

Microstructural Characterization of Zinc Alloy ZA27 with Modification and Heat Treatments

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Abstract. The influence of Ti and Zr incorporated modification and heat treatments on microstructure of ZA27 zinc alloy were investigated in this work. The results of XRD and optical microscopy analyses showed that modification with the addition of 0.03 wt.% Ti and 0.05 wt.% Zr changed the morphology of primary α -Al dendrite in ZA27 alloy from large branch-shape to small flower-shape without variation of phase constitution. It has been proposed that the segregation of Ti and Zr elements in the front of solidification interface influenced solute distributions and constitutional supercooling, and resulted in the change in growth pattern of block α -Al dendrite and in the formation of secondary dendrite. It was found that modification improved the distribution of η -Zn phase in α -Al matrix after solution heat treatment at 370°C for 10h, and obviously restrained the coarsening of eutectics during anneal heat treatments at 320°C for 3h and 18h, respectively.

Introduction

High aluminum zinc based alloys have got rapid development as a new type of nonferrous alloy. ZA27 alloy is a kind of high strength cast alloy with a number of good mechanical performances, such as low density than copper and ferrous alloys, and high maximum tensile strength, good abrasive resistance, good load bearing, moderate heat conductivity and electric conductivity, etc. Now, ZA27 alloy has become an excellent substitute of wear-resistant materials, such as copper based alloys and cast irons, to manufacture wear-resistant parts, such as shaft sleeves, turbines, sliding blocks, etc. Moreover, ZA27 alloy is still of great application prospect in mould making industry [1]. Nonetheless, high aluminum zinc based alloys including ZA27 alloy are not desirable to be used in the fabrication of many important parts due to their inferior plasticity and toughness. Generally, ZA27 alloy needs to be improved in strength and toughness by means of modification and heat treatment, as well as other technological methods. Regarding to modification, many modifiers, such as boron, lithium, titanium, zirconium and rare earth elements, have been proved to enhance the plasticity and toughness of ZA27 alloy substantially through effectively grain refinement [2-4]. However, to date the modifying approach and effect of modifiers for ZA27 alloy is still lack of deep understanding, and the modifying mechanism has not got consistent opinion [5-7]. There is still lack of theoretical direction for modification of ZA27 alloy and lack of the understanding of heat treatment method [8].

According to the binary phase diagram of Al-Zn alloys [9], as shown in Fig.1, the solidification process and microstructure evolution of ZA27 alloy is fairly complex due to the existence of uniform grain, eutectic and segregation and other reactions on the non-balanced solidification condition. It is expectable that these reactions will be influenced to some extent by adding modification agents. For this reason the present work investigated the effect of Ti and Zr elements as incorporated modifiers, and the effect of some kind of subsequent heat treatments on the microstructure evolution of ZA27 alloy.

