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Preparation of nanocrystal modificator and its modification mechanism

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Abstract: In order to increase the modifying effect, the Cu-P master alloy was rapidly solidified with melt-spin method, and the nano-sized ribbon was gained at 10^5−10^6 ℃/s. Subsequently, ZL109 alloy was modified by nanocrystal and massive Cu-P master alloy, respectively, with molten metal casting method. The results show that the microscopic structure of ZL109 alloy modified by nanocrystal Cu-P master alloy is better than that modified by massive Cu-P master alloy, the original crystal silicon and eutectic silicon are refined more effectively and the mechanical properties are increased evidently: the tensile-strength is increased by 25%, the elongation is increased by 32.26% and the hardness is increased by 17.2%. Therefore, the melt-spin treatment is a feasible method to improve the modifying effect of Cu-P master alloy.

Key words: Cu-P master alloy; ZL109 alloy; melt-spin; rapid solidification; nanocrystal; modification; refinement

1 Introduction

Nowadays, the constant development of automobile engine towards high speed and high pressure leads to higher and higher demands for properties of engine piston. In order to improve the performance of piston, the massive Cu-P master alloys are often added to molten Al-Si alloys prior to casting in industrial practice. Though the Cu-P master alloy can effectively modify the shape of Si phase in aluminium alloys and alleviate the impairment of Si phase to matrix[1−2], it has some evident flaws such as high melting point, melting difficulty, high density, easy deposition and segregation [3−4]. Therefore, it is necessary to improve the modifying effect of Cu-P master alloy.

On the other hand, though the rapid solidification technique has become an important method to study amorphous or monotectic microstructure, it is mostly limited to study the relationship between amorphous or monotectic microstructure and their preparation method[5−7], and the influence of rapid solidification on the modifying effect of Cu-P master alloy has not been studied in detail yet. The present study attempts to fill this gap by a detailed study on the rapid solidification of Cu-P master alloys and its modifying mechanism on ZL109.

2 Experimental

In this research, the modifying object is ZL109 alloy, whose compositions are listed in Table 1, and the modificator is Cu–8%P (mass fraction) alloy.

Table 1 Chemical composition of ZL109 alloy (mass fraction %)

Chemical composition	Theoretical value	Experimental value
Si	11.0−13.0	14.04
Cu	0.5−1.5	1.03
Mg	0.8−1.3	1.38
Ni	0.8−1.5	1.02
Fe	0.7	0.26
Ti	0.2	−
Mn	0.2	−
Zn	0.2	−
Al	Bal.	Bal.

As the key process of the whole research, the rapid solidification of Cu-P intermediate alloy is crucial. The Cu-P intermediate alloy is melt-spin in LZK-12A type

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vacuum rapid quenching furnace, and a ribbon of Cu-P intermediate alloy with about 50 μm in thickness was gained. Subsequently, the ZL109 alloy was modified respectively with massive and ribbon Cu-P intermediate alloys at 700−750 ℃. The addition of Cu-P intermediate alloy is 0.4%[8], and the testbars are cast in a metal mould. The tensile test was carried out with SHT5305 type computer control electric-hydraulic servo universal test machine. After the tensile test rods were fractured, the fractographic analysis was performed on Philips XL30W/TMP Scanning Electron Microscope. The metallographic structures were observed on optical microscope and the degree of hardness was measured.

In order to determine the microstructure of the ribbon, DTA, XRD and TEM analysis were made with Philips X'pert MPD and Philips TECNAI−F20 Transmission Electron Microscope.

