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Thermodynamics of effect of modification on microstructure of Al-Si alloy melt①

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Abstract: Thermodynamic law of interaction between modification element and alloy melt has been analyzed, and the effect of modification element on electrical resistivity of melt has been studied. It was found that, in a certain range of concentration, there exists a 'node' where the alloy melt reconstruction will occur. An extreme value appeared in the relationship curve of melt's resistivity and modification element's concentration corresponding to the 'node', where the solidified structure of the alloy changed remarkably.

Key words: Al-Si alloy melt; thermodynamics; modification **Document code:** A

1 INTRODUCTION

Modification of phase Si has been used widely as an effective way to improve the properties of Al-Si alloy. But the studies on the acting behavior of modification elements in the alloy have not broken away from the experimental pattern, in which the modification effect was evaluated on the basis of solidification structure and properties. The main reason resulting in this situation is that the effect of modification element in alloy melt can not be discussed deeply into the melt structure. If we could reveal the interaction law between the modification element and the melt, and express it by the variation of sensitive physical characteristics from the point of the variation of melt structure, and research the relativity among the variation of melt structure and sensitive physical properties and solidification structure, the behavior of modification element in the process of alloy melting and solidifying can be evaluated, and scientific basis can also be provided for reasonable control of the modification technology.

2 THERMODYNAMIC ANALYSIS

When we study the microstructure of melt, the SRO (Short Range Order) area existing in the melt can be looked as a big molecule, which has the energy level of electron, vibration and rotation and can exchange energy with the particles reacting with it[1~4]. The SRO area is characterized by stability. When no modification element is added, reaction between the SRO areas can only occur selectively[5,6]; when there is atom of modification element in the melt, and it has a reaction with any atom in the SRO area, there forms an activation entity of (A + MO) which could be called the activated complex. The redistribution of electrons which occurs at this time in SRO will affect its size and stability.

Based on the above analysis, this process can be presented by the following formulae:

$$A_n + MO \rightarrow A_{n-1} + (A + MO)^{\dagger} \quad (1)$$

$$(A + MO)^{\dagger} \rightarrow A + MO_l \quad (2)$$

or

$$(A + MO)^{\dagger} \rightarrow AMO \quad (3)$$

where A is the atom in SRO; † is the activated atom group; MO is the atom of modification element.

If the atom of MO exists in melt in form of a big molecule, it is marked with MO_p, then the reaction can be described as

$$A_n + MO_p \rightarrow A_{n-1} + MO_{p-1} + (A + MO)^{\dagger} \quad (4)$$

$$(A + MO)^{\dagger} \rightarrow A_l + MO_l \quad (5)$$

From the above formulae, we can see that the ultimate product of the reaction is synthesis entity, or free atom of A and MO. All of these depend on the bonding energy between A and MO atom in the melt, which is related with the concentration of MO.

Regular solution is a kind of solution close to actual solution. Except that mixing enthalpy does not equal zero, other characteristics of its formation are the same as those of the ideal solution. The thermodynamic law derived from regular solution can be widely used to study and analyze the alloy solution[7].

Based on the principle of regular solution, the

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mixing free energy ΔG^M of solution can be described by the following formula:

$$\Delta G^M = \Delta G^{id} + G_e^E = RT(X_A \ln X_A + X_B \ln X_B) + RT\alpha X_A X_B = RT(X_A \ln X_A + X_B \ln X_B) + \lambda X_A X_B \quad (6)$$

where X_A and X_B are concentrations of component A and B respectively; λ is a constant which has no relation with composition and temperature for regular solution.

On the basis of formula (6), a point c_0 can always be found in ΔG^M - X_B figure of regular solution[7]:

$$\partial^2 G/\partial c_0^2 = 0$$

In long wave limit, the related function $S_{\infty}(0)$ of concentration-concentration can be expressed by[8]

$$S_{\infty}(0) = \frac{RT}{\left(\frac{\partial^2 G}{\partial c^2}\right)_{R,T}} \quad (7)$$

$S_{\infty}(0)$ is related with structure factor and decided by diffraction approach. Now that the variation of $\partial^2 G/\partial c^2$ with concentration c_{MO} is not monotonic, $S_{\infty}(0)$, $S(0, c, T)$, the short range arrangement and the mean coordination number will change similarly, and some reconstruction in the melt will proceed.

