Thermophysical properties of undercooled liquid Co–Mo alloys

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Abstract

Using electromagnetic levitation in combination with the oscillating drop technique and drop calorimeter method, the surface tensions and specific heats of undercooled liquid Co–10 wt% Mo, Co–26.3 wt% Mo, and Co–37.6 wt% Mo alloys were measured. The containerless state during levitation produces substantial undercoolings up to 223 K (0.13TL), 213 K (0.13TL) and 110 K (0.07TL) respectively for these three alloys. In their respective undercooling ranges, the surface tensions were determined to be 1895/C0.31(T/L C0 1744), 1932/C0.33(T/L C0 1682), and 1989/C0.34(T/L C0 1607) mN m−1. According to the Butler equation, the surface tensions of these three Co–Mo alloys were also calculated, and the results agree well with the experimental data. The specific heats of these three alloys are determined to be 41.85, 43.75 and 44.92 J mol−1 K−1. Based on the determined surface tensions and specific heats, the changes in thermodynamics functions such as enthalpy, entropy and Gibbs free energy are predicted. Furthermore, the crystal nucleation, dendrite growth and Marangoni convection of undercooled Co–Mo alloys are investigated in the light of these measured thermophysical properties.

§1. Introduction

Liquids can be deeply undercooled below their freezing temperature TL, as has been reported by Fahrenheit (1724) and Turnbull (1950). Owing to the metastable state of undercooled liquid, the thermophysical properties, such as specific heat and surface tension, are less understood than the normal liquid. Therefore, the thermophysical properties in the undercooled regime are of great research interest (Fecht and Jonson 1988, Sommer 1990, Rajeswari and Raychaudhuri 1993, Egry et al. 1995, Wang et al. 2002). With the specific heat, one can calculate the enthalpy change ΔHLS, the entropy change ΔSLS and thus the Gibbs free energy difference ΔGLS between the undercooled liquid and crystalline solid during the solidification process. Knowledge of C_p(ΔT) also gives some information about the velocity of crystal growth (Ivantsov 1947), the short-range order in undercooled liquid (Nelson et al. 1982), the glass transition trend (Battezzati and Baricco 1987, Battezzati 1990) and the glass transition temperature (Kauzmann 1948). The surface tension value and its temperature dependence are essential for describing Marangoni flow, which affects the crystal–melt interface shape (Campbell et al. 2001) and contributes to the

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formation of the so-called ‘spoke pattern’ on the melt surface during the growth of a single crystal by the Czochralski method (Przyborowski et al. 1995). Meanwhile, the viscosity of undercooled liquid can be theoretically predicted from the surface tension. This together with the Gibbs free energy difference, makes the prediction of nucleation rate as a function of undercooling possible.

So far, there have been only a few studies on the thermophysical properties of undercooled liquid metals and alloys of high melting point because of the experimental difficulties. At high temperatures, especially when the temperature exceeds 1273 K, any physical contact with the container wall will induce immediate nucleation, and thus the metastable undercooling region is hard to access. In this case, the containerless processing technique and non-contact measurement methods, which will not disturb the metastable state of undercooling, have to be developed. Electromagnetic levitation is an elegant way to process liquid metals in a containerless way, which avoids surface contamination of the sample and can keep the undercooling state for a long duration. Electromagnetic levitation in combination with oscillating-drop method can measure the surface tension of undercooled liquid, while its combination with the drop calorimeter method provides possibilities to determine the specific heat of undercooled liquid. In recent years, these two methods have been widely applied to determine the surface tension (Egry et al. 1995, 1996) and specific heat of undercooled liquid (Sommer 1990, Barth et al. 1993, Wang et al. 2002).

Co–Mo binary alloy is attracting research interest in that it is an important constituent subsystem of many Co-based superalloys, which can find many applications in aerospace industry. This article deals with the measurement of the surface tensions and the specific heats of highly undercooled Co–10 wt% Mo, Co–26.3 wt% Mo and Co–37.6 wt% Mo alloys. In addition, on the basis of the measured thermophysical properties, the Gibbs free-energy difference and the relative nucleation rate are calculated for a comparison with the calculated results by several approximate models for $\Delta G_{1S}$. Meanwhile, the dendrite growth and Marangoni convection of the Co–Mo alloy system are investigated.

§ 2. Experimental procedure

Experiments were performed with an electromagnetic levitation facility, as illustrated in figure 1. A 30 kW high frequency generator operating at 300–450 kHz is used for power supply, which is connected to a conically shaped coil. The levitation coil was placed in a vacuum chamber, which is evacuated to about $1 \times 10^{-4}$ Pa and backfilled with a gas mixture of Ar, He and H$_2$. Co–Mo master alloys were prepared from 99.997% pure Co and 99.97% pure Mo in an ultrahigh-vacuum arc melting furnace and each sample has a mass of 0.8–0.9 g. During experiments, the sample was levitated and melted by inductive heating. Then He with an addition of 25% H$_2$, which flowed through liquid N$_2$, was blown towards the sample in order to achieve high undercooling. When the liquid was undercooled to an expected temperature, the flow rate of the blowing gas was adjusted to keep this undercooling for 15–40 s. The temperature was recorded with an infrared pyrometer. The surface oscillations are detected with a photodiode focused on the top side of the sample through a spectroscope. Having passed a low-pass filter with a threshold of 110 Hz and an amplifier, the signal was recorded with a sampling rate of 800 Hz to avoid aliasing. After analogue-to-digital conversion with a sampling rate of up to 100 kHz, fast Fourier transformation is performed off line in order to obtain the oscillation spectra.
The surface tension is calculated according to the famous Rayleigh (1987) equation:
\[
\gamma = \frac{3\pi M \omega_R^2}{8}.
\] (1)

