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Effects of combined addition of Y and Ca on microstructure and mechanical properties of die casting AZ91 alloy

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Abstract: A series of die casting heat-resistant magnesium alloys based on Mg-Al system were developed for automotive application by adding Y and various amounts of Ca. The mechanical properties and microstructures of die casting AZ91 alloy with combined addition of Y and Ca were investigated by optical microscopy, scanning electronic microscopy, X-ray diffractometry and mechanical property test. The results show that the combined addition of Y and Ca can refine the as-die-cast microstructure, result in the formation of Al_2Ca phase and Al_2Y phase, and inhibit the precipitation of $Mg_{17}Al_{12}$ phase. The combined addition of Y and small amount of Ca has little influence on the ambient temperature tensile properties, but increasing the content of Ca can improve significantly the tensile strength at both ambient and elevated temperatures. It is found that for AZ91-1Y-*x*Ca alloy, the hardness and the elevated temperature tensile strength increase, while the elongation decreases with increasing the addition of Ca. The mechanism of mechanical properties improvement caused by the combined addition of Y and Ca was also discussed.

Key words: die casting magnesium alloy; AZ91Mg alloy; yttrium; calcium; microstructure; tensile property

1 Introduction

In order to solve environmental problems and economic efficiency, manufacturing of lightweight and high strength materials for automotive application attracted extensive attention in recent years[1]. Die casting magnesium alloy products are increasingly used in automotive industry due to its low density, high specific strength and specific stiffness, good castability and better damping capacity and so on, which can reduce the mass of car, fuel oil consumption and exhaust-gas discharge. So magnesium alloys are considered an excellent choice for mass reduction of automobile up to now[2−3]. The AZ91 alloy is the most favored die casing magnesium alloy for automotive components such as cam covers, crankcase, oil pan and clutch housing. However, its relatively low strength and poor creep strength at elevated temperatures make the alloy unsuitable for many key automotive constructional components such as engine housing and transmission housing, which restrain the application of AZ91 alloy unfortunately[4].

In recent years, great attempts adopting the method of adding alloy elements such as rare earth (RE), Ca, Si, Bi, Sn and Sb to the AZ91 alloy were done to improve the elevated temperature properties of the alloy[5−11]. Among rare elements, Y is considered a more effective alloying element that can affect the properties of magnesium alloy, especially the elevated temperature mechanical properties. Consequently, some magnesium alloys containing Y were developed such as WE54 alloy and WE43 alloy. But the castability and higher cost of WE series alloys also strongly restrict their applications [12−13]. In some studies, it was proved that the addition of Y to AZ series alloys can enhance mechanical properties both at ambient and elevated temperatures [14−17], especially, the ultimate tensile strength of die casting AZ91-1Y alloy still maintains a higher value at 180 ℃[5]. The Ca is relative chapter than RE element, which can provide an effective prevention for ignition and oxidation of magnesium alloys during melting [18−19]. Adding Ca to AZ91 magnesium can refine the microstructure, improve the elevated temperature properties and the corrosion resistance of magnesium alloys[4, 8, 20−23]. However, these studies mainly focus on the effect of an individual alloy element on microstructures and properties of AZ91 alloy, while the studies

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about the effect of combined addition of Y and Ca on die casting AZ91 alloy are rare. Therefore, it is significant to study the effects of combined addition of Y and Ca on microstructure and properties of magnesium alloys so as to develop the heat-resistant die casting magnesium alloys with lower cost. In this work, the Y combined with Ca was added into the die casting AZ91 alloy. The microstructure, mechanical properties at room and elevated temperature of AZ91-1Y-*x*Ca alloys were studied.

2 Experimental

In the present experiments, the commercial AZ91 alloy was chosen as master alloy. The alloying elements Y and Ca were added in the form of Mg-9.7Y alloy and pure metal, respectively. The AZ91 alloy was firstly melted in a steel crucible resistance furnace under a mixed atmosphere of 0.03% SF_6 and 99.97% N_2 (volume fraction), and then 1.0% Y combined with Ca of 0.5%, 1.0% and 1.5% (mass fraction) were added into the molten alloy at 720 ℃, respectively. The melt was held at 720 ℃ for 30 min to ensure that the elements Y and Ca can dissolve completely. Subsequently, the melt was poured into a BUHLER 530 t cold chamber die casting machine. The die cast specimens with a gauge length of 100 mm and a diameter of 6 mm were produced at pouring temperature of 680 ℃, mold temperature of 200 ℃, injection velocity of 3 m/s. Their chemical compositions are listed in Table 1.

