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Al-Si-P master alloy and its modification and refinement performance on Al-Si alloys

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Abstract

An Al-Si-P master alloy has been developed by an *in-situ* reaction and the electron probe microanalyzer (EPMA) results show that there are many pre-formed AlP particles contained in the master alloy. Silicon introduced into the system plays an important role in remarkably improving the distribution and content of AlP particles due to their similar crystal structure and lattice parameters. ZL109 alloys have shown fast modification response to the addition of 0.5% Al-15Si-3.5P master alloy at 720°C, with a mass of primary Si precipitating in size of about 15 μm. Also, coarse primary Si grains in Al-30Si alloy can be refined dramatically from 150 μm to 37 μm after the addition of 2.0% Al-15Si-3.5P master alloy at 850°C. The P recovery of the Al-15Si-3.5P master alloy is much higher than that of a Cu-8.5P master alloy due to the pre-formed AlP particles.

Keywords: Al-Si alloys; Al-Si-P master alloy; primary Si; P recovery; modification; refinement

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1. Introduction

Considerable interest in replacing cast iron with Al alloys has been concentrated on the automotive industry to improve energy efficiency and meet environmental requirements [1-2]. Among them, eutectic and hypereutectic Al-Si alloys have been widely used due to their excellent combination of properties such as low thermal expansion and high wear resistance as well as good castability [3-5]. Since the desirable combination of mechanical properties of eutectic and hypereutectic Al-Si alloys depends on the primary Si grain size to a large extent, the modification and refinement of primary Si are studied more widely with increasing usage [6].

It is well established that refinement of primary Si can be achieved by several methods such as mechanical or electromagnetic stirring [3, 7], rheocasting and thixocasting means [8-9], rapid cooling [10] and melt inoculation by adding P, As, and rare earth (RE) elements [4, 11-12]. Among the chemical modifiers, P is generally used due to the AlP particles formed in melt on which primary Si can effectively nucleate. P can be added into the melt in many forms such as red phosphorus, phosphate salt, and Cu-P master alloy. However, red phosphorus and phosphate salt are less utilized mainly due to pollution, unstable modification efficiency, and a lower P recovery. On the other hand, a Cu-P master alloy is not suitable for a flame furnace and an electrical resistance furnace due to the higher melting point and density [13]. In addition, Al-Cu-P and Al-Fe-P master alloys mentioned in Refs. [1, 14] have the disadvantages of contamination of Cu or Fe composition.

In this study, a new type of Cu-free and Fe-free Al-based master alloy containing phosphorus, Al-Si-P master alloy, has been developed and its modification and refinement performances on eutectic and hypereutectic Al-Si alloys were investigated. In addition, the comparison between the new master alloy and the Cu-8.5P master alloy was also discussed.

2. Experimental

Commercial purity Al (99.85%), Si (99.5%), and other commercial purity elements were used to produce ZL109 alloy, Al-30Si alloy (all compositions quoted in this work are in wt.% unless otherwise stated) and their chemical compositions are listed in Table 1. A series of Al-Si-P master alloys and a Cu-8.5P master alloy were from Shandong Shanda Al&Mg Melt Technology Co. Ltd.

The ZL109 alloy was melted in an electrical resistance furnace at 720°C and kept for about 30 min. After treatment

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with 0.5% C_2Cl_6 for 15 min, modification treatment was operated by adding 0.5% Al-15Si-3.5P master alloys. Then the samples were poured into a cast iron mold (70 mm × 35 mm × 20 mm) preheated to 150°C at different holding times. The treatment of the Al-30Si alloy with 2.0% Al-15Si-3.5P master alloy was performed at 850°C with the same procedures as mentioned above. The comparisons between Al-15Si-3.5P and Cu-8.5P master alloys were carried out with an addition of 200 ppm P at 780°C.

Table 1. Chemical compositions of experimental alloys wt.%

Alloy	Si	Cu	Ni	Mg	Fe	Al
ZL109	12.15	0.99	0.70	1.10	0.16	Bal.
Al-30Si	30.50	0.02	0.01	0.06	0.48	Bal.

