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Microstructure and mechanical properties of ZA62 based magnesium alloys with calcium addition

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Abstract: As-cast microstructure and mechanical properties of Mg-6Zn-2Al-0.3Mn (ZA62) alloys with calcium addition were investigated. The as-cast microstructure of the base alloy ZA62 consists of the α-Mg matrix and eutectic phase $Mg_{51}Zn_{20}$. The $Mg_{51}Zn_{20}$ eutectic was gradually replaced by MgZn phase and $Mg_{32}(Al,Zn)_{49}$ phase when calcium is added into the base alloy. Further addition of calcium leads to the increase of grain boundary phases and formation of a new quaternary Mg-Zn-Al-Ca eutectic compound. In comparison with the base alloy, the increase of calcium addition to the base alloy results in the reduction of both strength and ductility at ambient temperature, but increase at elevated temperatures due to the thermal stability of Ca-containing phases. At elevated temperatures, the creep resistance of ZA62 based alloys containing calcium is significantly higher than that of AZ91 which is the most commonly used magnesium alloy.

Key words: magnesium alloys; ZA62 alloys calcium; creep properties

1 Introduction

Magnesium alloys are increasingly used in the automobile industry in order to reduce the mass thereby cut down the fuel consumption and pollution. However, inferior elevated temperature mechanical properties of conventional Mg alloys, such as AZ91 and AM60 based on Mg-Al system, limit the application of these alloys to temperatures below 120 ℃[1]. Some magnesium alloys containing rare earth developed in past decades exhibit high creep resistance at elevated temperatures above 150 ℃, however, the castability of these alloys is poor and the cost is too high for applications in automobile products[2−3]. Therefore, it is pressing to develop some new magnesium alloys with good creep properties, acceptable castability and low cost. Recent investigations reveal that alloys based on Mg-Zn-Al ternary system are promising to meet the above requirements[4].

So far, most of the researches concerning Mg-Zn-Al based alloys focused on the alloys with high Zn (>8%, mass fraction) and Al (>5%, mass fraction) concentrations[5], and it was reported that calcium addition significantly improved the mechanical properties at elevated temperatures[6−7]. ANYANWU et al[7] revealed that the mechanical properties of Mg-Zn-Al alloys were much higher than that of the conventional alloy AZ91D mentioned above, because high Zn content caused the formation of $Mg_{32}(Al, Zn)_{49}$ (τ) and MgZn intermetallic compounds with higher thermal stability than that of the β phase, which is the main secondary phase in Mg-Al base alloys. Furthermore, the enhancement of thermal stability of Mg-Zn-Al based alloys was achieved by small amount of calcium addition, which leads to the improvement of creep resistance at elevated temperature, as reported in Refs.[8−11]. In this work, small amount of calcium is added to Mg-Zn-Al based alloys with relatively low Zn and Al contents in comparison with the alloy in the previous investigations, and the microstructure and creep properties of the alloys

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were investigated.

2 Experimental

Five alloys were prepared in a mild steel crucible under the protection of mixed gas atmosphere of SF6 (1%, volume fraction) and CO_2 (Bal.). The compositions are listed in Table 1. The base composition of the alloys was Mg-6Zn-2Al-0.3Mn (alloy 1, ZA62). Different amounts of calcium were added to the other alloys in order to observe the effect of calcium addition and variation of calcium concentration on the microstructure and mechanical properties. The melt was held at 690 ℃ for several minutes, then poured into metal moulds made of cast steel.

