Investigation of Strengthen Phase Mg_2Si Growth Mechanism on Al -20Si Alloy In-situ Synthesis Composites

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Abstract: Al-20Si alloy in-situ synthesis composites were prepared by using in-situ synthesis technique. By means of the German ZEISS Axioskop2 optical micrograph, the microstructures of Al-20Si alloy in-situ synthesis composites were investigated. The evolvement rule of Mg_2Si microstructure was analyzed. The growth mechanism of Mg_2Si was studied. The results indicate that Al-20Si alloy in-situ synthesis composites are prepared successfully when the certain contents of magnesium are added in Al-20Si alloy melt. The morphology of primary Mg_2Si is the coarse block and eutectic Mg_2Si begin to appear which the morphology is the Chinese characters-like shape or stripe ones when the content of magnesium is 8%. While the coarse block of Mg_2Si decrease, and the morphology of Mg_2Si is Chinese characters-like shape, dendritic shape and fishbone shape with 6% magnesium. In the process of Mg_2Si growth, Mg_2Si push out more aluminum to solid-liquid interface, so the redistribution of solute elements happens in solid-liquid interface. The equilibrium structure of interface is that of the minimum free energy. Mg_2Si growth mechanism is in conformity with the interfacial energy minimum principle.

Hypereutectic Al-Si alloys have excellent properties, such as low coefficient of linear expansion, corrosion resistance, high wear resistance, good dimensional stability, suitable for casting, low casting cost, and other characteristics. Hypereutectic Al-Si alloy is a kind of light wear-resistant alloy ideal for pistons of automobile, motorcycle and others[1-3]. Adding certain mass fraction of Mg in hypereutectic Al-Si alloy melt, Mg forms authigenic Mg_2Si with Si. With small density of Mg_2Si (1.99kg/m^3), high elastic modulus (120GPa), low coefficient of thermal expansion(CTE $=7.5\times10^{-6}$ K^{-1})[4-6], Mg_2Si is ideal reinforcement for hypereutectic Al-Si alloy composite. The hypereutectic Al-Si alloy composites have not only advantages of high strength, high hardness, low coefficient of thermal expansion and etc., but also characteristics of good interface bonding and thermodynamic stability, with dispersive small Mg_2Si reinforcements in hypereutectic Al-Si alloy[7-8]. Its performances have been greatly improved compared to traditional hypereutectic Al-Si alloy.

Using Al-20% Si hypereutectic alloys for study, in situ synthesis of Mg_2Si[9-10], Al-20% Si alloy situ composites were prepared with different mass fraction of Mg in the alloy melt. We observed reinforced phase Mg_2Si microstructure evolution process with different magnesium

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content and studied growth mechanism of reinforced phase Mg_2Si. Provide an important experimental basis for further studies of solution treatment and mechanical properties.

Test methods and procedures

Test alloys

Used industrial pure aluminum (with Al99.7%), aluminum-silicon master alloy (with Si50%), and industrial pure magnesium (with Mg99.9%) as raw materials for test. Smelted test alloys in SG2-3-10 crucible resistance furnace with melting temperature of 720˚C. Used KSW-4D-11 resistance furnace temperature controller for temperature control. After reaching the set temperature, respectively added 8% and 6% mass fraction of Mg and stired well. At the same time added a small amount of modifier Sr for modification process. Casted in metal mold after degassing and refining with casting temperature of 700˚C. The ingot size is φ70mm × 120mm after casting. The samples obtained are numbered a, b of the two samples. By Magix (PW2424) X-ray fluorescence spectrometer for component analysis, the actual composition (mass fraction) of the alloy is shown in Table 1.

Table 1 Hypereutectic Al-Si alloy composition for test

Sample Code	a	b
Al Content	71.8	73.2
Si Content	20.1	20.8
Mg Content	7.75	5.6
Margin	Impurity	Impurity

Microstructure detection

Get ingot samples after casting. Cut off the samples and took a wafer with about 10mm thick. Then removed fan-shaped block (over the center) with the arc length of about 25mm in the wafer, taking the fan-shaped block as metallurgical sample. The metallographic sample had been processed by pre-grinding, rough grinding, fine grinding, polishing, etching it with 10% HF solution. The microstructure morphologies of the samples were observed with German-made optical microscope ZEISS Axioskop2.