Under terrestrial levitation conditions the sample is distorted from its perfect spherical shape owing to gravity and the existence of magnetic field. As a result, the expected single Rayleigh frequency \(\omega_R\) will shift and split into five peaks in the spectrum. Cummings and Blackburn (1991) considered the influence of the magnetic field and derived the following frequency sum rule to obtain the Rayleigh frequency:
\[
\omega_R^2 = \frac{1}{5} \sum_{m=-2}^{2} \omega_{2,m}^2 - 2\overline{\omega}_t^2
\] (2)

with
\[
\overline{\omega}_t^2 = \frac{1}{3} (\omega_x^2 + \omega_y^2 + \omega_z^2),
\] (3)

where \(\omega_{2,m}\) are the frequencies of the surface oscillation for the \(l = 2\) mode; \(\omega_x, \omega_y\) and \(\omega_z\) are the translational frequencies of the droplet’s centre of mass along the direction of the axis \(x, y\) and \(z\) axes respectively and \(\overline{\omega}_t\) is the mean translational frequency, which is often 4–7 Hz according to the shape of coil, the mass of the droplet and the levitation condition.

Figure 2 is a typical oscillation spectrum of a levitated droplet. Apparently, the Rayleigh frequency is split into five peaks around 43 Hz. The lower-lying set of peaks corresponds to the translational frequency. Such spectra were obtained at different temperatures, the surface tension being determined according to equation (2).

Having recorded the oscillation signal, the power of rf induction heating was switched off and the sample was dropped into an adiabatic Cu calorimeter, whose mass is 1317.5 g. The details of the adiabatic calorimeter has been described elsewhere (Barth et al. 1993). Under adiabatic condition, after determining the temperature change \(\delta T\) of the calorimeter block, the enthalpy change of the undercooled melt is given by:
\( H(T) - H(293 \text{ K}) = \frac{M}{m} C_{PS} C_{Cu} \delta T + C_{PS}^{293 \text{ K}} (T_e - 293) + \frac{Q_{\text{lost}}}{m}, \) \( (4) \)

where \( H(T) \) is the enthalpy of the levitated droplet, \( H(293 \text{ K}) \) the reference enthalpy at 293 K, \( M \) the mass of calorimeter block, \( C_{PS} C_{Cu} \) the specific heat of calorimeter block which is calibrated as 0.386 Jg\(^{-1}\)K\(^{-1}\), \( C_{PS}^{293 \text{ K}} \) the specific heat of the sample at 293 K, \( m \) the mass of the sample, \( T_e \) the final equilibrium temperature of calorimeter block and \( Q_{\text{lost}} \) the heat loss of the droplet during its fall into the calorimeter. Considering the convection and thermal radiation, \( Q_{\text{lost}} \) can be expressed as

\[ Q_{\text{lost}} = A \varepsilon_b \sigma (T^4 - T_0^4) t_D + A(T - T_0) \int_0^{t_D} \alpha_c \, dt. \] \( (5) \)

Here, \( A \) is the surface area of the sample, \( \varepsilon_b \) the emissivity, \( \sigma \) the Boltzmann constant, \( T \) the temperature before the sample dropping, \( T_0 \) the ambient temperature, \( t_D \) the drop time, about 0.2 s, and \( \alpha_c \) the heat transfer coefficient of inert gas. When the enthalpy change of the sample is determined from equation (4), the specific heat of the sample can be derived directly from:

\[ C_P^L = \frac{\partial [H(T)]}{\partial T} = \frac{\partial [H(T) - H(293 \text{ K})]}{\partial T}. \] \( (6) \)

\section*{§3. Results and discussion}

Figure 3 is the upper left part of the Co–Mo binary alloy phase diagram, in which the locations of the selected compositions are indicated. Co–10 wt% Mo and Co–26.3 wt% Mo are single-phase alloys and Co–37.6 wt% Mo is a two-phase eutectic alloy. During experiments, these three Co–Mo alloys were undercooled by up to 223 K (0.13\( T_L \)), 213 K (0.13\( T_L \)) and 110 K (0.07\( T_L \)) respectively. Within their respective temperature ranges, the surface tensions and the specific heats were measured.
Figure 3. Selected compositions and obtained undercoolings designated in the Co–Mo binary alloy phase diagram.

