

Effect of Ca on crystallization of Mg-based master alloy containing spherical quasicrystal

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Abstract: Spherical icosahedral quasicrystalline phase (*I*-phase) was obtained by introducing Ca into Mg-Zn-Y alloy under conventional casting conditions. Due to the addition of Ca, Mg₄₅Zn₅₀Y_{4.5}Ca_{0.5} primary *I*-phase, which is thermodynamically stable and homogeneously distributed, was generated instead of decahedral quasicrystalline phase during the solidification process; the morphology of primary *I*-phase in the solidification microstructure changed from petal-like one (60–80 μm) to spherical one (≤15 μm). When the mass fraction of Ca reaches 0.05%, spherical *I*-phase with the largest quantity, highest spheroidization rate and highest circular degree can be obtained. Meanwhile, due to the changed morphology and the decreased size of primary *I*-phase, the hardness of Mg-Zn-Y-Ca master alloy is reduced. The application of spherical *I*-phase as particulate reinforced phase provides great opportunities for the improvement of strength and toughness of magnesium alloys.

Key words: magnesium alloy; Ca; spherical quasicrystal; crystallization; microstructure

1 Introduction

Since quasicrystals in Mg-Zn-RE system were discovered in 1990s, great progress has been made on Mg-based quasicrystal research. However, many issues such as microstructure, morphology, formation mechanism, mechanical properties and physical properties of quasicrystals, are expected to be further studied. Meanwhile, the application of quasicrystals is limited, far from the bright future that people have expected. In a context that research on magnesium alloys becomes a worldwide hot issue, through making use of superior properties of quasicrystals and employing proper fabrication process, high performance magnesium alloys containing quasicrystals can be developed, thus widening applied range of quasicrystal materials and providing a new way for the research and development of high-strength and high-toughness magnesium alloys. Developing high performance magnesium alloys containing quasicrystals is of great significance from the viewpoint of academic research and engineering application, and is one of the most important research subjects in the field of new materials[1].

For the preparation of high-temperature heat resistance magnesium alloys, a series of rare earth alloys with high strength, high heat and corrosion resistance were developed by adding rare earth elements into magnesium alloys. However, high cost of rare earth elements limited the application of rare earth magnesium alloys. Therefore, it is urgent to develop heat resistance magnesium alloys with low cost and high performance[2–4], so as to meet the extensive demands of automobile industry.

The addition of low-cost Ca into magnesium alloys can heighten the oxidating combustion temperature of magnesium alloy, refine the microstructure, and improve room-temperature mechanical property and elevated-temperature heat resistance[5–10]. If Ca can modify the morphology of the quasicrystal phase in magnesium alloys, new application value of Ca will be disclosed. Therefore, in this study the effect of Ca on Mg-Zn-Y quasicrystal phase was investigated by introducing Ca into quasicrystal containing Mg-Zn-Y master alloy.

2 Experimental

Initially, a master alloy, Mg-10%Ca (mass fraction),

was prepared by induction melting under Ar atmosphere using magnesium (99.99%) and calcium (99.99%) raw materials. Then, Mg-Zn-Y-Ca melt with the expected chemical composition (shown in Table 1) was prepared using the master alloy, magnesium (99.99%), zinc (99.99%) and yttrium (99.99%) raw materials. Finally, the melt was poured into a metal mold with inner diameter of 30 mm and height of 120 mm to form final samples.

Table 1 Chemical compositions of quasicrystal containing Mg-Zn-Y-Ca alloy (mass fraction, %)

Alloy	Zn	Y	Ca	Mg
1	45.500	2.500	0.025	Bal.
2	45.000	2.500	0.050	Bal.
3	44.000	2.500	0.100	Bal.
4	43.000	2.500	0.250	Bal.
5	41.000	2.500	0.500	Bal.

Constituent phases were identified by X-ray diffractometry (Y-2000) and transmission electron microscopy (TEM, H-800). The phase compositions were analyzed by electron dispersive spectroscopy (EDS) in scanning electron microscopy (SEM, JSM-6700F). Brinell hardness of quasicrystal containing Mg-Zn-Y and Mg-Zn-Y-Ca master alloys was examined by hard-meter (HB-3000B).

