Specific heat and related thermophysical properties of liquid Fe-Cu-Mo alloy

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The specific heat and related thermophysical properties of liquid Fe_{77.5}Cu₁₃Mo_{9.5} monotectic alloy were investigated by an electromagnetic levitation drop calorimeter over a wide temperature range from 1482 to 1818 K. A maximum undercooling of 221 K (0.13 T_m) was achieved and the specific heat was determined as 44.71 J·mol⁻¹·K⁻¹. The excess specific heat, enthalpy change, entropy change and Gibbs free energy difference of this alloy were calculated on the basis of experimental results. It was found that the calculated results by traditional estimating methods can only describe the solidification process under low undercooling conditions. Only the experimental results can reflect the reality under high undercooling conditions. Meanwhile, the thermal diffusivity, thermal conductivity, and sound speed were derived from the present experimental results. Furthermore, the solidified microstructural morphology was examined, which consists of (Fe) and (Cu) phases. The calculated interface energy was applied to exploring the correlation between competitive nucleation and solidification microstructure within monotectic alloy.

high undercooling, specific heat, monotectic alloy, thermophysical property, rapid solidification

The thermophysical properties of undercooled liquid metals and alloys have aroused great research interest in the field of materials physics in recent years^[1-6]. Specific heat, one of the most important thermophysical properties, has a significant influence on developing the current solidification theory^[3-6]. Due to the metastable state of undercooled alloy melts, the conventional experimental methods cannot be applied to determining their thermophysical properties. This results in great difficulty to obtain these important data. Therefore, the thermodynamic research of highly undercooled metals and alloys has been in the qualitative or semi-quantitative state.

Up to now, the experimental data for undercooled metals and alloys are still very scarce, although there have been some reports. In the recent literature, only the measurements of some pure metals and simple binary alloys are available. For monotectic alloys, the second liquid phase L_2

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always acts as the leading phase to nucleate owing to the lower liquid/liquid interface energy when temperature drops to their monotectic temperatures. Once L_2 phase begins to nucleate, the local concentration is favorable for the nucleation of solid phase, resulting in great difficulty to obtain a large undercooling. Therefore, the investigations on the thermophysical properties of monotectic alloys are seriously limited due to the lack of fundamental undercooled data. Electromagnetic levitation can avoid the contamination from crucible walls and obtain a high degree of undercooling. Meanwhile, the drop calorimetric method is applicable to specific heat measurements^[4–8].

Fe-Cu-Mo ternary alloy is a typical monotectic system and has a good prospect for industrial applications. The objective of this work is to determine the specific heat of undercooled liquid $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ ternary alloy using the drop calorimetric method in combination with electromagnetic levitation. The related thermophysical properties, including the excess specific heat, thermal diffusivity, thermal conductivity and sound speed, are derived on the basis of the experimental results. And their temperature dependence is also revealed by theoretical predictions. Furthermore, the rapid solidification of ternary monotectic alloy is investigated under high undercooling conditions.

1 Experimental procedure

$\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ alloy samples were prepared from 99.999% pure Fe, 99.999% pure Cu and 99.999% pure Mo in an arc melting furnace and each sample had a mass of 0.85 g. The experiments were performed by an electromagnetic levitation facility, which was evacuated to 10^{-5} Pa and back-filled with a mixed gas of argon, helium and hydrogen in the volume ratio of 6:3:1. During the experiment, the sample was levitated and melted by rf induction heating. The temperature was monitored by an infrared pyrometer. A He gas flow refrigerated by liquid nitrogen was blown toward the sample to achieve high undercooling. When an ideal undercooling was attained, the gas flow rate was adjusted to maintain the alloy melt at this undercooling for about 5 s. Then, the power of the rf induction heating was switched off and the levitated sample would drop into an adiabatic copper calorimeter. The temperature difference between the calorimeter shell and the calorimeter block was monitored by a Eurotherm 818P4 unit. When the temperature of the calorimeter shell was higher or lower than that of the calorimeter block, the resistance heating would begin or stop to ensure that the calorimeter is practically adiabatic. The temperature rise of the adiabatic copper block was measured by Pt100 resistance.