The fluctuation of concentration in the melt can be described by the following rule[9]:

$$P = A\exp(-\Delta G/kT) \quad (8)$$

where P is a factor of probability of concentration fluctuation; A is a constant.

When infinitesimal quantity fluctuation ΔX is formed in melt whose concentration is c_{MO}, that is $c(X) = c(X + \Delta X)$, and $c(X) = c(X - \Delta X)$, expand the Taylor's series at the point of $X = c_{MO}$, then obtain:

$$\Delta G = \frac{1}{2}\left[G(X + \Delta X) + G(X - \Delta X)\right] - G(X)$$
$$= \frac{1}{2}\left[G(X) + \frac{1}{1}(\Delta X)\frac{\partial G}{\partial X} + \frac{1}{2}(\Delta X)^2\frac{\partial^2 G}{\partial X^2} + \cdots + G(X) - \frac{1}{1}(\Delta X)\frac{\partial G}{\partial X} + \frac{1}{2}(\Delta X)^2\frac{\partial^2 G}{\partial X^2} - \cdots\right] - G(X)$$
$$= \frac{1}{2}\frac{\partial^2 G}{\partial X^2}(\Delta X^2)$$

$$\Delta G = \frac{1}{2}\frac{\partial^2 G}{\partial c_{MO}^2}(\Delta X^2) \quad (9)$$

Substitute formula (9) into formula (8), then obtain:

$$P = A\exp\left(\frac{-\Delta X^2\left(\frac{\partial^2 G}{\partial c_{MO}^2}\right)}{kT}\right) \quad (10)$$

Because the variation of $\partial^2 G/\partial c_{MO}^2$ is not monotonic, variation of formula (10) is not monotonic either. The mean square deviation of concentration fluctuation can be expressed by the formula as bellow:

$$(\Delta c_{MO})^2 = \frac{kT}{\frac{\partial^2 G}{\partial c_{MO}^2}} \quad (11)$$

Similarly, the variation of $(\Delta c_{MO})^2$ is not monotonic either.

According to thermodynamic and statistic physics[8,10], the physical nature of the relationship of $(\Delta c_{MO})^2$ and $\partial^2 G/\partial c_{MO}^2$ can be analyzed by formula (11): because of the result of formulae (1) ~ (5), the primary structure based on short range order A_n will be replaced by the structure based on short range order AMO as c_{MO} increased. The difference of the two kinds of melt is in the maximum probability of concentration fluctuation. Change from a concentration fluctuation to another should pass such a state that the distribution of particles is in the largest disorder, and the melt structure is homogeneous.

From above analysis we can see that, because of extreme value existing in every situation, some change will occur in composition-physical characteristic curve corresponding to structure transition taking place in melt.

The analysis from the point of thermodynamics as above showed that, when microscale modification element was added into alloy melt, they might react with melt, which would make microstructure change and then cause sensitive physical characteristic of melt to change.

3 EFFECT OF MODIFICATION ELEMENTS Ce AND Sr ON RESISTIVITY OF Al-Si ALLOY MELT

A rotation magnetic field method was used to measure the specific resistivity, and the whole process was shielded by argon.

From the isothermal curve (Fig.1) of resistivity (ρ) of melt added Ce, we can see that the resistivity decrease sharply with addition of 0.01 %Ce and it decreases slowly when addition increases to 0.03 %Ce. The curve begins to increase until the addition reaches 0.05 %Ce which corresponds to the point of the lowest resistivity of melt.

From the isothermal curve of resistivity of melt with addition of Sr, we can see that resistivity decreased after Sr was added. The resistivity had a small fluctuation at the point of 0.05 %Sr and reached the lowest at the point of 0.075 %Sr. When more Sr was added, there was a tendency of increase, and from Fig.2 we can see that the point of 0.075 %Sr was corresponding to the transformation point of melt structure.