All the metallographic specimens were cut from the same position of the casting samples and then mechanically ground and polished through standard routines. Statistical analysis was conducted to determine the average size of primary Si. It is necessary to quickly prepare the specimens for the Al-Si-P master alloy to avoid oxidation and hydrolysis of AlP particles. Microstructure analysis was carried out with high scope video microscope (HSVM) and JXA-8840 electron probe microanalyzer (EPMA). The P content in ZL109 alloys modified by Al-15Si-3.5P and Cu-8.5P master alloys was measured using the emission spectrometer (QSN750, Germany).

3. Results and discussion

3.1. Microstructure characters of Al-Si-P master alloys

The EPMA analysis of Al-40Si-1.5P and Al-15Si-3.5P master alloys is shown in Figs. 1 and 2, respectively. From Fig. 1(a), it can be seen that there are many dark particles surrounding the primary Si phase with a length of about 20 μm. The chemical composition of site A shown in Fig. 1(a) is about 43.73 wt.% Al, 40.03 wt.% P, and 16.24 wt.% Si. Also, these dark AlP particles mostly present as radiated morphology inside primary Si phases and some of them are alongside the primary Si at the lower reaction temperature, as shown in Fig. 1. Granular AlP may precipitate at the region with a higher P concentration, and they also often combine with primary Si, which results from the higher reaction temperature, as shown in Fig. 2. Therefore, it can be concluded that the sizes and morphologies of AlP particles depend on the reaction temperature and P content during the formation process [15]. In addition, AlP particles cannot distribute uniformly in the Al melt due to their poor wettability, and they often float on the melt or adsorb on the inner walls of the vessels. However, the silicon introduced into the master alloy system parcels up AlP particles, and plays an important role in improving the distribution and content of AlP due to their similar crystal structures and lattice parameters, as evident from Figs. 1 and 2.

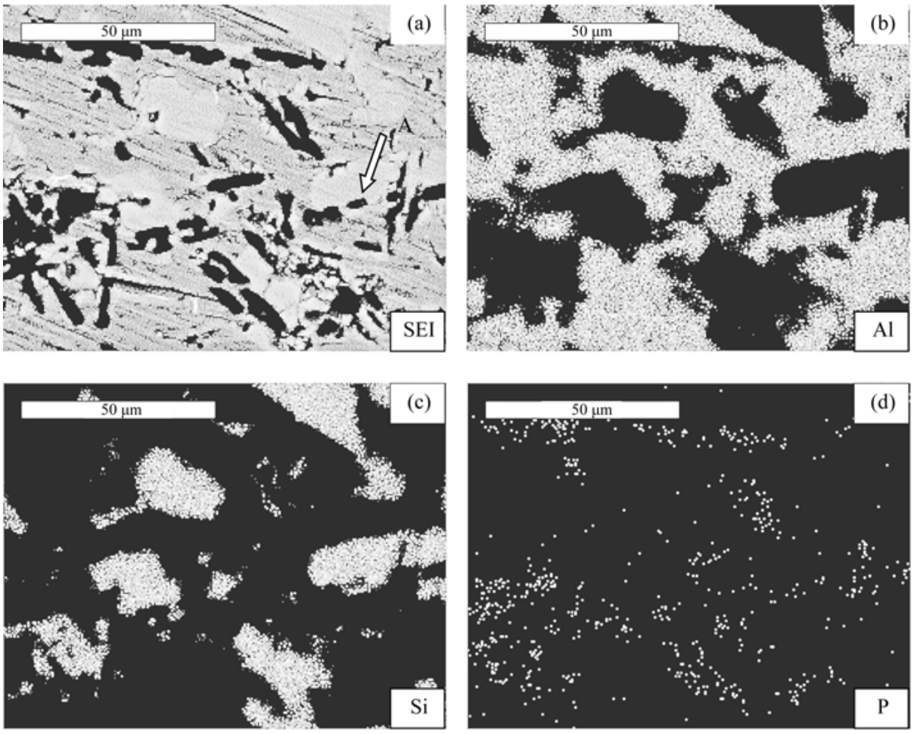

Fig. 1. EPMA analysis of the Al-40Si-1.5P master alloy: (a) SEI and (b-d) X-ray images for elements Al, Si, and P respectively.

