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Author(s)	Xu, Jun; Qiao, Zhiyu; Han, Xiujun et al.
Citation	Zeitschrift für Metallkunde. 2004, 95(11), p. 1001-1004
Version Type	VoR
URL	https://hdl.handle.net/11094/26441
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Measurement and calculation of surface tension of undercooled liquid Fe-20 wt.% Cu alloy

Using electromagnetic levitation in combination with the oscillating drop technique, the surface tension of liquid Fe-20 wt.% Cu alloy above and below the liquidus temperature was measured. The containerless state during levitation produces substantial undercooling up to 156 K. In the experimentally covered temperature range, the surface tension of Fe-20 wt.% Cu alloy was determined as $1.658 - 2.234 \times 10^{-4} (T - 1736)$ N/m. According to Butler's equation and STCBE software, the surface tension of Fe-20 wt.% Cu alloy was also calculated. A good agreement was found between the calculated and experimentally measured values within the error limits. The different sign of the temperature dependences of the calculated and measured surface tensions is preliminarily discussed.

Keywords: Surface tension; Fe–Cu alloy; Undercooled liquid

1. Introduction

The surface tension of liquid metals plays an important role in those metallurgical processes, which are related to free surface, such as welding and surface melting. During these processes, the structures and some thermodynamic characteristics of materials can change strongly in the metastable undercooled regime. Therefore, the knowledge of the surface tension in the undercooled regime is indispensable to understand these processes from a physicochemical point of view. However, it is very difficult to measure the surface tension of undercooled liquid alloys, since at high temperatures any physical contact between the container wall and the alloy melt will induce immediate nucleation, and thus the metastable undercooled state is hard to access [1]. Electromagnetic levitation is an elegant method to process liquid metals in a containerless way. In recent years, electromagnetic levitation combined with the oscillating drop technique has been widely applied to measure the surface tension of undercooled liquid metals [2–7]. Nevertheless, the experimental determination of surface tension is very time and money consuming. It is impossible to measure surface tensions of all alloy systems in the whole composition range. Recently, several methods for calculating the surface tension [8–15], such as STCBE (Surface Tension Calculation based on Butler's Equation) [13] and STCGM (Surface Tension Calculation based on Geometric Model) [13] have been developed towards obtaining sufficient and reliable data for practical use.

The objective of the present paper is to study the surface tension of the undercooled liquid Fe-20 wt.% Cu alloy experimentally using electromagnetic levitation combined with the oscillating droplet technique and theoretically using Butler's equation with the excess thermodynamic data from the SGTE database [16].

2. Surface tension measured by the oscillation drop technique

2.1. Theoretical background and experimental procedure

The surface tension is related to the frequency of the surface oscillation of a levitated sample according to Rayleigh's equation [2, 17]:

$$\sigma = \frac{3}{8} \pi m \omega_R^2 \quad (1)$$

where σ is the surface tension, ω_R is the Rayleigh frequency and m is the droplet mass.

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 ω_R will shift and split into five peaks in the spectrum. Cummings and Blackburn [17] considered the influence of magnetic field and derived the following frequency sum rule to obtain the Rayleigh frequency:

$$\omega_R^2 = \frac{1}{5} \sum_{m=-2}^2 \omega_{2,m}^2 - 2\bar{\omega}_l^2 \quad (2)$$

with

$$\bar{\omega}_l^2 = \frac{1}{3} (\omega_x^2 + \omega_y^2 + \omega_z^2) \quad (3)$$

where $\omega_{2,m}$ are the frequency of the surface oscillation for the $l = 2$ mode; ω_x , ω_y , and ω_z are translational frequencies of the droplet's center of mass along the direction of axes x , y , and z ; $\bar{\omega}_l$ 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.

