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Microstructure and tensile properties of AE42-based magnesium alloys with calcium addition

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Abstract: The as-cast microstructure of AE42 was of typical dendritic and composed of the α matrix and some needle-shaped interphases $Al_{11}RE_3$. A small amount of Ca addition results in significant microstructural refinement and formation of a new phase Al_2Ca, which showed two kinds of morphologies, lamellar and tiny granular. The former distributes on grain boundaries and the later is within the matrix grains. With the increase of Ca addition the volume fraction of Al-RE compound ($Al_{11}RE_3$) decreases, but Al_2Ca increases. Addition of Ca causes a significant increase of yield strength of the alloy both at ambient and elevated temperatures, but a little decrease of the ductility. With calcium addition the ultimate strength decreases at ambient temperature and 150 ℃, but increases at 175 ℃ and 200 ℃.

Key words: AE42-based magnesium alloys; calcium; microstructure; tensile properties

As the lightest applied structural alloys, magnesium alloys offer a good combination of mechanical properties, corrosion resistance and castability[1,2]. In recent years, research and development of magnesium alloys have been greatly promoted by the lightweight requirement in the automotive industry[2]. Though some magnesium alloys, such as AZ91 and AM60, have been used in automotive products for recent years, they are limited to some noncritical parts due to the restriction of strength and creep resistance at elevated temperatures.

Rare earth (RE) elements are very important alloying elements for heat-resistant magnesium alloys. Small amounts of misch metal addition to Mg-Al based alloys result in significant increase of strength as well as creep resistance at elevated temperatures. Recent developments have revealed that the addition of calcium to Mg-Al based alloys is also very effective in improving creep resistance of the alloys at elevated temeratures[3,4]. In the present investigation, the effect of calcium additions to alloy AE42, which contains 2% of misch metal, at both ambient and elevated temperatures has been studied with the aim of developing new heat resistant magnesium alloys.

1 Experimental Procedure

Five alloys were prepared; their compositions are listed in Tab. 1. The base alloy was alloy 1, the composition of which was in the range of the specified alloy AE42. Different amounts (from 0.5% to 2.0%) of calcium were added to the other four alloys. Calcium addition was performed by adding a master alloy Mg-30Ca with 30% Ca. The rare earth elements used in the present investigation are lanthanum-rich misch metal (MM), the compositions of which are listed in Tab.2. Melting of the alloys was conducted in a mild steel crucible under the protection of a mixed gas atmosphere of SF_6(1% by volume) and CO_2(bal.). After the alloying elements were dissolved, the melt was held at 720 ℃ for a few minutes then poured into permanent molds made from cast iron. The chemical compositions of prepared alloys were analyzed by inductively coupled plasma (ICP) and the results are also listed in Tab.1, from which it can be seen that the analyzed compositions of the alloys is in good agreement with the designed compositions.

Tab.1 Chemical compositions of the alloys studied %

Alloy No.	Designed compositions					Analyzed compositions				
	w(Al)	w(RE)	w(Ca)	w(Mn)	w(Mg)	w(Al)	w(RE)	w(Ca)	w(Mn)	w(Mg)
1	4.0	2.0		0.3	Bal	3.9	1.8		0.4	Bal
2	4.0	2.0	0.5	0.3	Bal	4.1	2.1	0.7	0.2	Bal
3	4.0	2.0	1.0	0.3	Bal					Bal
4	4.0	2.0	1.5	0.3	Bal	3.9	1.9	1.4	0.2	Bal
5	4.0	2.0	2.0	0.3	Bal	4.1	1.9	1.6	0.2	Bal

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Tab.2 Chemical composition of the misch metal (RELa-80, GB/T 4153—93, Chinese Specification)

Element	w (La)	w(Fe)	w(Si)	w(S)	w(P)
Composition/%	>80	<0.5	<0.07	<0.02	<0.01

Tensile specimens with a gauge section of 18.0 mm × 3.5 mm × 2.0 mm were cut by electric spark machining from the ingots prepared. Microstructures of the alloys were characterized on selected specimens using optical microscope (OM) and scanning electron microscope (SEM). Microanalysis and crystal structure of precipitates were carried out by X-ray energy dispersive spectroscopy (XEDS) and X-ray diffraction (XRD), respectively.

2 Results

2.1 Microstructure

Fig.1 shows the optical micrographs taken from the as-cast specimens of the alloys prepared.

