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Application of CX-type modifiers in Al-Si alloys

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Abstract: The modification effect of CX-type (CX means the modifiers that have long effective term) modifiers applied in ZL108 and ZL104 Al-Si alloys has been studied in detail. The results show that the morphologies of the eutectic silicon and the primary silicon can be modified and refined simultaneously. The modification effect acts quickly and can maintain a period of 8 h by the CX-type modifiers. The CX-type modifiers increase the mechanical properties of Al-Si alloys and improve the service properties of machine parts made of Al-Si alloys (such as piston and cylinder *etc.*). In modifying processes, the amount of the addition of CX-type modifiers is smaller than that of any other modifiers, and the modifying procedures are simple. There are no smoke, no dust, and no irritant smell in modifying processes using CX-type modifiers. Therefore, the CX-type modifiers have advantages in economy and environment protection.

Key words: Al-Si alloys; CX-type modifier; double modification; strontium; phosphorus; sodium

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Al-Si alloys are well-known casting alloys with high wear resistance, low thermal-expansion coefficient, good corrosion resistance, and it can improve mechanical properties at a wide range of temperatures. These properties led to the application of Al-Si alloys in the automotive industry, especially for cylinder blocks, cylinder heads, pistons, and valve lifters [1-6]. The Na-salts, Al-Sr alloys, Sb, and phosphorous powder are usually used in the production of Al-Si alloy castings as the modifier [2]. Because of the defaults such as high cost, the environment pollution, or short modifying period *etc.*, these are not ideal modifiers of Al-Si alloys. The CX-type (CX means the modifiers that have long effective term) modifiers which were studied in recent years are a new type modifiers of Al-Si alloys [3,4]. They have overcome the defects of traditional modifiers, and can be used in hypoeutectic Al-Si alloys and hypereutectic Al-Si alloys. The economical and technological effects are outstanding.

1 Experiment procedures

The alloys used in the experiments were ZL104 Al-Si alloy in which the content of Si is 8.0%-10.5% and ZL108 alloy in which the content of Si is 11.0%-13.0% (mass fraction). The alloys were melted in the electric resistance crucible furnace. The melting temperature was 720-760℃. When the alloy was melted, certain amount of modifier (0.1% to ZL108 alloy cast in permanent mould, and 0.2 % to ZL104 alloy cast in sand mould) was plunged into the molten bath with a plunger. The molten alloy was slowly stirred in the treating process. After the modifier reaction was fully completed, the molten alloy was refined according to the requirement of production. Then, the molten alloy was slag-off and poured into the permanent or sand mould to make the specimens which sizes were ϕ12 mm and ϕ30 mm, respectively. The ZL108 alloy was also cast into pistons which were assembled in the 493Q type engine to examine the quality of piston materials.

In addition, the red phosphorous powder and the Na-salts were used as the modifiers of ZL108 alloy and ZL104 alloy for comparing experiments respectively. The amount of the addition of red phosphorous is 0.1% to ZL108 alloy, and the amount of the addition of Na-salts modifier is 1.4%-2.0% to ZL104 alloy.

The effects (such as the microstructure, the mechanical properties of alloys, the service properties of castings and the technical economical benefit *etc.*)

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of CX-type modifiers were synthetically evaluated with the national standards: GB10849-89 (The Modification of Cast Al-Si Alloys), GB1173-86 (Cast Al Alloys), JB3931-85 (The Technical Requirement of Piston Used in Automobile Engine and Motor Engine), and the standard (JB3932-85) which is related to metallography.

2 Experimental results and analysis

2.1 The modification effect of CX-type modifier on ZL108 Al-Si Alloy

The experimental results are shown in **figure 1** and **table 1**. Figure 1 shows the results of microstructures and mechanical properties of ZL108 Al-Si alloy which was treated with 0.1% CX-type modifier and 0.1% red phosphorous powder respectively, and the melting ZL108 alloy was kept for 8 h after the modifiers were added into the molten alloy. Table 1 shows the results under the same conditions as above, in addition, in maintained time the melting alloy was kept for 8 h. It is shown that the modification effects of CX-type modifier are better than that of the red phosphorous powder. The eutectic silicon was modified and the primary silicon was obviously refined by the modification of CX-type modifier. The time in which the CX-type modifier remained the modification effects is at least 8 h. And the tensile strength for normal temperature (σ_b) and high temperature ($\sigma_{b,\,300℃}$) were both increased.