3 Results and discussion

3.1 Crystallization process of quasicrystal

With proper mole ratio among magnesium, zinc and yttrium, the quasicrystal phase (*I*-phase) can be generated during the crystallization of Mg-Zn-Y alloy. In the solidification microstructure of quasicrystal containing Mg-Zn-Y master alloy, the quasicrystal phase can be either petal-like icosahedral phase (*I*-phase) or bacillary decahedral phase (*D*-phase)[11–12].

For the crystallization of quasicrystal containing Mg-Zn-Y alloy, it can be seen from vertical cross section of $Mg_{40-x}Zn_{60}Y_x$ in Mg-Zn-Y ternary phase diagram[13] that, when the chemical composition of the melt was Mg_3Zn_6Y , $(Zn, Mg)_5Y$ crystal phase was first generated while the melt temperature reduced to 960 K, and then *I*-phase formed by a peritectic reaction, $L+(Zn, Mg)_5Y \rightarrow I$ -phase, at 900 K; when Y content was low in the melt such as $Mg_{37}Zn_{60}Y_3$, *I*-phase was initially generated in the solidification process followed by the formation of (*I*-phase+ α -Mg) eutectic microstructure at 673 K. Therefore, solidification microstructure of Mg-Zn-Y ternary alloy under normal casting condition, a multiphase microstructure, was composed of primary *I*-phase and *D*-phase, (*I*-phase+ α -Mg) lamellar eutectic structure, the primary α -Mg and MgZn crystal phase (shown in Fig.1). Fig.1(a) shows SEM micrograph of

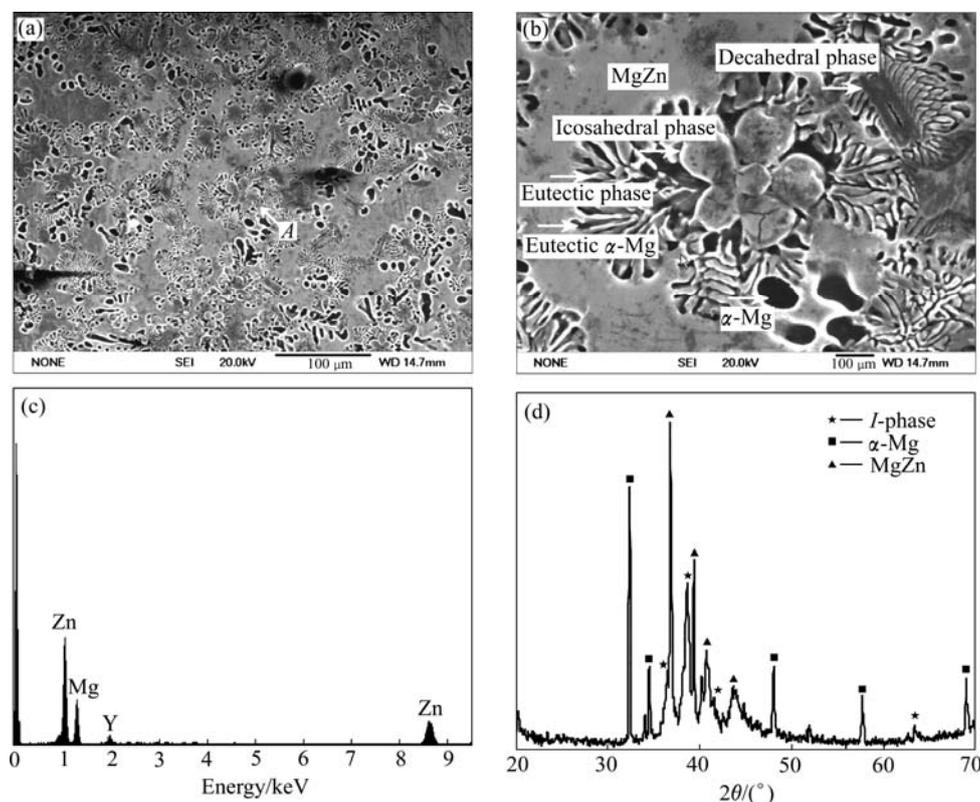


Fig.1 Microstructure analysis of quasicrystal containing Mg-Zn-Y master alloy: (a) SEM image of quasicrystal; (b) Magnified SEM image of *I*-phase marked by arrow in Fig.1(a); (c) EDS spectrum of petal-like *I*-phase in Fig.1(b); (d) XRD pattern of quasicrystal

quasicrystal containing Mg-Zn-Y master alloy. Fig.1(b) shows magnified SEM micrograph of the *I*-phase marked by an arrow in Fig.1(a). From Fig.1(b) it is clear that lamellas surrounding petal-like *I*-phase are (*I*-phase + α -Mg) eutectic microstructures, gray matrix is MgZn crystal phase, and parallel *D*-phase is upper right. Fig.1(c) shows EDS analysis of petal-like *I*-phase in Fig.1(b); Fig.1(d) shows XRD pattern of quasicrystal containing Mg-Zn-Y master alloy.

