INFLUENCES OF TRACE ADDITIONS OF STRONTIUM AND PHOSPHORUS ON ELECTRICAL RESISTIVITY AND VISCOSITY OF LIQUID Al-Si ALLOYS①

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ABSTRACT The electrical resistivity and viscosity of liquid hypoeutectic Al-7% Si and hypereutectic Al-18% Si alloys, and the influences of trace strontium and phosphorus on them were investigated. The trace additions of the two elements increase the electrical resistivity. At the precipitation temperatures of primary phase, the electrical resistivity exhibits a discontinuity for all experimental Al-Si alloys. In the discontinuity the electrical resistivity, respectively, decreases and increases abruptly for Al-7% Si alloys and Al-18% Si alloys. Phosphorus and strontium both have some effects on the discontinuity temperature and the jump value of electrical resistivity of Al-18% Si alloys, but strontium hardly has effect on them in Al-7% Si alloys. The trace additions of strontium and phosphorus increase the viscosity of the experimental alloy.

Key words electrical resistivity viscosity Al-Si alloy liquid metal modification

1 INTRODUCTION

Al-Si alloys are widely used because of their excellent combination of properties, including good castability, corrosion and wear resistance. Their solid mechanical and physical properties have been studied extensively[1-3]. It is found that trace Na, Sr, Sb(referred to as modifying elements) can change eutectic silicon from flake to fibrous morphology, and trace P and S(refining elements) can refine primary silicon crystal, hence a number of properties like ultimate tensile strength, ductility, wear resistance are improved obviously[4-5]. The previous experiments have shown that the trace addition of some elements also changes the liquid properties such as viscosity, electrical resistivity and surface tension of Al-Si alloys. For example, the viscosity of Al-1.65% Si containing trace sodium increases 40 times[6]. The great increase of viscosity facilitates to create porosity, misrun and oxidation inclusion in ingot or casting, to degrade the product quality. Strontium is also an excellent modification element, and its modifying effect may hold for 8 h, but sodium only 30 min. Therefore, strontium-containing modification agent has great potential application in foundry practice. However, to present authors' knowledge it considerably lacks of research on the influences of strontium on the physical properties of liquid Al-Si alloys. Phosphorus is a conventional refining agent of hypereutectic Al-Si alloy. The electrical resistivity of Al-Si alloys containing 0%~10% P was once studied by Samsonov *et al* by using the electrodeless rotational magnetic field method[7]. Here further experiments will be conducted by the DC four-probe measuring method.

2 EXPERIMENTAL METHODS

The master alloy with 25% Si was prepared from 99.99% pure Al and high purity silicon (99.999%) by melting in a graphite crucible

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under argon protection. To avoid inhomogeneity of silicon, the alloy was remelted one time. The experimental alloys with 7% Si and 18% Si were obtained from dilution of the master alloy in alumina crucible. Al-5% Sr master alloy prepared from 99.99% pure Al and 99.9% pure Sr was used for strontium-modified treatment. Strontium content of the alloys in this paper means the addition amount in the experiment, but strontium almost had no burning loss when it was added. The addition of phosphorus adopted red phosphorus+ C_2Cl_6. The final impurity content of phosphorus in the alloy is about 0.05%.

Resistivity measurements were performed by the D C four-probe method using an alumina cell fitted with four tungsten electrodes. The geometrical constant of the cell was calibrated by measuring the resistivity of triple-distilled mercury. The electrical resistivity was measured successively in a sequence from high to low temperature under the condition of extremely slow cooling rate (about 0.5 ℃/min). The measuring apparatus and full experimental details were described in the literature[8]. Maximum gap of temperature between two measuring points is less than 10 ℃. The viscosity measurements were performed by the oscillating-vessel method. Viscosities were calculated by the revised Knappwost equation:

$$\eta = [(\lambda - \lambda_0)/k\rho_m]^2 \rho \qquad (1)$$

Above equation can further transform into:

$$v = [(\lambda - \lambda_0)/k\rho_m]^2 \qquad (2)$$

In Eq. (1) and (2) η is dynamic viscosity, v kinematic viscosity, λ and λ_0 the logarithmic decrements in load and empty crucible states, ρ_m and ρ the densities of experimental alloy in melting point and measuring temperature, k a constant relating to measuring apparatus. k was calibrated by high-pure tin, the tin's viscosities and densities have been measured by Iida *et al*[9], their data were quoted in our present calculation.

