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Specific heat of superheated Al-10Sr alloy melts①

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[Abstract] The specific heat of superheated Al-10Sr melts was determined at different heating rates between 1 K/min and 20 K/min using a differential scanning calorimeter (DSC). As a whole, the specific heat increases with increasing temperature. A hump is observed on the specific heat curve at the temperature corresponding to the phase boundary temperature dependent on heating rate. Moreover, the hump shifts to higher temperature in the measured temperature range from about 840 ℃ to 890 ℃ with increasing heating rate. At certain temperature in the higher superheated zone, the specific heat of the melt as a function of temperature shows a sharp rise. The result indicates that disorder zone fraction begins to increase while atom clusters fraction decreases at the breaking temperature.

[Key words] superheat; Al-10Sr alloy melts; specific heat; heating rate; quasi-polycrystalline modeling
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1 INTRODUCTION

The Al-Sr master alloy system is one of the new-type modifier which can improve the microstructures and enhance mechanical performances. For example, it can promote the formation of fibrous silicon by retarding the growth rate of silicon. It has been found that the difference of microstructures in Al-Sr master alloys resulted in different modifying structure and properties of modified Al-Si alloys[1~4]. Compared with ingot master alloys, the modifying effect of electrolytic and rapidly solidified Al-Sr master alloys increased by 40% and 50%, respectively[5].

The thermodynamic properties are useful for the production, application and theoretical study of alloys[6]. At the same time, specific heat is one of the most fundamental thermodynamic properties of matter. Calculations of change in enthalpy or entropy of a substance with temperature require a knowledge of the temperature dependence of heat capacity[7]. Temperature dependence of the specific heat may be due to the change in the chemical short-range order associated with the chemical bonds[8]. With respect to high melting-point metals at temperatures above 1000K, there is a little information available on this metastable regime[9]. The heating rate strongly affects the extent of liquid diffusion. In this paper, we mainly report the results of specific heat measurements for the superheated Al-Sr alloy melts at different heating rates between 1 K/min and 20 K/min. And the mechanisms are also discussed.

2 EXPERIMENTAL

The samples were prepared by molten salt electrolysis pure aluminum melt as cathode and $SrCl_2$-KCl as electrolyte. The enthalpy of fusion ΔH and the specific heat C_p of liquid phases were measured with a differential heat-flow calorimeter (Netzsch DSC 404) applying a method of comparison with sapphire as the reference standard. Calibration measurements on pure gold, nickel and indium samples showed that the deviations from literature values are smaller than 3% for specific heat and enthalpy of fusion values, which is adequate for this investigation. Al-10Sr in the sample crucible used for the specific heat measurements were about 40mg. The samples were heated to 1 200 ℃ at different heating rates of 1 K/min, 5 K/min, 10 K/min, 15 K/min, and 20 K/min, respectively. However, the cooling rates were all 20 K/min.

3 RESULTS

Fig. 1 shows the specific heat of superheated Al-10Sr melt at different heating rates as a function of temperature. A hump has been observed on the curve of C_p. It occurs at around 840 ℃, 850 ℃, 860 ℃, 870 ℃, 890 ℃ for different heating rates of 1 K/min, 5 K/min, 10 K/min, 15 K/min, 20 K/min, respectively. According to Al-Sr phase diagram, these temperatures correspond to the phase boundary temperature. It should be noted that the melting solid is constitutionally superheated and therefore the melting interface may develop Mullins-Sekerka type instabilities. Another possibility would involve the loss of local equilibrium. In general, loss of local equilibrium is normally associated with interface speed that approach a characteristic diffusive speed. Moreover, the hump shifts to higher temperature with increasing heating

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rates. The major portion of the sample melts on a hump initiated at a higher temperature.