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

Alloy	Al	Zn	Y	Ca	Mg
AZ91	8.89	0.61	−	−	Bal.
AZ91-1Y-0.5Ca	8.77	0.59	0.92	0.47	Bal.
AZ91-1Y-1.0Ca	8.53	0.55	0.95	1.12	Bal.
AZ91-1Y-1.5Ca	8.92	0.63	1.16	1.45	Bal.

The tensile tests were carried out on a CSS-55100 electric multiple-purpose testing machine at test temperature ranging from room temperature to 200 ℃. After holding for 15 min to ensure the stability of test temperature, the tensile specimens were tested at a cross-head traveling rate of 1.0 mm/min and then air cooled in furnace following fracture. The chemical compositions of the studied alloys were analyzed by inductively coupled plasma (ICP). The scanning electron microscopy samples were ground and polished before being etched with a solution of 4% nitric acid (volume fraction) + ethyl alcohol. The microstructure and phase analysis were performed by optical microscopy (OM) and scanning electron microscopy (SEM) (Hitachi S-3400N) with an energy-dispersive spectroscopy (EDS). The phases in the alloys were identified by a Rikakn D/maxr X-ray diffractometer.

3 Results and discussion

3.1 Microstructures of as-die-cast AZ91-1Y-*x*Ca alloys

Fig.1 shows the microstructures of as-die-cast AZ91-1Y-*x*Ca alloys. It can be found that the microstructure of as-die-cast AZ91 alloy exhibits a typical dendritic morphology, which is composed of primary *α*-Mg solid solution and $Mg_{17}Al_{12}$ intermetallic phases, and $Mg_{17}Al_{12}$ phase shows discontinuous distribution along grain boundaries, as shown in Fig.1(a). With the combined addition of 0.5% Ca and 1.0% Y to AZ91 alloy, the grain size in microstructure decreases (see Fig.1(b)). Further increasing Ca content can cause the change of microstructure from dentritic to equiaxed, and increase the amount of interphases, as shown in Fig.1(c). When 1.5% Ca and 1.0% Y are combinedly added to AZ91 alloy, the grains are remarkably refined, and the average grain size is 20−30 μm, as shown in Fig.1(d).

The SEM images of the AZ91-1Y-*x*Ca alloys are shown in Fig.2. As shown in Fig.2(a), the $Mg_{17}Al_{12}$ phases of AZ91 magnesium alloy precipitate mainly at grain boundaries. These precipitates are scattered at the grain boundaries in discontinuous long strip, while inside the grains are in fine particle structure. As shown in Fig.2(b), some short rod-like and block phases appear, and some phases with plate and network structure can be observed. Fig.3 shows the magnification SEM micrograph and EDS pattern for these new phases. The EDS analysis reveals that the compositions of short rod-like phases are similar to those of block phases that are mainly composed of Al, Y, Zn and Mg. The compositions of block phase are 61.60%Al (molar fraction), 25.8%Y, 0.012% Zn and Mg balance (see point *A* in Fig.3(a)), and the molar ratio of Al and Y is about 2:1 at point *A*, which may be considered as Al_2Y phase by ignoring effect of Zn and Mg[12], while the plate and network phases are mainly composed of elements Al and Ca, and the compositions of point *B* in Fig.3(a) are 23.17%Al, 1.02%Ca, 0.0075% Zn and Mg balance. It has been found that the plate phases exhibit a lamellar structure as a result of Ca dissolving in $Mg_{17}Al_{12}$ phase, which agrees with some study results[4, 24].