Comparing the above test results, we can see that, the influence mechanisms of Ce and Sr on resis-

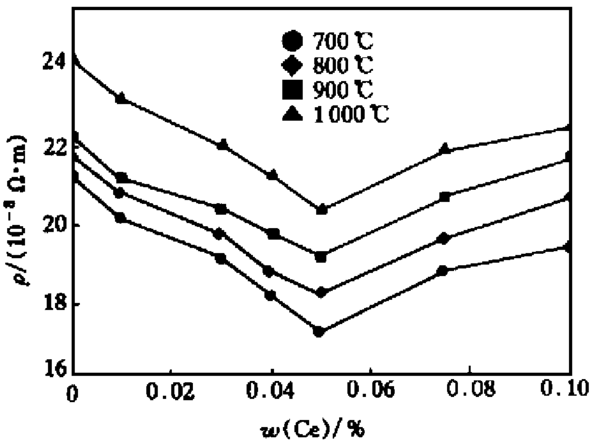

Fig.1 Relationship between resistivity of Al-12%Si + Ce and Ce addition

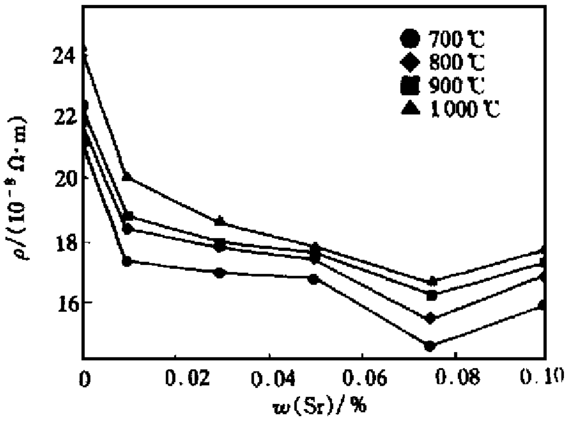

Fig.2 Relationship between resistivity of Al-12%Si + Sr melt and Sr addition

tivity of melt were similar. There was a node for every element, corresponding to which the state of melt would change. This could be represented by physical characteristic (resistivity) and also by solidification structure.

4 EFFECT OF Ce AND Sr ON EUTECTIC STRUCTURE OF Al-Si ALLOY

The microstructures of eutectic Si in alloys with different Sr contents are shown in Fig.3. We can see from this figure that, the modification element has