Under adiabatic conditions, after determining the temperature rise of calorimeter block, the enthalpy change of liquid alloy is determined by

$$H(T) - H(293) = \frac{M}{m} C_{P1} \delta T + C_{P2} (T_e - 293) + \frac{Q_{\text{lost}}}{m}, \quad (1)$$

where $H(T)$ is the enthalpy of the sample in the superheated or undercooled state, $H(293)$ the reference enthalpy at 293 K, T the temperature of the alloy sample when dropping, M the mass of calorimeter block, C_{P1} the specific heat of calorimeter block which is calibrated as $0.386 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ in advance, m the mass of the sample, C_{P2} the specific heat of the sample at 293 K, $\delta T = T_e - T_0$ the temperature rise of the calorimeter, T_e the equilibrium temperature of the calorimeter, T_0 the room temperature, and Q_{lost} the heat loss. This heat loss during dropping cannot be absorbed by the calorimeter, therefore, it should be compensated in eq. (1). Considering the heat loss mainly resulting from thermal convection and heat radiation, Q_{lost} can be expressed as

$$Q_{\text{lost}} = A\varepsilon_h\gamma(T^4 - T_0^4) + A(T - T_0)\int_0^{t_D}\alpha_c dt, \quad (2)$$

where A is the surface area of the sample, ε_h the emissivity, γ the Stefan-Boltzmann constant, t_D the drop time, and α_c the heat transfer coefficient of the inert gas, which is determined by

$$\alpha_c = \frac{\lambda_g}{D}[2 + 0.6(v_r D \rho_g / \eta_g)^{1/2}(c_g \eta_g / \lambda_g)^{1/3}], \quad (3)$$

where λ_g is the thermal conductivity, ρ_g the density, η_g the viscosity, D the diameter of the liquid sample, and v_r the drop velocity.

When the enthalpy change of the sample is determined by eqs. (1)–(3), the specific heat can be derived directly by

$$C_{\text{PL}} = \frac{\partial[H(T)]}{\partial T} = \frac{\partial[H(T) - H(293)]}{\partial T}. \quad (4)$$

It can be seen that the specific heat can be obtained just from the temperature rise of the calorimeter without considering the detailed mechanism of phase transformation during solidification.

2 Results and discussion

2.1 Specific heat of undercooled liquid alloy

The specific heat of liquid $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ ternary monotectic alloy was determined. According to eqs. (1)–(4), the experimental results of this alloy are presented in Figure 1, which gives the relationship between the enthalpy change and temperature within the temperature range from 1482 to 1818 K. A maximum undercooling of $\Delta T_{\text{max}} = 221$ K ($0.13 T_L$) was obtained. The enthalpy change shows a good linear relationship with temperature. The following equation can be derived after the regression of the measured data:

$$H(T) - H(293) = 97.96 + 44.71T \quad (\text{J} \cdot \text{mol}^{-1}). \quad (5)$$

Figure 1 Measured enthalpy difference as a function of temperature.

Accordingly, by the definition of eq. (4), the specific heat of liquid $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ ternary monotectic alloy in the experimental temperature regime is

$$C_{\text{PL}} = 44.71 \quad (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}). \quad (6)$$

After an extensive survey of the relevant literature, it was found that no reference data is available to be compared with the present experimental results due to great experimental difficulty. For pure Fe, Cu and Mo, the specific heat has been measured previously. Their values at melting points are 44.40, 31.46 and 54.69 J·mol⁻¹·K⁻¹, respectively. By comparing the specific heat of liquid Fe_{77.5}Cu₁₃Mo_{9.5} ternary monotectic alloy with those of pure Fe, Cu and Mo, it is evident that this value is lower than that of pure Mo but larger than those of pure Fe and Cu. According to Neumann-Kopp's rule, the specific heat was also calculated by using the values of pure metals, which is equal to 43.7 J·mol⁻¹·K⁻¹. The measured result is a little larger than this approximately estimated result.

Previously, the experimental investigations have been done on pure metals and binary alloys. It revealed generally that, for pure metals with low melting points, the specific heat of undercooled melts increases with the decreasing temperature. This kind of metals includes Bi, In, Sn, etc.^[9]. Their C_{PL} values are usually measured by DSC method. Al is an exceptional case because its C_p value keeps roughly constant although its T_m is not high^[10]. However, for pure metals whose melting temperatures are higher than 873 K, the specific heat is nearly independent of temperature in a large temperature regime from normal liquid to undercooled state. Co, Ni, Fe, Zr, Mo, etc. belong to this case and the electromagnetic levitation drop calorimeter is frequently employed to measure their C_{PL} values due to its effective heating and large undercooling. For binary alloys, although the available data are still scarce, some experimental results seem to show a similar temperature-independent variation tendency according to their melting temperatures, such as Ni-Cu, Ni-Fe, Ti-Al and Co-Mo alloys^[5-7]. Ni_{70.2}Si_{29.8} alloy is an exceptional case although its melting temperature is up to 1488 K^[4]. For Fe_{77.5}Cu₁₃Mo_{9.5} ternary monotectic alloy, its specific heat is also nearly independent of temperature within the undercooling regime of 221 K in the experiments. It seems that this is in good agreement with the above inferences. It should be pointed out that the C_{PL} values of alloys should be the function of composition. Only one alloy was investigated from Fe-Cu-Mo ternary system in this work, therefore, the relationship between the specific heat and composition of Fe-Cu-Mo alloy should be investigated further. And the temperature dependence of specific heat for ternary alloys should also be given more attention.

