Effects of ZnS modification on primary Si in hypereutectic Al-Si alloy

Cheng-dong Li¹, Chuan-hao Sun¹, Wen-qiang Si², *Mei Zhao¹, Man-man Lu¹, Lei Zhang¹

1. College of Materials Science and Engineering, Qingdao University of Science & Technology, Qingdao 266042, China

2. Shandong Yinguang Yuyuan Light Metal Precise Forming Co., Ltd., Linyi 273400, China

Abstract: A new modifying agent, ZnS, was used as a refiner to modify primary silicon in hypereutectic Al-Si alloy. The factors affecting the modification results, including addition level of ZnS and holding time, were investigated. The results showed that the average size of the most effectively modified primary silicon was 28.5 μm when the ZnS mixed powder addition was 0.15wt.% with a holding time of 10 min. More important, the average size of primary silicon could remain below 40 μm despite the holding time extending to 120 min, which means ZnS is a promising modifying agent of primary Si in industrial applications.

Key words: ZnS; primary silicon; hypereutectic Al-Si alloy; modification

CLC numbers: TG146.21

Document code: A

Article ID: 1672-6421(2017)02-093-05

As an important cast alloy, hypereutectic Al-Si alloy has a low expansion coefficient and density, good cast performance and high wear resistance. However, with the increasing of silicon content, a large number of coarse and irregular lumps of primary silicon and needle-like eutectic silicon can be observed, which seriously decreases the comprehensive performance of the alloy. Therefore, primary silicon must be refined to achieve the fine dispersive Si phase with desirable properties^[1,2]. It was found that adding modifier is the most popular and effective method to refine the primary silicon^[3-5]. The effective refinement of primary Si can be obtained through the addition of some modifiers, such as P^[4-6], rare earth (RE)^[7,8], etc. However, the use of P can result in serious air pollution, and the costly RE used to refine primary Si is poor effective. So, researchers have been looking for new and more efficient and effective modification agents for Al-Si casting alloys.

According to research^[9], Al-ZnS master alloy was used as a new refiner, and the primary silicon could be refined from more than 80 μm to 20 μm . Fan et al. also researched the modification performance of ZnS on primary Si in hypereutectic Al-Si alloy and came to the same conclusion^[10], in which ZnS was synthesized by chemical reaction using Zn and Na₂S. Nevertheless,

Na₂S is so deliquescent in the air that it is not favorable for storage. The ZnS synthesized by direct chemical reaction of Zn and S can be stored trouble-free, and the yield was very high, but research concerning the refinement and modification behavior of ZnS on Al-Si alloy hardly can be found. To investigate the recession degree of ZnS modification synthesized by Zn and S and the optimal addition level, the effects of ZnS addition amount and holding time on Al-Si alloy were investigated.

1 Experimental procedure

According to the study of hypereutectic Al-Si alloy, the shrinkage of Al-Si alloy was the lowest when the content of silicon was between 22wt.%–25wt.%^[11]. Therefore, Al-24wt.% Si alloy was chosen to be the base alloy in this study. Figure 1 shows the microstructure of Al-24Si alloy without ZnS addition. Primary silicon particles exhibit coarse irregular and star-shaped morphologies in the as-cast alloy, which will drastically degrade the mechanical properties of the castings, and the average size of primary Si is up to about 107.7 μm .

A novel and simple synthetic method for ZnS composite was a chemical reaction using zinc and sublimed sulfur with 99.9% purity. A 33 g zinc block and 3 g pressed sulfur powder were placed into a proportionately sized graphite crucible covered by another bigger crucible, heated to 700 °C and held for 6 min^[9]. In order to ensure a complete reaction, and excessive amount of zinc was added. ZnS mixed powders were collected as modifying agent in this

*Mei Zhao

Female, born in 1974, Ph.D. Research interests: nano materials and technology.

E-mail: Zhaomei@qust.edu.cn

Received: 2016-10-21; Accepted: 2016-12-20

Fig. 1: Micrograph of unmodified Al-24Si alloy

experiment. According to the mass fraction of sulfur added, the content of ZnS in the mixed powder is 25.4%.

Al-24wt.%Si alloy was heated to 900 °C and held for 15 min. Then the temperature of the melt was decreased gradually. The ZnS refiner wrapped in aluminum foil was added into the melt at 800 °C and stirred. After the slag of the melt was skimmed, the melt was poured into a steel mold preheated to about 200 °C. Samples with dimensions of $\Phi 20$ mm $\times$ 65 mm were obtained.

Microstructure analysis was carried out on the Al-24wt.%Si alloy samples by optical microscopy (OM) and electron scanning microscopy (SEM) to investigate the influence of ZnS on primary Si phases. Metallographic specimens were all cut from 25 mm above the bottom of the metallurgical samples. The size of primary silicon crystals was the average value of 100 measurements. Samples 1, 2, 3, 4, 5 correspond to addition level of 0.05wt.%, 0.1wt.%, 0.15wt.%, 0.2wt.%, 0.25wt.% ZnS mixed powder, respectively.