Table 1 Chemical compositions of alloys (mass fraction, %)

Alloy No.	Designed composition					Analyzed composition				
	Mg	Zn	Al	Ca	Mn	Mg	Zn	Al	Ca	Mn
ZA62	Bal.	6.0	2.0	−	0.3	Bal.	5.69	1.94	−	0.25
ZAX6202	Bal.	6.0	2.0	0.2	0.3	Bal.	5.75	1.89	0.16	0.27
ZAX6205	Bal.	6.0	2.0	0.5	0.3	Bal.	5.72	1.86	0.47	0.24
ZAX6210	Bal.	6.0	2.0	1.0	0.3	Bal.	5.91	2.03	1.08	0.22
ZAX6220	Bal.	6.0	2.0	2.0	0.3	Bal.	5.84	1.91	1.87	0.24

Tensile specimens with a gauge section of 18 mm×3.2 mm×1.8 mm were cut by wire electrode cutting machining from the ingots, and tensile tests were performed using a CMT5105 Electronic Universal Testing Machine. Creep tests were conducted on the as-cast specimens of cylindrical geometry with dimensions of d10 mm×10 mm using RD2-3 high-temperature creep testing machine. Constant load tests were conducted on 70 MPa at 150 ℃ and 175 ℃. The temperature was maintained constant within ±2 ℃ during testing. The results of tensile and creep tests were based on the average of two or three specimens for each alloy on each test condition. Microstructural observations of the alloys were carried out using optical microscopy (OM) and scanning electron microscopy (SEM). Microanalysis and identification of the phases presented in the prepared alloys were performed by energy dispersive X-ray spectroscopy (EDAX) and X-Ray diffractometry (XRD), respectively.

3 Results and discussion

3.1 Microstructure

Fig.1 shows the microstructures of as-cast alloys. It can be seen that the as-cast microstructure of alloy ZA62 consisted of the α-Mg matrix and interphase particles. Calcium addition in the base alloy caused the increase of volume fraction of interphases and an interphase network can be observed in alloy ZAX610, in which 1% (mass fraction) calcium was added. Grain boundaries in the alloys were observed in the specimens during annealing process, as shown in Fig.2. The grain size of the alloys decreased with the increase of calcium addition. After annealing at 340 ℃ for 120 h, the interphases observed in the microstructure of as-cast alloy ZA62 were basically dissolved in the α-Mg matrix, however, small amount of interphases still appeared in the specimens of alloys with calcium addition after annealing, as shown in

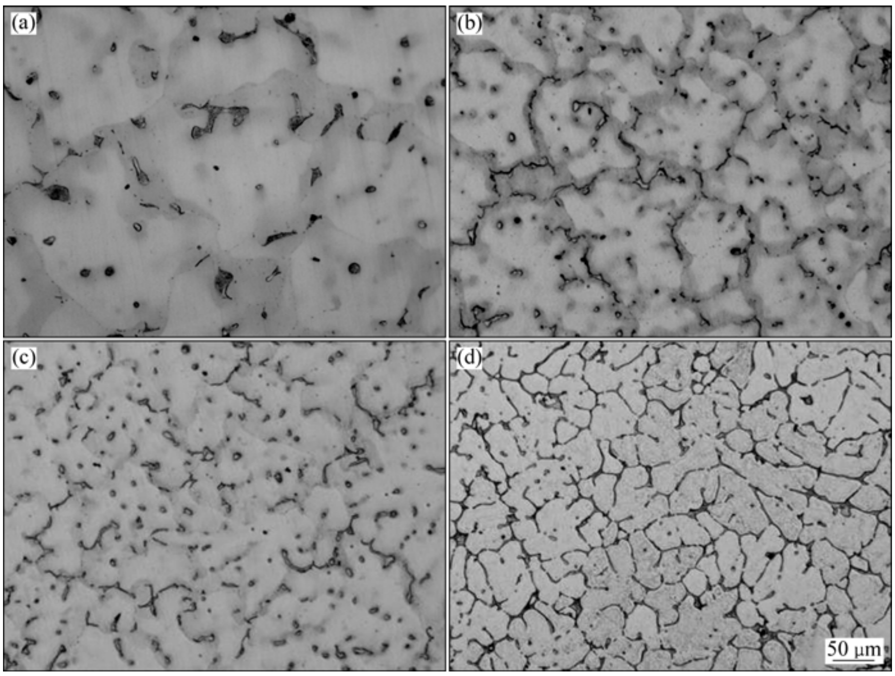

Fig.1 Optical micrographs of as-cast alloys: (a) ZA62; (b) ZAX6202; (c) ZAX6205; (d) ZAX6210