Several models have been developed previously to describe the relationship between specific heat and undercooling owing to the limited experimental data on specific heat of undercooled melts. One is the well-known model of Turnbull^[11] who proposed that the specific heat value of undercooled melt is approximately equal to that of crystalline solid at the same temperature. The excessive specific heat is, therefore, equal to zero:

$$\Delta C_{PL} = 0. \quad (7)$$

Thompson and Spaepen^[12] thought that the excessive specific heat value ΔC_{PL} is equal to the ratio of enthalpy difference ΔH_m divided by the melting point temperature T_m :

$$\Delta C_{PL} = \frac{\Delta H_m}{T_m}. \quad (8)$$

On the basis of the model of Thompson and Spaepen, Battezzati and Garrone^[13] gave another equation:

$$\Delta C_{PL} = 0.8 \times \frac{\Delta H_m}{T_m}. \quad (9)$$

A further proposal is Dubey-Ramachandrarao's model^[14], which is based on the free volume model of liquids and yields

$$\Delta C_{PL} = \Delta C_P^m \left(\frac{2T^3 + 3T^2\Delta T - \Delta T^3}{2T^3} \right), \quad (10)$$

where the ΔC_P^m value is equal to that in eq. (8).

The excessive specific heat was computed as a function of undercooling, as shown in Figure 2. The calculated results by Turnbull, Thompson and Spaepen, and Battezzati and Garrone are equal to 0, 9.9 and 7.9 J · mol⁻¹ · K⁻¹, respectively. With the increase of undercooling, the results from both experimental data and Dubey-Ramachandrarao's model become larger and larger. Although there exists a deviation of about 4 J · mol⁻¹ · K⁻¹, the increasing tendencies with undercooling are in good agreement.

Figure 2 Excessive specific heat versus undercooling.

2.2 Related thermodynamic properties

Furthermore, the present measured specific heat of undercooled Fe_{77.5}Cu₁₃Mo_{9.5} ternary monotectic alloy can be applied to computing the relevant thermodynamic properties, such as the enthalpy change ΔH_{LS} , the entropy change ΔS_{LS} and the Gibbs free energy difference ΔG_{LS} etc. They are of great importance in the research on crystal nucleation and growth. After determining the specific heat, they are expressed as

$$\Delta H_{LS} = \Delta H_m - \int_T^{T_m} \Delta C_{PL}(T) dT, \quad (11)$$

$$\Delta S_{LS} = \frac{\Delta H_m}{T_m} - \int_T^{T_m} \frac{\Delta C_{PL}(T)}{T} dT, \quad (12)$$

$$\Delta G_{LS} = \Delta H_{LS} - T \Delta S_{LS}. \quad (13)$$

According to the experimental results and the above eqs. (11)–(13), the enthalpy change, the entropy change, and the Gibbs free energy difference are calculated as functions of undercooling. The results are given in Figure 3. With the increase of undercooling, ΔH_{LS} and ΔS_{LS} decrease, whereas ΔG_{LS} increases. This reveals that the thermodynamic driving force of phase transformation becomes larger and larger with undercooling. In order to compare the thermodynamic properties derived from the experimental result with those obtained by the previous models, ΔH_{LS} , ΔS_{LS} and ΔG_{LS} are calculated as functions of undercooling. Figure 3 gives the calculated results by

Turnbull's model as an example, which are shown as the dashed line. With the increase of undercooling, the deviations between the experimental solid line and the approximate dashed line become larger and larger. For ΔH_{LS} and ΔS_{LS} , it is rather remarkable. The calculated values by the conventional model lead to almost constant ΔH_{LS} and ΔS_{LS} . This cannot reflect the actual situation of the change in enthalpy and entropy during solidification. For ΔG_{LS} , although there seems to be only a little difference, it has a remarkable effect on the nucleation kinetics. This indicates that the calculated results by traditional estimation methods can only describe the solidification process under low undercooling conditions. Only the experimental results can reveal the reality under high undercooling conditions.