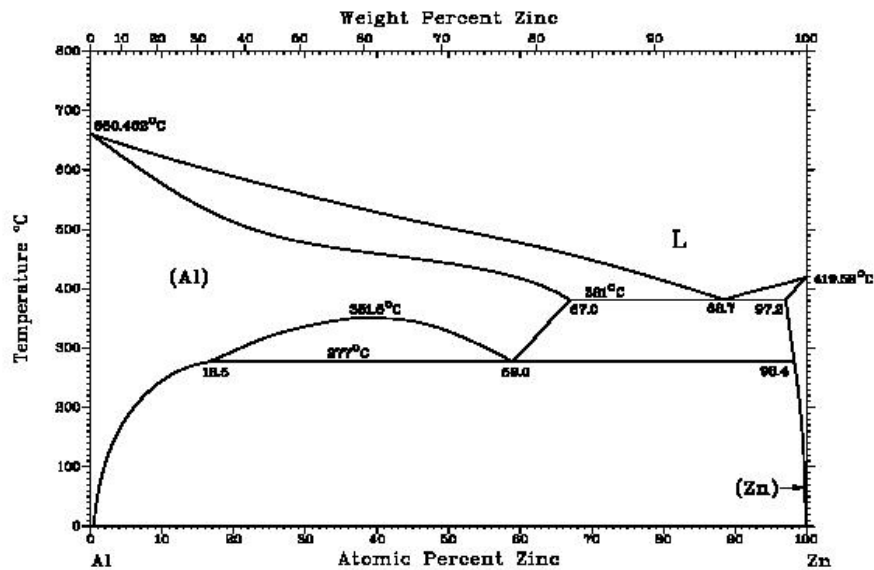


Fig.1. Equilibrium binary phase diagram of Al-Zn alloys

Experimental procedures

Materials and preparation: The raw materials used in this study were commercial pure aluminum, pure zinc, pure magnesium and Al-10%Cu (mass fraction) master alloy. The modifiers Ti and Zr elements were induced by the Al-3%Ti and Mg-33%Zr master alloys. Pure Zn, Al ingots and Al-10%Cu master alloy were first melted at 720°C by use of electrical resistant furnace in a stainless steel crucible. After refined by ZnCl₂ with manually stirring, pure Mg was added into the melt subsequently and pre-modified samples were cast after standing for 5-10min. Then the Al-3%Ti and Mg-33%Zr master alloys were added into the melt with stirring. Finally the melt was poured to metal mould to get modified samples. The chemical compositions of the cast ZA27 alloy with and without modification were listed in table 1.

Table.1. Chemical composition of ZA27 alloys investigated (% , mass fraction).

element	Al	Cu	Mg	Ti	Zr	Zn
without modification	25.4	2.4	0.10			balance
with modification	26.1	2.3	0.12	0.03	0.05	balance

Heat treatments: The solution heat treatment and anneal heat treatment were conducted on the as-cast samples of the experimental ZA27 alloys. Both alloys with and without modifications were heat treated in the same regime. The solution samples were heated to 370°C and held for 10 hours in an electric furnace and quenched in water immediately. The annealing samples were heat treated at 320°C and held for 3 and 18 hours, respectively, and cooled in air.

Microstructural characterization: All samples were etched using 4% Nital after pre-grinding and polishing, and observed under an optical microscopy, Zeise 200 MAT type. Grain size and volume fraction of phase was measured by use of the image analysis software (MZLY). The phase components of the investigated alloys were determined by means of X-ray diffraction (XRD), DX-2000 type. Differential thermal analysis (DSC) was conducted for both alloys with and without modification, by using the apparatus of NETZSCH STA-409PC type.

Results

As-cast microstructures: The XRD spectrums of investigated ZA27 alloys with and without modification are shown in Fig.2. It indicates that both alloys are composed of α -Al, η -Zn and ϵ -CuZn₅ phases, which means that no phase composition change occurs in ZA27 alloy after Ti and Zr incorporated modification. Fig.3 shows the DSC curves of the alloys, it reveals that the alloys

undergo eutectic reaction and monotectoid reaction during solidification and cooling processes, respectively. It is obvious that the modification increases the monotectoid temperature and decreases the eutectic temperature and melting point of ZA27 alloy.