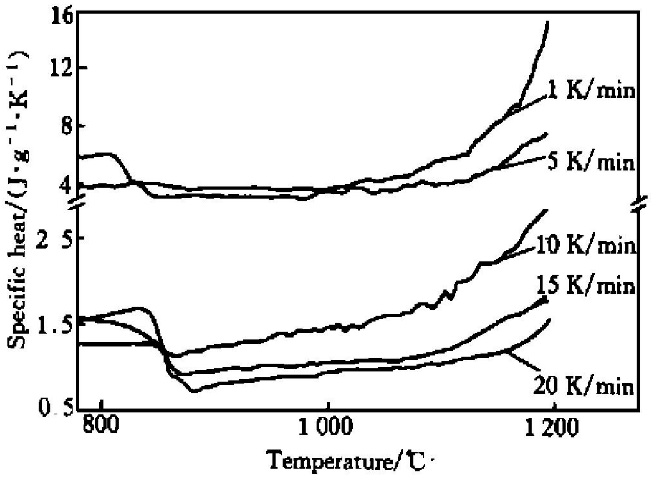

Fig. 1 Temperature dependence of specific heats for superheated Al-10Sr alloy melts at different heating rates

At higher temperatures, however, the specific heats for melts show a remarkable increase with increasing temperature. It can be seen from Fig. 1 that higher temperatures exceed the phase boundary temperatures by about 200 ℃. Moreover, the slower the heating rate is, the more remarkable the ascending trend is. Especially, the specific heat-temperature curves for the heating rate of 1 K/min and 10 K/min appear in a sharp increase trend at around 1 040 ℃.

The DSC curves obtained for Al-10Sr alloy melts at different heating rates are illustrated in Fig. 2. It still indicates that the increasing trend of DSC curves at lower heating rate becomes more remarkable than those at higher heating rates, and the superheated melts vary with heating rates in the temperature range from 880 ℃ to 1 200 ℃. The variation with heating rates depends on the structure of superheated melts.