3.1. Surface tension of undercooled Co–Mo alloys

The measured surface tensions of Co–10 wt% Mo, Co–26.3 wt% Mo and Co–37.6 wt% Mo alloys are demonstrated in figure 4. Obviously, the surface tension increases continuously and linearly with decreasing temperature. Data analysis shows that

\[
\sigma_{\text{Co–10 wt\% Mo}} = 1895 - 0.31(T - 1744) \text{ mN m}^{-1}
\]

(7)

\[
\sigma_{\text{Co–26.3 wt\% Mo}} = 1932 - 0.33(T - 1682) \text{ mN m}^{-1}
\]

(8)

\[
\sigma_{\text{Co–37.6 wt\% Mo}} = 1989 - 0.34(T - 1607) \text{ mN m}^{-1}
\]

(9)

Figure 5 illustrates the relationship between the surface tension and the weight fraction of Mo in these three alloys. To reveal the changing tendency of the surface tension with increasing Mo content, the surface tension data of liquid pure Co (Han et al. 2002) is also added to figure 5. From the \(\sigma–C\) curves at different temperatures, it is seen that the surface tension does not increase linearly with increasing the weight fraction of Mo but follows a two-order polynomial function relationship.

To evaluate the measured surface tension data, the Butler (1935) equation was applied to calculate the surface tensions of the Co–Mo alloys. Butler equation is expressed for the surface tension \(\sigma\) of any A–B binary liquid solution as follows:

\[
\sigma = \sigma_A + \frac{RT}{A_A} \ln \left(1 - N_B^S \right) + \frac{1}{A_A} G_{E_S}^A(T, N_B^S) - \frac{1}{A_B} G_{E_B}^A(T, N_B^B)
\]

(10)

with

\[
A_X = 1.901N_0^{1/3}V_X^{2/3}
\]

(11)

where \(R\) is the gas constant, \(T\) the temperature, \(\sigma_X\) is the surface tension of pure liquid X (X = A or B), \(N_0\) is Avogadro’s constant, \(V_X\) is the mole volume of liquid X, \(N_X^S\) and \(N_X^B\) are mole fractions of a component X in the surface phase and the bulk phase, and \(G_{E_S}^X(T, N_B^S)\) and \(G_{E_B}^X(T, N_B^B)\) are partial excess Gibbs energies of X.
in the surface phase and in the bulk phase respectively. For $G_X^{ES}(T, N_B^S)$, different models have been proposed, but they can be summarized as (Tanaka and Iida 1994)

$$G_X^{ES}(T, N_B^S) = \beta G_X^{EB}(T, N_B^S),$$

where $\beta$ is a parameter corresponding to the ratio of the coordination number $Z$ in the surface phase to that in the bulk phase, $Z^S/Z^B$. $\beta$ is often chosen as 0.75 or 0.83.
in the literature for liquid alloy. $G_{X}^{E}(T, N_{B}^{B})$ can be derived from $G^{E}(T, N_{B}^{B})$, which is often obtained from database or calculation of the phase diagram. For the Co–Mo binary alloy system (Davydov and Kattner 1999),

$$G_{Co-Mo}^{E} = X_{Co}X_{Mo}[(-7020.2 + 43.036T) + (6523.4 + 2.012T)(X_{Co} - X_{Mo})]. \quad (13)$$

From equations (10)–(13), and with the parameters listed in table 1, the surface tensions of Co–10 wt% Mo, Co–26.3 wt% Mo and Co–37.6 wt% Mo liquid alloys were calculated. It should be mentioned that in the literature there are two different surface tension values for liquid Mo at its melting point, namely 1.915 and 2.25 N m$^{-1}$. During calculations, these two values are both used for calculating the surface tension of Co–Mo alloys. The calculated results of these three alloys are superimposed on their respective $\sigma$–$T$ curves. Apparently, the determined surface tension of Co–10 wt% Mo agrees well with the calculated result, and the experimental results of Co–26.3 wt% Mo and Co–37.6 wt% Mo are a little lower, but within 1% deviation of the calculated results using $\sigma_{Mo} = 1.915 - 0.0003(T - T_{m})$, and within 2% deviation of the calculated value using $\sigma_{Mo} = 2.25 - 0.0003(T - T_{m})$.

Having obtained the surface tensions of Co–10 wt% Mo, Co–26.3 wt% Mo and Co–37.6 wt% Mo alloys, the viscosities of these three alloys can be predicted from the following expression (Egry 1993):

$$\eta = \frac{16}{15} \left( \frac{M}{kT} \right)^{1/2} \sigma, \quad (14)$$

where $M$ is the absolute atomic mass and $k$ the Boltzmann constant.

| Table 1. Thermophysical parameters of liquid Co and Mo used for the calculations. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| $T_{m}$ (K) | $\rho$ (kg m$^{-3}$) | $\sigma_{m}$ (Nm$^{-1}$) | $d\sigma/dT$ (Nm$^{-1}$ K$^{-1}$) |
| Co | 1766 | 7760 – 0.988($T - T_{m}$)$^{a}$ | 1.875$^{b}$ | –0.000 322$^{b}$ |
| Mo | 2880 | 9350 – 0.5($T - T_{m}$)$^{c}$ | 1.915$^{d}$; 2.25$^{c,d}$ | –0.000 30$^{c}$ |

$^{a}$ Campbells (1983).
$^{b}$ Han et al. (2002).
$^{c}$ Iida and Guthrie (1993).
$^{d}$ Keene (1993).
The predicted viscosities of these three alloys are illustrated in figure 6. To be compatible with the generally accepted formula for the temperature dependence of viscosity, namely \( \eta(T) = \eta_0 \exp(A/RT) \), a fit with an Arrhenius dependence of viscosity on temperature is used. Data regression shows that

\[
\eta_{10\text{wt}\%\text{Mo}} = 1.948 \exp\left(\frac{10947}{RT}\right),
\]

\[
\eta_{26.3\text{wt}\%\text{Mo}} = 1.967 \exp\left(\frac{11387}{RT}\right),
\]

\[
\eta_{37.6\text{wt}\%\text{Mo}} = 2.035 \exp\left(\frac{11456}{RT}\right).
\]

Apparently, the addition of the element Mo to a Co–Mo alloy will increase its viscosity. Owing to the lack of the viscosity data in the literature, deviation of the predicted viscosities from experimental data cannot be evaluated.