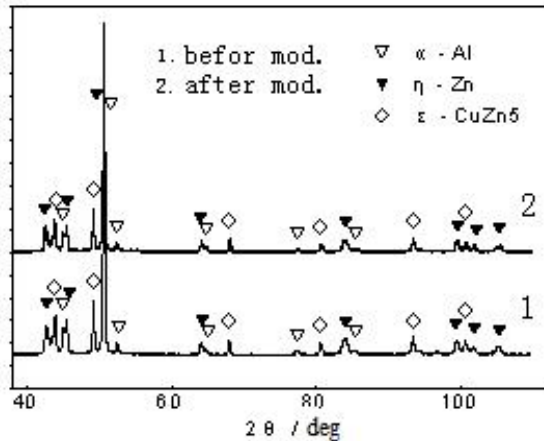


Fig.2. XRD patterns of as-cast ZA27 alloys

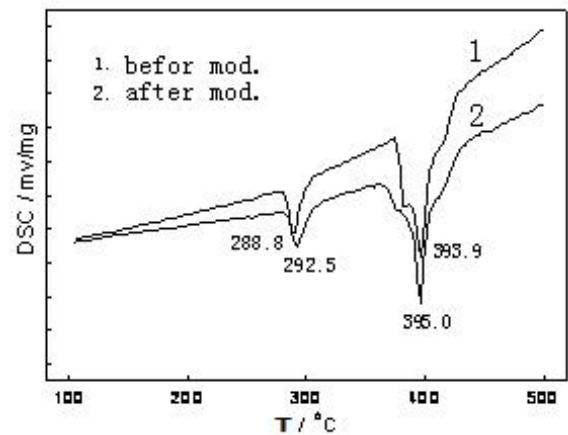
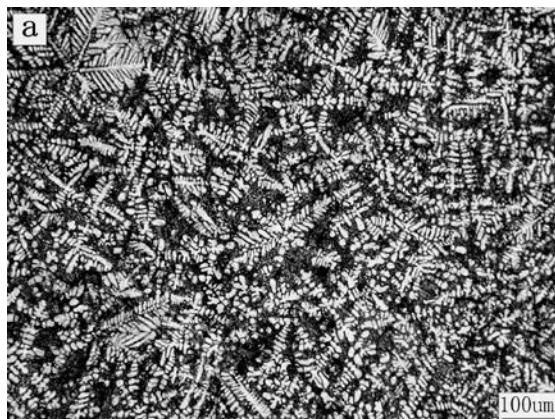


Fig.3. DSC curves of ZA27 alloys

Microstructures of as-cast ZA27 alloy with and without modification are shown in Fig.4. Without modification, the microstructure of ZA27 alloy is composed of developed integral dendrites of primary α -Al solid solution and eutectics between them. The volume fraction of primary α -Al dendrite is large above 65% and its mean length is about 200 μ m with no growth directionality, as shown in Fig.4(a). From the high magnification image, Fig.4(b), it can be seen that the secondary dendrite arms are very developed with the secondary dendrite arms spacing (SDAS) of about 10 μ m. The black spots between SDAS are η -Zn phase and the areas between primary dendrite are lamellar α + η eutectics mingling with fine ϵ -CuZn₅ compound. With modification, the microstructure of ZA27 alloy is still composed of integral primary dendrite and eutectics between them, as shown in Fig.4(c), but the shape of α -Al dendrites is changed to small and uniform petal shaped dendrite from the previous coarse developed dendrite without modification. The volume fraction of α -Al dendrite is decreased somewhat to about 55%. Same as the unmodified alloy, the dendrites of modified alloy grows without directionality during solidification. Rare secondary arms or only a few bulges form on the primary dendrites. The mean length of the dendrites is about 50 μ m. From the high magnification image, Fig.4(d), it can be seen that the first dendrites of the modified alloy are short and thick in comparison with that of unmodified alloy, and seem petal shaped due to rare secondary dendrites. But a number of oval α -Al dendrites of about 10 μ m are dispersed among the petal shaped primary dendrites. The volume fraction of eutectics between dendrite is slightly larger and the distribution of eutectics is more uniform than that of unmodified alloy.