In order to identify the new phases formed in the

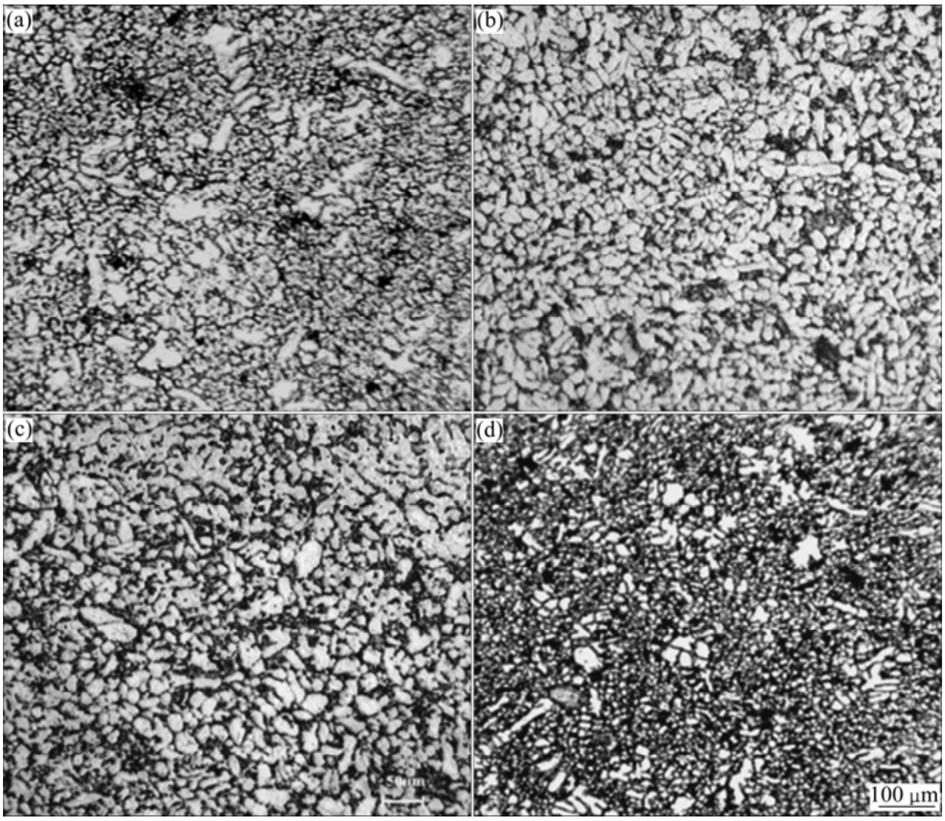

Fig.1 Microstructures of AZ91-1Y-*x*Ca alloys: (a) AZ91 alloy; (b) AZ91-1Y-0.5Ca alloy; (c) AZ91-1Y-1.0Ca alloy; (d) AZ91-1Y-1.5Ca alloy

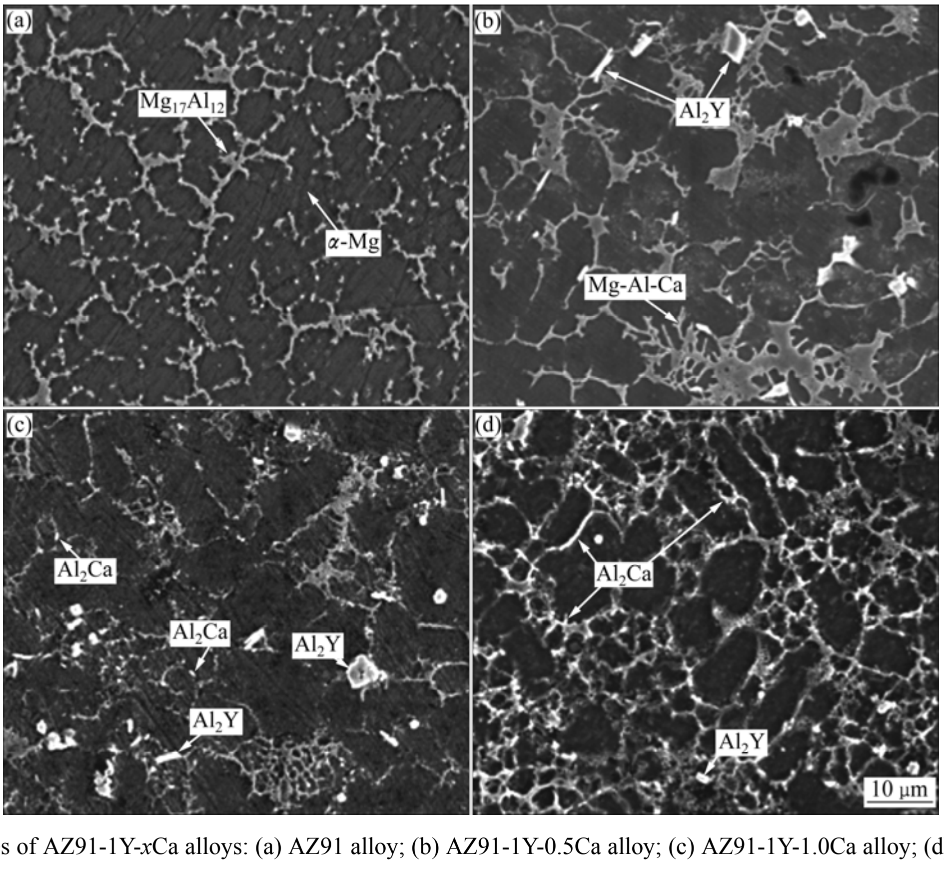

Fig.2 SEM images of AZ91-1Y-*x*Ca alloys: (a) AZ91 alloy; (b) AZ91-1Y-0.5Ca alloy; (c) AZ91-1Y-1.0Ca alloy; (d) AZ91-1Y-1.5Ca alloy