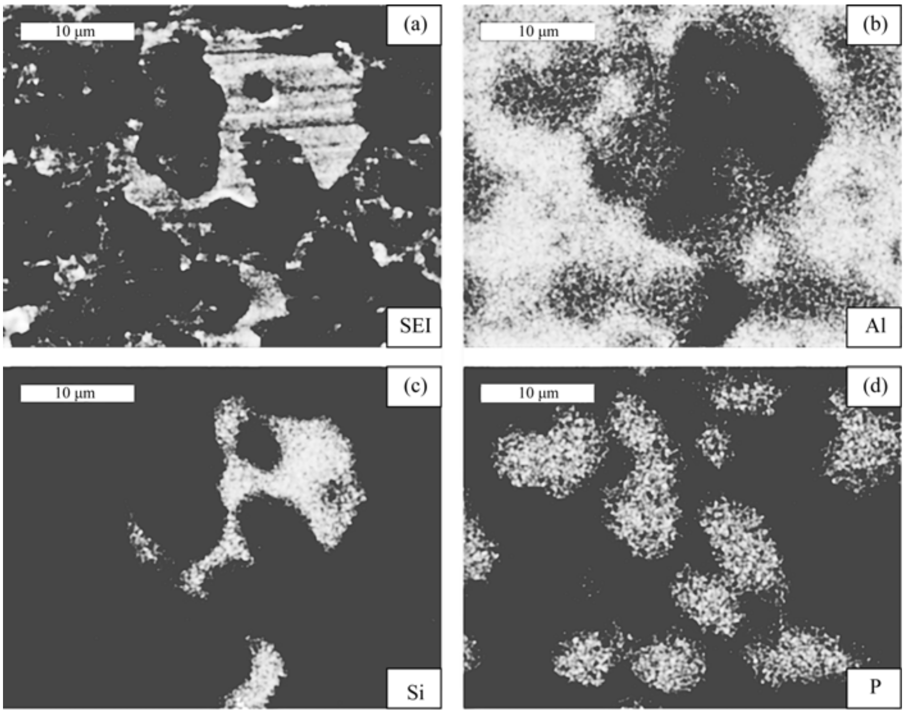

Fig. 2. EPMA analysis of the Al-15Si-3.5P master alloy: (a) SEI and (b-d) X-ray images for elements Al, Si, and P respectively.

3.2. Modification and refinement performance of Al-Si-P master alloys

Fig. 3 shows the microstructures of eutectic ZL109 alloys before and after addition of the Al-15Si-3.5P master alloy. It can be seen that the typical microstructure of eutectic Al-Si alloys is composed of α-Al dendrites and acicular eutectic Si, without primary Si. As evident in Fig. 3(b), ZL109 alloys have shown fast modification response to the addition of the Al-Si-P master alloy, with a mass of primary Si precipitating in size of about 15 μm using statistical analysis.

Fig. 4 shows the microstructure of Al-30Si alloys before and after treatment by the Al-15Si-3.5P master alloy. Primary Si in unrefined Al-30Si alloys presents irregular morphologies such as coarse platelet and star-like, which will crack the Al matrix easily, and that has been considered to be the main limit to their commercial use. After the addition of 2.0% Al-15Si-3.5P master alloy at 850°C, the average size of primary Si is dramatically refined from 150 μm to 37 μm and the morphology changes to block-like, as shown in Fig. 4(b). Fig. 5 presents the EPMA analysis of primary Si in the Al-30Si alloy with the addition of 2.0% Al-15Si-3.5P master alloy. It can be seen clearly that the elements Al and P exist in the center of primary Si, and it is proved to be AlP by means of EPMA quantitative analysis illustrated in Fig. 6.