Fig. 3 shows solidification enthalpy changes ΔH

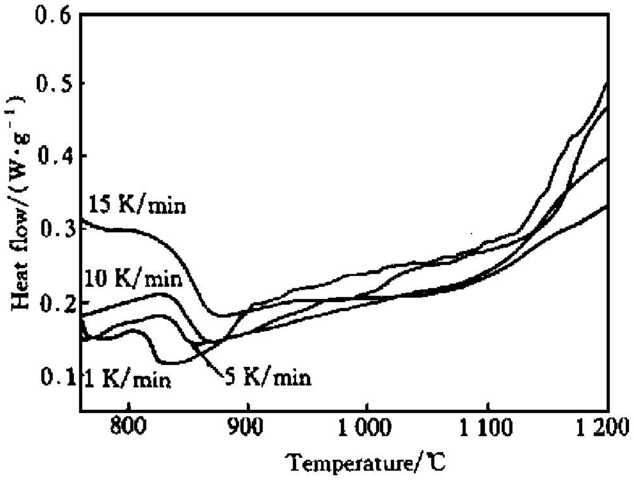

Fig. 2 DSC curves of superheated Al-10Sr alloy melts at different heating rates

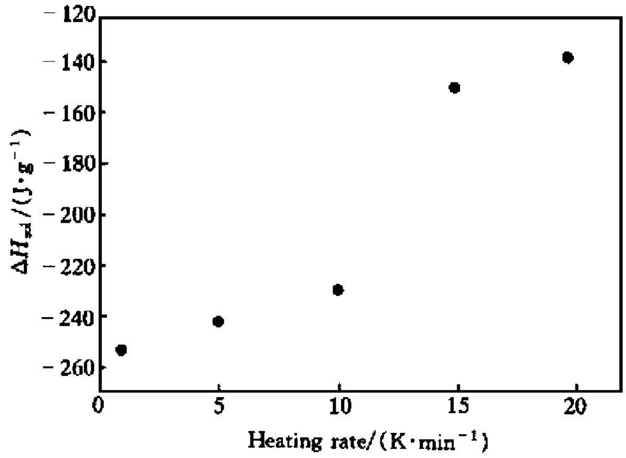

Fig. 3 Solidification enthalpy of Al-10Sr alloy melts at different heating rates

in solidifying process which is defined as

$$\Delta H = \int_{T_1}^{T_2} \tilde{c}_p \mathrm{d}T \qquad (1)$$

where T is absolute temperature, $\tilde{c}_p$ is specific heat of melt; and a, b, c are parameters. The ΔH reaches a maximum at the heating rate of 1 K/min. The ΔH at the heating rate of 20 K/min is smaller than that of the other heating rates, which shows that the atom disorders zones at higher heating rate still remain during solidification.

4 DISCUSSION

As seen in Fig. 1, different effects are observed in the temperature dependence of the specific heat for the Al-10Sr alloy melts at different heating rates.

Conservation of heat is described as

$$c_p T = c_p \frac{\mathrm{d}T}{\mathrm{d}t} + L \frac{\mathrm{d}f_\mathrm{L}}{\mathrm{d}t} \qquad (2)$$

where c_p and f_L are the specific heat and the heat of fusion, respectively. The parameter T is the imposed heating temperature prior to the start of melting[10].

The major portion of the alloy melts at a higher temperature, which increases towards the liquidus temperature with increasing heating rates. Accordingly, the hump shifts to higher temperature in the measured temperature range. Moreover, the majority of the enthalpy input is absorbed near the liquidus temperature. The high melting speed was obtained in these experiments at higher heating rate. An expression for the melting speed(v_m) is given by

$$v_\mathrm{m} = \frac{1}{3}\frac{R^3}{r_i^2}\frac{T}{[L/c_p + (T_\mathrm{l} - T_\mathrm{s})]} \qquad (3)$$

where R is the radius of spherical grains. The radius $r \in [0, R]$ is divided into a solid region $r \in [0, r_1]$ and a liquid region $r \in [r_1, R]$; the melting speed is obviously rapid enough to cause a loss of local equilibrium at the melt interface in the Al-Sr alloy system.

The increased heating rates may involve the loss of local equilibrium. The atmosphere temperature in the furnace is in excess of the inner temperature of the sample with increasing heating rate that results in the sample melting at higher temperature. Therefore, the hump shifts to higher temperature with increasing heating rate at the melting boundary temperature.

The quasi-polycrystalline modeling could be described for superheated melt to be composed of atom clusters and disorder zones with thermodynamically metastable characteristic. Atom clusters and disorder zones continuously locally disappear and regenerate because of energy fluctuation[11]. Any physical property of the metal melt, and Φ, is the comprehensive effects of atom clusters and disorder zones, which is described as

$$\Phi = \Psi_{pa3}\Phi_{pa3} + \Psi_{k\Lambda}\Phi_{k\Lambda} \quad (4)$$

where $\Phi_{k\Lambda}$ is partial properties of atom clusters, Φ_{pa3} is partial properties of disorder zones, Ψ_{pa3} and $\Psi_{k\Lambda}$ are relative fraction of disorder zones and atom clusters. The bulk fraction occupied by various atom clusters and disorder zones depends on the melt temperature. As the temperature reaches a given value, the atom clusters fraction decreases while disorder zones fraction increases with increasing temperature. Generally, the higher temperature, where c_p has a remarkable increase, corresponds to that the disorder zones fraction begins to increase, while atom clusters fraction begin to decrease, as shown in Fig. 1.

5 CONCLUSIONS

Temperature dependence of the specific heat for superheated Al-10Sr alloy melts is affected by the heating rate. As a whole, the measured c_p increases with increasing temperature. The temperatures corresponding to the phase boundary shift to the higher values in the temperature range from 840 ℃ to 890 ℃ with increasing heating rates. At certain higher temperature, the c_p value sharply increases. Moreover, the slower the heating rate is, the more remarkable the ascending trend is. The result denotes that the disorder zones fraction begins to increase, while atom clusters fraction begins to decrease at certain temperature.

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