Density of Ni–Cr Alloy in Liquid and Solid-Liquid Coexistence States

Kusuhiro Mukai and Feng Xiao

Department of Materials Science and Engineering, Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan

A modified sessile drop method was developed to obtain the precise density values for liquid nickel and nickel-chromium alloy in liquid and solid-liquid coexistence states. The density of liquid nickel decreases linearly with increasing temperature in the range from the melting point to 1923 K. The density at the melting point and the thermal expansion coefficient of liquid nickel are \(7.91 \text{ Mg m}^{-3}\) and \(1.81 \times 10^{-3} \text{ K}^{-1}\), respectively. The density of nickel-chromium alloy in liquid or solid-liquid coexistence state decreases linearly with increasing the temperature and chromium concentration in the alloy. The temperature coefficient of density of nickel-chromium alloy changes at the liquidus temperature. The absolute value of the temperature coefficient of density in solid-liquid coexistence state is larger than that in liquid state.

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1. Introduction

The density of liquid nickel and nickel-chromium alloy in liquid and solid-liquid coexistence states is the most important thermophysical property for investigating the structure of nickel-chromium alloy in liquid and solid-liquid coexistence states, studying the solidification modes of nickel-chromium alloy and simulating the liquid nickel-chromium alloy flow in the casting process.

The density of liquid nickel was measured by the gamma radiation attenuation method, the maximum bubble pressure method, the levitated drop method, the direct Archimedean method, and the large drop method. However, there is a large scatter in the reported density values of liquid nickel and its temperature dependence. At static condition, the sessile drop method is available to measure the density under precisely controlled oxygen partial pressure. But in the case of smaller drop, the error accompanied with measurement can not be neglected due to the smaller volume. While in the case of larger drop, the symmetry of drop profile is not good. It will result in more serious error. Furthermore, the difficulty of determining the boundary between the sessile drop and the substrate also results in error.

The data on the density of nickel-chromium alloy in liquid and solid-liquid coexistence states is seldom and it was only measured by Eremenko and Naidich with large drop method in the chromium concentration of 8.96–57.06 mass%.

In order to obtain more precise density of liquid nickel and nickel-chromium alloy in liquid and solid-liquid coexistence states, the authors have measured by a modified sessile drop method developed by Mukai et al. Larger volume of the sample is adopted and the symmetry of drop profile is improved in this method.

2. Experimental

2.1 Principle of measurement

The principle of the modified sessile drop method is shown in Fig. 1. A sample is charged into a horizontal alumina (99.9 mass% \(\text{Al}_2\text{O}_3\)) crucible (24.00 mm in OD, 14.00 mm in ID, 6.00 mm in depth). When temperature of the furnace is higher than the melting point of nickel or the solidus temperature of nickel-chromium alloy, a drop with smooth surface is formed above the upper end of the crucible with a volume of \(V_2\). \(V_1\) is the inner volume of crucible at experimental temperature. The total volume of the sample, \(V\), is the sum of \(V_1\) and \(V_2\). The sample mass, \(m\), is calculated from the change of the sample mass before and after the experiment and the experimental time. It is discussed further in 3.1.1. The density, \(\rho\), can be obtained from eq. (1):

\[
\rho = \frac{m}{V} \tag{1}
\]

The shape of \(V_2\) shown in Fig. 1 can be taken as rotational symmetry around axis \(z\) and its volume is composed of \(N - 1\) horizontal sections. Then, the total volume of sample can be computed as shown in eq. (2).

\[
V = V_1 + V_2 = \pi[D^2H_1 - (4 - \pi)(D - 2R)R^2](1 + \alpha_V)
\]

\[
/4 + \pi \sum_{i=1}^{N} (A_1z^2 + B_1z + C_1)dz \tag{2}
\]

where, \(D\) is the inner diameter of the crucible, \(H_1\) is the depth of alumina crucible, \(R\) is the radius of the bottom corner of crucible, \(\alpha_V\) is the volume expansion of the crucible, \(P_i\) (here \(i = 1, 2, 3, \cdots, N\)) are the measuring points, which are used...
as points of coordinate for computation, \( N \) is the number of measuring points, and \( A_i, B_i, C_i \) are the constants of the function, which represents the profile of liquid sample between horizontal section \( i - 1 \) to that of \( i \).