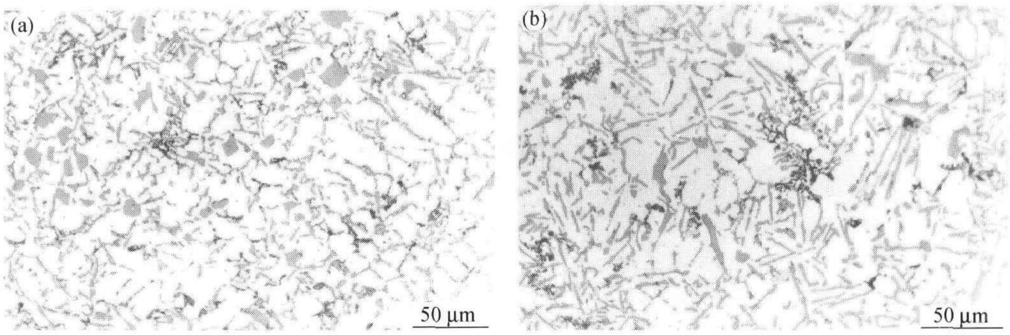

Figure 1 Microstructure of ZL108 Al-Si alloy modified with CX-type modifier and red phosphorous powder respectively, (a) modified with CX-01 modifier; (b) modified with red phosphorous powder.

Table 1 The modification effect of different modifier on ZL108 Al-Si alloy

Modifier	Addition / %	Primary Si size / μm	Eutectic Si size / μm	σ_b / MPa	$\sigma_{b,(300℃)}$ / MPa	HB
CX-01	0.1	<40	<60	355-360	≥104	121
Red P	0.1	100-120	100-120	340-350	≥ 80	121

Note: The specimens were made of the molten alloy which was kept for 8 h after modifying.

Since the modifiers were applied in ZL108 alloy to make pistons, the service properties of the piston of ZL108 Al-Si alloy modified with CX-type modifier were tested. The results are listed in **table 2**. It can be seen that the data of properties are above the requirements of standards.

Table 2 Some properties of the engine with the piston made of ZL108 alloy modified by CX-01 modifier

Targets	Running time / h			Standard requirement	conclusion
	0	300	600		
Maximum power (3600 r/min) / kW	55.04	55.44	55.89	53±2.2	Up to Standard
Maximum torsion moment (2000 r/min) / (N·m)	165.9	168.5	168.6	165±5	
Minimum oil consumed content / ($g\cdot kW^{-1}\cdot h^{-1}$)	216.2	211.1	231.8	241	
The ratio of fuse / %	0.4	0.3	0.37	0.8	

2.2 The modification effect of CX-type modifier on ZL104 Al-Si alloy

The microstructure of ZL104 alloy treated with 0.2% CX-02 modifier is shown in **figure 2**. The molten ZL104 alloy was kept for 1, 6, 7 h respectively after being treated with the modifier. The specimens were cast in sand mould. Some of the specimens were heat-treated with T6 procedure. The mechanical properties of the alloy are listed in **table 3**. The specimens were in heat-treated state or in as cast state.

Comparing with the Na-salts modifier, the amount of addition of CX-type modifier was only 10%-14% of the addition amount of Na-salts modifier which was used in common industry production. However, the modification time of CX-02 modifier could last more than 7 h. It is 3-5 times as long as that of the Na-salts modifier. The morphology of the eutectic silicon was modified into the fiber form by CX-02 modifier, which is as same as the form by the Na-salts modifier. The mechanical properties of ZL104 alloy treated with CX-02 modifier are higher than that required in national standards.