A schematic diagram of the apparatus is shown in Fig. 1. The apparatus was accurate enough to measure reliably the surface tension of undercooled liquid metals [19]. The Fe-20 wt.% Cu master alloy was prepared from 99.9 % pure Fe and 99.999 % pure Cu by rf heating under argon atmos-

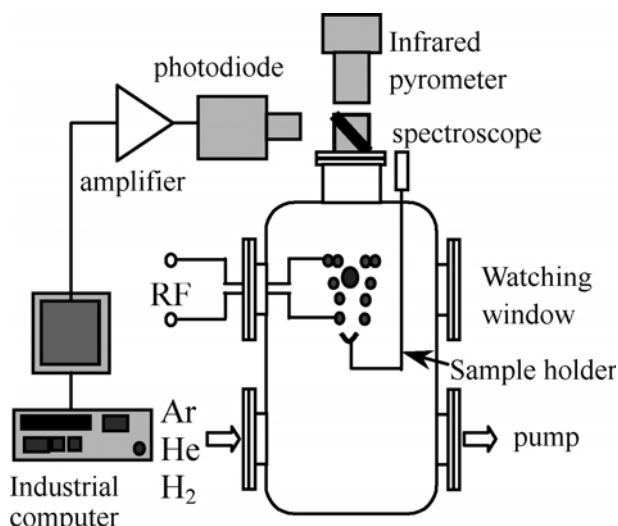


Fig. 1. Schematic of electromagnetic levitation facility for measuring the surface tension.

phere and each sample has a mass of about 0.85 g. For the power supply, a 25 kW frequency generator operating at 300–450 kHz was used. The levitation coil was placed in a vacuum chamber, which was evacuated to less than 2×10^{-4} Pa and backfilled with a gas mixture of argon, helium, and hydrogen in the ratio of 6 : 3 : 1. The sample was levitated and melted by inductive heating during the experiments. Furthermore, helium with an addition of 22.1 % hydrogen was passed through liquid nitrogen and blown toward the sample to achieve high undercooling. The temperature was measured by an infrared pyrometer, and the surface oscillations were detected by a photodetector focused on the topside of the sample through a spectroscope. The signal was passed through a low-pass filter with a threshold of 110 Hz and an amplifier. It was recorded with a sampling rate of 800 Hz to avoid aliasing. After analogue/digital conversion with a sampling rate up to 100 kHz, FFT (Fast Fourier Transformation) was performed offline in order to obtain the oscillation spectra.

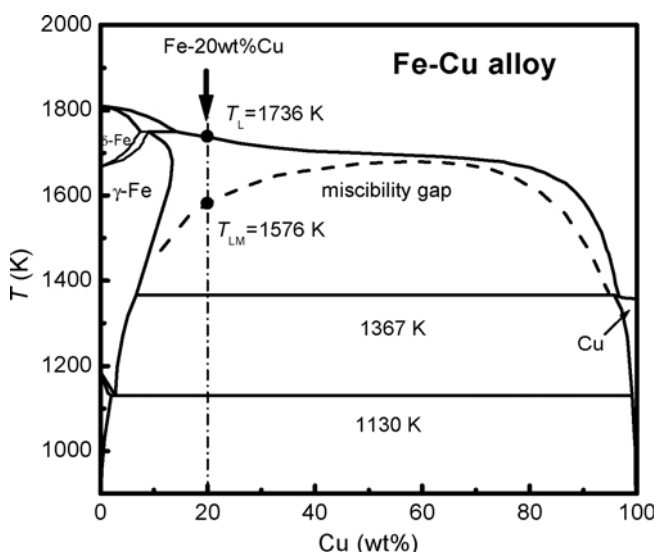


Fig. 2. Selected alloy shown in the phase diagram of the Fe–Cu alloy with a metastable miscibility gap presented as dashed line.

2.2. Measurement of the surface tension of liquid and undercooled Fe-20 wt.% Cu

Figure 2 is the phase diagram of the Fe–Cu binary alloy system. Obviously, there exists a metastable miscibility gap [20] in the phase diagram. Once the alloy is undercooled by more than 163 K, the homogeneous liquid alloy will separate into two different liquid phases, i.e. $L \rightarrow L_1(\text{Fe-rich}) + L_2(\text{Cu-rich})$. On the other hand, the evaporation of copper will become serious at high temperatures. Therefore the temperature should be kept in a suitable range. In the present work, the temperature was controlled between 1580 K and 1900 K, which corresponds to an undercooling of 156 K and a superheating of 164 K. Thus, there is no phase separation during the experiment and the mass loss is less than 0.6 %. Figure 3 presents the relationship between surface tension and temperature for Fe-20 wt.% Cu alloy in the experimentally covered temperature range. A linear regression analysis of the data gives:

$$\sigma_{\text{Fe-20wt\%Cu}} = 1.658 - 2.234 \times 10^{-4}(T - 1803 \text{ K}) [\text{N/m}] \quad (3)$$

Considering the volatilization of copper, the signal collection and the resolution of the FFT transformation, the experimental error is estimated to be 3–4 %. The error bar is also superimposed in Fig. 3.