3 Results and discussion

3.1 Rapid solidification result and analysis of intermediate alloy

The differential thermal analysis result of Cu-P rapid quenching ribbon is shown in Fig.1. During the temperature rising process, there is only one endothermic peak corresponding the melting point of Cu-P intermediate alloy, and there are no vitrification transition and hypo-crystalloid transition peaks (or trough). This primarily indicates that in this experiment there is not a large number of amorphous structure occurred in the ribbon[8−9]. However, as differential thermal analysis belongs to relatively rough analysis method, the tiny quantity of amorphous structures in ribbon is difficult to detect with it, and the XRD analysis results are shown in Fig.2. It can be seen from Fig.2 that the intermediate alloy mainly consists of Cu and Cu_3P. The diffraction peaks in Fig.2(a) are sharp, which is the character of typical crystal diffraction. The bottom in Fig.2(b) is higher than that in Fig.2(a), and there are a large number of approximately diffuse scattering peaks in Fig.2(b). The less the grain size, the wider the diffraction peaks width. The diffraction peaks of amorphous structure are thoroughly diffuse scattering peak, so it can be concluded that there is no obvious amorphous structure in melt-spin Cu-P, but the grain size is very small[10]. In order to ascertain that whether the nano- grains occur in melt-spin Cu-P, TEM analysis is made and the result is shown in Fig.3. It can be seen from Fig.3(a) that the Cu_3P particles disperse evenly in matrix, some of them are round or near-spherical. Most of these particles are about 30−50 nm in size, several are about 50−100 nm. Equal thickness stripes[11] found on these particles (as shown in circle and ellipse) indicates that these particles are polyhedron and their surfaces are rather plain. Multi-crystal diffraction spots of melt-spin Cu-P are shown in Fig.3(b).

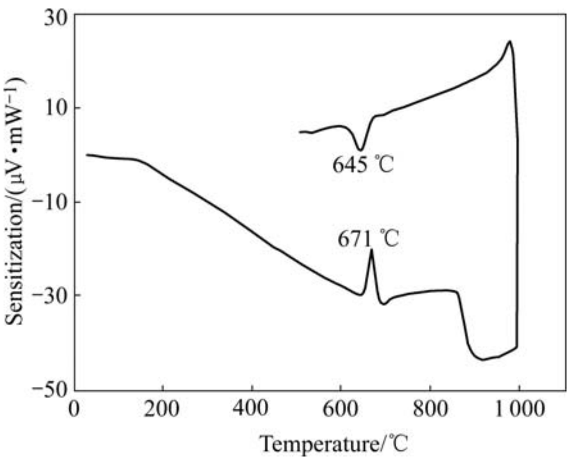

Fig.1 DTA curve of Cu-P melt-spin ribbon

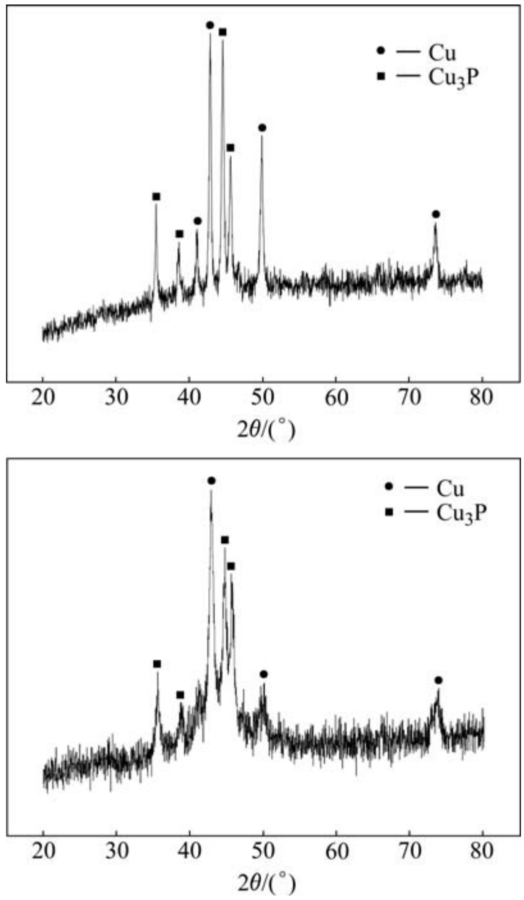

Fig.2 XRD patterns of Cu-P intermediate alloy (a) and melt-spin (b)

So it can be concluded from above results that under the existing cooling speed in this experiment, the melt-spin Cu-P consists of multi-crystal nano-particles and a little amount of amorphous structures.