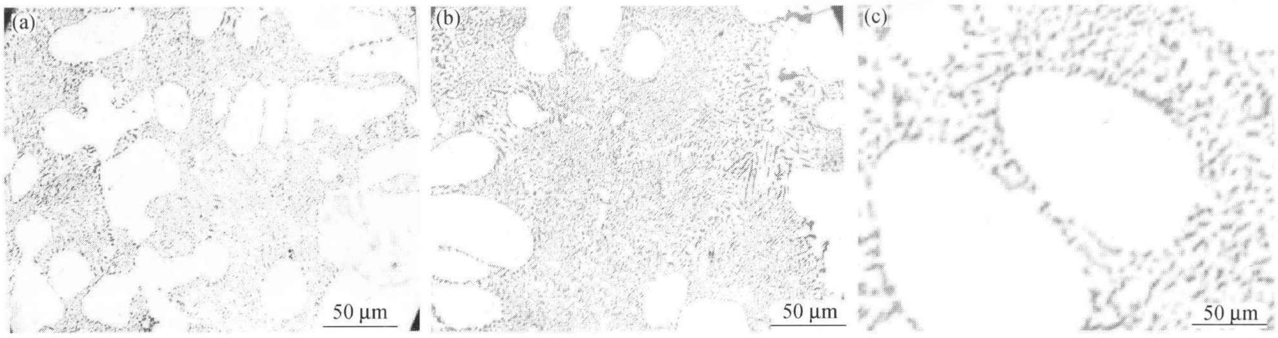

Figure 2 Microstructure of ZL104 treated with CX-02 modifier, (a) modified 1 h; (b) modified 6 h; (c) modified 7 h.

Table 3 Mechanical property of the alloy treated with CX-02 modifier

Treatment state	σ_b / MPa	δ / %	Requirement in standard		Conclusion
			σ_b / MPa	δ / %	
As cast	210-225	3-6.1	≥ 150	≥ 2.0	Up to Standard
T6	250-280	224	≥ 230	≥ 2.0	

Note: The size of specimens is Φ 30 mm, which were cast in sand mould.

2.3 The examination results of the experimental environment

When the alloys were treated with the CX-type modifiers, the noxious substances in the experimental field were detected with a detector which is a HL-205 type portable detector made in China. Under the conditions of natural air convection, the detector had not alarmed. This proves that there are no noxious gases released in the modifying process. There were only small yellow flame observed when the plunger was taken out from the molten alloys. There were not smoke and irritant or awful smell in the modifying process. All above show that the CX-type modifiers can improve the working conditions and are not harmful to human and equipment.

2.4 The modification mechanism of CX-type modifier

The CX-type modifiers are mainly composed of Na-salts, Sr-salts and phosphide. When the CX-type modifiers are added into the molten alloys, at the melt temperature of Al-Si alloys, the following chemical reactions can take place, because the free energy of these chemical reactions are negative.

$$2Sr(NO_3)_2+5C+2Mg = 2Sr+2MgO+2N_2\uparrow+5CO_2\uparrow,$$

$$\Delta G^{\ominus}_{1000} = -2323774.8 \quad (J/mol) \qquad (1)$$

$$6NaF + Al = Na_3AlF_6 + 3Na$$

$$\Delta G^{\ominus}_{1000} = -13935 \quad (J/mol) \qquad (2)$$

The following reactions between phosphate and carbon can take place in Al-Si alloy melt.

$$2NaPO_3 + C = 2Na + P_2O_5 + CO \qquad (3)$$

$$P_2O_5 + 5C + 2Al = 2AlP + 5CO$$

$$\Delta G^{\ominus}_{973} = -1182.5 \quad (kJ/mol) \qquad (4)$$

$$P + Al = AlP$$

$$\Delta G^{\ominus}_{973} = -210.4 \quad (kJ/mol) \qquad (5)$$

It can be seen from the above calculation that according to the thermodynamic principle, compounds in modifier can decompose the atomic state sodium (Na), strontium (Sr), and phosphorous (P), and there are no harmful substances decomposed. Of course, phosphorous can also combine with Na to form Na_3P, but according to the study results, P and Na have no counteractive effect in certain proportion [6].