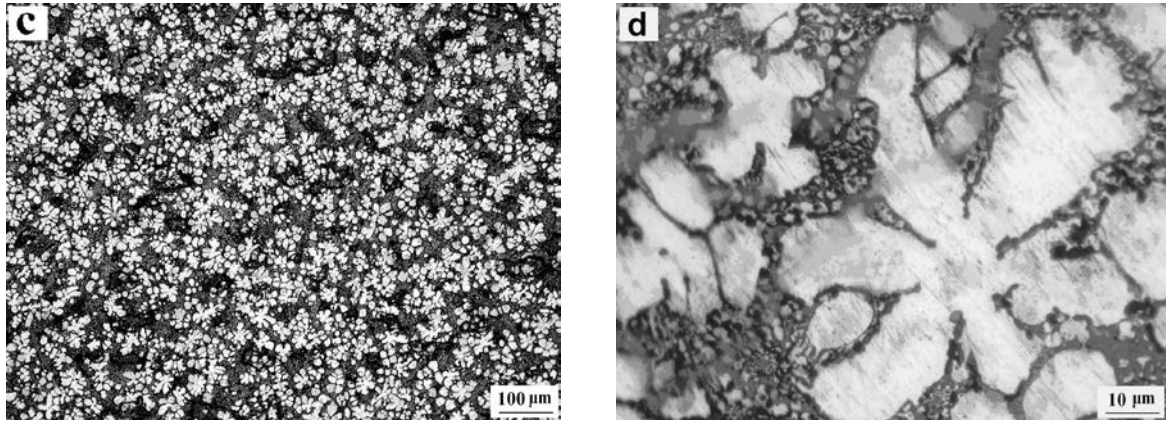


Fig.4. As-cast microstructures of ZA27 alloy, a, b un-modified; c, d modified

Solution heat treatment: Fig.5 shows the microstructures of investigated ZA27 alloy with and without modification after solution heat treatment at 370°C for 10 hours and quenched in water immediately. It is clear that the outlines of original coarse dendrites still appear in the unmodified alloy, and the volume fraction of α -Al phase increased greatly to about 80%, as shown in Fig.5(a). The details are shown in the high magnitude image, Fig.5(b). It can be found that no full independent dendrite really exists, and the fine lamellar eutectics and ϵ particles of as-cast alloy are completely decomposed. The β phase in eutectic is dissolved into α -Al matrix, and η phase is aggregated to interrupted blocks with ϵ phase dissolved. So that a typical two-phase microstructure of α and η is shaped by solution heat treatment on as-cast unmodified ZA27 alloy. With respect to the microstructure of modified ZA27 alloy, the outlines of original as-cast petal disappear after solution heat treatment due to the interconnect of primary dendrites resulted from the dissolution of intergranular structures, as shown in Fig.5(c). The volume fraction of α -Al phase increases enormously to above 80 percent. From the high magnitude image, Fig.5(d), it can be seen that a typical α and η two-phase structure forms by solution heat treatment due to the full decomposition of eutectics and dissolution of ϵ phase, just like that of unmodified alloy. But the η phase is more dispersive and uniform than that of unmodified alloy.

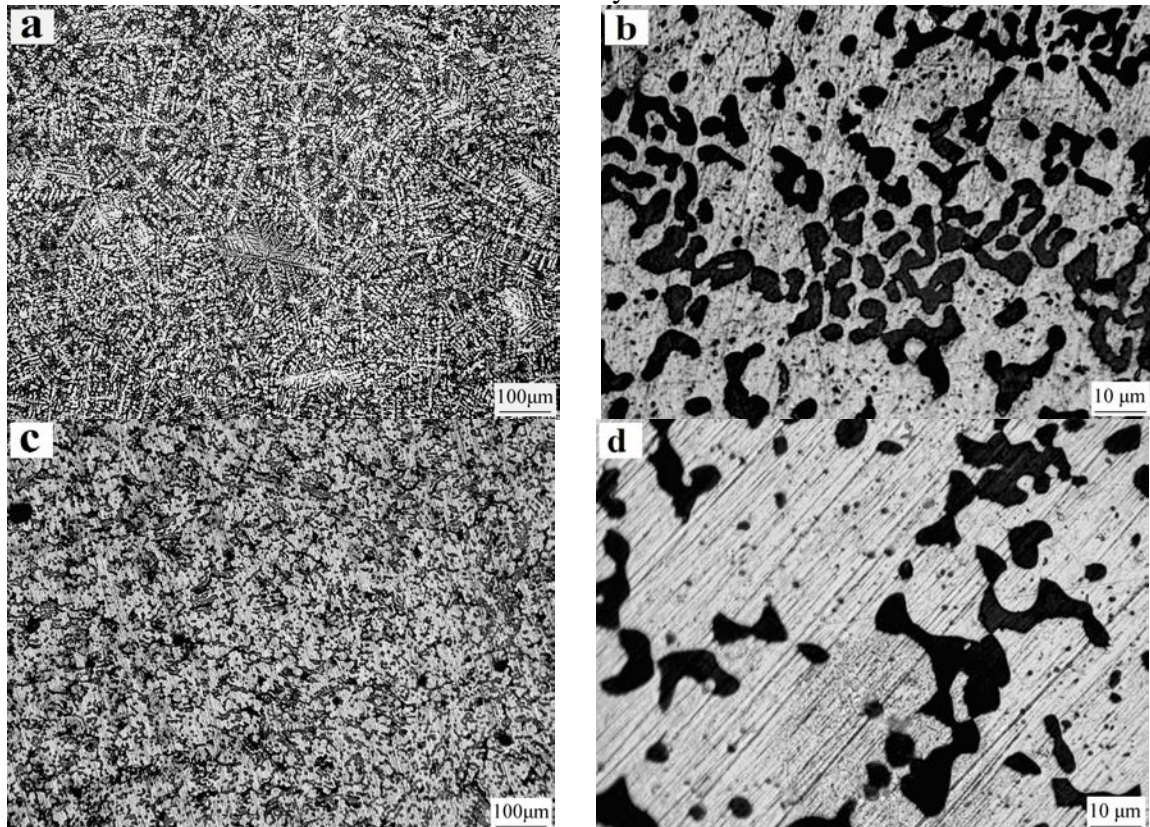
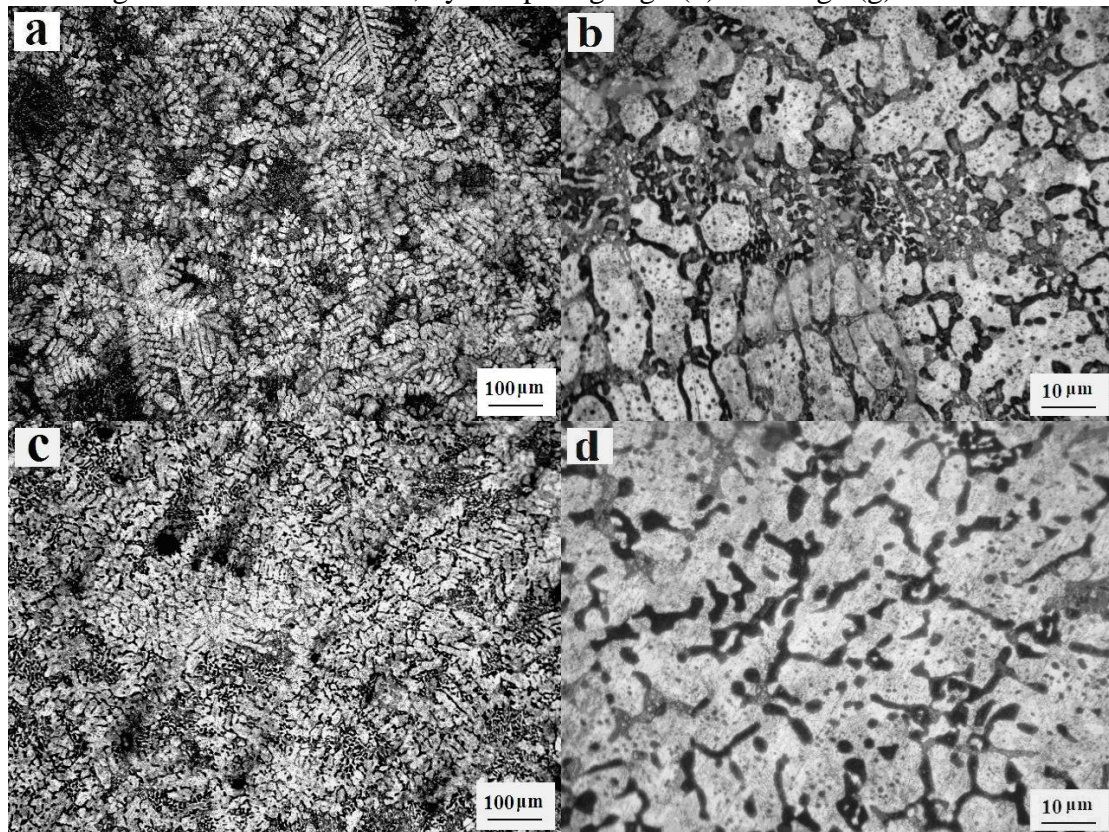