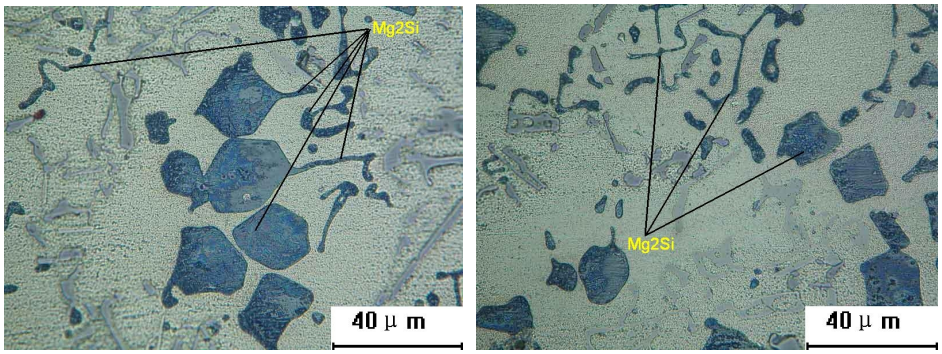

Figure 1 Al-20% Si alloy microstructure containing Mg 8%

Microstructure of specimen

In the Al-Mg-Si ternary alloy system, Al-Mg-Si composes pseudo-binary eutectic system with

eutectic temperature of 595˚C and eutectic composition of Al-8.9Mg_2Si[11]. Combined with Al-Mg_2Si -Si ternary phase diagram[12-14], it can be seen that, in figure 1, near spherical white area is primary α-A1 microstructure and gray fibrous dense tissue is eutectic silicon and blue or black block-like form is primary Mg_2Si phase. From Mg_2Si indicated in figure, it can be seen that the microstructure is similar to eutectic composition microstructure of the Al-Mg_2Si pseudo-binary eutectic system, but primary Mg_2Si phase is more and Al-Mg_2Si eutectic portion gradually appears.

As shown in Figure 2, component of microstructure is in the vicinity of eutectic composition of Al-Mg_2Si pseudo-binary eutectic system, when adding 6% magnesium in the alloy. Its morphology is shown in Figure 2. Black microstructure is binary eutectic Mg_2Si and more complete network-like microstructure is ternary eutectic crystals(α-Al+Mg_2Si+Si) in the figure. For morphology of eutectic Mg_2Si, some are full-developed characters like, dendritic, as well as fish-bone morphology, and even five star-shaped petals. This microstructure is ideal microstructure of hypereutectic Al-20% Si with reinforced phase of situ Mg_2Si.

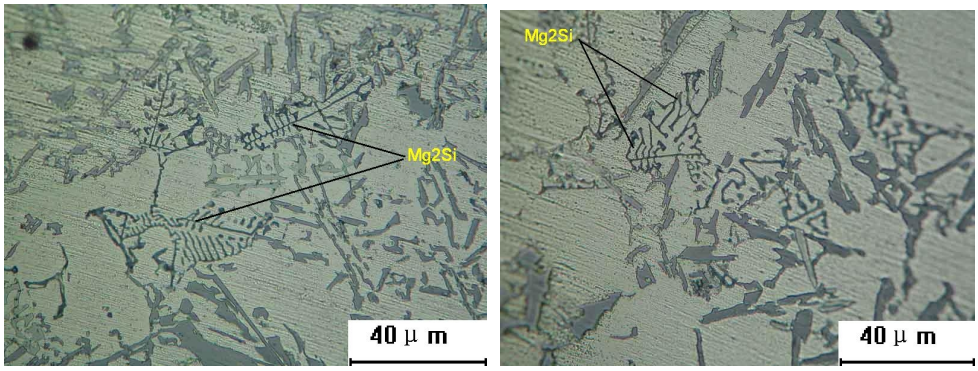

Figure 2 Al-20% Si alloy microstructure containing Mg 6%

Growth mechanism of enhanced phase Mg_2Si

Formation process of enhanced phase Mg_2Si

According to equilibrium phase diagram[15] of Mg-Si binary alloy, the eutectic reaction temperature is 638.8˚C，L→α(Mg)+Mg_2Si, and Si mass fraction of eutectic alloy is 1.34%, the mass ratio of the two eutectic microstructures respectively 95.9% and 4.1%. In hypereutectic Al-20% Si alloy, Si content is greater than 1.34%, so the primary crystal phase is Mg_2Si and eutectic reaction also occurs at 638.8˚C. According to Mg-Si binary alloy equilibrium phase diagram and the microstructure shown in Figure 1 and Figure 2, it indicates that Mg_2Si phase produced by binary and ternary eutectic crystal reaction is of irregular lumps or characters like, while eutectic composition(α-Al+Mg2Si+Si) generated through ternary eutectic reaction is of reticular distribution. In crystallization process, firstly Mg_2Si phase is crystallized and then binary eutectic reaction L→α(Al)+Mg_2Si occurs and then ternary eutectic reaction (α-Al+Mg_2Si+Si). The primary crystal Mg_2Si phase is block-like or polygon, while Mg_2Si phase produced through binary and ternary eutectic reaction is of irregular characters shape or fishbone-like.