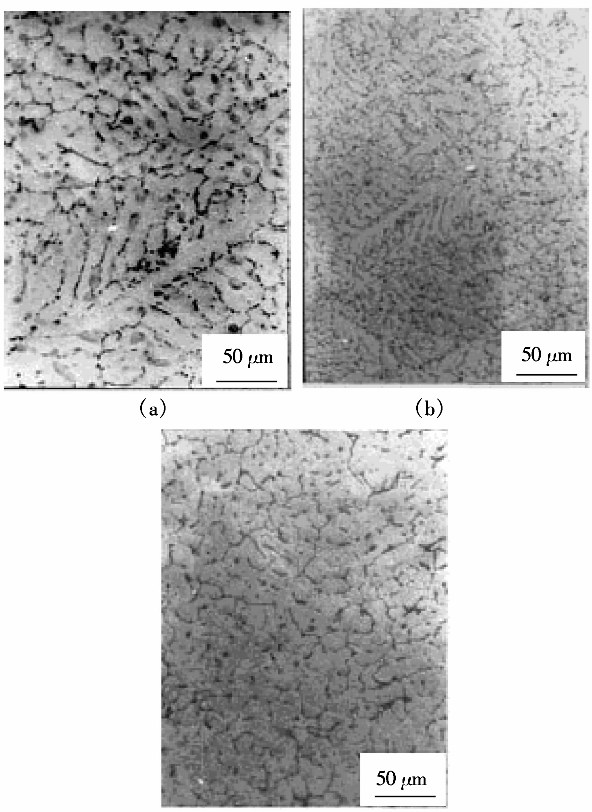

Fig.1 As-cast micrographs of AE42 system alloys. (a) Alloy 1; (b) Alloy 2; (c) Alloy 5

The as-cast microstructure of alloy 1 (Fig.1(a)) exhibited typical dendritic morphology. With 0.5% of Ca addition, the dendrites in as-cast microstructure were significantly refined, as shown in Fig. 1 (b). Further increase of calcium concentration caused the change of as-cast microstructure from dendritic to equiaxed (Fig. 1 (c)). Interphase particles can be observed in the interdendritic areas and at grain boundaries.

Fig.2 is an SEM micrograph of as-cast alloy 1, which shows some needle-shaped particles. Microanalysis was performed on these particles and the results showed that they contained aluminum and rare earth elements La and Ce. Fig.3 is an XRD pattern taken from as-cast alloy 1 (AE42), in which all the peaks were indexed as arising form the α-Mg matrix and an intermetallic compound $Al_{11}La_3$. Thus the particles observed in Fig.2 were identified as an Al-La compound $Al_{11}La_3$ with some cerium substituting lanthanum. The molecular formula of this compound can be written as $Al_{11}RE_3$.