Fig.5. As-dissolved microstructure of ZA27 alloys, a, b-unmodified; c, d-modified

Anneal heat treatment: Fig.6 shows the microstructures of investigated ZA27 alloys with and without modification after annealing at 320°C and holding for 3 hours and 18 hours respectively. For holding 3 hours, both alloys with and without modification remain the same shape of their as-cast primary α -Al dendrites, in spite of the increase of the volume fraction of α -Al phase, as shown in the low magnitude images of Fig.6(a) and Fig.6(e), respectively. From the high magnitude images, Fig.6(b) and Fig.6(f), it can be seen that annealing for 3 hours causes the structure between dendrites of both alloys coarse and lamellar apparently, and facilitates the precipitation of fine punctiform η phase within the α -Al dendrite. Prolonging the annealing time to 18 hours, the outlines of α -Al dendrites of both alloys with and without modification are still distinguishable though they change to somewhat fuzzy due to the increase of volume fraction and the interconnection of α -Al dendrites, as shown in Fig.6(c) and Fig.6(g). From the high magnitude images, Fig.6(d) and Fig.6(h), it can be seen that the eutectics between dendrites are decomposed thoroughly and aggregated to block η phase. The precipitates of η phase within α -Al dendrite aggregate to scatter and grow obviously. Reversely, it is found that a few α -Al precipitates appear within η phase blocks. Furthermore, monotectoid reaction happens in anneal treatment of both alloys, which is the gray thin lamella structure in the high magnitude image, Fig.6(b, d, f and h), this is not found in the condition of solution heat treatment. It can be seen that the incorporated Ti and Zr modification restrains monotectoid reaction in the condition of short time anneal, that is annealing for 3 hours at 320°C, by comparing Fig.6(b) with Fig.6(f), and promotes it in the condition of long time anneal, that is annealing for 18 hours at 320°C, by comparing Fig.6(d) with Fig.6(g).