### 2.2 Experimental procedure

The experimental apparatus consisted of a LaCrO₃ heating furnace, a gas purifier, an oxygen sensor, a photographic system, and a digital system (computer). In order to maintain air-tightness of the reaction chamber, a double tube structure was adopted in the study. The tubes were made of high purity alumina. Both ends of the tubes were sealed with water-cooled stainless steel caps. The temperature was measured with a B-type thermocouple, which was positioned directly under the alumina crucible.

The atmosphere in the alumina tube was replaced by argon passed through a gas purifier and further deoxidized by Mg chip heated at 823 K after evacuation with a rotary pump. The oxygen partial pressure in argon, \( P_{O_2} \), was measured with an oxygen sensor of ZrO₂–CaO solid electrolyte. The sample is not oxidized during the experiment because the oxygen partial pressure in argon is lower than \( 1 \times 10^{-19} \) MPa.

The photographs of liquid alloy drop were taken every 0.3 ks after holding at a given temperature for 0.6 ks.

The nickel and chromium concentration in alloy was analyzed by radio frequency inductively coupled plasma (I.C.P.) emission spectrometry and oxygen concentration in the alloy was obtained by the oxygen and sulfur analyzer.

### 3. Results and Discussion

#### 3.1 Measurement error of the modified sessile drop method

Since the measurement errors of sample mass and volume are the two main sources of measurement error of density, the absolute measurement error and relative measurement error of density can be deduced from the definition equation, eq. (1) and expressed by the following equations:

\[
dρ = \frac{\partial ρ}{\partial m}dm + \frac{\partial ρ}{\partial V}dV \quad (3)
\]

\[
dρ/ρ = dm/m + dV/V \quad (4)
\]

where, \( dm/m \) is the measurement error of the sample mass and \( dV/V \) is the measurement error of the sample volume.

The measurement error of sample volume includes the error arisen from the number of measuring points of the drop, the error from the profile measurement of the liquid sample surface, the error from the machining accuracy of crucible, and the error from the thermal expansion of alumina crucible. All of the sources of measurement error are analyzed as follows.

#### 3.1.1 Measurement error of sample mass (\( dm/m \))

It is very important to take an optimum sample mass for evaluating the precise volume of sample. In the case of modified sessile drop method, if the sample mass is too small, the inner volume of crucible is not occupied completely with liquid sample. Then, the measured volume is assumed larger than real volume. In contrary, if the sample mass is too much, the symmetry of liquid sample becomes worse. This also results in incorrect measurement of volume. By preliminary experiments, the optimum sample mass for the measurement of each alloy with various chromium concentrations was determined to be from 9.8 to 10.0 g.

The sample mass was measured by using high accuracy electronic balance (0.1 mg of resolution). Change of the sample mass due to the evaporation of sample during the experiment can be expressed in Fig. 2. \( \Delta m = m_0 - m_f \) was less than 29.7 mg in the present experiment. Then the sample mass for calculating the density can be expressed by the following equation under the assumption that the evaporation mass at the temperature lower than the solidus is much less than that at the temperature higher than the solidus:

\[
m = m_0 - (m_0 - m_f)t/t_f \quad (5)
\]

where, \( m_0 \) is the sample mass before the experiment, \( m_f \) is the sample mass after the experiment, \( t \) is the time from the beginning of density measurement to take the photographs and \( t_f \) is the whole time of density measurement at the temperature higher than the solidus.

The maximum error of density arisen from the mass loss of sample can be expressed by the following equation:

\[
dm/m = [(m_0 - m_f)t/m_0] \times 100\% < \pm 0.06\% \quad (6)
\]

#### 3.1.2 Error arisen from the number of measuring points (\( dV/V \)_n)

As shown in Fig. 1, the volume \( V_2 \) of semi ellipse sphere can be taken as a cone composed of \( N \) paraboloids (proportion of axis is \( H_2/(D/2) \), \( z \geq 0 \)). When \( N \) is larger than 40, the relative error is around \( \pm 0.0015\% \). In this study, the point \( N \) on surface profile of liquid sample is taken 60 to 80. The error can be controlled less than \( \pm 0.0015\% \).