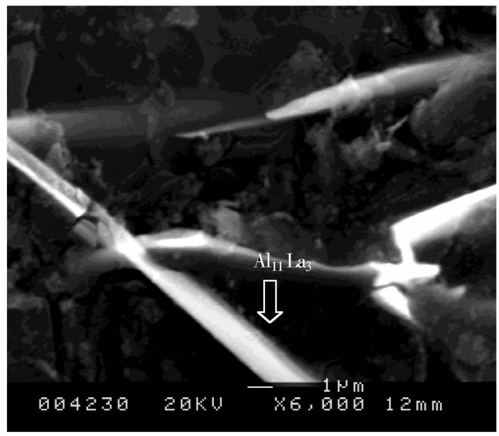

Fig.2 SEM micrograph of alloy 1

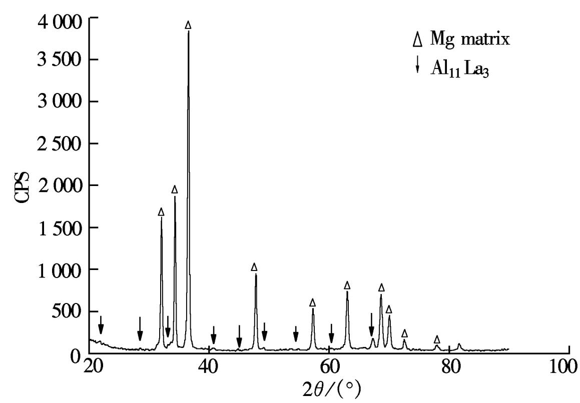

Fig.3 XRD pattern of alloy 1

With addition of calcium to the base alloy, some new interphase particles formed in as-cast microstructure. In Fig. 4, a lamellar phase, which seemed as an eutectic product, appeared at the grain boundaries by SEM of alloy 5. The chemical compositions of these lamellas determined by XEDS were approximately Al-31.7Ca-15.2Mg. Fig.5 is an XRD pattern of alloy 5, in which peaks were indexed as arising from three phases, α-Mg, $Al_{11}RE_3$ and Al_2Ca. Based on the result of XRD and microanalysis, the lamellar phase existing in as-cast alloy 5 can be identified as Al_2Ca. Al_2Ca was also observed in the other three alloys. Fig. 6 (a) is an SEM micrograph taken from an as-cast specimen of alloy 2, in which both Al_2Ca lamellas and $Al_{11}RE_3$ needles exist. Higher magnification SEM observation revealed some tiny granular particles distributing in the matrix grains and microanalysis showed that they had the same chemical composition with that of lamellar Al_2Ca, as shown in Fig.6(b). These two kinds of Al_2Ca are labeled as A-type and B-type, respectively, in Fig.6(b).

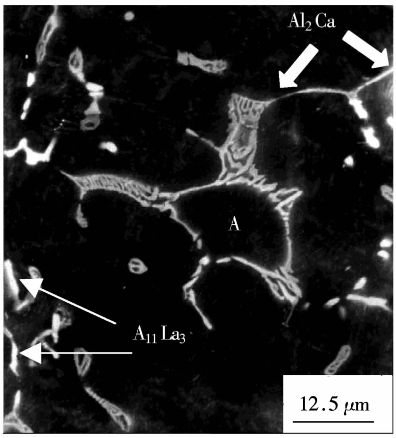

Fig.4 SEM micrograph of as-cast alloy 5

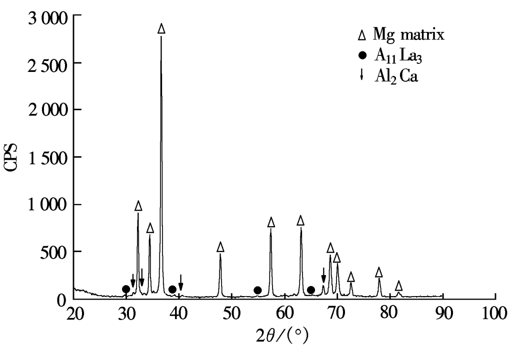

Fig.5 XRD pattern of alloy 5

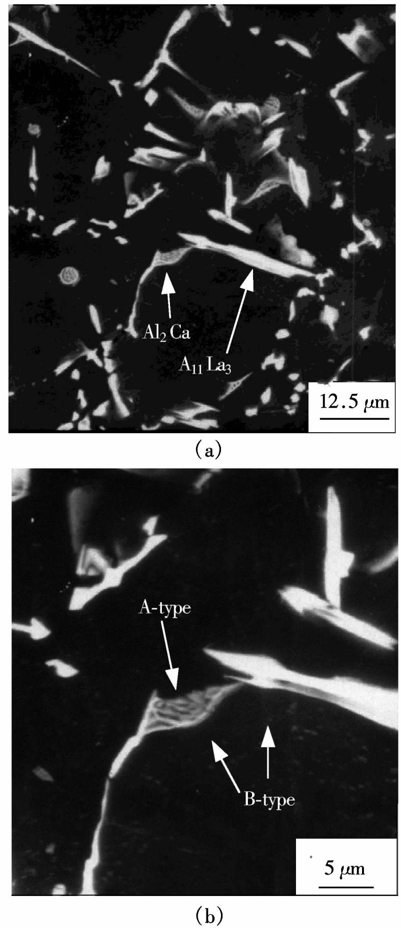

Fig. 6 SEM micrographs of as-cast alloy 2. (a) SEM micrograph of as-cast alloy 2; (b) Amplificatory micrograph of A zone

Fig.7 shows the SEM micrograph of as-cast alloy 4. In comparison with alloy 1 (see Fig.2), it can be seen that the size and volume fraction of $Al_{11}RE_3$ decreased and its morphology changed from needle shape to short-stick shape with the increase of calcium addition. Whereas, the volume fraction of Al_2Ca increased with the increase of calcium addition and it distributed on almost all the grain boundaries in alloys 4 and 5.

