causing the grain refinement.

However, when the addition of Ca increases to 1.5 wt%, the grains become coarser and the average grain size reveals a significant increase, as shown in Fig.1f. The SEM images of the peak-aged alloys are shown in Fig.3. It is found that the alloys are composed of α-Mg and dispersively distributed intermetallic precipitates. The second phases (Fig.3) are identified by the XRD results (Fig.2) and the EDS analysis (Table 3). The EDS analyses reveal that some Ca atoms dissolve into the $Mg_{41}Sm_5$ phases and the volume fraction of Ca atoms increases significantly with increasing of Ca content. As shown in Fig.3a, the bulk and particle-like phases in S1 alloy is the $Mg_{41}Sm_5$ phase containing Ca. With Ca content increases from 0.5 wt% to 1.0 wt%, some needle/rod-like Mg_2Ca phase is observed in S2 alloy. In addition, the distribution of $Mg_{41}Sm_5$ phase is more uniform. However, the bulk shaped Ca-containing $Mg_{41}Sm_5$ phase which is distributed at the grain boundaries exhibits a significant decrease in S3 alloy, while the Mg_2Ca phase and particle-like $Mg_{41}Sm_5$ phase in the interior of the grains increase. Meanwhile, the Mg_2Ca phase becomes coarse. The decrease of bulk shaped Ca-containing $Mg_{41}Sm_5$ phase distributed at the grain boundaries can weaken the dislocation pinning. Therefore, the increase of grain size of S3 alloy is possibly attributed to the weaker pinning effect.

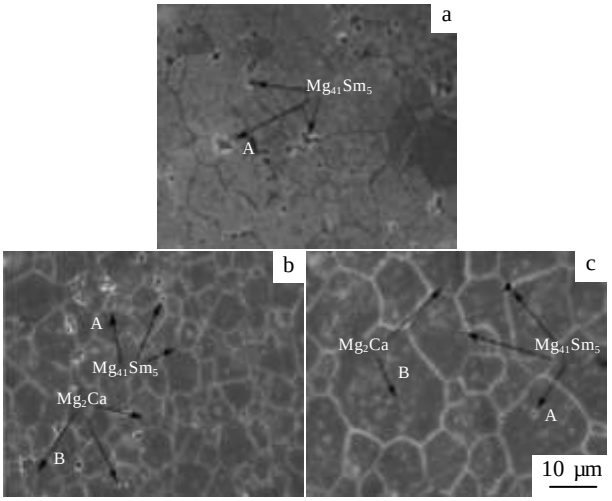

Fig.3 SEM images of Mg-Sm-Ca alloys as peak aged state: (a) S1 alloy, (b) S2 alloy, and (c) S3 alloy

Table 3 EDS results of the experimental alloys in Fig.3 (at%)

Position	Mg	Sm	Ca	Total
Fig.3a-A	87.72	11.77	0.51	100
Fig.3b-A	87.14	1.53	1.33	100
Fig.3b-B	93.42	0.84	5.74	100
Fig.3c-A	86.97	10.16	2.87	100
Fig.3c-B	91.71	1.13	7.16	100

2.2 Aging characteristics

Fig.4 shows the isothermal aging curves of S1, S2, and S3 alloys aged at 200 °C for 170 h. The hardness values HV of the three alloys as extruded state are 590, 670 and 630 MPa, respectively. The hardness increases gradually with the increase of aging time, and the peak hardnesses of the three alloys were obtained after aging for 48 h. The peak hardness HV values of the three alloys are 710, 820 and 740 MPa, respectively. The S2 alloy exhibits the best age-hardening behavior with a maximum peak hardness value of 820 MPa. It is suggested that the addition of Ca can improve the hardness of the alloy. The improved age-hardening behavior of the alloy is attributed to grain refinement strengthening and the increase of the volume fraction of the second phase. However, the excess Ca addition (1.5 wt%) will weaken age-hardening behavior and decrease the peak hardness value.