#### 3.1.3 Error arisen from the profile measurement of the liquid alloy surface (\( dV/V \)_p)

The error for numerical input can be less than \( \pm 0.1 \) mm. The magnification between photographed image of the drop and the real one was more than 10 times. Therefore, the measurement error \( \Delta \) arisen from numerical input is less than \( \pm 0.01 \) mm. The density error arisen from the profile measurement can be expressed by the following equation under the assumption that \( V_2 \) is a half of ellipsoid:

\[
(|ρ - ρ_0|/ρ_0) \times 100\% \approx (ΔV_{max}/V_0) \times 100\%
\]

\[
= [(V_0 - π[D^2H_1 - (4 - π)(D - 2R)^2](1 + αV)/4

\]

\[
- π \int_0^{H_2+Δ} (A_1z^2 + B_1z + C_1)^2dz]/V_0]

\]

\[
\times 100\% < \pm 0.40\% \quad (7)
\]
where, \( \rho \) is the measured value of density, \( \rho_0 \) is real value of density, \( V_0 \) is real value of volume, and \( \Delta V_{\text{max}} \) is the maximum error of volume measurement arisen from profile measurement.

In order to verify the calculated error in eq. (7), an example of the density variation of liquid sample with time is shown in Fig. 3. At constant temperature, the variation of density is only attributed to the numerical input of drop profile. The difference among 11 measured data at constant temperature was within \( \pm 0.38\% \). The standard deviation \( \sigma = (\sum \varepsilon^2/n)^{1/2} \) (\( \varepsilon \): an absolute error, \( n \): the number of measurements) was less than \( 2.60 \times 10^{-3} \text{ Mg m}^{-3} \). The relative error of density is consistent with the above analysis of eq. (7).

### 3.1.4 Error arisen from the machining accuracy of crucible \( (dV/V)_m \)

\( V_1 \) in eq. (2) is equal to the inner volume of alumina crucible at experimental temperature. The measurement error of \( V_1 \) depends on accuracy of machining and thermal expansion of alumina crucible.

As shown in Fig. 1, the corner of inner wall of crucible was machined to be a circular shape in order to secure that there is no gap in the contacting area between liquid sample and inner wall. For the purpose of obtaining more precise value of \( V_2 \) from the photographic image, the top of alumina crucible was machined into a slope. The error caused by the accuracy of machining can be deduced by the method as follows. At first, the inner volume of crucible at room temperature can be calculated by measuring the practical values of internal diameter and depth. Then, high pure mercury whose density is well known is charged into a crucible. In order to ensure the inner volume of crucible occupied completely by mercury, an alumina plate with flat and smooth surface is set on the surface of mercury and pressed to the crucible. The surplus mass of mercury is pressed out from the crucible. Inner volume of the crucible can be calculated from the mass of mercury left in the crucible and its density. The difference between calculated value and measured value is regarded as the volume error caused by the machining of crucible. Then the density error arisen from the machining accuracy of crucible can be expressed by the following equation:

\[
(\rho_C - \rho_m) \times 100\% = \left( \frac{|V_m - V_C|}{V_C} \right) \times 100\%
\]

where, \( \rho_C \) is the density value from the calculated value of inner volume of crucible, \( \rho_m \) is the density value from the measured value of inner volume of crucible, \( V_C \) is the calculated value of inner volume of crucible, \( V_m \) is the measured value of inner volume of crucible, \( m_{\text{Hg}} \) is the mass of mercury occupying the inner volume of crucible, and \( \rho_{\text{Hg}} \) is the density of mercury.

### 3.1.5 Error arisen from thermal expansion of alumina crucible \( (dV/V)_t \)

Thermal expansion of alumina crucible is the other main source of measurement error of density. The linear expansion of alumina material was measured as shown in Fig. 4 from the photographed image of crucible on naga film by using a gauging microscope (minimum gauge unit is 0.001 mm) in the temperature range from 1439 to 1923 K in the courses of temperature rising and falling. Compared with the size of crucible at room temperature (298 K), the linear expansion is from 0.93 to 2.09\% in the above temperature range, and the volume expansion is from 2.82 to 6.40\%. The maximum difference between the two courses is about \( \pm 1.91\% \) of the thermal expansion.