Figure 3 Calculated thermodynamic properties versus undercooling. (a) Enthalpy change; (b) entropy change; (c) Gibbs free energy difference.

2.3 Thermal conductivity and thermal diffusivity

Based on the experimental measurements, some other thermophysical parameters can be derived from the C_{PL} value. The thermal diffusivity, κ , as a function of temperature can be predicted by the following relation:

$$\kappa = \lambda / (\rho \cdot C_{PL}), \quad (14)$$

where λ is the thermal conductivity, and ρ the density. Wiedemann-Franz-Lorenz law describes the relationship between thermal conductivity and electrical resistivity ρ_e , which reads^[15]

$$\lambda \cdot \rho_e / T = 2.45 \times 10^{-8} \text{ (W} \cdot \Omega \cdot \text{K}^{-2}\text{)}. \quad (15)$$

Owing to the lack of the experimental data for $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ alloy, its electrical resistivity is derived by Neumann-Kopp's rule with the data of pure Fe, Cu and Mo, which is written by

$$\rho_e = 90.8 + 0.013T \text{ (}\mu\Omega \cdot \text{cm}\text{)}. \quad (16)$$

According to eqs. (15) and (16), the thermal conductivity can be derived, which is expressed as

$$\lambda = \frac{2.45T}{90.8 + 0.013T} \text{ (W} \cdot \text{K}^{-1} \cdot \text{m}^{-1}\text{)}. \quad (17)$$

The calculated thermal conductivities are presented in Figure 4. There exists an approximately linear relation between λ and T . With the increase of temperature, λ also increases.

Figure 4 Thermal diffusivity and thermal conductivity versus temperature.

To obtain the thermal diffusivity, the density of $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ alloy is essential. The following relationship by Eötvös and Wiedeman can be employed to predict the density from surface tension^[16]:

$$\sigma \left(\frac{M_r}{\rho} \right)^{\frac{2}{3}} = K_c (T_c - T), \quad (18)$$

where M_r is the relative atomic mass, K_c a constant equal to $6.4 \times 10^{-8} \text{ (J} \cdot \text{K}^{-1})$ for liquid metals, and T_c the critical temperature at which the liquid-gas interface disappears. The surface tension of this alloy has been determined to be $\sigma = 1.588 - 3.7 \times 10^{-4} (T - T_m) \text{ (N} \cdot \text{m}^{-1})$ ^[17]. Thus, the temperature dependent density of liquid $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ alloy is obtained and expressed by

$$\rho = 7.5 - 1.49 \times 10^{-3} (T - T_m) \text{ (g} \cdot \text{cm}^{-3}). \quad (19)$$

In terms of the results of eqs. (6), (17) and (19), the thermal diffusivity is calculated and presented in Figure 4. A linear relationship yields

$$\kappa = -8.5 \times 10^{-7} + 4.4 \times 10^{-9} T \text{ (m}^2 \cdot \text{s}^{-1}). \quad (20)$$

In the governing equation for the temperature field in liquid alloys, the thermal diffusivity plays an important role in investigating their thermal history. It is always taken as a constant in traditional calculations. However, it is actually a function of temperature for the present alloy according to eq. (20). Therefore, it is essential to determine their thermophysical properties for the theoretical investigations of rapid solidification.

2.4 Sound speed in undercooled alloy melt

The sound speed is another important physical parameter, which is of importance in analyzing rapid crystal growth. On the basis of the density and the specific heat, the sound speed of liquid $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ alloy, u , can be predicted by^[18]

$$u = \left(\frac{1}{\rho k_s} \right)^{1/2}, \quad (21)$$

where k_s is isentropic compressibility, which is expressed as^[18]

$$k_s = \frac{\alpha^2 V_m T C_V}{C_{PL} (C_{PL} - C_V)}, \quad (22)$$

where V_m is the molar volume, C_V the specific heat at a constant volume^[18], and α the isobaric thermal expansivity, which is described as

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p. \quad (23)$$

Based on eqs. (6), (19), and (21)–(23), the sound speed of liquid $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ alloy is calculated (Figure 5). A polynomial expression between the sound speed and temperature yields

$$u = 11912 - 5.7T + 9.5 \times 10^{-4} T^2 \quad (\text{m} \cdot \text{s}^{-1}). \quad (24)$$

From the above relationship, it can be seen that the sound speed decreases with the increase of temperature. In the TMK eutectic growth and LKT/BCT dendritic growth models^[19,20], the sound speed in alloy melt plays an important role. Especially, the kinetic undercooling increases steeply under a high undercooling condition. The kinetic growth coefficient is closely related to the sound speed. Previously, it is always taken as a constant in the calculation of the kinetic growth coefficient. However, it is in effect a function of temperature for the present alloy according to eq. (24).