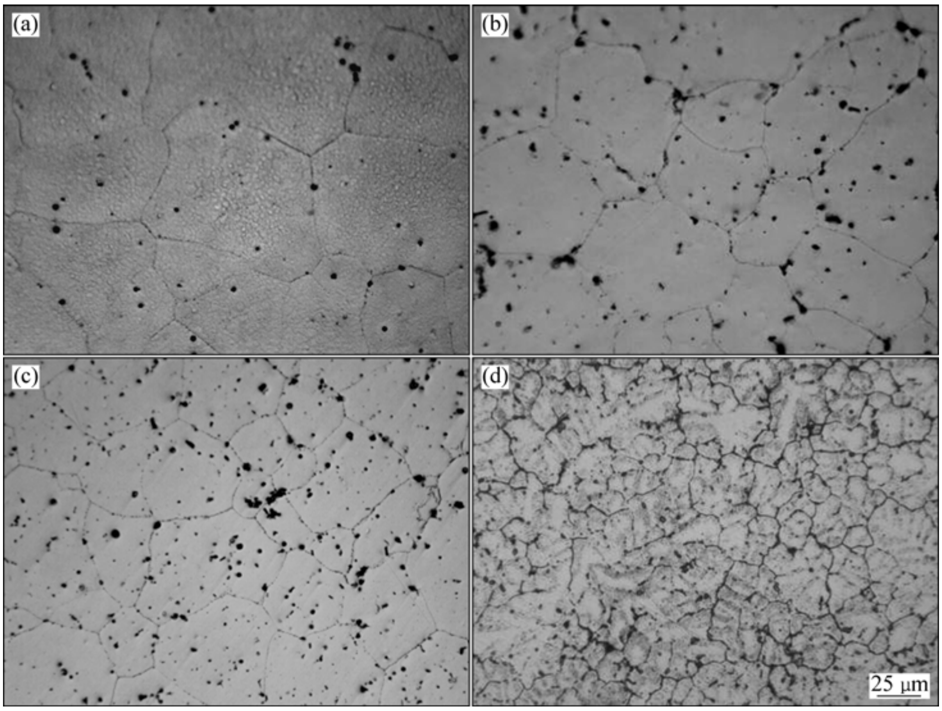

Fig.2 Optical micrographs of alloys after annealing treatment at 340 ℃ for 120 h: (a) ZA62; (b) ZAX6202; (c) ZAX6205; (d) ZAX6210

Figs.2(b)−(d).

The XRD patterns of different alloys are shown in Fig.3. It can be seen that all the peaks in the pattern taken from alloy ZA62 were indexed as α-Mg and $Mg_{51}Zn_{20}$ (ε) phases. In the XRD patterns taken from alloys with calcium addition, peaks of MgZn and $Mg_{32}(Al,Zn)_{49}$ (τ) phases appeared and other peaks were not able to be indexed according to PDF cards.

In order to identify the phases, SEM observation as well as microanalysis was performed, and the results are shown in Fig.4 and Table 2. Based on the XRD patterns and results of microanalysis, it can be presumed that:

1) The dense lamellar eutectic in alloy ZA62 (the area pointed by arrow *A* in Fig.4(a)) is the ε phase, which has a bct structure (space group *Immm* with lattice parameter a=1.408 3 nm, b=1.448 6 nm, c=1.402 5 nm)[12].

2) With small amount of calcium addition, three intermetallic compounds appeared in the as-cast microstructure. The dense lamellar eutectic in alloy ZAX6205 (the area pointed by arrow B in Fig.4(b)) is the ε phase, the same with that in alloy ZA62. The coarse block phase, pointed by arrow *C* in Fig.4(b), is the τ phase, which has a bcc structure (space group T^5_h, a=1.416 nm)[12] with a little amount of calcium dissolved in it. In the area pointed by arrow *D* in Fig.4(b), there is the hexagonal MgZn phase with space group of *P63/mmc*[13].