The measurement error of volume arisen from that of thermal expansion of alumina crucible can be calculated as follows.

\[
V = V_{\text{IRT}}(1 + \alpha_V(1 + \Delta \alpha_V)) + V_2
\]

when \( \Delta \alpha_V = 0 \),

\[
V_0 = V_{\text{IRT}}(1 + \alpha_V) + V_2
\]

then,

\[
\Delta V/V_0 = \left( V_{\text{IRT}} \cdot \alpha_V \cdot \Delta \alpha_V / [V_{\text{IRT}}(1 + \alpha_V) + V_2] \right) \times 100\%
\]
the surface of alloy drop comes to be not smooth because of the crystal at the surface. Thus, it is possible to measure the solidus temperature of alloy by observing the drop profile in the course of decreasing temperature. For example, the surface of alloy drop is smooth both in liquid and solid-liquid coexistence states as shown in Fig. 6(a), and it trends to be not smooth in the course of further decreasing temperature as shown in Fig. 6(b). Then the temperature at which the surface of drop changes into not smooth surface can be regarded as the solidus temperature of the alloy. On the other hand, the temperature coefficient for the density of alloy changes possibly at the solidus temperature and liquidus temperature. The two inflexions of the density-temperature curve are corresponding to the solidus temperature and liquidus temperature, respectively. In our experiment, one inflexion corresponding to the liquidus temperature did exist. It is further discussed in 3.4 “Density of nickel-chromium alloy”. Therefore, the solidus temperature and liquidus temperature of alloy can be evaluated by the observation of drop profile and the analysis of density value in relation to the temperature. The solidus temperature and liquidus temperature of the alloy evaluated with the method is shown in Fig. 7, which is close to that in the phase diagram of nickel-chromium alloy.23,24

![Image](image_url)

Fig. 6 Profile of alloy drop in liquid or solid-liquid coexistence state (a) and in solid state (b).

![Image](image_url)

Fig. 7 Comparison of the liquidus temperature and solidus temperature of alloy measured by a modified sessile drop method with that from the phase diagram.
This method can be particularly well suited to the determination of solidus temperature and liquidus temperature of some multi-component alloy.

3.3 Temperature dependence of density of liquid nickel

It is found experimentally that the temperature dependence of density for liquid metal and alloys is linear.\(^{25}\) If we follow Steinberg’s formula,\(^{25}\) the density data of liquid nickel can be represented by the following equation:

\[
\rho = \rho_m + k(T - T_m)
\]

(14)

where \(\rho_m\) stands for density at the melting point \(T_m\) and the temperature coefficient at constant pressure, \(k\), is expressed as follows:\(^{25}\)

\[
k = (\partial \rho / \partial T)_P = -\beta \rho_m
\]

(15)

where \(\beta = -(1/\rho_m)(\partial \rho / \partial T)_P\) is the thermal expansion coefficient of nickel.

The density of liquid nickel measured in this study is given in Fig. 8 together with literature values. The density at the melting point \(\rho_m\) and the thermal expansion coefficient \(\beta\) of liquid nickel are 7.91 Mg m\(^{-3}\) and 1.81 \(\times\) \(10^{-4}\) K\(^{-1}\), respectively. The measured result of \(\rho\) is expressed as follows:

\[
\rho/\text{Mg m}^{-3} = 7.91 - 1.43 \times 10^{-3}(T - 1728)
\]

\(\beta/\text{K}^{-1} = 1.81 \times 10^{-4}, 1728-1923\text{ K}\)

(16)

It is found that there is a large scatter in the density at the melting point \(\rho_m\), the temperature coefficient for the density and the thermal expansion coefficient \(\beta\) of liquid nickel obtained by various methods.\(^{1-17}\) The density at the melting point measured with modified sessile drop method in the present work is good agreement with values reported by Shiraiski and Ward,\(^{3}\) Kirshenbaum and Cahill,\(^{7}\) Saito and Sakuma,\(^{13}\) The thermal expansion coefficient \(\beta\) of liquid nickel is larger than the values obtained by other researchers except Benedicks \textit{et al.},\(^{11}\) Geld and Gertman,\(^{15}\) and is good agreement with values reported by Allen and Kingery,\(^{16}\) and Morita \textit{et al.}\(^{17}\)