3.2 Effect of Ca on crystallization of quasicrystal

Fig.2 shows the effect of addition of Ca on the microstructure of quasicrystal containing Mg-Zn-Y master alloy. It can be seen that the microstructure varies with the amount of Ca. When mass fraction of Ca is 0.02%, the morphology of the primary *I*-phase changes from petal-like to spherical (shown in Fig.2(b)). Adding 0.05%Ca, spherical *I*-phase with smaller size and homogeneous distribution and (*I*-phase+ α -Mg) lamellar

eutectic structure are obtained (see Fig.2(c)). With increasing the addition level of Ca up to 0.10%, the morphology of *I*-phase begins to transfer from spherical to petal-like, the quantity of spherical *I*-phase decreases and substantial lamellar quasicrystal phase appears (shown in Fig.2(d)). Further increase in the addition of Ca to 0.25%, the quantity of primary *I*-phase decreases obviously and there are few petal-like quasicrystals (shown in Fig.2(e)). It should be noted that there is almost no spherical *I*-phase and the quasicrystal phase only exists in the form of eutectic microstructure when 0.50% of Ca is added (shown in Fig.2(f)). Therefore, under normal casting condition, it is absolutely feasible that the addition of certain amount of Ca into the melt can change the formation process of quasicrystal containing Mg-Zn-Y alloy during the solidification process, avoid the formation of decahedral quasicrystal phase, generate thermodynamically stable and homogeneously distributed $Mg_{45}Zn_{50}Y_{4.5}Ca_{0.5}$ *I*-phase.