3.2 Modifying result and analysis of ZL109 alloy

The metallographic structure of as cast ZL109 with

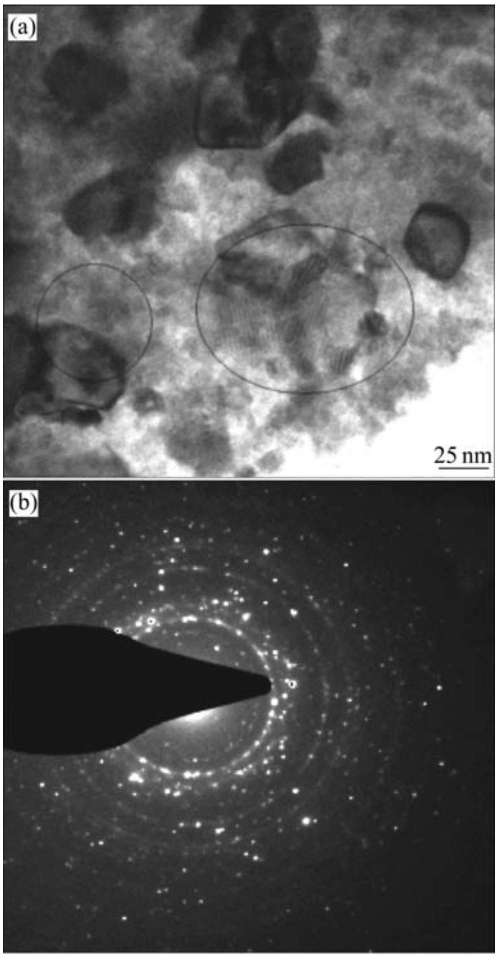

Fig.3 Microstructure and nanocrystal grain of intermediate alloy (a) and electron diffraction pattern of Cu-P intermediate alloy (b)

or without modificator is shown in Fig.4. Fig.4(a) illustrates that some block original crystal silicon and lots of eutectic silicon branch strongly disserve matrix and decrease its mechanical performance. After modified with the massive Cu-P(as shown in Fig.4(a)), the quantity of the original crystal silicon increases but the size decreases obviously. The eutectic silicon changes from dentrite into smaller rod or bone shaped. Whereas, the original crystal silicon in Fig.4(c) has been refined further compared with those in Fig.4(b). Some original crystal silicon changes to be globular and distributes more evenly. The eutectic silicon changes into short rod or dot shaped, the whole structure has been refined further and distributes more evenly. It is evident that the ribbon Cu-P can alter the size, distribution and shape of silicon phase more effectively than the massive Cu-P.

The mechanical properties of tensile sample of ZL109 are listed in Table 2. The strength and elongation of ZL109 are improved by modification treatment. But the properties of ZL109 alloy modified with the ribbon Cu-P are better than those with the massive Cu-P, which

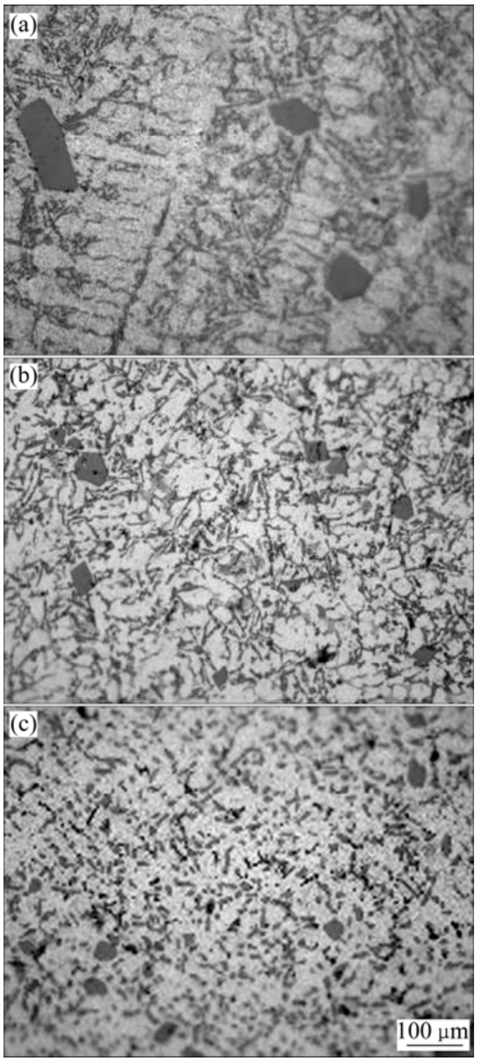

Fig.4 Metallographic structures of as-cast ZL109 alloy under different refining treatment conditions: (a) As-cast ZL109 without modification; (b) As-cast ZL109 alloy modified by massive Cu-P intermediate alloy; (c) As-cast ZL109 alloy modified by melt-spin Cu-P intermediate alloy

Table 2 Mechanical properties of tensile sample

Alloy	Tensile strength/MPa	Elongation/ %	HBS
ZL109[12]	325.0	–	125.0
Modified with mass Cu-P (T6)	384.4	3.1	119.5
Modified with ribbon Cu-P (T6)	480.9	4.0	140.0

indicates that the modifying effect of the melt-spin Cu-P is better than traditional massive ones.