3) With the increase of calcium addition in the base alloy, some coarse lamellar eutectic (shown by arrow E) can be observed in the as-cast microstructure, as shown in Fig.4(c). Microanalysis performed on the coarse lamellar eutectic phase showed that it has higher calcium concentration than other interphases mentioned above, as listed in Table 2. In the XRD pattern (Fig.3) taken from alloy ZAX6210, there are some unindexed peaks arising from unknown phases. Hence, it can be presumed that the unindexed peaks in the XRD pattern taken from alloy ZAX6210 arise from this coarse lamellar eutectic phase.

The isothermal sections of the Mg-Zn-Al ternary system at 335 ℃ is shown in Fig.5, which indicates that the equilibrium microstructure of the base alloy ZA62 consists of α-Mg matrix and $Mg_{51}Zn_{20}$ (ε) compound at 335 ℃. The ε phase is a high temperature phase existing

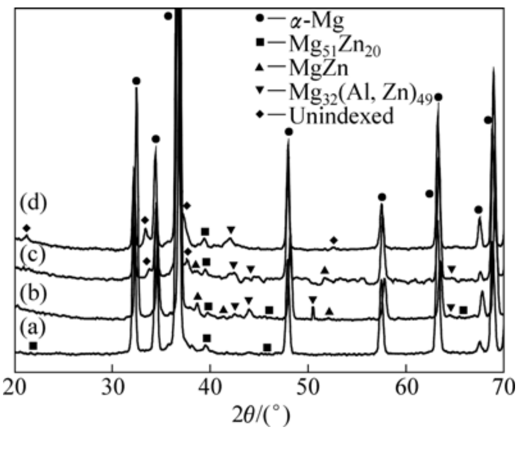

Fig.3 XRD patterns of as-cast alloys: (a) ZA62; (b) ZAX6202; (c) ZAX6205; (d) ZAX6210

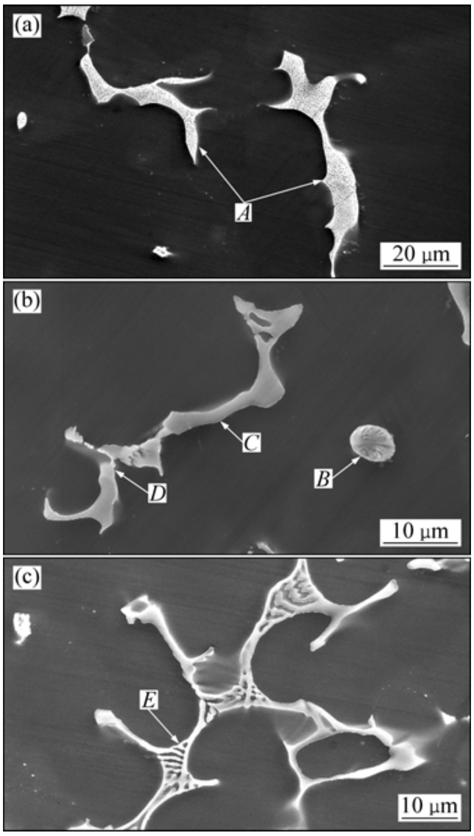

Fig.4 SEM images of as-cast alloys: (a) ZA62; (b) ZAX6205; (c) ZAX6210

Table 2 Results of microanalysis (mass fraction, %)