3.3. Comparison of modification effect and P recovery between Al-15Si-3.5P and Cu-8.5P master alloys

Fig. 7 shows the typical microstructures of ZL109 alloys modified by Al-15Si-3.5P and Cu-8.5P master alloys under the same experimental condition. It can be seen that compared with the Cu-8.5P master alloy, the modification performance of Al-15Si-3.5P master alloys is somewhat im-

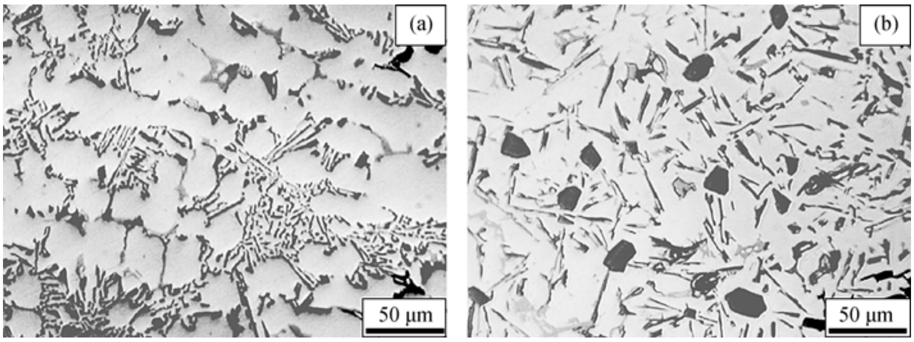

Fig. 3. Microstructures of eutectic ZL109 alloys at 720°C for 30 min: (a) unmodified and (b) modified by 0.5% Al-15Si-3.5P master alloy.

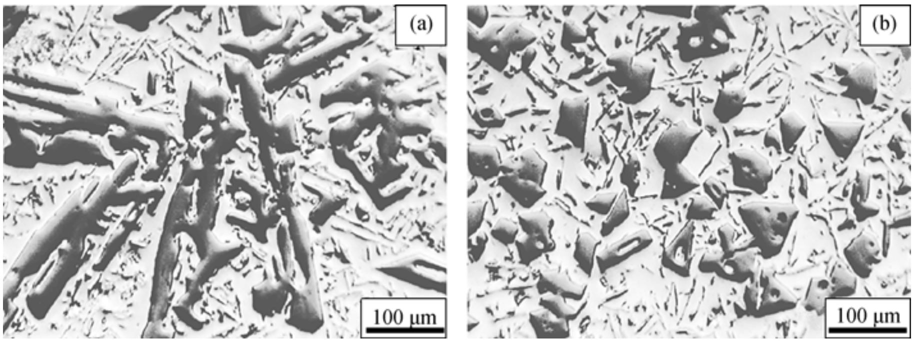

Fig. 4. Microstructures of Al-30Si alloys at 850°C for 30 min: (a) unrefined and (b) refined by 2.0% Al-15Si-3.5P master alloy.