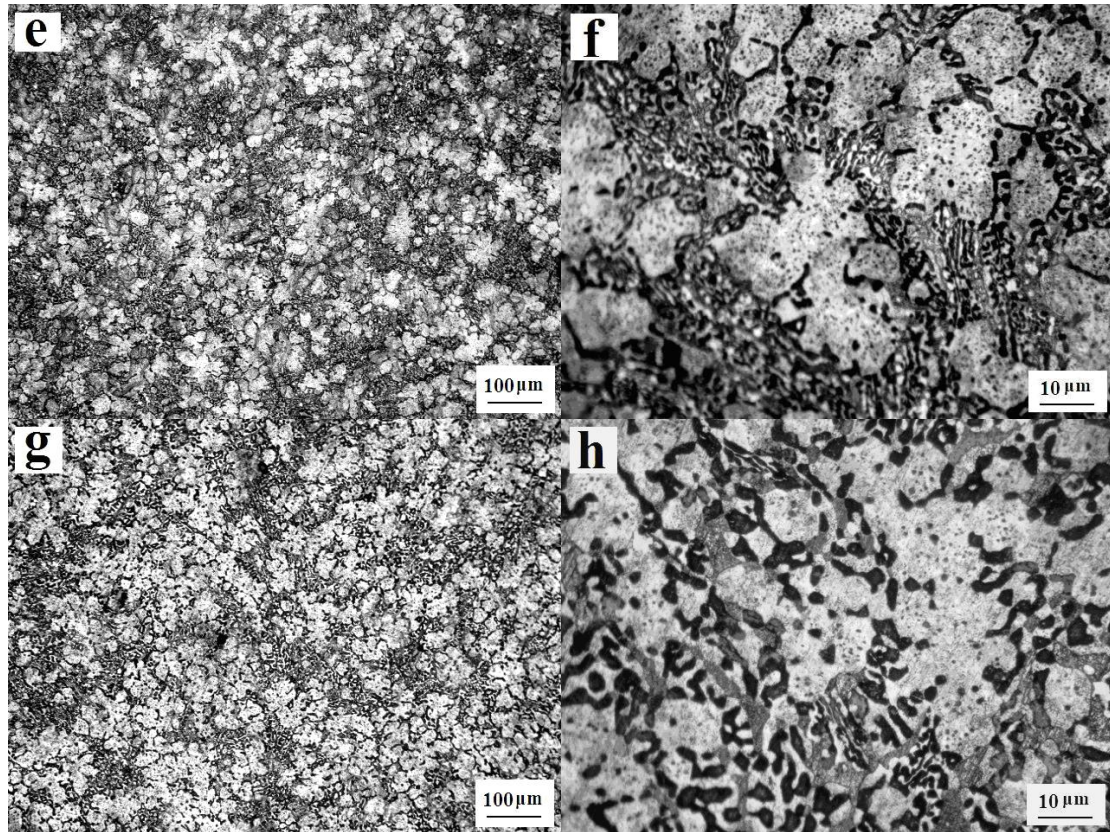


Fig.6. As-annealed microstructure of ZA27 alloys at 320°C, a, b: un-modified, 3h; c, d: unmodified, 18h; e, f: modified, 3h; g, h: modified, 18h