Among the above elements, phosphorous is combined with aluminum to form the high melting point compound AlP. AlP becomes the nuclear center of primary silicon [2]. While the silicon phase is growing, Sr and Na modify the eutectic silicon phase. The atoms of Na and Sr are absorbed on the TPRE (twin plane re-enter edge) place of {111} crystal plane in silicon phase. They obstruct the silicon crystal growing into flake form and force the silicon crystal to grow along the branch directions in <100> and <110> crystal directions of silicon. Recent study results show that a Si-Si covalent bond exists in the liquid of eutectic and hyper-eutectic alloys. Sr in the liquid Al-Si alloys has a capability of weakening the covalent bonds of Si-Si, suppressing the nucleation of the eutectic silicon phase [7].

Because the adsorption of Sr atom in the front of aluminum solidification plane, the crystallographic orientations of aluminum in eutectic and surrounding primary dendrites are identical [8]. Finally, the primary silicon crystallizes into mass morphology, and the eutectic silicon grows into round end fiber morphology [7-14]. The SEM photography of microstructure in ZL108 alloy modified respectively with the CX-type modifier and the red phosphorous powder are shown in **figure 3**. It can be seen from figure 3 that the primary silicon and the eutectic silicon in Al-Si alloys can be simultaneously double modified with the CX-type modifier. However phosphorous can refine the primary silicon, but it can not modify the eutectic silicon, and the refinement effects of phosphorous on the primary silicon are not so better as that of CX-type modifiers.

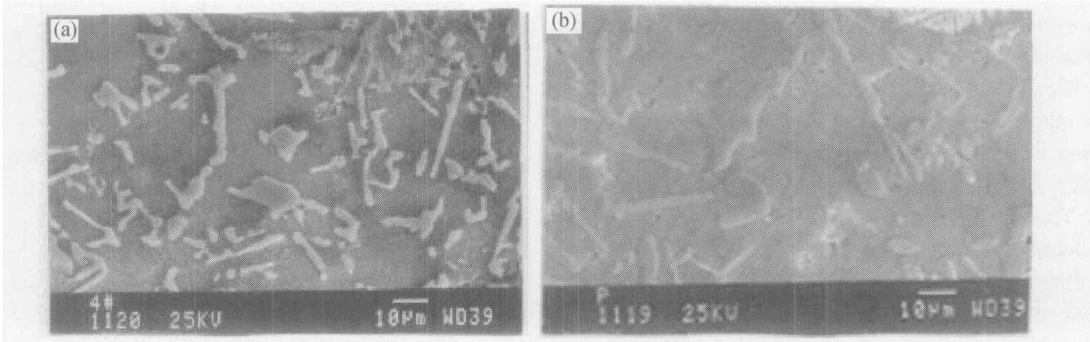

Figure 3 **The morphology of silicon phase in ZL108 alloy treated with different modifier, (a) modified with CX-01 modifier; (b) modified with red phosphorous powder.**

In the molten Al-Si alloy, the CX-type modifiers decompose into atomic state Na and Sr. First, the radium of Na atom (r_{Na} = 109 pm) is smaller than the that of Sr atom (r_{Sr} = 215 pm), the diffusing velocity of Na atom is faster than that of Sr atom, and Na atoms can be rapidly absorbed on TPRE (*i.e.* twin plane reentrant), Na can immediately produce the modifying effect on silicon phase. However, the modifying effect of Na is easy to fade. Contrarily, the radium of Sr atom is bigger than that of Na atom, and the diffusion velocity of Sr atom is slower than that of Na atom, so the atoms of Sr are absorbed on TPRE later. The modifying effect produced by Sr is later than that by Na. That is to say, the modification of strontium exists an incubative period. In addition, because the activity of Sr is less than that of Na, the atoms of Sr are not easy to diffuse to the surface of the molten alloy. Therefore, the oxidizing velocity of Sr is slower than that of Na, and the oxidized loss of Sr is smaller than that of Na, so Sr can maintain a long period of modifying effect. The modification effect of Sr is not easy to fade. The CX-type modifiers combine the advantages of Na and Sr, *i.e.* Na can quickly produce modifying effect and Sr can maintain a long period modifying effect. The CX-type modifier overcome the disadvantages of Na and Sr, *i.e.* Na is easy to fade and Sr is late to produce the modifying effect.