### 3.2. Specific heat of undercooled Co–Mo alloys

Figure 7 presents the relationships between the enthalpy change and the temperature of Co–10 wt\% Mo, Co–26.3 wt\% Mo and Co–37.6 wt\% Mo alloys. Within their respective temperature ranges, the enthalpy change shows a good linear relationship with the temperature. The linear regressions of the data for these three alloys are given by

\[
[H(T) - H(293 K)]_{10\text{wt}\%\text{Mo}} = -5303.4 + (41.85 \pm 1.51)T \text{ J mol}^{-1}
\]

\[
[H(T) - H(293 K)]_{26.3\text{wt}\%\text{Mo}} = -7261.0 + (43.75 \pm 1.79)T \text{ J mol}^{-1}
\]

\[
[H(T) - H(293 K)]_{37.6\text{wt}\%\text{Mo}} = -8174.4 + (44.92 \pm 1.67)T \text{ J mol}^{-1}
\]

As an example, table 2 listed the parameters necessary to calculate the enthalpy change of Co–26.3 wt\% Mo alloy. Apparently, the heat loss due to the convection and thermal radiation during free fall of a droplet can account for 0.7–1.05% of the enthalpy change according to the different gas environment.
Thus, according to equation (5), the specific heats of these three alloys are

\[ C_{PL}^{10\text{wt} \% \text{Mo}} = 41.85 \pm 1.51 \text{ J mol}^{-1} \text{ K}^{-1}, \]  
(21)

\[ C_{PL}^{26.3\text{wt} \% \text{Mo}} = 43.75 \pm 1.79 \text{ J mol}^{-1} \text{ K}^{-1}, \]  
(22)

\[ C_{PL}^{37.6\text{wt} \% \text{Mo}} = 44.92 \pm 1.67 \text{ J mol}^{-1} \text{ K}^{-1}. \]  
(23)
Table 2. Parameters necessary for calculating the enthalpy change of the Co–26.3 wt% Mo alloy.

<table>
<thead>
<tr>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
</tr>
<tr>
<td>1942</td>
</tr>
<tr>
<td>1795</td>
</tr>
<tr>
<td>1622</td>
</tr>
<tr>
<td>1560</td>
</tr>
<tr>
<td>1468</td>
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<tr>
<td>1747</td>
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<td>1879</td>
</tr>
<tr>
<td>1666</td>
</tr>
<tr>
<td>1689</td>
</tr>
<tr>
<td>1520</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$ (g)</td>
</tr>
<tr>
<td>0.798</td>
</tr>
<tr>
<td>0.85</td>
</tr>
<tr>
<td>0.85</td>
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<tr>
<td>0.85</td>
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<tr>
<td>0.852</td>
</tr>
<tr>
<td>0.85</td>
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<tr>
<td>0.845</td>
</tr>
<tr>
<td>0.846</td>
</tr>
<tr>
<td>0.79</td>
</tr>
<tr>
<td>0.80</td>
</tr>
</tbody>
</table>

| Temperature rise |
| $\delta T$ (K) |
| 1.859 38       |
| 1.781 25       |
| 1.579 69       |
| 1.570 31       |
| 1.453 13       |
| 1.765 63       |
| 1.906 25       |
| 1.656 25       |
| 1.562 50       |
| 1.429 69       |

| Balance temperature |
| $T_e$ (K) |
| 288.86     |
| 288.78     |
| 290.58     |
| 287.57     |
| 288.45     |
| 288.77     |
| 288.91     |
| 289.66     |
| 291.56     |
| 288.43     |

| Heat loss |
| $Q_{\text{lost}}$ (%) |
| 0.797       |
| 0.745       |
| 0.832       |
| 0.808       |
| 0.758       |
| 0.993       |
| 1.048       |
| 0.845       |
| 0.809       |
| 0.792       |

| Enthalpy change |
| $H(T) - H(293 \text{K})$ (J mol$^{-1}$) |
| 78,034.5       |
| 70,132.7       |
| 62,285.3       |
| 61,821.3       |
| 57,057.2       |
| 69,690.1       |
| 75,740.9       |
| 65,601.2       |
| 66,290.7       |
| 59,821.8       |
Figure 8 illustrates the dependence of the specific heats of Co–Mo alloys on the weight percentage of Mo. To show the tendency more clearly, the specific heat of undercooled liquid Co (Wang et al. 2002) is also added to figure 8. Apparently, the specific heat increases linearly with increasing Mo content. Data analysis shows that