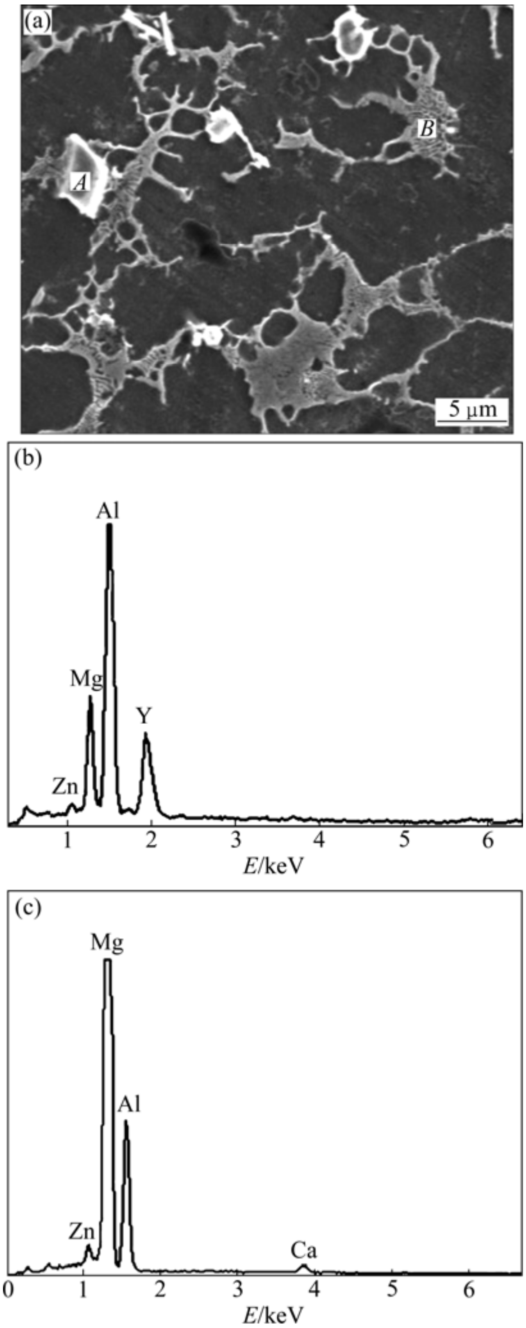

Fig.3 SEM micrograph and EDS pattern for AZ91-1Y-0.5Ca alloy: (a) SEM micrograph; (b) EDS pattern of point *A*; (c) EDS pattern of point *B*

alloy, X-ray diffraction (XRD) analysis was performed for AZ91-1Y-1.0Ca alloy, as shown in Fig.4. The AZ91-1Y-1.0Ca alloy consists of α-Mg solid solution, $Mg_{17}Al_{12}$ phase, Al_2Y phase and Al_2Ca phase, which indicate that the new Al_2Ca phase can precipitate from the matrix with increasing Ca content, compared with the microstructure of AZ91-1Y-0.5Ca alloy. The EDS analysis shows that a little granular bright phase distributed at grain boundaries is Al_2Ca phase (see Fig.2(c)). Fig.2(d) shows the SEM micrograph of AZ91-1Y-1.5Ca alloy. Compared with AZ91-1Y-1.0Ca alloy, it can be seen that the volume fraction of Al_2Ca phase increases obviously, and the Al_2Ca phase tends to distribute reticularly along all the grain boundaries. The morphologies of Al_2Y phase change from short rod-like and coarse block to fine block with the increase of Ca addition, which indicates that increasing Ca content can decrease the grain size of Al_2Y phase. The amount of $Mg_{17}Al_{12}$ phase can be decreased with decreasing Al content in AZ91 alloy. Similarly, when the Ca content in AZ91-1Y alloy is further increased, the amount of Al_2Ca phase increases with the more consumption of Al atoms in alloy, which decreases the amount of $Mg_{17}Al_{12}$ phase.