Element	*A*	*B*	*C*	*D*	*E*
Mg	77.1	65.5	40.3	46.7	73.6
Zn	22.8	27.4	32.7	41.6	10.2
Al	−	5.9	22.7	8.5	8.3
Ca	−	1.2	4.3	3.2	7.9

only at temperature above 300 ℃[14], and decomposes into the α-Mg and MgZn phases at temperature below 300 ℃, according to the Mg-Zn binary and Mg-Zn-Al ternary diagrams under the equilibrium condition. In the present study, however, the ε phase is observed in the as-cast microstructure of the base alloy and it is apparently due to non-equilibrium solidification. In the alloy with small amount of calcium addition, three interphases, ε, τ and MgZn are found in the as-cast microstructure, indicating that the addition of calcium promotes the eutectic decomposition of ε to α and MgZn phases. In the previous investigation, ANYANWU et al[7] proposed that small amount of calcium addition decreased the solubility of both Al and Zn in the α matrix and accelerated the formation of MgZn and τ phases. Both MgZn and τ phases exhibit higher thermal stability and higher melting points than the ε phase, which is obviously beneficial to high temperature mechanical properties of the alloys. When the amount of calcium addition to the base alloy increases to 1.0%, an unknown Mg-Zn-Al-Ca quaternary compound appears in the as-cast microstructure. The structure characteristic of this phase is not clear due to lack of information concerning Mg-Zn-Al-Ca quaternary system. A similar unknown Mg-Zn-Al-Ca quaternary phase was reported in the previous work concerning the microstructure of alloy ZA53 with calcium addition[15]. The mechanism of the formation of this kind of quaternary phase is poorly understood, and further study is underway.

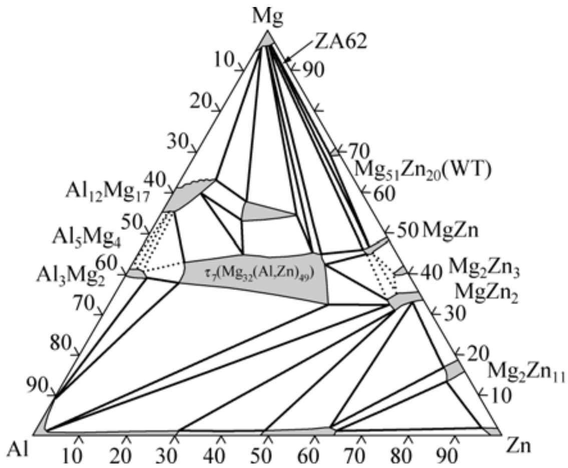

Fig.5 Isothermal section of Mg-Zn-Al ternary diagram at 335 ℃

3.2 Tensile properties

Table 3 lists the data of tensile tests of the as-cast alloys studied at ambient and elevated temperatures of 200 ℃. At ambient temperature, it can be seen that calcium addition resulted in the reduction of both strength and elongation. At 200 ℃, however, both yield and tensile strength increased with the increase of calcium addition and reached the maximum when 0.5% (mass fraction) calcium was added. Further increase of calcium addition caused the decrease of both strength and ductility. The variations of tensile properties for alloys ZA62 and ZAX6205 with the increase of temperature are shown in Fig.6. It can be seen that the strength of both alloys decreased with the increase of temperature. However, the reduction of strength for alloy ZAX6205 was much smaller than that of alloy ZA62, indicating 0.5% of calcium addition to the base alloy (ZA62) enhanced tensile properties at elevated temperatures.

The strength of alloys varies with grain size and the relationship usually follows the Hall-Petch equation: $\sigma_y=\sigma_0+kd^{-1/2}$[16−17]. In the present study, the grain size of calcium containing alloys decreases with the increase of calcium concentration, however, the yield strength of them does not thereby increase. The inconsistency between the results of tensile test and Hall-Petch equation is mainly accounted for the formation of the

Table 3 Mechanical properties of alloys at room temperature and 200 ℃

Alloy	Room temperature			200 ℃		
	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%
ZA62	228	101	10.2	118	73	20.1
ZAX6202	186	104	6.9	122	88	17.4
ZAX6205	162	98	6.0	127	90	9.0
ZAX6210	147	94	3.4	117	87	6.0
ZAX6220	119	87	2.0	108	75	5.6