Results and Discussion

As-cast microstructures: According to Al-Zn binary phase diagram, Fig.1, the solubility of Zn in Al is enormous at high temperature, with maximum solid solubility of 85wt.% at eutectic temperature (381°C). During equilibrium solidification process of ZA27 alloy, primary α -Al solid solution is firstly precipitated, then eutectic reaction, $L \rightarrow \alpha\text{-Al} + \eta\text{-Zn}$, happens at 381°C. With reduction of temperature, the solubility of Zn in Al falls clearly and monotectoid reaction, $\alpha\text{-Al} \rightarrow \alpha'\text{-Al} + \eta\text{-Zn}$, happens at 277°C. Within the subsequent cooling process, solubility of Zn in $\alpha'\text{-Al}$ decreases sharply to about 0.4% at room temperature. Similarly, solubility of Al in η -Zn also decreases to about zero at room temperature. When a small quantity of Cu exists in solidification process of ZA27 alloy, a part of Cu atoms dissolve in primary α -Al and the others are ejected to the melt of eutectics forming $\varepsilon\text{-CuZn}_5$ compound in the later period of solidification process. The ε phase is also regarded as CuZn_4 [10] or CuZn_3 [11], and distributes in grain boundaries in the form of $\varepsilon + \alpha$ binary eutectic or $\alpha + \eta + \varepsilon$ ternary eutectic. Tiny Mg in ZA27 alloy is commonly dissolved in α -Al and η -Zn. In the condition of nonequilibrium solidification, severe microsegregation occurs within α -Al solid solution and results in more eutectics in ZA27 alloy. The solute segregation will make the primary α -Al solid solution grow up to dendrite due to the enhanced constitutional supercooling effect, as shown in Fig.4(a, b). Eutectic reaction happens in the remainder melt between dendrites to form $\alpha + \eta$ and $\alpha + \eta + \varepsilon$ eutectic structures. The α -Al phase of the eutectics at narrow secondary arms is easy to adhere the primary α -Al dendrites forming divorced eutectic structure. The eutectics between dendrites are fine due to large degree of supercooling and high actual cooling rate, as shown in Fig.4 (b).

The solidification process and microstructure of ZA27 alloy will be remarkably affected by modification of tiny Ti and Zr addition. There are a few of modifying mechanism of Ti and Zr on ZA27 alloy. One point of view considers as that some intermetallic particles with high melting point, such as TiAl_3 , $\text{Al}_{15}\text{Ti}_2\text{Zn}$ and ZrAl_3 [12-14], will form first in the solidification process of the modified alloy due to much higher melting points of Ti and Zr than that of Al and Zn. These

intermetallic particles can act as heterogeneous nuclei of primary α -Al dendrite crystallization because of the favorable lattice matching of those particles with α -Al. Another point of view [15] suggests that peritectic reaction of TiAl_3 and ZrAl_3 with melt, that is $\text{L} + \text{Al}_3\text{Ti} \rightarrow \alpha\text{-Al}$, is the reason of Ti improving the nucleation of α -Al dendrite and meanwhile refining eutectic structure of ZA27 alloy in solidification process. Nonetheless, no TiAl_3 and ZrAl_3 has been found by XRD detection in this investigation. Moreover, Ti and Zr incorporated modification has not refined eutectic structure in spite of coarsening and homogenizing effect, though it really refined primary α -Al dendrite. So that it is thought that both heterogeneous nucleation and peritectic reaction are not suitable to explain the refining mechanism of primary α -Al dendrite by modification in the present investigation, due to no heterogeneous nucleation particles are detected and no isometric crystal nucleation of α -Al is observed. The probable modification mechanism may be that the segregation of Ti and Zr changes solutes distribution and the degree of constitutional supercooling of melt in front of primary α -Al dendrite, which impede the growth of dendrite and restrain the formation of secondary dendrite or cause it remelt and fall off, so that bring about the change of final growing morphology and the refinement of primary α -Al dendrite. The broken egg-like α -Al blocks near the margin of petaloid dendrite, as shown in Fig.4, can be considered as formed like this. Whereas the exact modifying mechanism of Ti and Zr on primary α -Al dendrite of ZA27 alloy and the effect on eutectic structure and the distribution of ϵ phase are still waiting for further investigation.