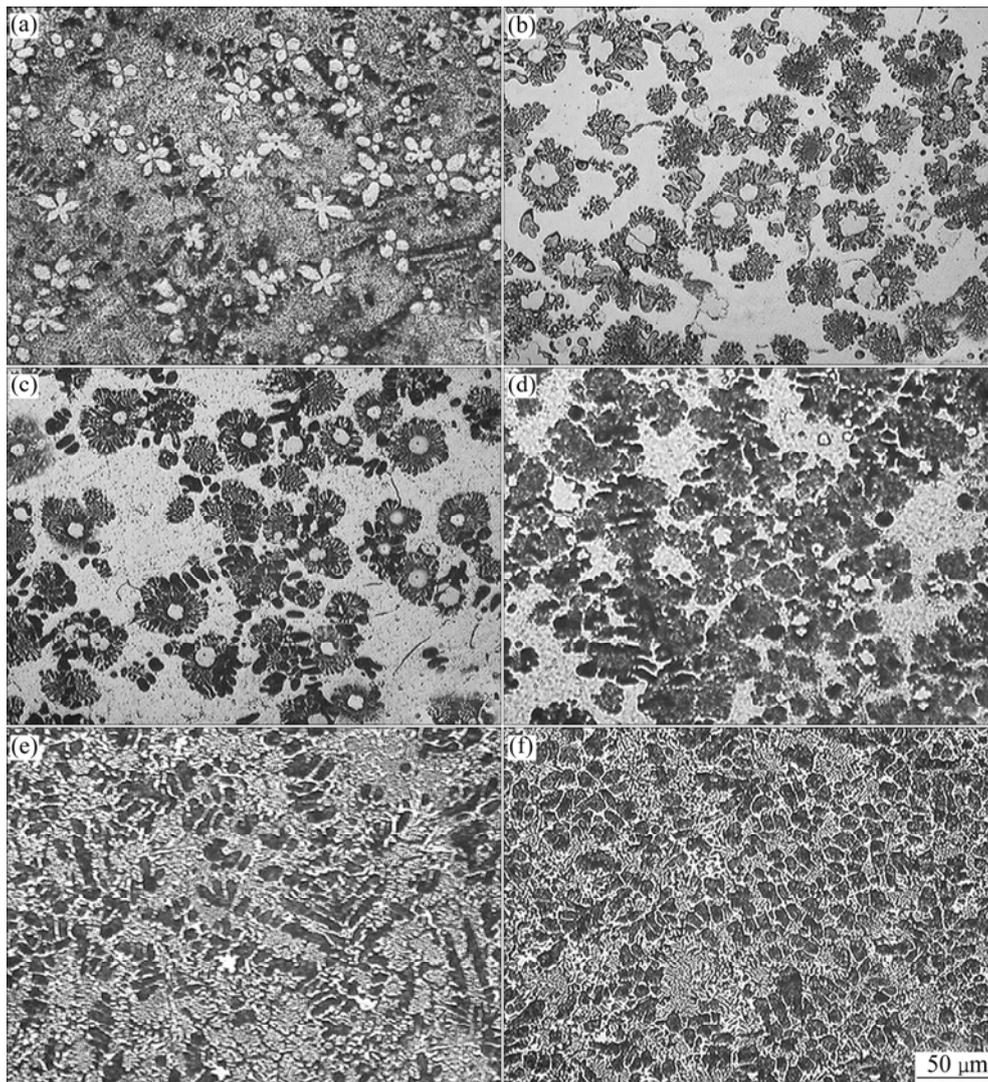


Fig.2 Effect of addition of Ca on microstructure of quasicrystal containing Mg-Zn-Y master alloy: (a) 0%Ca; (b) 0.02%Ca; (c) 0.05%Ca; (d) 0.10%Ca; (e) 0.25%Ca; (f) 0.50%Ca

Consequently, the morphology of *I*-phase is transformed from petal-like one to spherical one. Moreover, because of the addition of Ca, *I*-phase particle size is changed from large petal-like one (60–80 μm) to small spherical one ($\leq 15 \mu\text{m}$)[14–15].

Fig.3 shows the microstructure and phase analysis of quasicrystal containing Mg-Zn-Y-Ca master alloy. From Fig.3(a), it is clear that spherical *I*-phase is surrounded by lamellar quasicrystal inter-growth eutectic microstructure. TEM micrograph and diffraction spots of

quasicrystal containing Mg-Zn-Y-Ca master alloy are shown in Fig.3(b). XRD pattern of quasicrystal containing Mg-Zn-Y-Ca master alloy is shown in Fig.3(c). Figs.3(d) and (e) show EDS analysis of spherical *I*-phase (marked by *A* in Fig.3(a)) and lamellar quasicrystal phase (marked by *B* in Fig.3(a)), respectively; while Fig.3(f) shows EDS analysis of lamellar α -Mg phase (marked by *C* in Fig.3(a)). EDS analysis results in Figs.3(d) and (e) show that the primary spherical *I*-phase is surrounded by lamellar