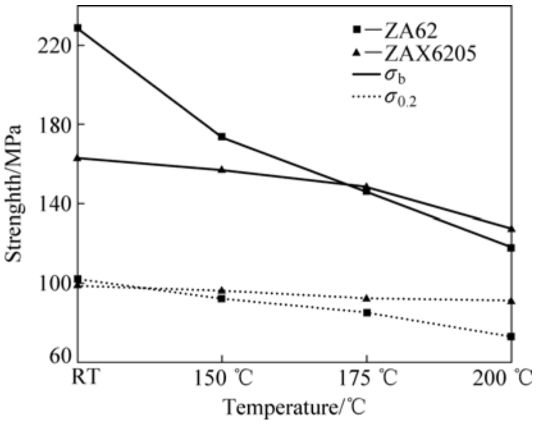

Fig.6 Tensile properties of alloys at different temperature

interphases in microstructure. As shown in Fig.1, the volume fraction of interdendritic compounds increases with calcium addition and a continuous network forms in the alloy with 1.0% of calcium addition. For most alloys, the intermetallic compounds with this kind of morphology are usually considered to be a main factor of deteriorating the tensile properties of the alloys at ambient temperature. In addition, the formation of interphases results in reduction of both Al and Zn dissolved in the α-Mg matrix, leading to the weakening of solid solution hardening caused by Al and Zn addition[7]. Therefore, both strength and ductility of the alloys decrease with the addition of calcium.

3.3 Creep properties

The tensile creep curves of the alloys tested at the applied stress of 70 MPa and elevated temperatures of 150 ℃ and 175 ℃ are shown in Figs.7(a) and (b), respectively. The results of the steady creep rate and 100 h creep strain of the alloys are listed in Table 4. The creep data of the as-cast AZ91 alloy is also shown so that the creep properties of the Mg-Zn-Al alloys and the conventional Mg-Al alloy can be compared. At 150 ℃, alloy AZ91 exhibited very poor creep resistance, its steady state creep rate and 100 h creep strain were much higher than those of alloy ZA62. Further improvement of creep resistance was achieved with calcium addition. The steady creep rate of the alloy ZAX6210 containing 1.0% calcium reached 2.3×10^{-9} s^{-1}, almost one order of magnitude lower than that of the base alloy.

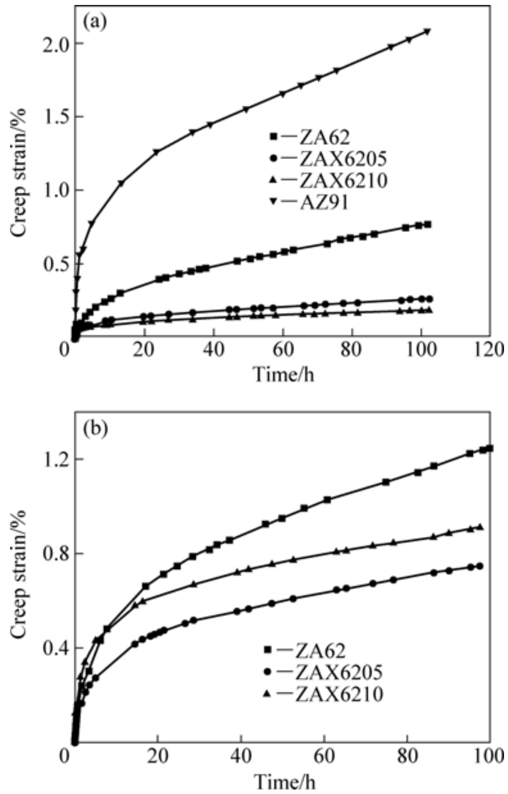

Fig.7 Creep curves of experimental alloys for 100 h: (a) At 150 ℃, 70 MPa; (b) At 175 ℃, 70 MPa

Table 4 Steady creep rate and 100 h creep strain of different alloys at 70 MPa

Alloy	150 ℃		175 ℃	
	ε/%	$\dot{\varepsilon}$ /10^{-9} s^{-1}	ε/%	$\dot{\varepsilon}$ /10^{-9} s^{-1}
ZA62	0.76	13.2	1.25	17.9
ZAX6205	0.25	3.7	0.75	8.6
ZAX6210	0.17	2.3	0.91	9.0
AZ91	2.05	28.0	−	−