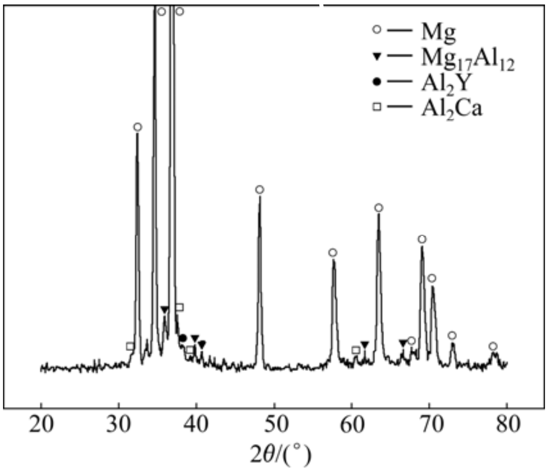

Fig.4 XRD pattern of AZ91-1Y-1.0Ca alloy

3.2 Mechanical properties of as-diecast AZ91-1Y-*x*Ca alloys

Fig.5 shows the mechanical properties of as-die-cast AZ91-1Y-*x*Ca alloys at different temperatures. It can be noted that the combined additions of Y and Ca have little influence on the ultimate strength at ambient temperature, but can obviously improve the yield strength at ambient temperature and the tensile strength at elevated temperature, while the ductility of the alloys decreases with increasing Ca content at tested temperature. The tensile strength of the AZ91 alloys with the combined additions of Y and Ca at 150 and 200 ℃ are higher than those of the AZ91 alloy. At 200 ℃, the highest ultimate tensile strength and yield strength of the AZ91-1Y-1.5Ca alloy are 218.3 and 131.26 MPa, respectively, which are about 89.7% and 53.6% higher than those of the AZ91 alloy, respectively, and the AZ91-1Y-1.5Ca alloy at 200 ℃ exhibits better ductility. Fig.5(d) shows the hardness of AZ91-1Y-*x*Ca alloys. The combined additions of Y and Ca can increase the hardness of AZ91 alloy, and the hardness of the alloys slightly increases with increasing Ca content.