3. Calculation of the surface tension of liquid Fe-20 wt.% Cu based on Butler's equation

Considering that the surface of the molten solution can be treated as a “surface phase”, which is in equilibrium with the bulk phase, Butler [21] derived the relationship between surface tension and thermodynamic properties as follows:

$$\begin{cases} \sigma = \sigma_i + \frac{RT}{S_i} \ln \frac{X_i^s}{X_i^b} + \frac{1}{S_i} ({}^E G_i^s - {}^E G_i^b), \\ \sum_{i=1}^n X_i^{s,b} = 1, \quad 0 \leq X_i^{s,b} \leq 1, \end{cases} \quad i = 1, 2 \dots n \quad (4)$$

where σ and σ_i are the surface tension of the solution and the pure component i , respectively; T is the absolute tempera-

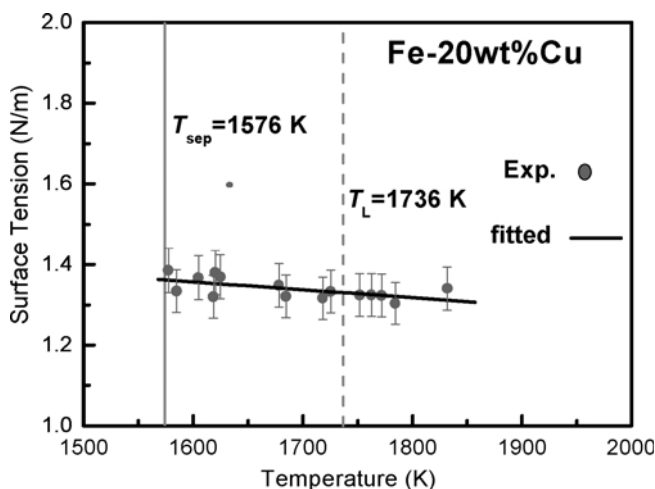


Fig. 3. Measured surface tension of the liquid Fe-20 wt.% Cu alloy versus temperature.

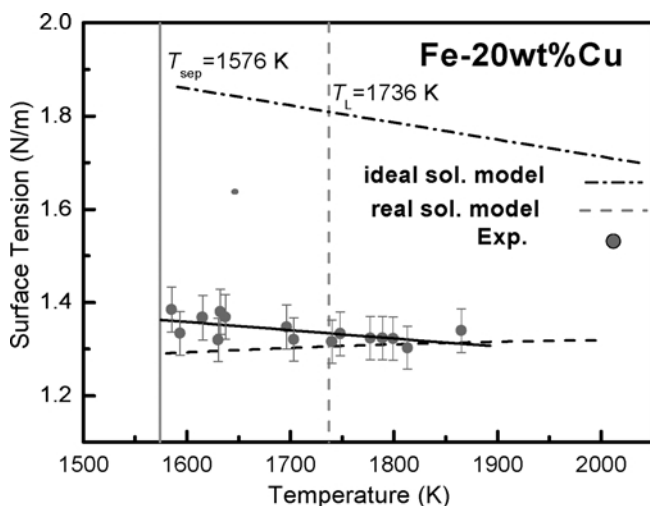


Fig. 4. Experimental and calculated surface tension of liquid and undercooled Fe-20 wt.% Cu.

ture; R is the gas constant; X_i^s and X_i^b are the molar fractions of component i in the surface phase and bulk phase, respectively; S_i is the monolayer of component i ; ${}^E G_i^s$ and ${}^E G_i^b$ are partial excess Gibbs energies of component i in the surface and bulk phase, respectively. The following assumptions were made for the further calculation.

(1) ${}^E G_i^s$ has the same formula as ${}^E G_i^b$, and the excess Gibbs energy is proportional to the coordination number

$${}^E G_i^s = \frac{Z^s}{Z^b} {}^E G_i^b = \beta {}^E G_i^b \quad (5)$$

where Z^s and Z^b are coordination numbers in the surface phase and the bulk phase, respectively. For alloy systems, β is in the range of 0.75–0.83 [11, 13, 22], and $\beta = 0.75$ [13] is used in the present work. ${}^E G_i^b$ can be obtained directly from a thermodynamic database or from the literature.