Microstructures after heat treatment: The purpose of heat treatment for ZA27 alloy is to eliminate dendritic segregation and abnormal structure [16]. In the present investigation, solid solution heat treatment at 370°C for 10 hours and quenching in water subsequently offered the alloy of apparent two phase microstructure, led to the interconnection of individual original dendrites and the elimination of eutectic structure and ϵ compound among dendrites. This is due to the sufficient atomic diffusion of alloy at high temperature for long time, which makes dendritic segregation homogenize, the strip α -Al in eutectic and ϵ phase decompose into α -Al phase, and the strip η phase in eutectic grows through aggregating each other. This two phase microstructure is unstable and in favor of enhancing plasticity and toughness of the alloy. It can be seen in Fig.5 that after solid solution heat treatment the blocks of η phase mainly distribute at the original grain boundaries of as-cast primary α -Al dendrite, which means that the as-cast microstructure has significant influence on as-solid solution heat treated microstructure in ZA27 alloy. Modification by the addition of tiny Ti and Zr elements facilitates the solid solution heat treatment process of ZA27 alloy due to the fact that much uniform as-solid solution heat treated microstructure of modified alloy is obtained in comparison to unmodified alloy.

The heat treatment of annealing at 320°C for different times showed that in the case of short time heat preservation the volume fraction of α -Al in ZA27 alloy increased not obviously, which indicated that eutectics and compounds at grain boundaries were not dissolved sufficiently. But the elimination of dendritic segregation and the coarsening of eutectics meant that short range atomic diffusion was still conducted in such situation. Moreover, a great number of dispersive precipitates of η phase appeared in α -Al dendrites during the subsequently cooling process. It can be seen from Fig. 6 that the eutectics in modified ZA27 alloy after 3 hour annealing were finer apparently than that of unmodified alloy. This is just right reverse to the as-cast condition and indicates that the modifiers Ti and Zr block atomic diffusion in annealing process. In the present investigation, the eutectic reaction temperatures of ZA27 alloy with and without modification were 393.9°C and 395.0°C , the monotectoid reaction temperatures were 288.8°C and 292.5°C , respectively. This meant that modification by trace Ti and Zr increased the eutectic and monotectoid temperatures of ZA27 alloy, as shown in Fig.3. So that, in the case of annealing for 3 hours at 320°C , the eutectics were refined by modification of trace addition of Ti and Zr, which is beneficial to improve the mechanical properties of ZA27 alloy. Prolonging the holding time of annealing to 18 hours, the volume fraction of α -Al in ZA27 alloy obviously increased. This shows that the eutectics and compounds in the alloys were fully dissolved and two phase microstructure like solid solution heat treated microstructure was obtained after long time atomic diffusion during annealing. But there are a lot of dispersive precipitates of η phase in α -Al solid solution due to the slow cooling rate in

comparison to quenching. Seeing the details of microstructure in Fig.6 (c,d) and Fig.6 (g,h), it can be found that the eutectics and compounds at grain boundaries in unmodified alloy were fully dissolved due to entirely atomic diffusion, and the outline of primary α -Al dendrite was vague seriously due to the fact that α -Al dendrites were integrated by the attachment of α -Al phase in eutectic. The η phase in eutectics was aggregated to block and distributed at the original grain boundaries after 18 hours annealing. However, the outlines of independent α -Al dendrites were still clear considerably in the modified ZA27 alloy after 18 hours annealing. It indicates that the α -Al phase in eutectic was not adhered completely to the primary α -Al dendrite though the eutectics is coarsened seriously and the presence of thick lamellar of α -Al and η phase blocks. This indicates again that modification by trace Ti and Zr can hinder the atomic diffusion in ZA27 alloy during annealing process.

Conclusions

(1) Incorporated modification by the addition of trace Ti and Zr changed coarse primary α -Al dendrite in as-cast ZA27 alloy to fine petaloid dendrite without secondary arms, though the phase constituent was not varied. The mechanism of modification is probably that the existence of tiny Ti and Zr atoms changed the solute distribution and the degree of constitutional supercooling, and obstructed the growth of α -Al dendrites and the formation of secondary dendrites.

(2) Solid solution heat treatment for 10 hours at 370°C fully eliminated the existence of eutectics and compounds of ZA27 alloy with and without modification. Modification by trace Ti and Zr improved the uniform distribution of η phase after solid solution heat treatment.

(3) Annealing for 3 hours at 320°C not changed the morphology of primary α -Al dendrite in both modified and unmodified as-cast ZA27 alloys, but caused eutectics and ϵ particles coarsen and fine η phase particles precipitate within primary α -Al dendrite. Modification can restrain the coarsening of eutectics effectively. Prolonging annealing time to 18 hours, two phase structure of block η phase and α -Al dendrites was obtained. Modification resulted to the refining of lamellar eutectic structure of α -Al and η -Zn phases due to the obstruction of atomic diffusion by the addition of Ti and Zr.

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