3 EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Electrical resistivity

Below liquidus, with the decrease of temperature, the continuous precipitation of primary phase (α-Al or Si) resulted in formation of some pores in the measured conductor in the cell, so the measuring data displayed in the digital voltmeter appeared irregular fluctuation, and then became invalid. Therefore, the lowest measuring temperature was limited for different alloys during our test. Fig. 1 shows the electrical resistivities of Al-7% Si alloys with 0.08% and 0.15% Sr and without Sr in the temperature range of 600~1050 ℃ (below 600 ℃, the measuring data displayed irregular fluctuation). The electrical resistivities of Al-18% Si alloys in the range of 640~1050 ℃ are shown in Fig. 2. It is found that there is a discontinuity at about 615 ℃ for Al-7% Si alloys and between 666~671 ℃ for Al-18% Si alloys, in which the electrical resistivity of Al-7% Si alloys drops, whereas Al-18% Si alloys' rises. This result is attributed to the precipitation of primary α-Al (Al-7% Si alloys) or primary silicon (Al-18% Si alloys). However, in the experiments of Samsonov *et al* who used the electrodeless method to measure the electrical resistivity[7], only in hypereutectic Al-Si alloy the discontinuity exhibited, but there was no discontinuity in hypoeutectic Al-Si alloy. Silicon crystal is a semiconductor, its appearance certainly leads to an abrupt increase of the electrical resistivity. On the contrary, aluminum is a good conductor, primary αAl precipitation should also give rise to an abrupt decrease. Based on this viewpoint, our experimental results are reasonable. The temperatures of discontinuity and the increments of the electrical resistivity in the discontinuity are given in Table 1. The trace additions of strontium hardly change those values of Al-7% Si alloys. For Al-18% Si alloys the trace addition of strontium or phosphorus has some effects on them, strontium decreases, but phosphorus increases both values. In the whole measuring region, the trace additions of strontium increase the electrical resistivity of Al-7% Si alloy, and 0.15% Sr grains greater increment than 0.08% Sr. The additions of both 0.15% Sr and 0.05% P increase the electrical resistivity of Al-18% Si alloy obviously. On an average, the former raises 2.5 μΩ·cm, and the latter raises 2 μΩ·cm.

Table 1 Temperatures and jump values of electrical resistivity of Al-7%Si and Al-18%Si alloys in discontinuity

Alloys	Temperature in discontinuity/ ℃	Jump value / μΩ·cm
Al-7Si	615	- 1.21
Al-7Si-0.08Sr	615.5	- 1.24
Al-7Si-0.15Sr	614.5	- 1.19
Al-18Si	669	0.74
Al-18Si-0.15Sr	666	0.49
Al-18Si-0.05P	671	0.97

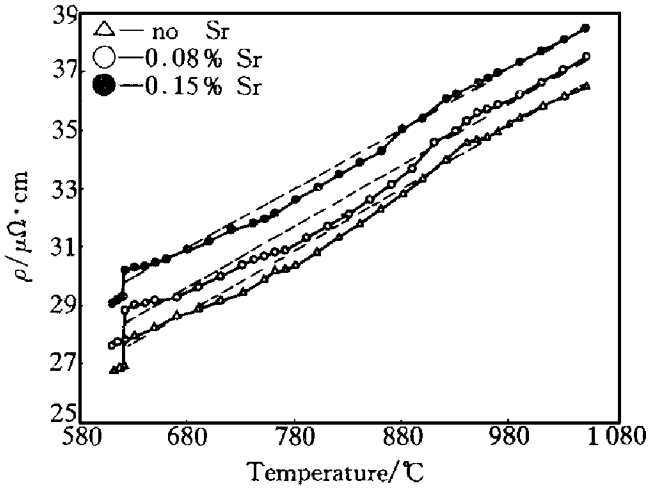

Fig. 1 Electrical resistivities of liquid Al-7Si alloys with and without strontium