2.3 Mechanical properties of the peak-aged alloys

Fig.5 shows tensile properties of S1, S2 and S3 alloys as peak-aged state at room temperature. It can be seen that Ca

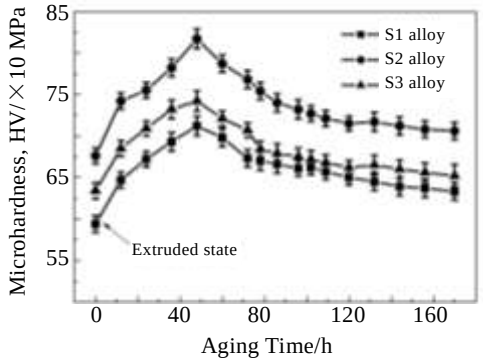

Fig.4 Aging hardening curves of the extruded Mg-Sm-Ca alloys

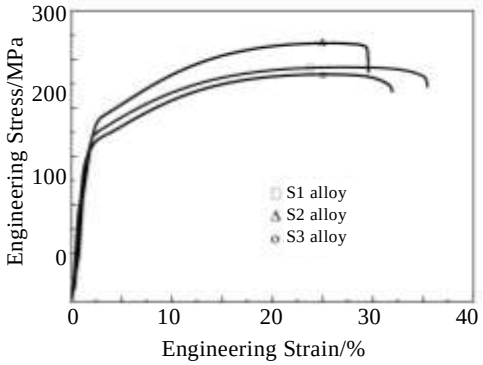

Fig.5 Engineering stress-strain curves of the Mg-Sm-Ca alloys as Peak-aged state

addition has a significant effect on mechanical properties. The values of UTS, YS and elongation of S1 alloy are 242 MPa, 174 MPa and 30%, respectively. The UTS and YS of the alloys increase upon adding 1.0 wt% Ca, but the elongation decreases. When the Ca content is up to 1.5 wt%, the UTS and YS of the alloys obviously decrease and the values of UTS and YS are 234 MPa and 164 MPa, respectively, with an elongation of 26%. The S2 alloy exhibits the relatively optimal UTS, YS and elongation of 267 MPa, 189 MPa and 24%, respectively.

Fig.6 shows the tensile fracture surfaces of the peak-aged S2 alloy. A great number of dimples and tearing ridges are observed on fracture surface. Some second phase particles are observed within these dimples. These deep dimples, which are associated with the drawing of particles, indicate that a certain amount of plastic deformation is involved prior to rupture. Thus, the fracture mode of peak-aged S2 alloy exhibits a quasi-cleavage with a large amount of dimples.

It is seen from Fig.5 that the tensile strength of the alloy increases when the Ca content increases from 0.5 wt% to 1.0 wt%. According to the Hall-Petch relation[13], the grain

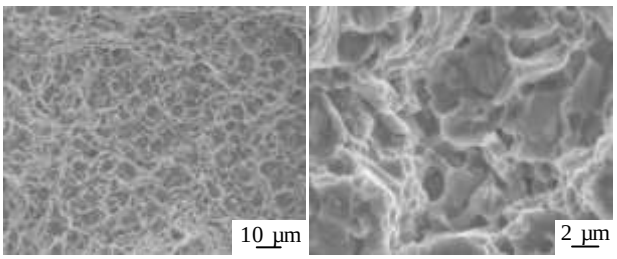

Fig.6 Tensile fracture morphologies of S2 alloy

refinement results in an obvious increase of tensile strength of S2 alloy. The smaller the grain size, the larger the deformation resistance, thus resulting in an increase of the strength. Meanwhile, the increasing of Mg_2Ca phase will make resistance to the dislocation movement, and thus the tensile strength of S2 alloy is improved. In addition, it was reported that Ca might also play an important role in enhancing thermal stability of the Mg-RE phase [11]. However, the Mg_2Ca phase is a brittle phase, and the decrease of elongation of S2 alloy can be associated with the increase of brittle Mg_2Ca phase.

Compared with S2 alloy, adding of 1.5 wt% Ca brings a detrimental effect on the tensile strength. The decrease of tensile strength can be attributed to the following three factors: (1) The grain size of S3 alloy increases which leads to the decrease of tensile strength. (2) The excess Ca causes the coarsening of Mg_2Ca phase in the matrix. The presence of these coarse Mg_2Ca phases promotes the initiation and the propagation of cracks, resulting in an adverse effect on the ultimate tensile strength[14]. (3) It was reported that magnesium alloys with the higher Ca addition are susceptible to hot cracking[15]. It can be preliminarily inferred that the reduction of strength by adding 1.5 wt% Ca is possibly related to the weakening effect of interfacial micro-cracks associated with the relatively higher hot cracking tendency. However, compared with S2 alloy, the elongation of S3 alloy increases slightly. It is possibly attributed to the weaker pinning effect which is caused by the decrease of bulk $Mg_{41}Sm_5$ phase distributed at the grain boundaries.

3 Conclusions

1) With the Ca content increases from 0.5 wt% to 1.0 wt%, the grains of the alloys are significantly refined. However, excess Ca addition (1.5 wt%) will cause a significant increase of the grain size. The S2 alloy shows the smallest grain size of 5.1 μm (under T5 condition).