3.3 Discussion

In the present investigation, the combined additions

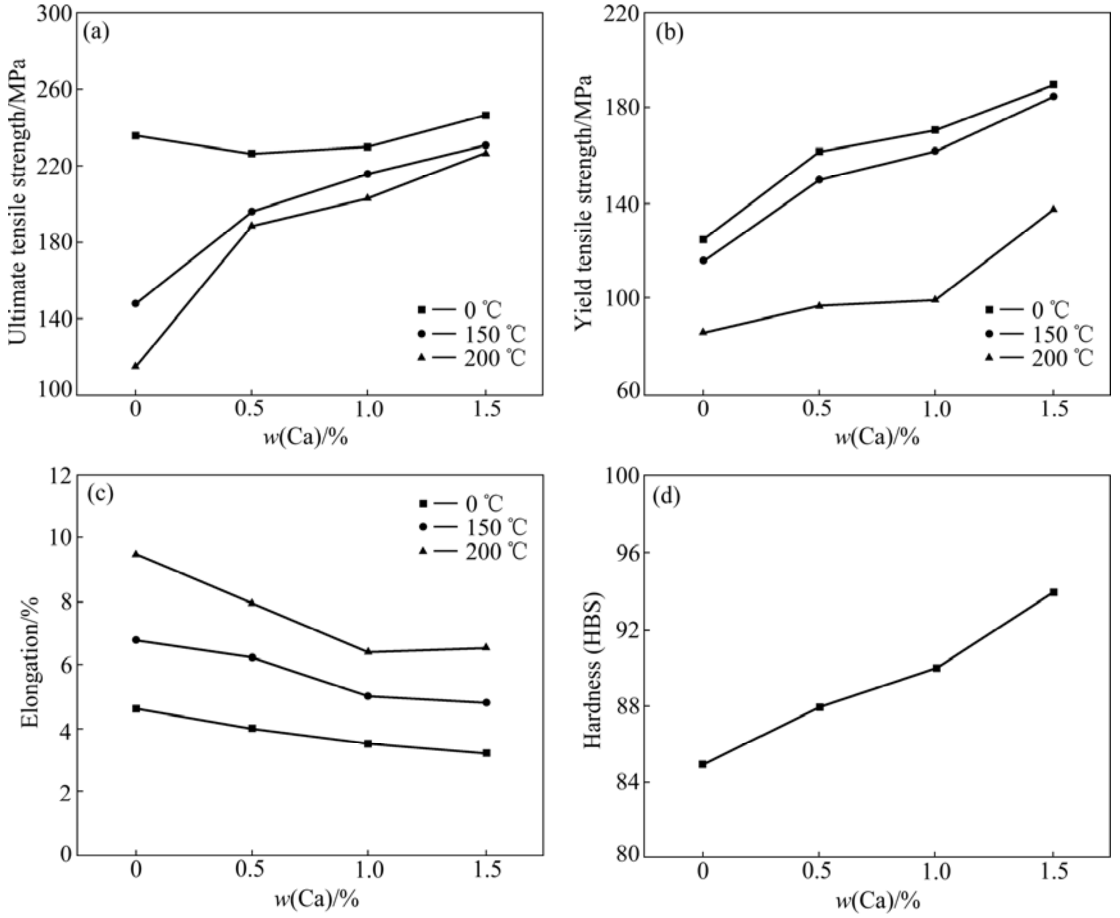

Fig.5 Mechanical properties of as-die-cast AZ91-1Y-*x*Ca alloys at different temperatures: (a) Ultimate tensile strength; (b) Yield strength; (c) Elongation; (d) Hardness at ambient temperature

of Y and Ca to AZ91 alloy can refine the as-die-cast microstructures of alloy significantly, and increasing Ca content will have more obvious refined effect on the microstructure of alloy. Generally, the effect of solute on the grain refinement may be the result of the formation of some particles that can act as potent nucleation sites for magnesium and cause the constitutional undercooling generated by the growth of a grain adjacent to a nucleation particle suspended in the melt[25−26]. The constitutional undercooling was simplified as the growth restriction factor (GRF). According to Ref.[27], GRF can be defined as follows:

$$\mathrm{GRF}=\sum_i m_i c_{0,\,i}(k_i-1) \tag{1}$$

where m_i is the slope of the liquidus line, c_0 the initial composition, and k_i the equilibrium partition coefficient for element *i*. A large GRF can result in the effective grain refinement. Due to the strong segregation of Ca in magnesium alloy, GRF increases, consequently, and refines the microstructure of magnesium alloy obviously [27]. At the same time, the rare earth element Y, as a surface reactive element of magnesium, also can refine microstructure. Accordingly, it can be found that the combined additions of Y and Ca have an obvious refinement effect on the grain size of AZ91 magnesium alloy.

The yield strength of AZ91-1Y-*x*Ca alloys both at ambient and elevated temperatures increases with increasing Ca content, which can be explained by the well-known Hall-Petch relation. Because *K* coefficient in magnesium alloys reaches high values in the range of 200−300 MPa·μm$^{-1/2}$, so the grain refinement will increase the yield strength. However, the combined addition of 1.0%Y and small amount of Ca (lower than 1.0%) can slightly decrease the ultimate tensile strength at ambient temperature. When the Ca content reaches 1.5%, the ultimate tensile strength increases contrarily. WANG et al[20] reported that the ambient ultimate tensile strengths of AZ91-*x*Ca alloys decrease with increasing Ca content ranging from 0.5% to 2.0%, due to the formation of brittle Al_2Ca phase and its reticular distribution along grain boundaries. This implies that in present study, the combined additions of Y and Ca have little effect on the ambient ultimate tensile strength, and the ultimate tensile strength can be improved with increasing Ca content. The reason for slight decline in ambient ultimate tensile strength is because of the formation of coarse block and rod-like Al_2Y phase, while the increase of ambient ultimate tensile strength of AZ91-1Y-1.5Ca alloy results from the microstructure improvement, refinement of Al_2Y phases and dispersion strengthening with Al_2Ca phases and Al_2Y phases. Unfortunately, the combined addition of Y and Ca can decreases the elongation at 150 ℃, results in the formation of Al_2Ca phase and Al_2Y phase, and inhibits precipitation of $Mg_{17}Al_{12}$ phase. With increasing Ca content, the more the amount of Al_2Ca phase, the less the amount of $Mg_{17}Al_{12}$ phase. The brittle Al_2Ca phase and Al_2Y phase formed at grain boundaries can increase the brittleness of alloy, thereby resulting in worse ductility of alloy. Because the microhardness of Al_2Ca and Al_2Y is higher than that of $Mg_{17}Al_{12}$, the hardness of alloy increases with the combined addition of Y and Ca, and further increase with increasing Ca content.