Fig.5 shows the tensile fracture photograph of ZL109 alloy modified by melt-spin Cu-P. The fracture of ZL109 alloy modified by melt-spin Cu-P takes on typical ductile rupture feature. There are many various sizes of round or elliptic dimple on the micro-fracture, which is the basic character of micro-fracture of the assemble micro-hole. The assemble process of the micro-hole fracture contains micro-hole formation, growing up, aggregation even rupture. The formation of micro-hole is due to the second-phase (or impurity) fragmentation, or due to the second-phase (or impurity) disengagement from matrix interface. For this study, the second-phase particles include Si, Cu_3P and Mg_2Si.

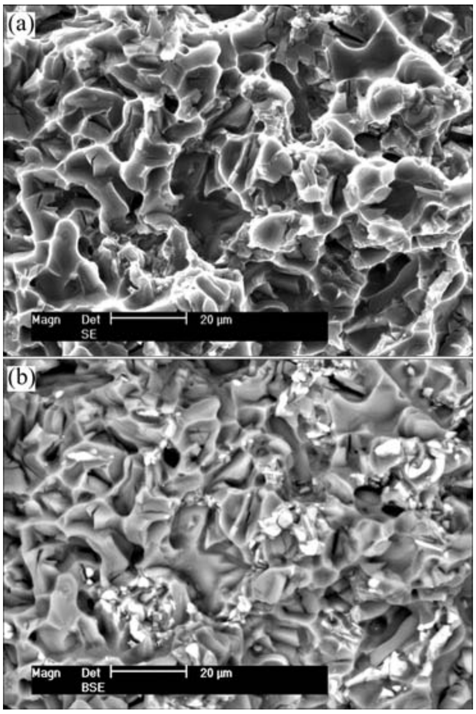

Fig.5 Fracture photograph of tensile sample of ZL109 alloy modified by melt-spin Cu-P

In conclusion, the rapid modification has improved the modifying effect of melt-spin Cu-P obviously, and the reason may be as follows.

1) In the view of nucleation, when the Cu-P massive alloy was added into Al-Si melt, AlP was generated during the interaction between Cu_3P and aluminium melt at about 800 ℃. With high melting point (1 000 ℃), AlP is not easy to decompose in aluminium melt. Moreover, with the same crystal structure and similar lattice constant with Si, AlP tends to become the heterogeneous nuclear of Si. During the process of melt-spin Cu-P, the microstructure of Cu-P intermediate alloy was refined, the pre-nucleus Cu_3P in master alloy was increased, and a large number of modifying nucleus AlP was produced in liquid aluminum in subsequent melting process. Hence Si phase is refined more effectively by ribbon Cu-P massive alloy[13].

2) In the view of interface effect, there are abundant grain boundaries in nano-material, and the atoms of the interface occupy quite a large ratio. Abundant grain boundaries and local atom structure increase the free energy of nano-structure material, and make it in unstable state. Hence the rapid solidification greatly increases the surface area and interface energy of particles Cu_3P and increases the wetting property with aluminium melt. It is more easily for thin ribbon Cu-P master alloy to be added and melted. Additional appropriate agitation makes the nano-particles distribute more evenly in aluminum melt. Therefore, the melt spin treatment enhances the modifying velocity and quality of Cu-P master alloy.

3) In the view of dispersive reinforcement, it is difficult for all the particles in intermediate alloy to react with aluminium melt to produce nucleus of heterogeneous nucleation after being added into aluminum melt. Thus lots of nano-crystals may reserve in matrix acting as dispersive reinforcement particles. Some nanocrystals distribute on the grain boundaries of aluminum alloy. When the grain boundaries move, these nano-crystals are dragged, which nail the grain boundaries, enhance the moving resistance of the grain boundaries and increase strength. In addition, the nano-crystal can be seen as perfect crystal with few dislocations in it[14−15], even if a small quantity of dislocations exist inside crystal grains, they are difficult to breed because of short of the stress that is necessary for F-R dislocation to initiate. When the moving dislocations in matrix meet these nano-crystals, the stress to round or cut the nano-crystals increases sharply, which improves the alloy strength accordingly.