2.2 Tensile properties

Tab.3 lists the tensile properties of the as-cast alloys at ambient and elevated temperatures. At ambient temperature, calcium addition resulted in an increase of yield strength but slight decrease of ductility. The highest yield strength obtained from alloy 5 reached

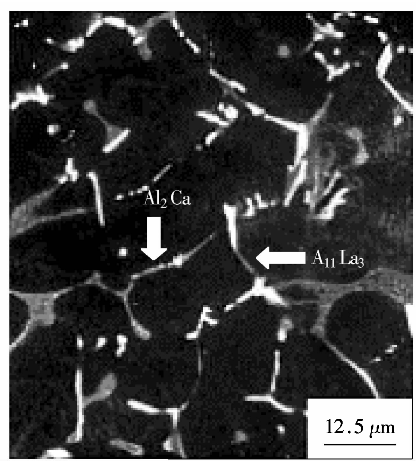

Fig.7 SEM micrograph of as-cast alloy 4

as high as 107 MPa, 53% higher than that of AE42 alloy. The ultimate strength was correlated with tensile ductility, and it decreased with decreasing ductility. At 150 ℃, the change of tensile properties with the increase of calcium additions was similar to that at ambient temperature, however, both yield and ultimate strength increased with the increase of calcium concentration when the test temperature rose to 175 ℃

and 200 ℃. Fig. 8 shows the curves of tensile properties of the alloys studied vs. temperature. It can be seen that the yield strength of all the alloys studied at elevated temperatures was lower than that at ambient temperature. For the alloys with calcium additions, the reduction of yield strength caused by the increase of temperature was less than that of the bass alloy (alloy 1). At 200 ℃ the yield strength of alloy 5 was 85 MPa, 52% higher than that of the base alloy at the same temperature, indicating that calcium addition was effective in strengthening Mg-Al-RE based alloys at elevated temperatures.

Tab.3 Tensile properties of the alloys at ambient and elevated temperatures

Alloy No.	Room temperature			150 ℃			175 ℃			200 ℃		
	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%
1	188	70	9.8	144	68	14.2	115	65	15.1	78	56	20.3
2	178	80	4.3	140	77	11.7	121	70	14.3	92	65	18.4
3	154	84	2.6	136	82	10.6	122	75	12.7	112	69	17.8
4	138	100	2.4	131	87	10.1	125	83	12.1	115	75	16.4
5	131	107	1.8	128	90	9.0	125	87	11.0	118	85	16

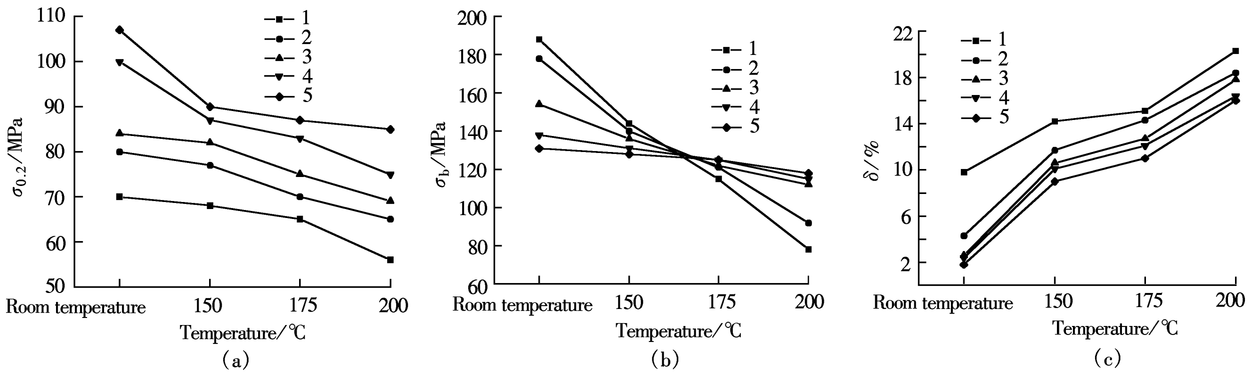

Fig.8 Curves of tensile properties vs. temperature. (a) Yield strength; (b) Ultimate strength; (c) Elongation