$$C_{PL} = 40.63 + 0.11553C_{Mo} \text{ J mol}^{-1} \text{ K}^{-1}. \quad (24)$$

3.3. Thermodynamic functions $\Delta H_{LS}$, $\Delta S_{LS}$ and $\Delta G_{LS}$

Having obtained the specific heats of undercooled liquid Co–Mo alloys, one can rigorously calculate the dependences of the enthalpy difference $\Delta H_{LS}$, entropy difference $\Delta S_{LS}$, and thus the Gibbs free energy difference $\Delta G_{LS}$ on the undercooling according to their respective expressions:

$$\Delta H_{LS} = \Delta H_{m} - \int_{T}^{T_m} (C_{PL} - C_{PS}) \, dT, \quad (25)$$

$$\Delta S_{LS} = \Delta S_{m} - \int_{T}^{T_m} \frac{C_{PL} - C_{PS}}{T} \, dT, \quad (26)$$

$$\Delta G_{LS} = \Delta H_{LS} - T \Delta S_{LS}, \quad (27)$$

where $C_{PS}$ is the specific heat of the crystalline solid and $\Delta H_{m}$ the melting enthalpy, both of which can be determined conveniently with a commercial differential scanning calorimeter. Figure 9 illustrates the calculated $\Delta H_{LS}$, $\Delta S_{LS}$ and $\Delta G_{LS}$ values of these three Co–Mo alloys. The parameters used during calculation are listed in table 3. It can be seen that, with increasing undercooling, $\Delta H_{LS}$ and $\Delta S_{LS}$ decrease, whereas $\Delta G_{LS}$ increases. Meanwhile, at the same undercooling level these three thermodynamic functions all increase with increasing Mo content.

Previously, owing to the lack of specific heat data on the undercooled melt, especially on alloy melts of high melting temperature, several models have been proposed to estimate the Gibbs free energy difference. Turnbull (1950) assumed a zero specific heat difference $\Delta C_{f}$ between the undercooled liquid and the crystalline solid which resulted in the linear approximation:
Jones and Chadwick (1971) suggested that $\Delta C_P$ could be represented by a ‘suitable’ value, which is mostly often chosen as the difference $\Delta C_P^f$ at the melting temperature. This yields the following relation:

$$\Delta G_{LS} = \frac{\Delta H_m \Delta T}{T_m}. \quad (28)$$

Figure 9. Enthalpy change $\Delta H_{LS}$, entropy change $\Delta S_{LS}$, and Gibbs free-energy $\Delta G_{LS}$ of Co–Mo alloys versus undercooling.
Following some empirical considerations, Singh and Holz (1983) approximated $\Delta G_{LS}$ as

$$\Delta G = \frac{\Delta H_m}{T_m} \Delta T - \frac{\Delta C_p^f(\Delta T)^2}{T_m + T}. \quad (29)$$

On the basis of the free-volume model of liquids, Dubey and Ramachandrarao (1984) proposed another expression for $\Delta G_{LS}$:

$$\Delta G = \frac{\Delta H_m}{T_m} \Delta T - \frac{7T}{T_m + 6T}. \quad (30)$$

To confirm whether these models can describe the thermodynamic functions quantitatively, $\Delta G_{LS}$ for Co–26.3 wt% Mo alloy was calculated as an example by the aforementioned four models and compared with that calculated by its rigorous expression on the basis of the experimentally determined specific heat data. The calculated results are shown in figure 10. Obviously, at small undercoolings, these four models agree well with rigorous expression for $\Delta G_{LS}$ on basis of the experimentally determined specific heat. However, with increasing undercooling, deviation occurs. Moreover, the higher the undercooling, the larger is the deviation. When undercooling reaches 600 K, the deviation amounts to 4.57%, 2.19%, 3.09% and 1.81% respectively for these four models. Of these approximation models, the Dubey–Ramachandrarao model depicts $\Delta G_{LS}$ the best.
3.4. Crystal nucleation rate

With the Gibbs free-energy difference calculated rigorously and the viscosity derived from the measured surface tension data, we can go one step further to calculate the nucleation rate according to the classical nucleation theory (Turnbull 1956, Spaepen and Turnbull 1976): 

\[
I = \frac{10^{36}}{\eta} \exp \left( \frac{-16\pi \gamma^3}{3k_B T \Delta G_{LS}^2} f(\theta) \right),
\]

where \( \eta \) is the viscosity, \( k_B \) the Boltzmann constant, \( f(\theta) \) the heterogeneous nucleation factor given by \( f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2/4 \) and \( \gamma \) the solid–liquid interfacial energy, which can be calculated from the interfacial model of Spaepen (1975) and Spaepen and Meyer (1976).