4 Conclusions

1) The Cu-P intermediate alloy is rapidly solidified with melt-spin method. DTA,XRD and TEM analysis show that, under the cooling speed of 10^5−10^6 ℃/s, the microstructure of the ribbon consists of nano- grains, and the number of Cu_3P in Cu-P intermediate alloy increases while the grain size of Cu_3P decreases from 5−40 μm to about 30−50 nm, which produces more modifying nucleus AlP in liquid aluminum in the subsequent melting process. So the modifying effect of Cu-P intermediate alloy is improved.

2) The mechanical properties of ZL109 alloy modified by melt-spin Cu-P intermediate alloy are higher than those modified by massive ones: the tensile-strength is increased by 25%, the elongation coefficient is increased by 32.26% and the hardness is increased by 17.2%. Therefore, the melt-spin treatment is a feasible method to improve the modifying effect of Cu-P master alloy.

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References

[1] PRASADA RAO A K, DAS K, MURTY B S, CHAKRABORTY M. Microstructural and wear behavior of hypoeutectic Al-Si alloy (LM25) grain refined and modified with Al-Ti-C-Sr master alloy [J]. Wear, 2006, 261: 133−139.

[2] ROBLES HERN´ANDEZ F C, SOKOLOWSKI J H. Thermal analysis and microscopical characterization of Al-Si hypereutectic alloys [J]. Journal of Alloys and Compounds, 2006, 419: 180−190.

[3] LIU Xiang-fa, QIAO Jin-guo, LIU Yu-xian, LI Shi-tong, BIAN Xiu-fang. Modification performance of the Al-P master alloy for eutectic and hypereutectic ZL109 alloys [J]. Acta Metallurgica Sinica, 2004, 40(5): 471−476. (in Chinese)

[4] YAO Shu-fang, MAO Wei-min, ZHAO Ai-min, ZHONG Xue-you. The development of refining and modification of cast ZL109 alloy [J]. Foundry, 2000, 49(9): 512−515. (in Chinese)

[5] LARA-RODRIGUEZ G A, GONZALEZ G, FLORES-ZÚÑIGA H, CORTÉS-PERÉZ J. The effect of rapid solidification and grain size on the transformation temperatures of Cu-Al-Be melt spun alloys [J]. Materials Characterization, 2006, 57(3): 154−159.

[6] BARROS A M, TENO´RIO J A S. Calorimetric study of Ni3Al alloys produced by rapid solidification [J]. Intermetallics, 2005, 13: 137−140.

[7] OCHIN P, KOLOMYTSEV V, PASKO A, VERMAUT P, PRIMA F, PORTIER R. Phase transformations in rapidly solidified $(Ti\text{-}Zr)_{50}(Ni\text{-}Cu\text{-}Sn)_{50}$ alloys [J]. Materials Science and Engineering A, 2006, 438/440: 630−633.

[8] WU Yu-ying, LIU Xiang-fa, LIU Xiang-jun, BIAN Xiu-fang. Cu-P base master alloy with low melting point and its modification effect [J]. Spec Cast Nonferrous Alloys, 2004, 3: 69−70. (in Chinese)

[9] GLORIANT T, GREER A L. Al-based nanocrystalline composites by rapid solidification of Al-Ni-Sm alloys [J]. Nanostructured Materials, 1998, 10(3): 392−393.

[10] ZHANG Hong-wen, WANG Jian-qiang, LU Ke. Kinetics of crystallization nucleation and growth in rich metallic glass [J]. Acta Metallurgica Sinica, 2002, 38(6): 609−612.

[11] DING Bing-jun. Nanomaterial [M]. Beijing: Machine Industry Press, 2004: 17.

[12] LIU Da-li, QI Pi-xiang. New style aluminium piston [M]. Beijing: Defense Industry Press, 1999: 8.

[13] GREER A L, BUNN A M, TRONCHE A, EVANS P V, BRISTOW D J. Modeling of inoculation of metallic melts: Application to grain refinement of aluminium by Al-Ti-B [J]. Acta Mater, 2000, 48: 2823−2835.

[14] HU Lan-qing. Investigation of metal nanocrystallization and its mechanism [D]. Taiyuan: Taiyuan University of Technology, 2005.

[15] WARD D K, CURTIN W A, QI Y. Mechanical behavior of aluminum–silicon nanocomposites: A molecular dynamics study [J]. Acta Materialia, 2006, 54: 4441−4451.

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