3 Discussions

In the present investigation microstructural observations revealed that the addition of a small amount of Ca to AE42 refined the as-cast microstructures significantly. Generally, the effect of solute on the grain refinement may be the result of the formation of some particles which act as the potent nucleation sites for magnesium and the constitutional undercooling generated by the growth of a grain adjacent to a nucleant particle suspended in the melt[5, 6]. The constitutional undercooling was simplified as the growth restriction factor (GRF). According to Ref.[7], GRF can be defined by

$$\sum_i m_i C_{0,1}(k_i - 1)$$

where m_i is the slope of the liquidus line, C_0 is the initial composition, and k_i is the equilibrium partition coefficient for element i. A large GRF results in the effective grain refinement. The previous investigation[7] reported that the strong segregation of Ca in magnesium led to the increase of GRF, consequently refined the microstructures of magnesium alloys obviously. This is consistent with the results of the present work.

Tensile tests in the present investigation showed that the yield strength of AE42 based alloys increased with the increase of calcium addition at both ambient and elevated temperatures. According to the Hall-Patch formula, the reduction of grain sizes causes the increase of yield strength, therefore, the increase of yield strength at ambient temperature in the result of grain refinement. At elevated temperatures, however, fine grain structure is usually not beneficial to improvement of yield strength as well as creep resistance due to easy slipping of grain boundaries. The ternary AE42 alloy exhibits high yield strength and creep resistance at temperatures below 150 ℃. The strengthening effect of RE in the AE42 alloy at elevated temperatures is attributed to the formation of $Al_{11}RE_3$, which is metallurgically stable as seen in the related phase diagrams[8] and would be expected to yield effective grain boundary strengthening and resistance to flow during creep loading[9]. However, recent studies have shown that $Al_{11}RE_3$ compound decomposes to Al_2RE and Al[10] and the latter forms $Mg_{17}Al_{12}$, which is low temperature intermetallic compound[11], thereby decreasing the elevated temperature strength. With the increase of Ca addition to the base alloy AE42, Al_2Ca replaces $Al_{11}RE_3$. In comparison with $Al_{11}RE_3$, Al_2Ca is more stable[12] and would not decompose or dissolve into the α matrix even after solution treatment at 450 ℃ for 24 h[13]. SEM observations reveal that Al_2Ca exhibits two morphologies, lamellar and tiny granular. According to the Mg-Al-Ca phase diagram[14], lamellar Al_2Ca, distributing at grain boundaries of the α matrix, is one phase of eutectic product and the tiny granular Al_2Ca particles are precipitated from the matrix after solidification. When tensile test is performed at elevated temperatures, these two kinds of Al_2Ca play important roles to inhibit grain boundary gliding and dislocation slipping. This accounts for the significant improvement of yield strength of the AE42 alloy with calcium addition at elevated temperatures.

4 Conclusions

1) The as-cast microstructure of AE42 alloy is typical dendritic and composed of the α matrix and $Al_{11}RE_3$ compound.

2) Calcium addition to the AE42 alloy causes the formation of a new phase Al_2Ca, which shows two kinds of morphologies, laminar and tiny granular. The former distributes on grain boundaries and the later is within the matrix grains.

3) Small amount of calcium addition to the AE42 alloy causes significant refinement of as-cast microstructure.

4) Addition of calcium results in significant improvement of yield strength of alloys at both ambient and elevated temperatures, but a slight decrease of ductility.

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Ca 对 AE42 镁合金的显微组织和拉伸性能的影响

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摘要: AE42 的铸态组织主要包含了 α 镁和少量的针状 $Al_{11}RE_3$ 相, 呈典型的树枝晶分布.少量 Ca 的加入使合金组织细化并形成新相 Al_2Ca, Al_2Ca 主要呈现分布在晶界的层片状形貌和弥散在晶粒内部的颗粒状形貌.随着 Ca 的加入量增多, $Al_{11}RE_3$ 的体积百分比降低, 相应 Al_2Ca 含量增加.拉伸性能方面, Ca 的加入使合金的屈服强度在室温和高温下都有显著提升, 随之延伸率有少量降低.Ca 的加入还使合金在室温和 150 ℃ 下抗拉强度下降.温度的提高使 Ca 对抗拉强度的影响逐渐加大, 175 ℃和 200 ℃下, 随 Ca 含量的增加抗拉强度逐渐增大.

关键词: AE42 镁合金; Ca; 显微组织; 拉伸性能

中图分类号: TG146