In order to determine the influence of the deviation in \( \Delta G_{LS} \) between equations (28)–(31) and its rigorous expression on the nucleation rate, \( \log \left( \frac{I_{cal}}{I_{exp}} \right) \) is defined as the relative nucleation rate, where \( I_{cal} \) is the nucleation rate based on \( \Delta G_{LS} \) calculated by the aforementioned four models and \( I_{exp} \) is obtained by \( \Delta G_{LS} \) from its rigorous expression using the specific heat determined experimentally. Obviously, the relative nucleation rate reflects the deviation degree of approximation models from the experiment. Figure 11 shows the calculated relative nucleation rate of Co–26.3 wt% Mo alloy with a heterogeneous nucleation factor \( f(\theta) = 0.5 \) using the aforementioned approximation models. Since the Turnbull, the Jones–Chadwick, and the Dubey–Ramachandrarao models always show positive deviation from the rigorous expression of \( \Delta G_{LS} \), their relative nucleation rates are also positive. Within the undercooling range 0–400 K, \( \log \left( \frac{I_{cal}}{I_{exp}} \right) \) is larger than 4.2 and smaller than −3.7 for the Turnbull and the Singh–Holz models respectively. This means that the nucleation rates calculated from these two models deviate at least four orders and three orders respectively of magnitude from the experiment. Even for the Dubey–Ramachandrarao model, \( \log \left( \frac{I_{cal}}{I_{exp}} \right) > 1 \). This indicates that a minor deviation of \( \Delta G_{LS} \) will lead to a major deviation in the calculated nucleation rate. Therefore, in order to obtain the accurate nucleation rate, the specific heat of undercooled liquid must be measured quantitatively.

![Figure 11](image-url) Figure 11. Relative nucleation rate of Co–26.3 wt% Mo alloy calculated with different approximate models for \( \Delta G_{LS} \).
3.5. Rapid dendrite growth

Apart from the crystal nucleation, the thermophysical parameters also influence calculations in the rapid crystal growth under the high undercooling condition. In order to evaluate this influence, the crystal growth of Co–26.3 wt% Mo alloy was investigated with the specific heat determined experimentally and that extrapolated from the data of pure elements. The dominant crystal growth mechanism of Co–26.3 wt% Mo alloy in undercooled melt is dendrite growth. So far, the Lipton–Kurz–Trivedi (LKT) (1987) and Boettinger–Coriell–Trivedi (BCT) (1987) have been the most successful models to predict the rapid dendrite growth from highly undercooled liquid.

The LKT–BCT theory consists of two principal equations. The first equation is concerned with the relationship between the partial undercoolings and the bulk undercooling.

$$\Delta T = \Delta T_c + \Delta T_t + \Delta T_r + \Delta T_k.$$  \hspace{1cm} (33)

Here, $\Delta T_c$ is the solute undercooling, $\Delta T_t$ the thermal undercooling, $\Delta T_r$ the curvature undercooling and $\Delta T_k$ the kinetic undercooling. Of these four partial undercoolings, $\Delta T_t$ is related to the specific heat $C_{PL}$ by

$$\Delta T_t = \frac{\Delta H_m}{C_{PL}} Iv(P_t),$$ \hspace{1cm} (34)

where $P_t$ is the thermal Peclet number and $Iv(P_t)$ the thermal Ivantsov function.

The second equation relates the dendrite tip radius to the marginally stable wavelength of perturbations at the solid–liquid interface.

$$R = \frac{\Gamma/\sigma^*}{(\Delta H/C_{PL}) P_t \xi_t - \{2m_tC_0(1-k)P_c/[1-(1-k)Lv(P_c)]\} \xi_c},$$ \hspace{1cm} (35)

where $\Gamma$ is the Gibbs–Thomson coefficient, $\sigma^*$ is the stability constant equal to $1/4\pi^2$, $P_c$ is the solute Peclet number, $\xi_t$ and $\xi_c$ are the thermal and solute stability functions, $m_t = m_l(1 + \{k_e - k_v[1 - \ln(k_v/k_e)]/(1-k_c)\}$ and $m_l$ are the effective and equilibrium liquidus slopes respectively, $C_0$ is the alloy concentration, $\Delta H(C_p)$ is the solute Ivantsov function, $k_v = (k_v + V/V_d)/(1 + V/V_d)$ is the effective solute distribution coefficient, $k_e$ is the equilibrium partition coefficient, $V_d = D_L/a_0$ is the atomic diffusive speed, $D_L$ is the diffusion coefficient and $a_0$ is the characteristic diffusion length.

Another parameter related to the specific heat is thermal diffusivity $\kappa$, which is given by

$$\kappa = \frac{\lambda}{\rho C_{PL}}.$$ \hspace{1cm} (36)

$\kappa$ influences the crystal growth through the thermal Peclet number $P_t$:

$$P_t = \frac{VR}{2\kappa}.$$ \hspace{1cm} (37)

In the above two equations, $\rho$ is the density, $V$ is the dendrite growth velocity, $R$ is the dendrite tip radius and $\lambda$ is the thermal conductivity, which is closely related to the electrical conductivity $\rho_e$ via the Wiedemann–Franz law (Iida and Guthrie 1993)

$$\frac{\lambda \rho_e}{T} = 2.45 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}.$$ \hspace{1cm} (38)
Owing to the lack of data, the density and electrical conductivity of Co–Mo alloys have to be extrapolated linearly from the data of pure elements. From equations (37)–(39), the thermal diffusivity of liquid Co–26.3 wt% Mo alloy is given by

$$\kappa_{26.3\text{wt}\% \text{Mo}} = 3.5 \times 10^{-7} + 3.78 \times 10^{-9} \text{T m}^2 \text{s}^{-1}.$$  \hspace{1cm} (39)