It is observed that the combined addition of Y and Ca to the AZ91 alloy can obviously improve the tensile strength at elevated temperature. A previous study proposed that the sliding of grain boundaries is an important part of the deformation mechanism for some Mg-A1 based alloys at elevated temperature[28]. The shape and distribution of $Mg_{17}Al_{12}$ phase, as a main strengthening phase in the AZ91 alloy, play an important role in enhancing the ambient temperature strength. However, softening and coarsening of the $Mg_{17}Al_{12}$ phase will occur as a result of an increase in solid solubility with increasing temperature according to the phase diagram of Mg-Al, which impairs the strengthening effect of $Mg_{17}Al_{12}$ phase. The formations of Al_2Ca phase and Al_2Y phase with higher melting point suppress the formation of the low melting eutectic phase, $Mg_{17}Al_{12}$, resulting in increasing the metallurgical stability of the grain boundaries at elevated temperature. Meanwhile, the $Mg_{17}Al_{12}$ phase containing Ca also possesses higher thermal stability than the $Mg_{17}Al_{12}$ phase without Ca[29]. Both of these can depress the elevated temperature diffusion process at grain boundaries, which leads to an evident improvement in the elevated temperature tensile properties.

4 Conclusions

1) The combined addition of Y and Ca can refine the as-die-cast microstructure, result in the formation of Al_2Ca phase and Al_2Y phase, inhibit the precipitation of $Mg_{17}Al_{12}$ phase, and increasing Ca content can cause the refinement of Al_2Y phases.

2) The combined additions of Y and small amount of Ca have little influence on the ambient temperature tensile properties, but increasing Ca content can improve significantly the tensile strength at both ambient and elevated temperatures. For AZ91-1Y-*x*Ca alloys, the hardness and elevated temperature tensile strength increase, while the elongation decreases with increasing Ca content.

3) Among the studied alloys, the ultimate tensile strength and yield tensile strength of die casting AZ91-1Y-1.5Ca alloy at 200 ℃ can reach 218.3 and 131.26 MPa, compared with that of die casting AZ91 alloy, which increase by 89.7% and 53.6%, respectively.

References

[1] MORDIKE B L, EBERT T. Magnesium properties—applications—potential [J]. Materials Science and Engineering A, 2001, 302(1): 37−45.

[2] NICHOLAS J. High-performance magnesium [J]. Advanced Materials and Processes, 2005, 163(9): 65−67.

[3] ZHANG Chun-xiang, CHEN Pei-lei, CHEN Hai-jun, SHI Ai-ju, GUAN Shao-kang. Application and research progress of magnesium alloys in automobile industry [J]. Foundry Technology, 2008, 29(4): 531−534. (in Chinese)

[4] LUO A. Recent magnesium alloy development for elevated temperature applications [J]. International Materials Reviews, 2004, 49(1): 13−30.

[5] ZHANG Shi-chang, Cai Qi-zhou, WANG Li-shi, WEI Bo-kang. Mechanical properties of die cast AZ91 alloy containing Y and MM RE at elevated temperatures [J]. Special Casting & Nonferrous Alloys, 2005, 25(5): 287−290. (in Chinese)

[6] KHOMAMIZADEH F, NAMI B, KHOSHKHOOEI S. Effect of rare-earth element additions on high-temperature mechanical properties of AZ91 magnesium alloy [J]. Metallurgical and Materials Transactions A, 2005, 36: 3489−3494.

[7] YUAN Guang-yin, SUN Yang-shan, DING Wen-jiang. Effects of bismuth and antimony additions on the microstructure and mechanical properties of AZ91 magnesium alloy [J]. Materials Science and Engineering A, 2001, 308: 38−44.

[8] SUN Yang-shan, ZHANG Wei-min, MIN Xue-gang. Tensile strength and creep resistance of Mg-9Al-1Zn based alloys with calcium addition [J]. Acta Metallurgica Sinica, 2001, 14(5): 330−334.

[9] YUAN Guang-yin, SUN Yang-shan, DING Wen-jiang. Effect of Sb addition on the microstructure and mechanical properties of AZ91 magnesium alloy [J]. Scripta Materialia, 2000, 43(11): 1009−1010.

[10] XUE Feng, MIN Xue-gang, SUN Yang-shan. Microstructures and mechanical properties of AZ91 alloy with combined additions of Ca and Si [J]. Journal of Materials Science, 2006, 41(15): 4725−4731.

[11] HOSSEIN B, EHSAN S. Effect of rare earth elements addition on thermal fatigue behaviors of AZ91 magnesium alloy [J]. Journal of Rare Earths, 2009, 27(2): 255−258.

[12] ZHANG Shi-chang, WEI Bo-kang, CAI Qi-zhou, WANG Li-shi. Effect of mischmetal and yttrium on microstructures and mechanical properties of Mg-Al alloy [J]. The Chinese Journal of Nonferrous Metals, 2003, 13(1): 83−87. (in Chinese)

[13] ASM International Handbook Committee. Metals Handbook: Vol.2 [M]. OH: Metals Park, 1990.