(2) The partial molar surface area S_i of component i is equal to the molar surface area of this pure component, that is:

$$S_i = 1.09 N_0^{1/3} \left(\frac{M_i}{\rho_i} \right)^{2/3} \quad (6)$$

where N_0 is Avogadro's number, M_i the atomic weight of component i , and ρ_i the density of component i . The surface tension σ can be calculated with Eqs. 4–6 at the given temperature T and the bulk composition of component i , X_i^b .

Based on Butler's equation and using the STCBE program, the surface tensions of liquid and undercooled liquid Fe-20 wt.% Cu alloy have been calculated. The results are shown in Fig. 4 and the data of thermodynamic properties used for the calculation of the surface tension are listed in Table 1.

The dash-dotted line in Fig. 4 represents the surface tensions of the liquid and the undercooled liquid Fe-20 wt.% Cu alloy calculated with the ideal solution model (${}^E G_{\text{Fe-Cu}}^b = 0$). It is found that the agreement between measurement and this calculation is very poor. The Gibbs free energy of Fe–Cu alloy at various temperatures calculated using the data (${}^E G_{\text{Fe-Cu}}^b$) from the SGTE solution database is shown in Fig. 5. Apparently, the free energy of mixing of the Fe–Cu alloy system departs positively from ideal solution model in the whole composition range. Therefore, according to the standard formula [23], the relations between ${}^E G_m^b$ and ${}^E G_i^b$, ${}^E G_{\text{Fe}}^b$ and ${}^E G_{\text{Cu}}^b$ are calculated. Then

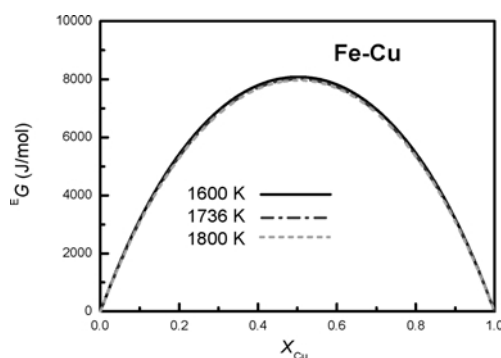


Fig. 5. Large positive departure of free energy of mixing from ideal solution model in the Fe–Cu alloy.

the surface tensions of the liquid and the undercooled liquid Fe-20 wt.% Cu alloy (dashed line in Fig. 4) are calculated using Butler's equation and the STCBE software in the temperature range of 1580–1900 K. From Fig. 4, there is a good agreement between the measurement and calculation using the data from the SGTE database within the error limits, and the degree of agreement is much better than the calculated value with the ideal solution model.

Although the agreement between the experimental and the calculated surface tensions is satisfactory, the temperature dependences of the experimental and the calculated surface tensions have different sign: $d\sigma/dT(\text{exp.}) < 0$ and $d\sigma/dT(\text{cal.}) > 0$. Recently, Lee et al. [24–26] showed that a positive temperature dependence can occur for liquid alloy

Component		Fe	Cu
M (kg · mol ^{−1})		0.05585	0.06354
ρ (kg · m ³)		8500−0.85 <i>T</i>	7938−0.71(<i>T</i> −1358)
σ (N · m ^{−1})		1.925−3.96×10 ^{−4} (<i>T</i> −1803)	1.33−2.3×10 ^{−4} (<i>T</i> −1358)
^E <i>G</i> _{<i>ij</i>} ^b		Cu−Fe	
(SGTE Solution Database [16])	<i>A</i> ₀	36087.987	
	<i>B</i> ₀	−2.3296885	
	<i>A</i> ₁	324.52964	
	<i>B</i> ₁	−0.032700618	
	<i>A</i> ₂	10355.386	
	<i>B</i> ₂	−3.6029763	
	^E <i>G</i> _{<i>ij</i>} ^b = <i>x</i> _{<i>i</i>} <i>x</i> _{<i>j</i>} ∑ [(<i>A</i> _{<i>n</i>} + <i>B</i> _{<i>n</i>} <i>T</i>) (<i>x</i> _{<i>i</i>} − <i>x</i> _{<i>j</i>}) ^{<i>n</i>}] J/mol <i>n</i> = 0, 1, 2 . . .		