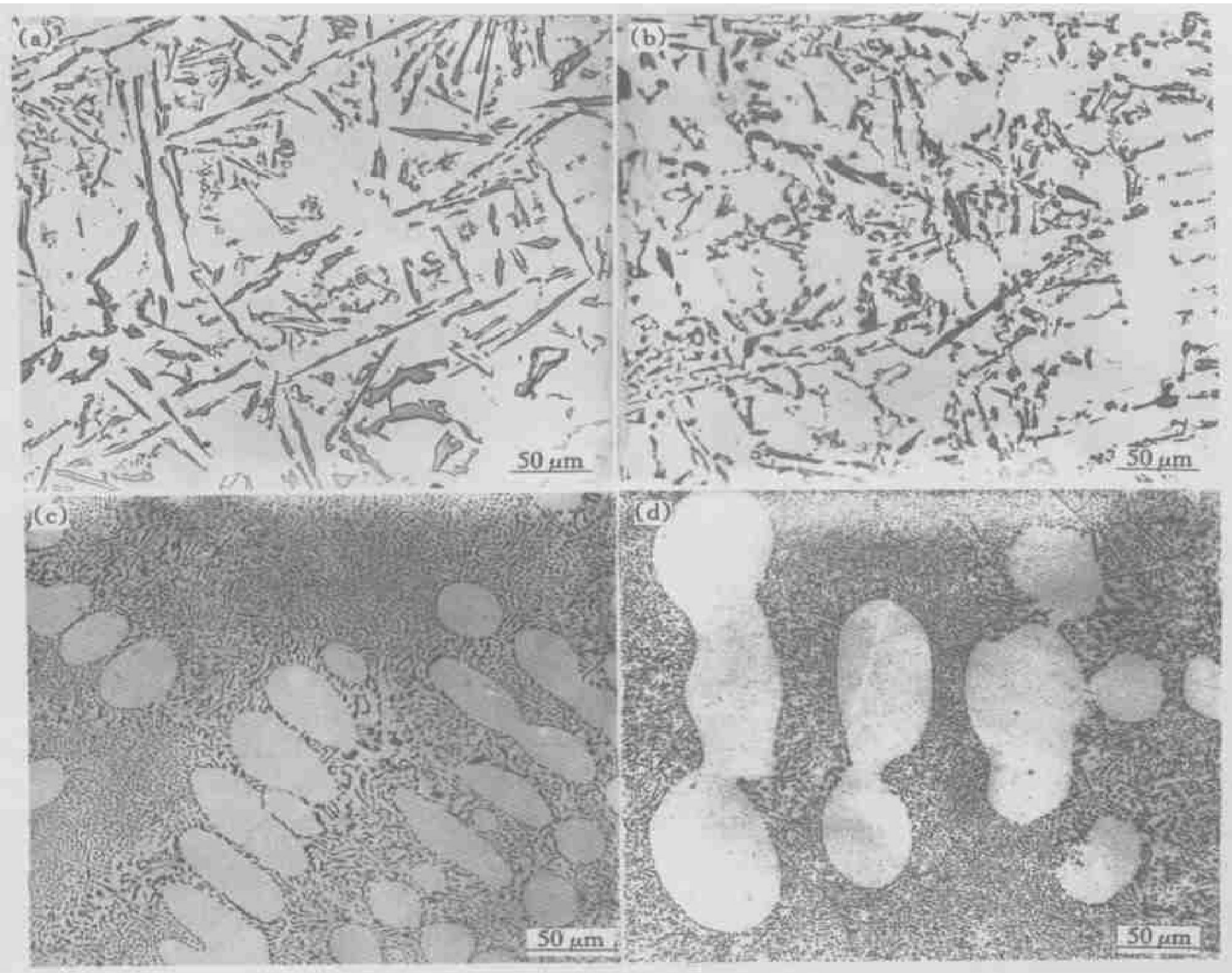

Fig.3 Microstructures of Al-12%Si + Sr alloy
(a) —No Sr; (b) —0.03%Sr; (c) —0.05%Sr; (d) —0.075%Sr

favorable modification effect when its content is in the range of 0.05% ~ 0.075%Sr. In this case, the tensile strength and elongation percentage of alloy are the highest, and the liquidus curve and eutectic transformation temperature decline to the lowest (see Fig. 4).

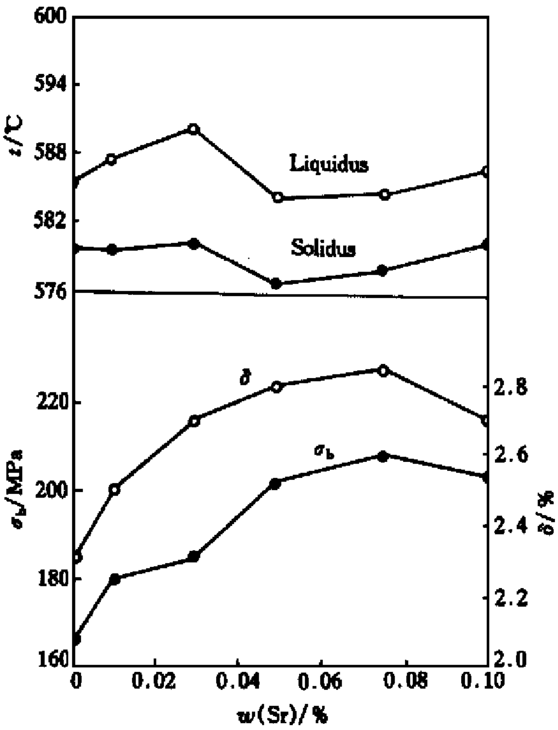

Fig.4 Relationship between crystallization point and mechanical properties of Al-12%Si + Sr alloy and addition quantity of Sr

5 CONCLUSIONS

1) As an effective method to improve the properties of alloy, modification not only played an important role during solidification, but also showed a special effect on improving the microstructure of melt. Modification element has brought into effect when the alloy was in liquid state.

2) As modification element was added, SRO arrangement and mean coordination number would change. Correspondingly, the composition of concentration fluctuation in melt would change too and some zigzag change appeared on the curve of concentration-physical characteristics.

3) Corresponding to the change of physical characteristics of the melt, the solidification structure of alloy changed, and the pattern of eutectic Si became finer and more homogenous and the branches grew very heavy.

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