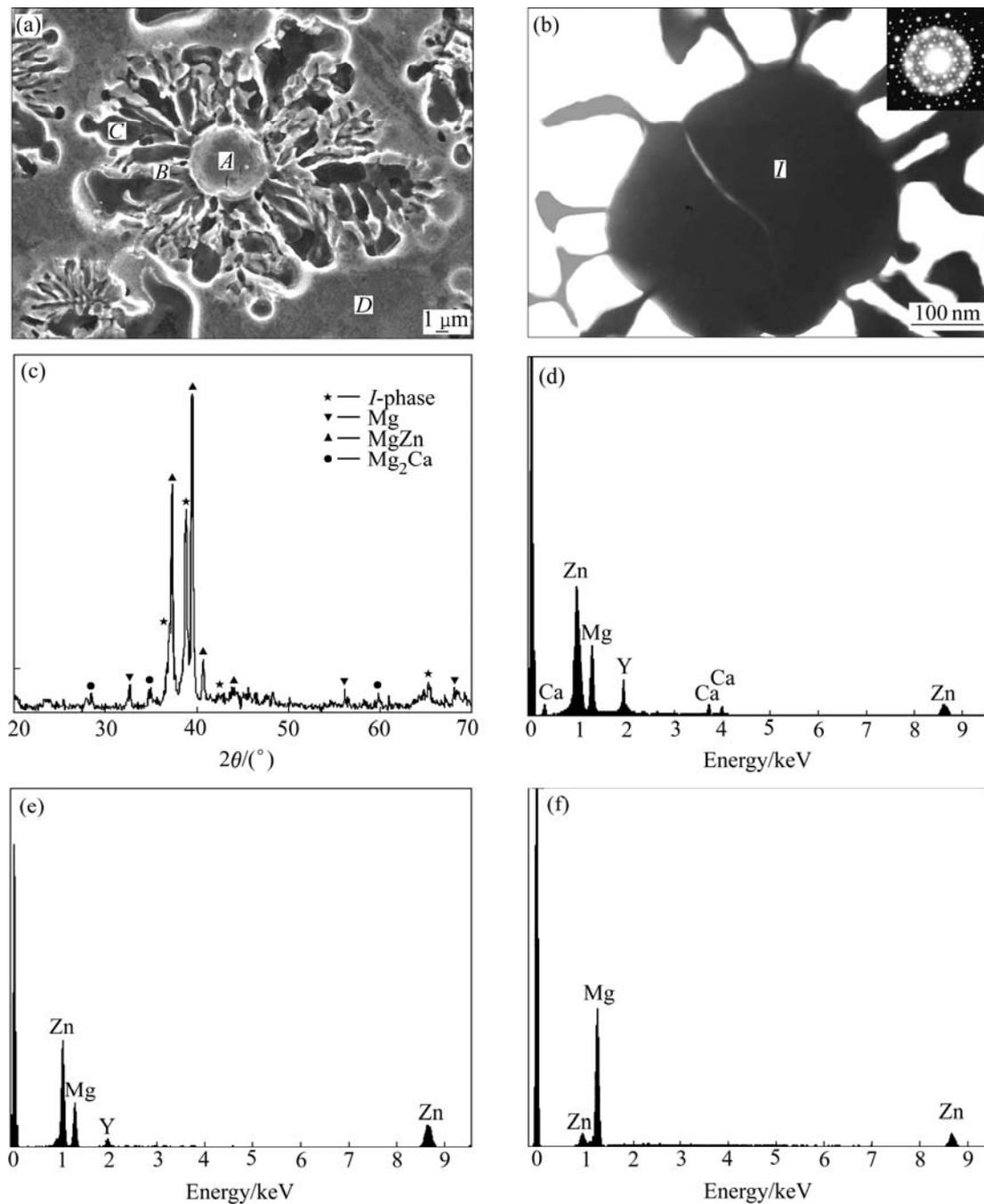


Fig.3 Microstructures of quasicrystal containing Mg-Zn-Y-Ca master alloy with mass fraction of Ca of 0.05%: (a) SEM image of spherical *I*-phase; (b) TEM image and diffraction spots of quasicrystal; (c) XRD pattern of quasicrystal; (d) EDS analysis of spectrum *A* in Fig.3(a); (e) EDS analysis of spectrum *B* in Fig.3(a); (f) EDS analysis of spectrum *C* in Fig.3(a)

quasicrystals that are generated through the eutectic reaction. Therefore, the solidification microstructure of Mg-Zn-Y-Ca alloy under normal casting condition, a multiphase microstructure, consists of $Mg_{45}Zn_{50}Y_{4.5}Ca_{0.5}$ spherical *I*-phase, $(Mg_{55}Zn_{42}Y_3)$ *I*-phase+ α -Mg lamellar eutectic structure, dendrite α -Mg, and MgZn crystal phase.

Fig.4 shows SEM micrograph and EDS analysis of the sample with mass fraction of Ca of 0.50%.

As optical micrograph in Fig.2 and SEM micrographs in Fig.3(a) and Fig.4(a) show, the quantity and size of the quasicrystal phase decrease with increasing addition level of Ca. When the addition level of Ca is 0.05%, primary spherical *I*-phase with largest quantity, highest spheroidization rate and highest circular degree can be obtained. Further increasing in the addition of Ca, the morphology of *I*-phase changes from spherical to petal-like, and the quantity of primary *I*-phase decreases. When 0.50% of Ca is added, primary spherical *I*-phase disappears while the quantity of lamellar quasicrystal phase increases. From the results mentioned above proper content of Ca is favorable to the formation of primary spherical *I*-phase, showing that Ca

is a spheroidizing element for the quasicrystal phase; excess content of Ca will suppress the formation of spherical *I*-phase and promote the formation of lamellar quasicrystal phase.