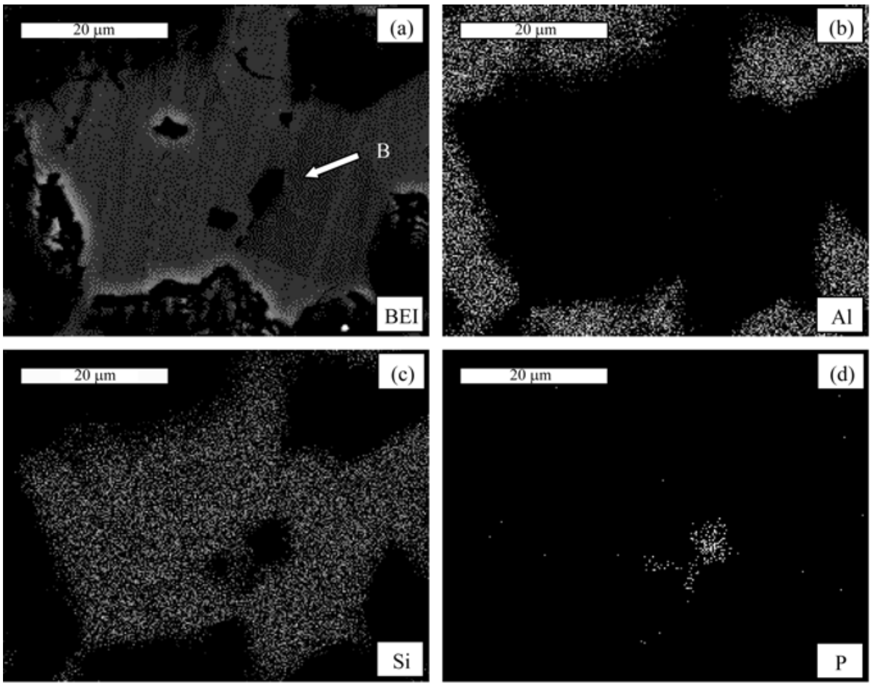

Fig. 5. EPMA analysis of the nuclei of primary Si in Al-30Si alloys: (a) BEI and (b-d) X-ray images for elements Al, Si and P, respectively.

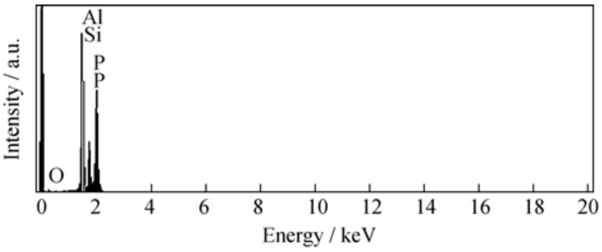

Fig. 6. EPMA quantitative analysis for site B in Fig. 5.

proved. It is clear that the average size of primary Si in ZL109 alloys modified by Al-15Si-3.5P master alloys is smaller than that of Cu-8.5P master alloys. Meanwhile, the morphology of primary Si is more regular.

Phosphorus concentration was compared between Al-15Si-3.5P and Cu-8.5P master alloys with an addition of 200 ppm P at 780°C, and the result is shown in Table 2. It can be seen that the P content in all samples increases with holding time, but in ZL109 alloy modified by the Al-15Si-3.5P master alloy it is much higher than that of the samples treated by the Cu-8.5P master alloy. At the holding time of 10 min, the recovery of P in ZL109 alloy modified by the Al-Si-P master alloy is about 40%, and it goes up to 60% when holding for 120 min. In comparison with that, with the holding time ranging from 10 min to 120 min, the recovery of P of the Cu-8.5P master alloy goes up from 10% to 45%, which is still lower than that of the Al-15Si-3.5P master alloy at the holding time of 30 min.

The eutectic Cu-8.5P master alloy is composed of α-Cu and Cu_3P phases. After its addition into the melt, the reaction $Cu_3P_{[l]} + Al_{[l]} \rightarrow 3Cu_{[l]} + AlP_{[s]}$ can occur. That is, there is a reaction process for the Cu-8.5P master alloy to form AlP and exhibit refinement effect on primary Si in Al-Si alloys. Zhang *et al.* [16] studied the microstructure and mechanical properties of hypereutectic Al-Si alloys modified

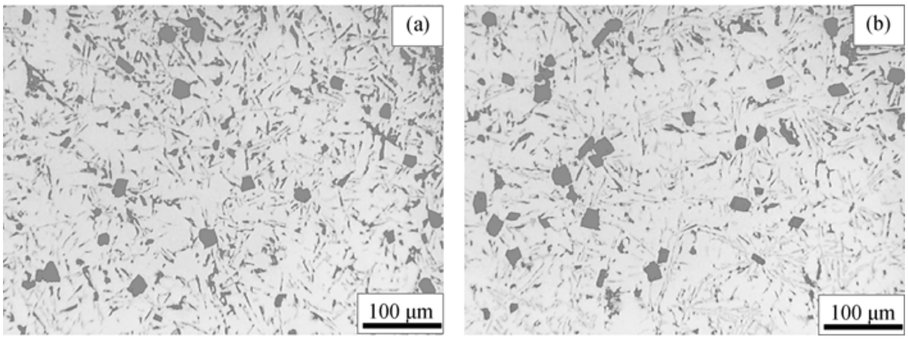

Fig. 7. Microstructures of ZL109 alloys: (a) modified by the Al-15Si-3.5P master alloy and (b) modified by the Cu-8.5P master alloy (the melting temperature was 780°C; the addition level of P was 200 ppm; the holding time was 60 min).