2 Results and discussion

2.1 Phase analysis and morphology of ZnS mixed powder

Figure 2(a) shows the X-ray diffraction (XRD) pattern of the ZnS mixed powder, where the diffraction peaks corresponding to (008), (110), (118) of cubic zincblende ZnS can be found. The reaction product is composed of Zn and ZnS, with no sulfur found, indicating that the sulfur is fully reacted with zinc.

Morphology of ZnS powders was observed by means of SEM. As shown in Fig. 2(b), the particles in the mixed powder are in a wide range of size from about 10 μm to micrometer even nanometer level.

Fig. 2: XRD pattern (a) and SEM image (b) of ZnS

2.2 Effect of ZnS modification on primary silicon

Microstructures of Al-24wt.%Si alloys with different addition amount of ZnS mixed powder are shown in Fig. 3. Figure 3(a) shows the microstructure of Al-24wt.%Si alloy with 0.1% ZnS mixed powder, in which the size of primary Si is reduced to 37 μm. However, some large size primary Si is still observed, and some primary Si is aggregated together. When the addition amount increases to 0.15%, the primary Si tends to segregate uniformly with the average size reducing to 28.5 μm. The morphology of primary Si tends to round shape. With the further increase of ZnS mixed powder amount to 0.2%–0.25%,

the primary Si, however, becomes larger and aggregates more seriously in some regions as indicated by the rectangular areas in Figs. 3(c), (d).

In order to show the change of the average size of primary Si, a line chart is drawn in Fig. 4(a). Obviously, with 0.15% ZnS mixed powder, i.e. 0.038wt.% ZnS, primary Si has the best refinement effect. Figure 4(b) shows the particle size distribution of primary Si in Al-Si alloy with 0.15% ZnS mixed powder, showing the strong improvement of refinement efficiency. It can be seen that the size of primary Si is concentrated at 25–35 μm, which follows a normal distribution. This indicates that ZnS particles are potent substrates to refine the primary Si in hypereutectic Al-Si alloy.

Fig. 3: Microstructures of Al-24Si alloys with different addition amounts of ZnS mixed powder: (a) 0.1%; (b) 0.15%; (c) 0.2%; (d) 0.25%

Fig. 4: Effect of ZnS content on primary silicon of Al-24wt.%Si alloy: (a) changes of primary size with different ZnS addition; (b) particle size distribution of primary Si in Al-24wt.%Si alloy with 0.15% ZnS mixed powder

2.3 Effect of holding time on primary silicon

In order to investigate the effect of holding time on ZnS modification effect, the microstructure of Al-24wt.%Si alloy with 0.15% ZnS mixed powder addition was observed. The microstructures in Figs. 5(a) to (d) correspond to the holding time of 10 min, 30 min, 60 min, and 120 min, respectively. It can be seen that the primary Si segregates uniformly when the holding time is 10 min (Fig. 5a). In Fig. 5(b), the distribution of primary Si is not as uniform as Fig. 5(a); some primary Si tends to come together. With the holding time further increasing, primary Si grows up, a few large size Si about 60 μm could be observed in Fig. 5(c) and 5(d), but change of the average size is very small.

It is obvious that the longer the holding time, the larger the average size, but the change is slow (Fig. 6). Even when the holding time reaches 120 min, the average size of primary Si is only 39.7 μm, which means that ZnS is still very effective in controlling the size of primary Si, and the modification of ZnS on the hypereutectic Al-24wt.%Si alloy possesses longevity. Therefore, we can conclude that ZnS is a promising modifying agent of primary Si in industrial applications.

Simultaneously, in Fig. 6, the data is fitted to describe the relationship between the size of primary Si and holding time. The result shows that they meet the linear function $Y=0.10X + 27.75$.

Fig. 5: Microstructures of Al-Si alloy + 0.15% ZnS with different holding times: (a) 10 min; (b) 30 min; (c) 60 min; (d) 120 min

Fig. 6: Effect of holding time on primary silicon of Al-24wt.%Si alloy with 0.15% ZnS mixed powder addition

2.4 Modification mechanism of ZnS on hypereutectic Al-Si alloy

Like AlP, the modification mechanism of ZnS on primary silicon can also be regarded as a heterogeneous nucleation^[2, 12-13]. Crystal silicon is a cubic structure with lattice parameter: $a=5.45 \text{ \AA}$, and ZnS is also a cubic zincblende structure with lattice parameter $5.41 \text{ \AA}$ when temperature is below $1,020^\circ\text{C}$. There is a suitable mismatch degree between the cubic zincblende ZnS and Si phase (0.33%), which is found to be smaller than that of the

Si/AlP, 0.42%. The lower the mismatch, the higher potential the heterogeneous nucleation likely to be. So, primary Si can nucleate heterogeneously on the solid ZnS particles with a cube-cube orientation relationship and solidify, promoting the modification of primary Si. Moreover, the interfacial free energy at the nucleating interface is one of the controlling factors in heterogeneous nucleation. ZnS particles dispersed in the mixed powder are swaddled by excess zinc, which can be solute in aluminum. Therefore, the massive wetting ZnS inoculants for Si come into being, which can reduce the interfacial energy to a lower level. The solidification process of Al-24wt.%Si alloys with ZnS modification is illustrated in Fig. 7.