3.3 Effect of Ca on macro-hardness of quasicrystal

The indentation test is customarily used to test and evaluate the mechanical properties of brittle materials. Due to high hardness of quasicrystal phase, porosity and high room-temperature brittleness usually existing in petal-like quasicrystals, most mechanical properties are tested indirectly by hardness experiments[16].

As shown in Fig.5, it can be seen that macro-hardness of the matrix of Mg-Zn-Y-Ca master alloy gradually decreases with the increase of Ca addition. This phenomenon may be explained as follows: on the one hand, the introduction of Ca into the Mg-Zn-Y ternary alloy results in the morphology evolution of quasicrystal phase in the matrix from petal-like to spherical, eliminates porosity in the quasicrystal phase and elevate the microstructure density of the quasicrystal containing master alloy; on the other hand, the addition of Ca reduces the quantity of primary

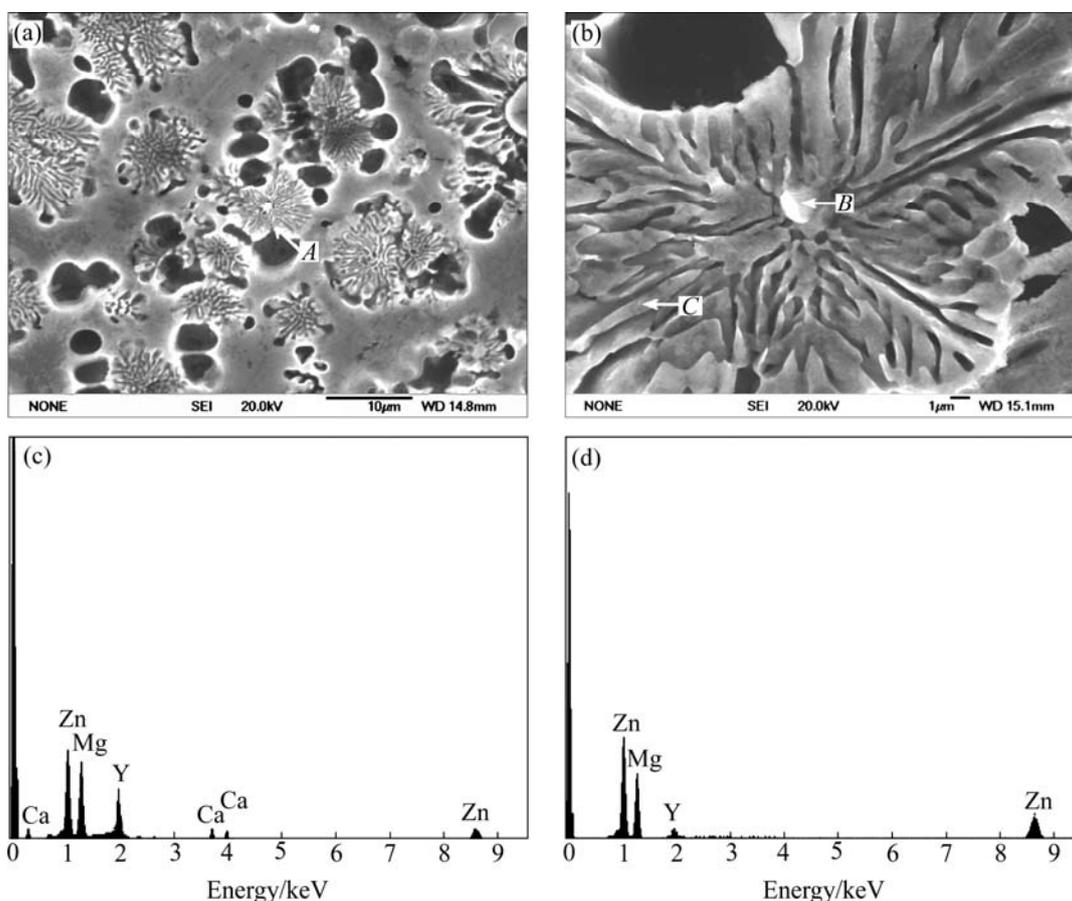


Fig.4 Eutectic structure analysis of quasicrystal containing Mg-Zn-Y master alloy with mass fraction of Ca of 0.50%: (a) SEM image of Fig.2(f); (b) Magnified SEM image of region marked by *A* in Fig.4(a); (c) EDS analysis of spectrum *B* in Fig.4(b); (d) EDS analysis of spectrum *C* in Fig.4(b)