Table 2. Comparison of P contents in ZL109 modified respectively by Al-15Si-3.5P and Cu-8.5P master alloys (the melting temperature was 780°C; the addition level of P is 200 ppm) ppm

Master alloy	Holding time / min					
	10	20	30	60	90	120
Al-15Si-3.5P	82	88	98	122	113	121
Cu-8.5P	18	34	40	57	79	88

with Cu-P master alloys, the change in Gibbs free energy (J) of the reaction mentioned above at 1073 K was calculated, and the value was equal to −79744 J, which was less than zero. It is clear from the value of change in Gibbs free energy that the reaction can occur spontaneously below 1073 K. Consequently, the formed AlP particles take as heterogeneous nuclei for primary Si due to their similar crystal lattice. Maeng *et al.* [1] found that a higher modification temperature is necessary for a Cu-P master alloy. It is reasonable to deduce that treatment temperature would influence the reaction rate and consequently impact the refinement effect.

In comparison with that, the Al-15Si-3.5P master alloy contains a large number of AlP particles as shown in Figs. 1 and 2. After adding it into the Al-Si melt, pre-formed AlP particles gradually start to dissolve, which results in the reductions in their size and the dissociation from large particles into smaller ones. Due to the lower solubility of phosphorus and the density difference, a large quantity of AlP particles cannot distribute uniformly in the melt. These undissolved AlP would become the dregs and float to the surface and cannot act as the nucleation sites of primary Si. During the solidification process, the solubility of P in the melt decreases with increasing temperature; P in solution reform lots of new AlP particles: $P_{[l]} + Al_{[l]} \rightarrow AlP_{[s]}$. Since AlP and Si have similar crystal structures and lattice parameters, primary Si can nucleate heterogeneously on solid AlP particles [17-21].

In short, there is a diffusion process of pre-formed AlP particles for the Al-15Si-3.5P master alloy, which is different from the Cu-8.5P master alloy with a reaction process. Therefore, a relatively stable refinement efficiency and higher recovery of P can be obtained after holding for a few minutes. Furthermore, the density and melting temperature of the Al-15Si-3.5P master alloy are similar to that of the Al-Si alloys, so it is much more beneficial for the master alloys to distribute uniformly in melt and display stable refinement efficiency.

4. Conclusion

It has been found that the Al-Si-P master alloy is an environmentally friendly modifier with good modification and refinement performances on eutectic and hypereutectic Al-Si alloys. For eutectic ZL109 alloys, a mass of primary Si precipitates with about 15 μm size after the addition of 0.5 % Al-15Si-3.5P master alloy at 720°C. The average size of coarse primary Si in the Al-30Si alloy can be remarkably decreased from 150 μm to 37 μm with the addition of 2.0% Al-15Si-3.5P master alloy at 850°C. Due to the pre-formed AlP particles, the P recovery of the Al-15Si-3.5P master alloy is much higher than that of the Cu-8.5P master alloy.

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References

[1] Maeng D.Y., Lee J.H., Won C.W., Cho S.S., and Chun B.S., The effects of processing parameters on the microstructure and mechanical properties of modified B390 alloy in direct squeeze casting, *J. Mater. Process. Technol.*, 2000, **105**: 196.

[2] Haque M.M. and Maleque M.A., Effect of process variables on structure and properties of aluminum-silicon piston alloy, *J. Mater. Process. Technol.*, 1998, **77**: 122.

[3] Robles Hernandez F.C. and Sokolowski J.H., Comparison among chemical and electromagnetic stirring and vibration melt treatments for Al-Si hypereutectic alloys, *J. Alloys Compd.*, 2006, **426**: 205.