As a general rule, the electrical resistivity of liquid metals and alloys can be expressed as a linear function of temperature. In the measuring range of liquid zone, we use the least-squares method to abtain the following equations(representation by the dotted lines in the Fig. 1 and Fig. 2) :

Al-7% Si: $\rho = 14.22 + 21.26 \times 10^{-3} T$

Al-7% Si-0.08% Sr: $\rho = 15.23 + 20.99 \times 10^{-3} T$

Al-7% Si-0.15% Sr: $\rho = 20.18 + 17.18 \times 10^{-3} T$

Al-18% Si: $\rho = 29.24 + 11.76 \times 10^{-3} T$

Al-18% Si-0.15% Sr: $\rho = 34.8 + 8.77 \times 10^{-3} T$

Al-18% Si-0.05% P: $\rho = 31.18 + 11.94 \times 10^{-3} T$

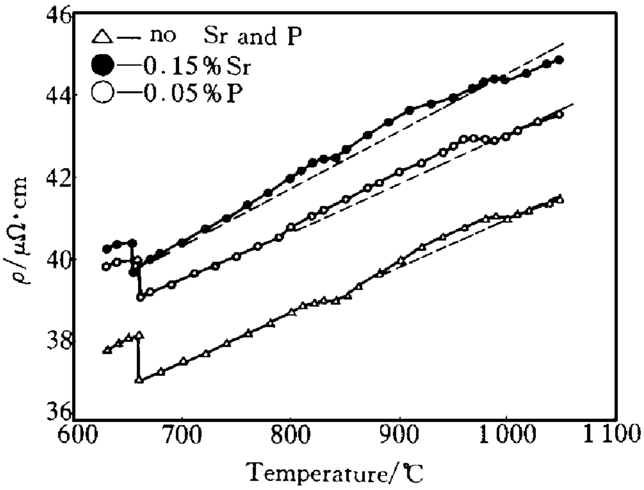

Fig. 2 Electrical resistivities of liquid Al-18Si alloys with and without trace element

In addition, an abnormal phenomenon can be found, i. e. at some temperatures an inflection or plateau in the electrical resistivity vs temperature occurs, such as 760~ 780 ℃ and 940~ 960 ℃ for Al-7% Si alloys, 835~ 850 ℃ and 980 ~ 1 000 ℃ for Al-18% Si alloys(see Fig. 1 and Fig. 2) . Meanwhile, the trace elements have some effects on them. The phenomenon may be explained by clusters existing in the liquid alloy. In lower liquid temperatures, there exist clusters of like or unlike atoms in liquid Al-Si alloys[10, 11]. With the increase in temperature of the melts, those clusters become unstable thermodynamically. Their elimination or formation results in the abnormal variation. On the other hand, it is also clear that the addition of trace strontium or phosphorus has effect on the clusters to a certain extent.

3.2 Viscosity

Fig. 3(a) shows the kinematics viscosity of liquid Al-7% Si alloys treated by 0.08% Sr and untreated. The trace addition of strontium increases the viscosity by about 50% ~ 150% in the range of measuring temperatures. Meanwhile, the increase of viscosity in the lower temperatures is obviously greater than that in the higher temperatures. Fig. 3(b) is the kinematics viscosity of liquid Al-18% Si alloys. The viscosity increases about 5~ 6 times in the experimental range after the trace addition of phosphorus is added. It is known that the fluidity of a metallic melt is inversely proportional to viscosity. Trace strontium and phosphorus increase the viscosity of Al-Si alloy melts, therefore in foundry practice, to maintain the good fluidity, it is neccesary to raise cast temperature properly.