Table 1. Thermodynamic properties used in the calculation for the surface tension of the liquid Fe–Cu alloy based on Butler's equation and STCBE software.

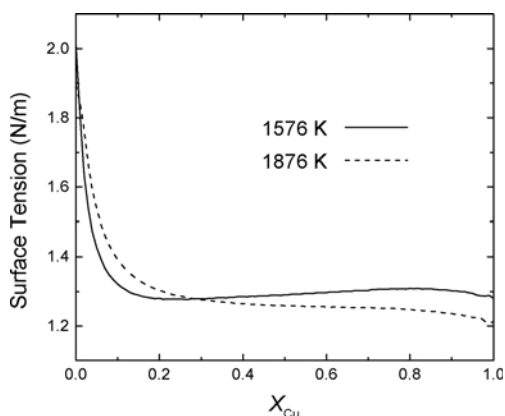


Fig. 6. Calculated surface tension of liquid Fe–Cu alloys at 1576 and 1876 K.

systems having a large positive mixing excess free energy or exhibiting a large difference in the surface tension of the component elements, especially in the low-temperature region. In Fig. 6, the calculated surface tensions of liquid Fe–Cu alloys at 1576 and 1876 K are given with the mole fraction of Cu in the bulk phase. When $0.01 < X_{\text{Cu}} < 0.28$, the calculated results at 1876 K have higher values than those at 1576 K, yielding a positive temperature dependence, whereas for $X_{\text{Cu}} > 0.28$ the temperature dependence shows negative values. The positive temperature dependence can be related to the change in the surface segregation of Cu with temperature. In Fig. 7, the molar fraction of Cu in the surface is shown with respect to that in the bulk. It is found that the molar fraction of Cu in the surface is 0.9 when that in the bulk reaches only a value of about 0.01 and 0.05 at 1573 and 1873 K, respectively. This distinguished surface segregation increases as the deviation of the activity from an ideal alloy becomes more positive, i. e., for a large positive mixing excess free energy [27]. Accordingly, due to the increase in the distinguished surface segregation of Cu with decreasing temperature, the calculated surface tensions have a positive temperature dependence when $0.01 < X_{\text{Cu}} < 0.28$. Nevertheless, the reason for the discrepancy in temperature dependence of the surface tension between the measurements and the calculated results is not clear at present. In order to further discuss this problem, it is anticipated to increase the reliability of both surface tension measurements and thermodynamic properties, such as the partial excess Gibbs energy in the bulk phase in the SGTE alloy solution database.

4. Conclusions

1. The surface tension of liquid Fe–20 wt.% Cu alloy was measured using the electromagnetic oscillating droplet technique in the temperature range of 1580–1900 K. The measured surface tension of the Fe–20 wt.% Cu alloy increases with decreasing temperature and the linear relationship between the surface tension and temperature can be expressed as $\sigma_{\text{Fe–20wt.\%Cu}} = 1.658 - 2.234 \times 10^{-4}(T - 1803 \text{ K})$ [N/m].
2. The surface tension of the alloy was also calculated in the temperature range of 1580–1900 K based on Butler's equation and STCBE software, which was in a good agreement with experimental values.

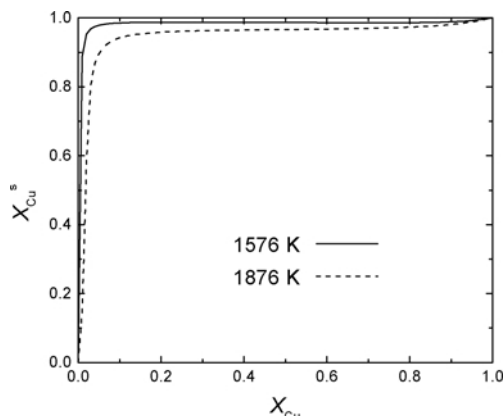


Fig. 7. Calculated surface concentration of liquid Fe–Cu alloys at 1576 and 1876 K.

Financial support of National Natural Science Foundation of China (No. 50071009) is greatly acknowledged.

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(Received January 12, 2004; accepted July 21, 2004)

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