[4] Liu X.F., Qiao J.G., Liu Y.X., Li S.T., and Bian X.F., Modification performance of the Al-P master alloy for eutectic and hypereutectic Al-Si alloys, *Acta Metall. Sin.* (in Chinese), 2004, **40** (5): 471.

[5] Asensio-Lozano J. and Suarez-Pena B., Effect of the addition of refiners and/or modifiers on the microstructure of die cast Al-12Si alloys, *Scripta Mater.*, 2006, **54**: 943.

[6] Yu L.N., Liu X.F., Ding H.M., and Bian X.F., A new nucleation mechanism of primary Si by peritectic-like coupling of AlP and TiB_2 in near eutectic Al-Si alloy, *J. Alloys Compd.*, 2007, **432**: 156.

[7] Lu D.H., Jiang Y.H., Guan G.S., Zhou R.F., Li Z.H., and Zhou R., Refinement of primary Si in hypereutectic Al-Si alloy by electromagnetic stirring, *J. Mater. Process. Technol.*, 2007, **189**: 13.

[8] Yu F.X., Cui J.Z., Ranganathan S., and Dwarakadasa E.S., Fundamental differences between spray forming and other semisolid processes, *Mater. Sci. Eng. A*, 2001, **304-306**: 621.

[9] Chen C.M., Yang C.C., and Chao C.G., A novel method for net-shape forming of hypereutectic Al-Si alloys by thixocasting with powder preforms, *J. Mater. Process. Technol.*, 2005, **167**: 103.

[10] Ge L.L., Liu R.P., Li G., Ma M.Z., and Wang W.K., Solidification of Al-50at.%Si alloy in a drop tube, *Mater. Sci. Eng. A*, 2004, **385**: 128.

[11] Yilmaz F., Atasoy O.A., and Elliott R., Growth structures in aluminum-silicon alloys Ⅱ. The influence of strontium, *J. Cryst. Growth*, 1992, **118** (3-4): 377.

[12] Wang Z.H., Mao X.M., Zhang J.L., and Ouyang Z.Y., Modification of Al-Si hypereutectic alloys by Sr-PM, *Spec. Cast. Nonferrous Alloys* (in Chinese), 2005, (4): 241.

[13] Liu X.F., Qiao J.G., Song X.G., Bian X.F., Zhu L.M., and Zhang Y.L., Application of Al-P master alloy to Al-Si piston alloy, *Spec. Cast. Nonferrous Alloys* (in Chinese), 2002, (6): 43.

[14] Kyffin W.J., Rainforth W.M., and Jones H., Effect of phosphorus additions on the spacing between primary silicon particles in a Bridgman solidified hypereutectic Al-Si alloy, *J. Mater. Sci.*, 2001, **36** (11): 2667.

[15] Li P.J., Kandalova E.G., and Nikitin V.I., Grain refining performance of Al-Ti master alloys with different microstructures, *Mater. Lett.*, 2005, **59**: 723.

[16] Zhang H.H., Duan H.L., Shao G.J., and Xu L.P, Microstructure and mechanical properties of hypereutectic Al-Si alloy modified with Cu-P, *Rare Met.*, 2008, **27** (1): 59.

[17] Ho C.R. and Cantor B., Heterogeneous nucleation of solidification of Si in Al-Si and Al-Si-P alloys, *Acta Metall. Mater.*, 1995, **43** (8): 3231.

[18] Wu Y.Y., Liu X.F., and Bian X.F., Effect of AlP on the eutectic nucleation in Ni-38wt.%Si alloys, *Mater. Sci. Eng. A*, 2006, **427**: 69.

[19] Cantor B., Impurity effects on heterogeneous nucleation, *Mater. Sci. Eng. A*, 1997, **226-228**: 151.

[20] Lescuyer H., Allibert M., and Laslaz G., Solubility and precipitation of AlP in Al-Si melts studied with a temperature controlled filtration technique, *J. Alloys Compd.*, 1998, **279**: 237.

[21] Beer S.Z., The solution of aluminum phosphide in aluminum, *J. Electrochem. Soc.*, 1969, **116** (2): 263.