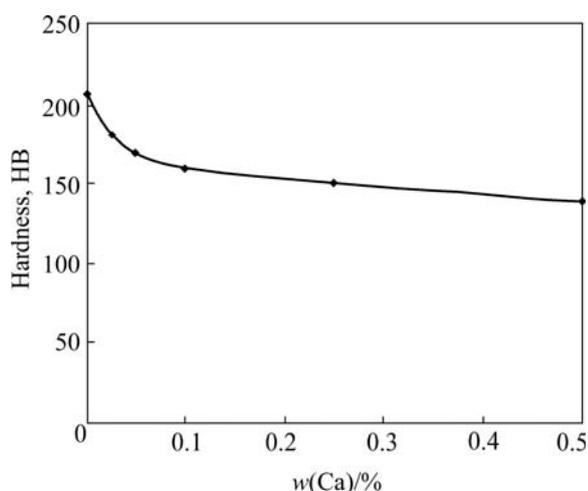


Fig.5 Effect of Ca addition on macro-hardness of Mg-Zn-Y-Ca alloy

quasicrystal phase, results in smaller volume fraction of primary quasicrystal phase in the matrix. The increase of hardness resulted from the elevated density is much higher than the decrease of hardness resulted from the reduced amount of *I*-phase. Therefore, lower macro-hardness of the matrix of Mg-Zn-Y-Ca master alloy can be obtained.

3.4 Mechanism analysis of Ca on crystallization of quasicrystal

The addition of Ca into quasicrystal containing Mg-Zn-Y master alloys can refine the grain and spheroidize the quasicrystal phase. To the matrix of quasicrystal containing Mg-Zn-Y master alloy, Ca is a surface-active element. So a small quantity of Ca added into Mg-Zn-Y master alloy will agglomerate at the solid-liquid interface. Consequently, on the one hand, constitutional undercooling occurs in local regions at the growing interface of primary quasicrystal phase, preventing the growth of the primary quasicrystal phase; on the other hand, the diffusion velocity of alloying elements slows down, suppressing the nucleation and growth of the primary quasicrystal phase. In addition, nucleating substances at the front of the diffusion layer can be activated by constitutional undercooling and provide substantial nucleating sites for the crystal phase, finally resulting in the grain refinement of the crystal phase. Grain-refining behavior of Ca on pure magnesium and its alloy may be explained by grain growth restriction theory, and the extent of Ca restricting the grain growth can be described by growth restriction factor (GRF). The GRF is a measure of the growth-restricting effect of solute elements on the growth of solid-liquid interface of new grains as they grow into the

melt by forming constitutional undercooling and slowing down the diffusion of solute atoms. The larger the GRF, the greater the growth-restricting effect of solute elements on the grain growth, that is, the more obvious the grain-refining effect [17]. Compared with other elements, Ca has a higher growth-restricting parameter [18]. Therefore, higher GRF of Ca can be obtained, thereby showing excellent grain-refining ability of Ca on the microstructure including the quasicrystal phase.

4 Conclusions

1) The addition of small amount of Ca into quasicrystal containing Mg-Zn-Y master alloy can change the morphology and size of primary quasicrystal phase. The morphology of primary *I*-phase in the solidification microstructure changes from petal-like one (60–80 μm) to spherical one ($\leq 15 \mu\text{m}$). The solidification microstructure of Mg-Zn-Y-Ca alloy under conventional casting condition, a multiphase microstructure, consists of $\text{Mg}_{45}\text{Zn}_{50}\text{Y}_{4.5}\text{Ca}_{0.5}$ spherical *I*-phase, $(\text{Mg}_{55}\text{Zn}_{42}\text{Y}_3 + \alpha\text{-Mg})$ lamellar eutectic structure, dendrite $\alpha\text{-Mg}$ and MgZn crystal phase.

2) When the mass fraction of Ca reaches 0.05%, spherical *I*-phase with highest spheroidization rate and highest circular degree can be obtained.

3) Hardness of quasicrystal containing Mg-Zn-Y master alloy decreases gradually with the addition level of Ca increasing.

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