As shown in Fig. 7, the ZnS, which homogeneously segregates in the melt, acts as the heterogeneous nucleation sites for primary Si. When adding ZnS refiner into the Al-24Si melt, a large quantity of ZnS particles distribute in the melt uniformly, the undissolved ZnS particles would become the slags and float to the surface and cannot act as the nucleation sites of primary Si during the solidification process. With the temperature decreasing, the ZnS particles dissolved in the melt would precipitate, then the primary Si nucleates and wraps around the ZnS nuclei to grow up to a compact particle. Therefore, an appropriate ZnS addition amount is necessary. Too little ZnS, there will not enough heterogeneous nucleation sites for primary Si; too much, ZnS particles easily tend to aggregation, and the effect of modification will be diminished.

Fig. 7: Schematic illustration of modification process of Al-24wt.%Si alloy with ZnS addition

3 Conclusions

(1) ZnS can significantly modify primary silicon. The average size of primary silicon is decreased from 107.7 μm to 28.5 μm by adding 0.15% ZnS mixed powder, i.e. 0.038wt.% ZnS.

(2) The primary silicon can be refined remarkably when the holding time is only 10 min. The size of primary Si of the castings changes so slowly even as the holding time reaches 120 min, the average size of primary Si is only 39.7 μm .

(3) The lattice parameters of Si and ZnS are much closer with a lattice mismatch of less than 1%. The primary Si can nucleate on the solid ZnS, whose synthetic method is easy and efficient. More importantly, the modification of ZnS shows good longevity, which means that ZnS is a promising modifying agent of primary Si in industrial applications.

References

- [1] Li Qinglin, Xia Tiandong, Lan Yefeng, et al. Effect of rare earth cerium addition on the microstructure and tensile properties of hypereutectic Al-20%Si alloy. *Journal of Alloys and Compounds*, 2013, 562: 25–32.
- [2] Guo Jian, Liu Ying, Fan Pengxu, et al. The modification of electroless deposited Ni-P master alloy for hypereutectic Al-Si alloy. *Journal of Alloys and Compounds*, 2010, 495: 45–49.
- [3] Liu Xiangfa, Qiao Jinguo, Liu Yuxian, et al. Modification performance of the Al-P master alloy for eutectic and hypereutectic Al-Si alloys. *Acta Metallurgica Sinica*, 2004, 40: 471–476.
- [4] Wu Yaping, Wang Shujun, Li Hui, et al. A new technique to modify hypereutectic Al-24%Si alloys by a Si-P master alloy. *Journal of Alloys and Compounds*, 2009, 477: 139–144.
- [5] Zuo Min, Liu Xiangfa, Sun Qianqian. Effects of processing parameters on the refinement of primary Si in A390 alloys with a new Al-Si-P master alloy. *Journal of Materials Science*, 2009, 44: 1952–1958.
- [6] Liu Xiangfa, Wu Yuying, Bian Xiufang. The nucleation sites of primary Si in Al-Si alloys after addition of boron and phosphorus. *Journal of Alloys and Compounds*, 2005, 391: 90–94.
- [7] Chang J Y, Kim G H, Moon I G, et al. Rare earth concentration in the primary Si crystal in rare earth added Al-21wt.%Si alloy. *Scripta Materialia*, 1998, 39: 307–314.
- [8] Chang J Y, Moon I G, Choi C S. Refinement of Cast Microstructure of Hypereutectic Al-Si Alloys Through the Addition of Rare Earth Metals. *Journal of Materials Science*, 1998, 33: 5015–5023.
- [9] Li Chengdong, Si Wenqiang, Zhao Mei, et al. A New Al-ZnS Master Alloy Designed for Modifying Hypereutectic Al-Si alloy and Its Refinement Performance on Primary Si. *Advanced Materials Research*, 2015, 1088: 242–244.
- [10] Al-Helal K W. New Approaches to Casting Hypereutectic Al-Si Alloys to Achieve Simultaneous Refinement of Primary Silicon and Modification of Eutectic Silicon. Brunel University, 2013.
- [11] Chang Fange, Jian Zengyun. Preparation of Aluminum-silicon Alloy without Shrinkage in the Solidification Process. *Foundry Technology*, 2005, 26: 300–302. (In Chinese)
- [12] Liu Xiangfa, Qiao Jinguo, Liu Yuxian, et al. Modification performance of the Al-P master alloy for eutectic and hypereutectic Al-Si alloys. *Acta Metallurgica Sinica*, 2004, 40: 471–476.
- [13] Zhang Hanghang, Duan Haili, Shao Guangjie, et al. Microstructure and mechanical properties of hypereutectic Al-Si alloy modified with Cu-P. *Rare Metals*, 2008, 27: 59–63.

This work was supported by the Applied Basic Research Programs of Qingdao, China (No. 14-2-4-50-jch).