Using the same method, the thermal diffusivities of Co–10 wt% Mo and Co–37.6 wt% Mo are calculated as

$$\kappa_{10\text{wt}\% \text{Mo}} = 3.73 \times 10^{-7} + 3.64 \times 10^{-9} \text{T m}^2 \text{s}^{-1}.$$  \hspace{1cm} (40)

$$\kappa_{37.6\text{wt}\% \text{Mo}} = 3.18 \times 10^{-7} + 3.93 \times 10^{-9} \text{T m}^2 \text{s}^{-1}.$$  \hspace{1cm} (41)

The calculated growth velocity $V$ of $\alpha$-Co dendrite in undercooled liquid Co–26.3 wt% Mo alloy is shown in figure 12, in which the solid curve is the $V–\Delta T$ curve using the specific heat $C_P = 43.75 \text{J mol}^{-1} \text{K}^{-1}$ determined experimentally, and the broken curve represents the calculated results using the specific heat $C_P = 38.4 \text{J mol}^{-1} \text{K}^{-1}$ extrapolated linearly from the data of pure elements. The physical parameters used during calculation are listed in table 4. The growth velocity of $\alpha$-Co dendrite determined experimentally (Wei and Herlach 1994) are also presented in figure 12. Apparently, the growth velocity calculated from $C_P = 43.75 \text{J mol}^{-1} \text{K}^{-1}$ agrees with the experimental result much better than that calculated from $C_P = 38.4 \text{J mol}^{-1} \text{K}^{-1}$. This again indicates the great importance of determining the thermophysical properties of undercooled metallic melts experimentally.

The effective solute distribution coefficient $k_v$ is a very important parameter during the crystal growth. With the specific heats from different sources, $k_v$ during the rapid crystal growth of undercooled liquid Co–26.3 wt% Mo alloy is calculated and shown in figure 13. Obviously, $k_v$ increases monotonically with increasing undercooling and, at an undercooling of about 80 K, there exists an anomalous point, which corresponds to the transition of $\alpha$-Co dendrite from solute-diffusion-controlled growth to thermal-diffusion-controlled growth. The calculated effective partition coefficient with the specific heat measured experimentally is a little higher.

![Figure 12. Experimentally determined and calculated growth velocity of $\alpha$-Co dendrite in Co–26.3 wt% Mo alloy.](image-url)
than that with the approximated specific heat. Moreover, this deviation is mainly focused on the stage of thermal diffusion controlled growth. This is understandable, since the specific heat is mainly related to the thermal undercooling $\Delta T_1$.

3.6. Marangoni convection

Marangoni convection is a fluid flow phenomenon, which is driven by surface tension differences along the surface. Together with other fluid flows, Marangoni convection can influence crystal growth by modifying the boundary layers ahead of the solid–liquid interface. In a microgravity environment, Marangoni convection is the main convection mechanism, thereby exerting great influences on the manufacturing of the new materials in outer space.

The surface tension differences can arise from the differences in temperature or in solute concentration. The former is called thermal Marangoni convection, and the latter solute Marangoni convection. These two Marangoni convections are mainly characterized by the thermal Marangoni $Ma_T$ and the solute Marangoni number $Ma_C$. These are defined as follows:

\[
Ma_T = \frac{\Delta \sigma}{\frac{1}{2} \rho \beta \Delta T_1}
\]

\[
Ma_C = \frac{\Delta \sigma}{\frac{1}{2} \rho D \Delta C}
\]

where $\Delta \sigma$ is the surface tension difference, $\rho$ is the density, $\beta$ is the thermal expansion coefficient, $\Delta T_1$ is the thermal undercooling, $D$ is the diffusion coefficient, and $\Delta C$ is the solute concentration difference.*
\[ Ma_T = \frac{\nabla T L^2}{\eta \kappa} \frac{\partial \sigma}{\partial T}, \]
\[ Ma_C = \frac{\nabla C L^2}{\eta D} \frac{\partial \sigma}{\partial C}, \]

where \( \nabla T \) is the temperature gradient, \( \nabla C \) is the concentration gradient, \( L \) is the characteristic length of the system, \( D = D_0 \exp \left(-\frac{Q}{RT}\right) \) is the solute diffusion coefficient, which can be approximated from empirical expressions, \( \frac{\partial \sigma}{\partial T} \) is the surface tension temperature dependence and \( \frac{\partial \sigma}{\partial C} \) is the surface tension concentration dependence.

The \( \frac{\partial \sigma}{\partial T} \) values for Co–10 wt% Mo, Co–26.3 wt% Mo and Co–37.6 wt% Mo alloys have been determined to be −0.31, −0.33 and −0.34 mN m\(^{-1}\)K\(^{-1}\) respectively. Compared with \( \frac{\partial \sigma}{\partial T} \), \( \frac{\partial \sigma}{\partial C} \) is more complex. From figure 5, it can be seen that \( \sigma \) at any temperature can be well fitted with a two-order polynomial function of solute concentration \( C_{\text{Mo}} \). For example, \( \sigma \) at 1600 K can be fitted with

\[ \sigma = 1933.8 - 0.3087C_{\text{Mo}} + 0.04335C_{\text{Mo}}^2. \]

Thus, at a given temperature, \( \frac{\partial \sigma}{\partial T} \) is a linear function of Mo content. The relationship of \( \frac{\partial \sigma}{\partial C}, C \) and \( T \) is presented in figure 14. For clarity, only \( \frac{\partial \sigma}{\partial C} \)–\( C \) curves at 1400, 1600, 1800 and 2000 K are illustrated.