Figure 5 Sound speed in undercooled alloy melt versus temperature.

2.5 Solidified microstructural morphology

In order to clarify the phase constitution of the $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ alloy solidified at different undercoolings, XRD analysis is employed to identify the different phases, as shown in Figure 6(a). It can be seen that the as solidified samples consist of (Fe) and (Cu) solid solutions. Only a very tiny diffraction angle offset occurs due to the solid solubility difference inside crystal grains at different undercoolings. Usually, macrosegregation comes into being when monotectic alloys solidify due to the large density difference. In the present experiments, no remarkable macrosegregation takes place, which is effectively suppressed by the containerless processing with electromagnetic levitation.

Under equilibrium conditions, the monotectic transformation of $L_1 \rightarrow (\text{Fe}) + L_2$ occurs when temperature drops to 1703 K. If solidification takes place at low undercooling, the morphology is characterized by very coarse and well branched (Fe) dendrites with interdendritic and intradendritic L_2 phase. With the increase of undercooling, (Fe) dendrites are refined and monotectic cells

form. They are characterized by fine spherical or rod-like $L_2(\text{Cu})$ phases homogenously distributed in the matrix of (Fe) phase, as shown in Figure 6(b). The $L_2(\text{Cu})$ and (Fe) phases grow in a coupled way during the formation of monotectic cells. Generally, the second liquid L_2 phase always acts as the leading phase to nucleate due to the smaller interface energy between the parent liquid phase and the second liquid phase.

In order to clarify this point of view, the interface energy of liquid/solid σ_{LS} and liquid/liquid $\sigma_{\text{L}_1\text{L}_2}$ was calculated according to the interface energy model^[21], as illustrated in Figure 7. σ_{LS} increases with the increase of undercooling, whereas $\sigma_{\text{L}_1\text{L}_2}$ decreases with the increase of undercooling. The $\sigma_{\text{L}_1\text{L}_2}$ value is on the magnitude of $10^{-2} \text{ J} \cdot \text{m}^{-2}$ and much smaller than that of σ_{LS} . According to the nucleation theory, the nucleation work is a function of σ^3 , and thus, liquid-liquid nucleation work is much smaller than liquid-solid nucleation work, which is one of the most important reasons why liquid-liquid nucleation is easier than liquid-solid nucleation. Once the $L_2(\text{Cu})$ phase begins to nucleate, the local composition is favorable for the nucleation of (Fe) phase. This results in the subsequent rapid solidification.

Figure 6 XRD analysis and monotectic microstructure of as solidified $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ alloy.

Figure 7 Interface energy versus undercooling.

3 Conclusions

The specific heat of undercooled liquid $\text{Fe}_{77.5}\text{Cu}_{13}\text{Mo}_{9.5}$ monotectic alloy was measured by com-

binning the electromagnetic levitation technique with an adiabatic drop calorimeter. A maximum undercooling of 221 K ($0.13T_L$) was achieved in the experiments. It was found that the enthalpy change shows an almost linear relationship within a wide temperature range from 1482 to 1818 K and the specific heat is determined to be $44.71 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The excessive specific heats were calculated on the basis of experimental results and the previous theoretical models for comparison. Only the values from Dubey-Ramachandrarao's model and experimental results have the similar increasing tendency with undercooling. Furthermore, the enthalpy change, the entropy change and the Gibbs free energy difference were also calculated, and they were compared with the traditional approximate models. It was revealed that the traditional approximate values of thermodynamic properties cannot reflect the reality during the rapid solidification. Meanwhile, the other thermophysical properties, including the thermal diffusivity, thermal conductivity and sound speed, were derived according to the present experimental results. All of them are dependent on undercooling. The phase constitution and microstructure morphology were examined. XRD analysis indicates that the as solidified samples consist of (Fe) and (Cu) solid solutions. The interface energy of liquid/solid and liquid/liquid was calculated and employed to explain the correlation between competitive nucleation and solidification microstructure within monotectic alloy.

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