Arrhenlus equation is a popular expression of experimental data of viscosity of liquid metals and alloys, over the limited temperature range, it gives excellent fit to the data of most metals and alloys. It is expressed as:

$$\eta = A\exp(E/RT) \qquad (3)$$

where η is the viscosity corresponding to the absolute temperature T, E the activation energy for viscous flow, R universal gas constant, A the pre-exponential factor. If η in Eq. 3 replaces by v (kinematic viscosity), Eq. 3 can be transformed to:

$$v = A\exp(E/RT) \qquad (4)$$

where E_v is the activation energy for viscous flow in kinematic condition, the other symbols have the same meaning as those in Eq. (3). In Fig. 3, solid-line curves result from the exponential regression of experimental data. It is found that our experimental data can obey exponential function well enough. The viscosity data further transformed into lg v, the following relationship of lg v with $1/T$ (reciprocal of the absolute temperature) can be obtained:

for Al-7%Si:

$$\lg(v\times 10^7) = -0.2105 + 856/T$$
$$E_v = 16.36\ \text{kJ/mol}$$

for Al-7%Si-0.08%Sr:

$$\lg(v\times 10^7) = -1.107 + 2191/T$$
$$E_v = 41.92\ \text{kJ/mol}$$

for Al-18%Si:

$$\lg(v\times 10^7) = -0.605 + 842/T$$
$$E_v = 16.11\ \text{kJ/mol}$$

for Al-18%Si-0.05%P:

$$\lg(v\times 10^7) = +0.544 + 1\,163/T$$
$$E_v = 22.25\ \text{kJ/mol}$$

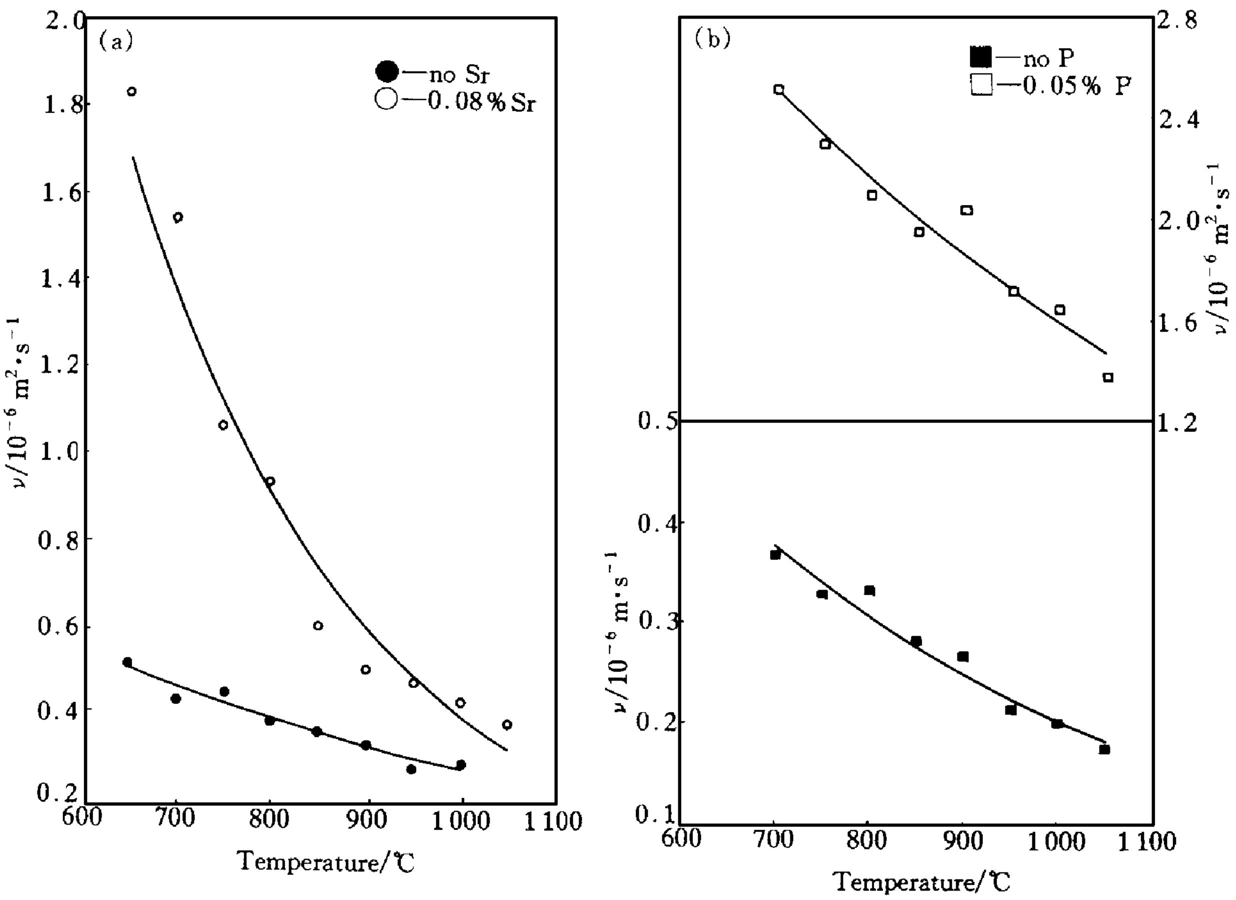

Fig. 3 Viscosities of liquid Al-Si alloys with and without trace elements *vs* temperature

(a) —Al-7Si alloy; (b) —Al-18Si alloy

Above results show that the trace additions of strontium or phosphorus increases E_v, it means that the trace elements reduce the ability of atomic movement, so the flow of the liquid alloys becomes more difficult.

4 DISCUSSION

For Al-7%Si alloy, primary α Al is precipitated in the discontinuity, the trace addition of strontium hardly changed the discontinuity temperature and the jump value. This shows that trace strontium does not influence the nucleation and growth of primary α-Al of the hypoeutectic alloy. Therefore, This gives further evidence to the suggestion that trace strontium used for modifying agent has no effect on α-Al, and only influences on silicon phase. In the case of Al-18%Si alloy, the discontinuity temperature and the jump value had obvious variation after strontium or phosphorus had been added. This means that strontium or phosphorus has some effect on the nucleus formation of primary silicon. The electrical resistivity of the mushy melt is relevant to the fraction of solid phase. Primary silicon precipitation leads to the increase of the electrical resistivity. As compared with the pure Al-18% Si alloy, the trace addition of strontium reduced the jump value, this less jump certainly resulted from the decrease of solid fraction of primary silicon. This indicates that strontium restrains the nucleation of primary silicon in hypereutectic Al-Si melt. On the contrary, the trace addition of phosphorus increased the jump value. By similar analysis, trace phosphorus promote the nucleation of primary silicon. In fact, phosphorus forms AlP compound in the hypereutectic melt, which is a heterogeneous nuclei of primary silicon[12].

It is known that trace sodium, which is a conventional modifying agent of Al-Si alloys, can result in a great increase of the viscosity of Al-Si alloys. The present experimental results indicate that the viscosity increase of the hypoeutectic Al-Si alloy from the strontium addition is lower. From this point, strontium is a better modifying agent of Al-Si alloys.

5 CONCLUSIONS

At the precipitation temperature of primary phase, these is a discontinuity in electrical resistivity *vs* temperature for the experimental Al-Si alloys. In the discontinuity the electrical resistivity of Al-7%Si alloys drops, whereas Al-18%Si alloys' rises. Phosphorus and strontium both have some effects on the discontinuity temperature and the jump value of electrical resistivity of Al-18%Si alloys, but Strontium hardly has effect on those of Al-7%Si alloys. The trace additions of strontium and phosphorus increase the electrical resistivity of liquid Al-Si alloys. The viscosity of liquid Al-7%Si alloy treated by 0.08%Sr increases by 50% ~ 150%, and the viscosity of liquid Al-18%Si alloy containing 0.05%P increases 5~ 6 times in the range of measuring temperature.

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