ε: 100 h creep strain; $\dot{\varepsilon}$: Steady creep rate

In comparison with the commonly used Mg-Al based alloys, such as AZ91 and AM60, the alloys studied show higher creep properties, which is attributed to the absence of $\beta(Mg_{17}Al_{12})$ phase discontinuous precipitation during casting and creep deformation. The discontinuous precipitation is considered to be the main factor responsible for the poor creep resistance of Mg-Al based alloys. Higher creep properties obtained from Mg-6Zn-2Al base alloys with small amount of calcium addition are obviously due to the formation of interphases distributing at grain boundaries. This is very similar to that of Al_2Ca in the Mg-(4−6)Al based alloys with 1%−2% (mass fraction) of calcium addition[18]. With high stability at elevated temperatures, the interphases observed in the as-cast microstructure of calcium containing alloys are effective on straddling and pinning the grain boundaries during creep deformation, leading to remarkable improvement of creep properties.

The distribution of calcium in the interphases raises their stability due to the relatively large size of calcium atom, which hinders the diffusion of the atoms at elevated temperatures, and improves the cohesive force for lower electronegativity of calcium according to the Pauli principle[19]. The stability of interphases is exhibited in the microstructure of alloy ZAX6210 after creep test at 175 ℃ and 70 MPa, as shown in (Fig.8). Only a few creep cracks exist in the block phase, but no cracks crossing the quarternary eutectic compound can be found.

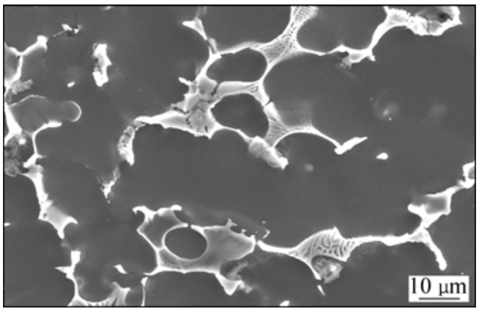

Fig.8 Microstructure of alloy ZAX6210 after creep at 175 ℃, 70 MPa for 100 h

At 175 ℃, after 100 h creep test, alloy ZAX6210 which has higher calcium concentration than alloy ZAX6205, showed a bit higher creep strain and steady creep rate. The decrease of creep resistance with the increase of calcium addition at 175 ℃ is probably accounted for the refinement of microstructure, which is also caused by the increase of calcium addition. Based on systematic investigations on creep behavior of Mg-Al based alloys, the creep mechanism for aluminum containing alloys was proposed as a mixed mode, controlled by both motion of dislocations and migration of grain boundaries. Apparently, grain boundary sliding is easy to occur in the alloy with smaller grain size. Therefore, the grain refinement caused by the increase of calcium addition might account for the slight reduction of creep resistance.

4 Conclusions

1) The as-cast microstructure of Mg-6Zn-2Al-0.3Mn (ZA62) alloy consists of *α*-Mg and eutectic phase $Mg_{51}Zn_{20}$. The eutectic $Mg_{51}Zn_{20}$ can be replaced by Ca-containing MgZn phase and $Mg_{32}(Al, Zn)_{49}$ phase when calcium is added into the ZA62 alloy.

2) The volume fraction of grain boundary in the alloy increases with the increase of calcium addition and an lamellar quaternary phase appears in the ZA62 based alloy with more than 0.5% (mass fraction) calcium addtion.

3) With the addition of calcium, both strength and ductility of the alloys drop at ambient temperatures, however, improved properties are obtained at elevated temperature due to the thermal stability of Ca-containing phases as compared to the ZA62 based alloy. At elevated temperature, the creep resistance of these Ca-containing alloys is significantly higher than that of commonly used magnesium alloy AZ91.

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