With the above characteristics, the CX-type modifiers can improve the morphology of silicon phase. The round end fiber morphologies of silicon phase can reduce the cutting effect of silicon phase to the matrix phase and the stress concentrating effect of flake form silicon phase. The improved form of silicon phase can improve the continuity of matrix structure. So the CX-type modifiers can improve the microstructure of Al-Si alloys and simultaneity increase the mechanical properties such as tensile strength and elongation of Al-Si alloys.

3 Conclusions

(1) The CX-type modifiers have double modification functions. They can simultaneously refine the primary silicon and modify the eutectic silicon in Al-Si alloys. They can improve the morphologies of the primary silicon and the eutectic silicon in Al-Si alloys. Therefore, they increase the mechanical properties such as tensile strength and elongation of Al-Si alloys.

(2) The amount of the addition of CX-type modifiers is small. Their modification effects can act quickly and can last up to 8 h. Their modification results are better than most other kinds of modifiers of Al-Si alloys.

(3) The operations of CX-type modifiers are simple. There is no smoke, no irritant or awful smell in the modifying process of using CX-type modifiers. They do not have the problem of environment pollution. CX-type modifiers are of advanced level in both technology and economy. They are used quite well by some companies.

References

[1] N. Saheb, T. Laoui, A.R. Daud, M. Harun, S. Radiman, and R. Yahaya, Influence of Ti addition on wear properties of Al-Si eutectic alloys [J], *Wear*, 249(2001), p.656.

[2] L.S. Li, *The Casting Alloys and It's Melting* (in Chinese) [M], Mechanical industry publisher, Beijing, 1989.

[3] S.F. Yao, *Research on the Modification and Refinement of Al-Si Alloys and the Removal of Excessive Mg and Zn from Al Alloys* (in Chinese) [D], University of Science and Technology, Beijing, 2001.

[4] S.F. Yao, X.Y. Zhong, and W.M. Mao, The development of refining and modification of cast Al-Si alloy (in Chinese) [J], *Foundry*, 49(2000), No.9, p.512.

[5] S.A. Kori, B.S. Murty, and M. Chakraborty, Development of an efficient grain refiner for Al-7Si alloy and its modification with strontium [J], *Materials Science and Engineering*, A283(2000), p.94.

[6] Z.X. Yin, The modification of hypoeutectic Al-Si alloys (in Chinese) [J], *Light metals*, 1998, No.9, p.52.

[7] X.F. Bian, W.M. Wang, S.J. Yuan, and J.Y. Qin, Structure factors of modified liquid Al-Si alloys [J], *Science and technology of advanced materials*, 2(2001), p.19.

[8] K. Nogita and A.K. Dahle, Eutectic solidification in hypoeutectic Al-Si alloys: electron backscatter iffraction analysis [J], *Materials Characterization*, 46(2001), p.305.

[9] S.Z. Lu and A. Hellawell, The mechanism of silicon modification in aluminum-silicon alloys: impurity induced twinning [J], *Metallurgical Transaction*, 18A(1987), p.1721.

[10] S.G. Shabestari and J.E. Gruzleski, Modification of Iron Intermetallics by Strontium in 413 Aluminum Alloys, *AFS Transactions*, 103(1995), p.285.

[11] M. Pekguleryuz, B. Closset, and J.E. Gruzleski, The Dissolution of Metallic Strontium in Liquid Aluminum and Liquid A356 Alloys, *Transactions*, 92(1984), p.109.

[12] B. Closset and J.E. Gruzleski, A study on the pure metallic strontium in the modification of Al-Si alloys, *AFS Transactions*, 90(1982), p.801.

[13] T.J. Hurley and R.G. Atkinson, Effects of Modification on Aluminum A-356 Alloys, *AFS Transactions*, 93(1985), p.291.

[14] Lu Shu-zu and A.Hellawell, Growth mechanism of silicon in al-si alloys [J], *Journal of Crystal Growth*, 73(1985), p.316.