[14] LI Jin-feng, GENG Hao-ran, YANG Zhong-xi, WANG Ying-zhi, CUI Feng, SUN Chun-jing. Effects of Y on microstructure and mechanical properties of AZ91 magnesium alloy [J]. Foundry, 2005, 54(1): 53−56. (in Chinese)

[15] ZHANG Shi-chang, WEI Bo-kang, LIN Han-tong. Effect of Y addition on microstructure and aging properties of Mg-9A1-1Zn alloy [J]. Transactions of Materials and Heat Treatment, 2003, 24(3): 23−26. (in Chinese)

[16] ZHANG Jing-huai, NIU Xiao-dong, QIU Xin, LIU Ke, NAN

Chang-ming, TANG Ding-xiang, MENG Jian. Effect of yttrium-rich misch metal on the microstructures, mechanical properties and corrosion behaviour of die cast AZ91 alloy [J]. Journal of Alloys and Compounds, 2009, 471: 322−330.

[17] WANG Xiao-qiang, LI Quan-an, ZHANG Xing-yuan. Effects of yttrium on microstructure and mechanical properties of AZ81 magnesium alloy [J]. Special Casting & Nonferrous Alloys, 2007, 27(5): 384−387. (in Chinese)

[18] FAN Chao, LI Hua-ji. Current state of research on ignition proof magnesium alloy [J]. Rare Metals Letters, 2005, 24(10): 1−4. (in Chinese)

[19] SAKAMOTO M, AKIYAMA S. Suppression of ignition and burning of molten Mg alloys by Ca bearing stable oxide film [J]. Journal of Materials Science Letters, 1997, 12: 1048−1050.

[20] WANG Qu-dong, CHEN Wen-zhou, ZENG Xiao-qin, LU Yi-zhen, DING Wen-jiang, ZHU Yan-ping, XU Xiao-ping. Effects of Ca addition on the microstructure and mechanical properties of AZ91 magnesium alloy [J]. Journal of Materials Science, 2001, 36: 3035−3040.

[21] FAN Yu, WU Guo-hua, GAO Hong-tao, ZHAI Chun-quan, ZHU Yan-ping. Effect of calcium on microstructure, mechanical properties and corrosion resistance of magnesium alloy [J]. The Chinese Journal of Nonferrous Metals, 2005, 15(2): 210−216. (in Chinese)

[22] NIU Jie-xin, XU Nai-xin, ZHANG Cheng-dian, CHEN Qiu-rong. Effect of alkaine-earth metals Ca and Sr on corrosion resistance of magnesium alloys [J]. Corrosion & Protection, 2008, 29(1): 1−6. (in Chinese)

[23] WU Guo-hua, FAN Yu, GAO Hong-tao. The effect of Ca and rare earth elements on the microstructure, mechanical properties and corrosion behavior of AZ91D [J]. Materials Science and Engineering A, 2005, 408: 255−263.

[24] WANG Feng, LIU Zheng, YU Bao-yi, ZHANG Kui. Effects of Ca addition on tensile properties and microstructures of hot-extruded AZ91 alloy tube [J]. The Chinese Journal of Nonferrous Metals, 2006, 16(s3): 1736−1740. (in Chinese)

[25] LEE Y C, STJOHN D H, HUTT J E C, DAHLE A K. Effect of grain refinement and silicon content on grain formation in hypoeutectic Al-Si alloys [J]. Materials Science and Engineering A, 1999, 259(1): 4−5.

[26] HUTT J E C, DAHLE A K, LEE Y C, STJOHN D H. Effects of growth restriction and effective nucleant potency on grain size and morphology in Al-Si and Al-Cu alloys [C]// Light Metals: Proceedings of Sessions, TMS Annual Meeting. Warrendale, PA: TMS, 1999: 685−692.

[27] DAHLE A K, LEE Y C, NAVE M D, SCHAFFER P L, STJOHN D H. Development of as-cast microstructure in magnesium-aluminum alloys [J]. Journal of Light Metals, 2001, 1(1): 61−72.

[28] HUMPLE P. Towards a cheap creep resistant magnesium alloy [J]. Materials Forum, 1997, 21(1): 45−56.

[29] DU Wen-wen, SUN Yang-shan, MIN Xue-gang, XUE Feng, WU Deng-yun. Influence of Ca addition on valence electron structure of $Mg_{17}Al_{12}$ [J]. The Chinese Journal of Nonferrous Metals, 2003, 13(6): 1274−1279. (in Chinese)

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