As Mg_2Si indicated in Figure 1, it can be seen that the microstructure close to the eutectic composition microstructure of Al-Mg_2Si pseudo-binary eutectic system, but primary Mg_2Si phase is

more and Al-Mg_2Si eutectic portion gradually appears. Mg_2Si is surrounded by α-Al eutectic[8]. a-A1 phase and Mg_2Si phase in hypereutectic Al-20% Si alloy composites are firstly generated as a primary crystal phase. Because of Mg content of 8% and higher proportion of the mass fraction, precipitates directly block shaped primary Mg_2Si in the liquid phase. When the temperature of the excess liquid reaches along the three-phase region in the phase diagram, A1+Mg_2Si pseudo-eutectic microstructures begin to form. Due to Mg_2Si lower temperature for formation in the pseudo eutectic microstructures, the atomic diffusion in the solid phase is more difficult. Additionally, due to easy nucleation at the grain boundaries and other reasons, most of them are in the a-Al phase interface or the a-Al phase, and grow into fibrous microstructure or characters like eutectic Mg_2Si, or grow up attaching on the primary crystal phase Mg_2Si. Therefore eutectic Mg_2Si is finer than primary crystal phase Mg_2Si.

Figure 2 shows the black microstructure is binary eutectic Mg_2Si and ternary eutectic crystal(α-Al+Mg_2Si+Si) is more complete network-like shape. Some of eutectic Mg_2Si morphologies are characters like, dendritic, as well as fish-bone, and even five star-shaped petals. In the actual non-equilibrium solidification conditions, a large number of binary eutectic microstructure(α-Al+Mg_2Si) are generated. Because the binary eutectic Mg_2Si growth depends on primary α-Al which pushes the binary eutectic Mg_2Si to the grain boundaries, binary eutectic Mg_2Si distributes in the grain boundaries. In addition, the primary crystal Mg_2Si nucleation rate is greater than other phases and eutectic microstructure is affected by diffusion factors. At this time, diffusion resistance to Mg and Si elements is greater. In the non-equilibrium solidification conditions, most of the binary eutectic microstructure has no chance to fully grow up and first precipitated Mg_2Si is growing up gradually slowly and thus primary crystal Mg_2Si microstructure is finer in figure 2. Eutectic Mg_2Si morphology is characters like or fish-bone and ternary eutectic crystals(α-Al+Mg_2Si+Si) have the maximum amount of production. This morphology is ideal microstructure for hypereutectic Al-20% Si alloy situ composites.

Solid-liquid interface structure and growth interface of enhanced phase Mg_2Si

Growth mechanism of crystal depends on solid-liquid interface structure, while final morphology of crystal depends on relative growth rate of crystal planes. External conditions (such as temperature, concentration, impurities, etc.) can change crystal morphology. Crystal growth environment and growth mechanisms are closely related.

According to the theory proposed by Jackson[16], balanced structure of the interface should be one with minimum free energy of interface. If you randomly add solid phase atoms on the flat interface leading to roughening interface, relative change $\frac{\Delta G_S}{NkT_0}$ of interfacial free energy △ Gs can be expressed as below:

$$\frac{\Delta G_S}{NkT_0}=\alpha x(1-x)+x\ln x+(1-x)\ln(1-x) \quad (1)$$

Where, N— Number of all positions available for atoms occupation on interface;

x— Fraction occupied by solid-phase atoms positions at all positions

$$\alpha=(\frac{L_0}{kT_0})(\frac{\eta}{\upsilon})\approx(\frac{\Delta Sm}{R})(\frac{\eta}{\upsilon}) \quad (2)$$

Where, L_0—Atomic latent heat of crystallization;

ΔSm —Melting entropy

η —The maximum possible number of neighboring atoms in the interface layer;

υ —Number of neighbors of one atom inside the crystal.

Equation (1) shows that, when $\alpha>2$, $\frac{\Delta G_S}{NkT_0}$ has respectively a minimum value in the much smaller x and close to one. That is, only a few lattice positions are occupied for the equilibrium structure of the interface or only a small space is left after most of the positions are occupied. Therefore, the flat interface is stable, and the greater α is , the more smooth the interface. Equation (2) shows that , α value depends on $\frac{\Delta Sm}{R}$ (which is determined by the thermodynamic properties of the system) and $\frac{\eta}{\upsilon}$ (referred as the interface orientation factor, and related to the crystal structure and the crystal face orientation on the interface). Solid-liquid phase interface of Mg_2Si phase is smooth interface(small crystal plane interface). From a macro-scale view, the solid-liquid interface is not smooth and jagged, but the atomic arrangement on the solid- liquid interface is smooth from the atomic scale view[17]. Smooth interface has strong crystallographic characteristics. The ability to pile up liquid atom is also not the same, because of different atomic density and interplanar spacing on different crystal planes. Therefore, the growth rate of various crystal planes is also bound to be different in the same supercooling degree. Generally, the liquid phase atoms are relatively easy to pile up to the crystal face arranging loosely, so the growth rate of the loose surface is faster than the growth rate of close-packed plane in the same supercooling degree. This results into that the fast-growing loose surface is gradually buried and crystal surface was gradually covered with close-packed surface. Hence the growth surface of Mg_2Si is composed of a number of close-packed small plane with angular lines at the microscopic scale. As interfacial energy of the close-packed surface is the minimum, this growth surface is consistent with principle that interfacial energy should be the minimum.