Assuming a temperature difference of 5 K and a 0.5 wt% difference in Mo content in a levitated droplet of \( 5 \times 10^{-3} \) m in diameter, \( Ma_T \) and \( Ma_C \) are calculated and presented in figure 15. Apparently, \( Ma_T \) increases and \( Ma_C \) decreases with reduction in temperature. Moreover, an increase in the Mo content increases \( Ma_C \) whereas it decreases \( Ma_T \) at a given temperature.

An interesting question about the thermal and solute Marangoni convection processes is which is the dominating mechanism. The answer depends on the thermal and solute profiles and the dependence of surface tension on the temperature and solute content. If the temperature and the concentration gradients have different signs, these two Marangoni convection processes are additive; otherwise they act in opposition. As for the latter case, which dominates the convection at a given coordinate \( r \) depends on the value of the combined surface tension gradient.
The $\sigma / \partial r$ values of Co–10 wt% Mo, Co–26.3 wt% Mo and Co–37.6 wt% Mo at different temperatures are presented in figure 16. Obviously, in a temperature range 1400–2000 K, the $\sigma / \partial r$ of these three Co–Mo alloys were negative. This indicates that thermal Marangoni convection dominates the total Marangoni convection process.

For a sphere-like geometry of a liquid drop, the flow velocity induced by Marangoni convection is approximated by (Malmejac and Frohberg 1987)

$$V_M = \frac{\Delta \sigma}{8 \eta},$$

where $\Delta \sigma$ is the difference in surface tension between the ‘cold’ and the ‘hot’ part of the drop and $\eta$ is the viscosity of the liquid.

With the derived viscosity from the surface tension, the flow velocity induced by thermal Marangoni convection and solute Marangoni convection are calculated and

$$\frac{\partial \sigma}{\partial r} = \frac{\partial \sigma}{\partial T} \frac{\partial T}{\partial r} + \frac{\partial \sigma}{\partial C} \frac{\partial C}{\partial r}.$$  (45)

Figure 15. Thermal Marangoni number $Ma_T$ and solute Marangoni numbers $Ma_C$ versus temperature.

Figure 16. Combined surface tension gradient of Co–Mo alloys versus temperature.
illustrated in figure 17. Apparently, the flow velocity induced by Marangoni convection is of the order of centimetres per second. Comparing the flow velocity induced by Marangoni convection with the growth velocity of Co–26.3 wt% Mo alloy shown in figure 12, Marangoni convection is important at small undercoolings \((\Delta T < 100 \text{ K})\) in the mass transport in front of the solid–liquid interface. With increasing undercooling, this role becomes smaller and smaller. At high undercoolings \((\Delta T > 200 \text{ K})\), this role can almost be neglected.

§4. CONCLUSIONS

The oscillating-drop technique and drop calorimeter method together with electromagnetic levitation were used to measure the surface tensions and specific heats of undercooled liquid Co–10 wt% Mo, Co–26.3 wt% Mo and Co–37.6 wt% Mo alloys. These three alloys were undercooled by up to 223, 213 and 110 K, respectively. Their surface tensions were determined to be \(1895 \pm 0.31(T - T_L)\), \(1932 \pm 0.33(T - T_L)\), and \(1989 \pm 0.34(T - T_L)\) mN/m. The surface tension of Co–Mo alloy was found to be a two-order polynomial function of Mo content. Based on the Butler equation, the surface tensions of these three Co–Mo alloys were calculated, and the results were in good agreement with the experimental data. Within a wide temperature regime around the liquidus temperature, the specific heats of these three alloys varied very little and were determined to be 41.85, 43.75 and 44.92 J mol\(^{-1}\) K\(^{-1}\) respectively. The specific heat of Co–Mo alloy is found to be a linear function of Mo content. The Gibbs free energy differences and the relative nucleation rates of Co–10 wt% Mo, Co–26.3 wt% Mo and Co–37.6 wt% Mo alloys were calculated according to the approximate models of Turnbull, Jones–Chadwick, Singh–Holz and Dubey–Ramachandrarao and compared with experimental data. Comparison shows that deviation exists between these four approximate models and experimental results. A minor deviation of the Gibbs free energy will cause a major deviation in the nucleation rate. Furthermore, the dendrite growth and Marangoni convection of Co–Mo alloy were investigated on the basis of the determined specific heats and surface tensions. The growth velocity of \(\alpha\)-Co dendrite in Co–26.3 wt% Mo alloy calculated from the specific heat determined experimentally agrees with the experimental result.
much better than that from the specific heat approximated linearly from the data on the pure elements. The thermal Marangoni number $Ma_T$ increases and the solute Marangoni number $Ma_C$ decreases with reduction in temperature, and an increase in Mo content increases $Ma_T$ but decreases $Ma_C$ at a given temperature. Whether the thermal or the solute component is the dominating mechanism of Marangoni convection depends on the profiles of temperature and concentration and the surface tension dependences of temperature and concentration. The flow velocity induced by Marangoni convection is of the order of centimetres per second, which indicates that Marangoni convection exerts great influence on mass transport at small undercoolings. However, at large undercoolings, this role can be neglected.

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