2) The alloys mainly contain α-Mg, $Mg_{41}Sm_5$ phase and Mg_2Ca phase. The amount of needle/rod-like Mg_2Ca phase increases gradually with the increase of Ca content. However, when the Ca content reaches 1.5 wt%, the amount of bulk Ca-containing $Mg_{41}Sm_5$ phase distributed at the

grain boundaries decreases significantly and the Mg_2Ca phase becomes coarse.

3) Adding 1.0 wt% Ca to Mg-4.0Sm alloy brings the best age-hardening behavior with the highest peak hardness of 820 MPa. The peak-aged S2 alloy exhibits the highest tensile strength. The increase of mechanical properties is mainly attributed to the grain refinement, the solution strengthening and the precipitation strengthening of Mg_2Ca phase and $Mg_{41}Sm_5$ phase.

References

1 Zhou Jixue, Yang Yuansheng, Tong Wenhui *et al*. *Rare Metal Materials and Engineering*[J], 2010, 39: 1899 (in Chinese)

2 Bi Guangli, Fang Daqing, Zhao Lei *et al*. *Journal of Alloys and Compounds*[J], 2011, 509: 8268

3 Barbagallo S, Cavaliere P, Cerri E *et al*. *Materials Science and Engineering A*[J], 2004, 367: 9

4 Li Daquan, Wang Qudong, Ding Wenjiang *et al*. *Transactions of Nonferrous Metals Society of China* [J], 2010, 20: 1311

5 Ding Hanlin, Liu Liufa, Kamado S *et al*. *Journal of Alloys and Compounds*[J], 2008, 456: 400

6 Zhang jinghuai, Liu Shunjuan, Leng Zhe *et al*. *Materials Science and Engineering A*[J], 2011, 528: 2670

7 Nie J F, Muddle B C. *Acta Materialia*[J], 2000, 48: 1691

8 Yan Yunqi, Zhang Tiejie, Deng Ju *et al*. *Rare Metal Materials and Engineering*[J], 2005, 34(5): 846 (in Chinese)

9 Li Yuncang, Hodgson P D, Wen Cui'e. *Journal of Materials Science*[J], 2011, 46: 365

10 Fei Houjun, Xu Guanglong, Liu Libin *et al*. *Transactions of Nonferrous Metals Society of China*[J], 2013, 23: 881

11 Jun J H, Park B K, Kim J M *et al*. *Key Engineering Materials*[J], 2007, 345-346: 557

12 Pan Yichuan, Liu Xiangfa, Yang Hua. *Journal of Wuhan University of Technology, Mater Sci Ed*[J], 2007, 22: 74

13 Li Mingzhao, Li Cong, Liu Xuguang *et al*. *Rare Metal Materials and Engineering*[J], 2009, 38(1): 7 (in Chinese)

14 Wu Guohua, Yu Fan, Gao Hongtao *et al*. *Materials Science and Engineering A*[J], 2005, 408: 255

15 John J B, Henry H. *SAE Transactions*[J], 2000, 109: 574

挤压态 Mg-Sm-Ca 合金的显微组织和力学性能

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摘　要：研究了挤压Mg-4.0Sm-*x*Ca (*x*=0.5, 1.0, 1.5, mass fraction%)合金经过200 ℃等温时效处理后的显微组织、时效硬化行为和力学性能。结果表明，随着Ca的添加，在镁基体中形成针/棒状的Mg_2Ca相、块状和颗粒状含Ca元素的$Mg_{41}Sm_5$相，合金的晶粒被细化、拉伸力学性能得到显著提高。在 T5（峰值时效）态下，Mg-4.0Sm-1.0Ca合金具有最细的晶粒，其大小约为 5.1 μm。随着Ca含量的增加，针/棒状的Mg_2Ca相逐渐增多，当Ca含量达到1.5%时，晶界处含Ca的块状$Mg_{41}Sm_5$相的量明显减少。在峰值时效态下，Mg-4.0Sm-1.0Ca合金具有最大的HV硬度值（820 MPa）以及最佳的力学性能，其抗拉强度、屈服强度和延伸率分别达到了267 MPa, 189 MPa 和 24%。合金力学性能的提高主要归因于晶粒细化、固溶强化以及Mg_2Ca相和$Mg_{41}Sm_5$相的析出强化。

关键词：Mg-Sm-Ca 合金；挤压−时效处理；显微组织；力学性能

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