Morphology evolution of enhanced phase Mg_2Si

According to the crystal growth theory[18], solute concentration distribution of the points on the solid-liquid interface is not uniform during polyhedral crystal growth with a small crystal plane growth mode. Therefore, oversaturated degree of points on the solid-liquid interface is different. Supersaturation unevenness is positive proportional to $b_{(\rho)}$ L/D for the points on the solid-liquid interface, wherein L is crystal size, D is the diffusion coefficient of the solute, $b_{(\rho)}$ represents the kinetic coefficient related to slope ρ of crystal plane and ρ is the crystal surface slope determined by the strongest level sources under given saturation conditions. The larger crystal size, the greater unevenness of supersaturation degree at various points on the solid-liquid interface. When the crystal size exceeds a critical value, the density difference of growth steps in the microscopic level on the solid-liquid interface has reached a critical value, which leads to the solid-liquid interface no

longer remaining flat and solid-liquid interface becomes buckling.

According to Mg-Si and Al-Mg-Si alloy phase diagram, when the Si content is higher, Si content of the melt gradually decreases while the amount of A1 gradually increases with the primary Mg_2Si precipitates growing during solidification of the alloy. Mg_2Si grows in a liquid phase with relatively low Si content and relatively high amount of A1, while Mg_2Si phase containing a higher amount of Si(60%). Additionally, crystallization latent heat diffusion is faster than the diffusion of atoms under test conditions. Therefore, more Al element will be discharged towards the front of solid-liquid interface and redistribution of solute elements occurs on the solid-liquid interface in the Mg_2Si growth process. As Mg_2Si phase is growing, a boundary layer with high-A1 and low-Si will be produced in the forefront of Mg_2Si phase. The boundary layer has two effects: one is to reduce the supersaturation of solute of the boundary layer and another is to reduce kinetic coefficients of the boundary layer. Thereby it will reduce the growth rate of primary Mg_2Si crystal boundary layer.

Size of the primary Mg_2Si is large enough, on the one hand, solid-liquid interface can start generating boundary layer with obvious high A1 and low Si, and on the other hand, supersaturation inhomogeneity of Si element on the solid-liquid interface also significantly increased. On the solid-liquid interface of primary Mg_2Si, there is a large growth rate at the position with greater supersaturation degree of Si elements and the growth rate is small at the position with smaller supersaturation degree. At the place with larger growth rate, Mg_2Si is easy to protrude beyond boundary layer with high A1 and low Si so as to increase growth rate, meanwhile excluding A1 element towards its lateral surrounding. For the part growing so fast as to protrude outside the boundary layer with high Al and low Si, Mg_2Si lateral growth rate is inhibited due to presence of the boundary layer with high A1 and low Si. Therefore, Mg_2Si has a faster growth rate which is perpendicular to solid-liquid interface. This will lead to the solid-liquid interface buckling. Due to the solid-liquid interface instability, the flat solid-liquid interface becomes consisting of a number of small convex and regular crystal planes, which produces many regular bulges.

In addition to the primary dendritic or polygonal Mg_2Si phase, there is irregular characters-like Mg_2Si phase formed by the eutectic reaction. After corrosion, it can be seen that characters-like Mg_2Si phase with irregular shape is indeed comprised of curved rod Mg_2Si. Its growing surface is also comprised of regular crystal surface, indicating that its growth mechanism is similar to the primary Mg_2Si. Eutectic Mg_2Si phase can also be attached to the primary Mg_2Si phase to grow up. Figure 1 also confirms this growth mechanism.

Conclusion

(1) Adding an appropriate amount of magnesium and prepared hypereutectic Al-20% Si alloy situ composites.

(2) Add different mass fraction of magnesium, the microstructure is different. When you add 8% Mg, massive primary Mg_2Si phase is more and characters-like or fibrous Mg_2Si also emerges. When you add 6% Mg, morphologies of Mg_2Si become characters-like, dendritic, and furthermore

of fish-bone morphology, or even appear as star-shaped petals.

(3) In the Mg_2Si growth process, it will discharge more Al element to the forefront of solid-liquid interface and produce redistribution of solute elements on the forefront of solid-liquid interface.

(4) Equilibrium structure of interface is structure with the minimum of interfacial free energy and Mg_2Si growth mechanism is in line with the principles that the interfacial energy is of minimum.

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