3.4 Density of nickel-chromium alloy

The density of six nickel-chromium alloys with different chromium concentration of 0–24.53 mass% measured by modified sessile drop method in this work is shown in Fig. 9 together with the result of Eremenko \textit{et al.}.\(^{18}\) According to the result measured by Eremenko \textit{et al.} with large drop method, the density of nickel-chromium alloy in the temperature range from 1673 to 1923 K is represented by straight lines, and the temperature coefficient of density is a constant over the above temperature range. In present work, the relationship between density of nickel-chromium alloy and the temperature can be represented by two straight lines over the temperature range higher than solidus temperature of alloy. The temperature coefficient of density changes at a temperature, that is correspond to the point of intersection of two density-temperature straight lines. This temperature can be regarded as the liquidus temperature of the alloy. The density of alloy decreases with increasing chromium concentration in the alloy. Anomalous chromium concentration dependence of the density obtained by Eremenko \textit{et al.} was not observed.

3.4.1 Density of liquid nickel-chromium alloy

As shown in Fig. 10, the density decreases linearly with increasing chromium concentration in alloy in the temperature range of 1733–1833 K. It can be described as follows:

1733 K \(\rho/\text{Mg m}^{-3} = 7.88 - 3.15 \times 10^{-2}C_{\text{Cr}}\text{(mass%)}\) (17)

\[r = 0.99\]

1753 K \(\rho/\text{Mg m}^{-3} = 7.84 - 3.01 \times 10^{-2}C_{\text{Cr}}\text{(mass%)}\) (18)

\[r = 0.99\]

1773 K \(\rho/\text{Mg m}^{-3} = 7.83 - 3.09 \times 10^{-2}C_{\text{Cr}}\text{(mass%)}\) (19)
The thermal expansion coefficient of liquid alloy fluctuates in the range of $1.27 \times 10^{-4} \sim 1.88 \times 10^{-4}$ K$^{-1}$ at various chromium concentration in the alloy.

Temperature coefficient for the density of liquid nickel-chromium alloy, $k$, in eqs. (23)–(29), changes with increasing chromium concentration as shown in Fig. 12. With the values of $k$, the following relation was obtained by using the least square method:

$$k \times 10^2/\text{Mg} \cdot \text{m}^{-3} \cdot \text{K}^{-1} = -0.143 + 1.73 \times 10^{-3} C_Cr(\text{mass%})$$

(30)

Therefore, a least-squares analysis of our data gives an equation for the density of liquid nickel-chromium alloy as a function of temperature and chromium concentration as follows.

$$\rho/\text{Mg} \cdot \text{m}^{-3} = (7.91 - 3.09 \times 10^{-2} C_Cr(\text{mass%}))$$

$$- (0.143 - 1.73 \times 10^{-3} C_Cr(\text{mass%}))$$

$$\times 10^{-2}(T - T_L) \quad (T_L \leq T \leq 1833 \text{ K})$$

(31)

where, $T_L$ is the liquidus temperature of nickel-chromium alloy.

3.4.2 Density of nickel-chromium alloy in solid-liquid coexistence state

Temperature dependence of the density of alloy in solid-liquid coexistence state is shown in Fig. 13. It can be described as follows:

$$\rho/\text{Mg} \cdot \text{m}^{-3} = 7.87 - 1.01 \times 10^{-2}(T - 1719)$$

(32)

$$\beta/\text{K}^{-1} = 1.28 \times 10^{-3}, \quad C_Cr(\text{mass%}) = 5.00$$

$latex \beta$ is the correlation coefficient of regression equation. At different temperature, $\partial \rho / \partial C_Cr$ is $-2.98 \times 10^{-2} \sim -3.15 \times 10^{-2}\text{Mg} \cdot \text{m}^{-3}(\text{mass%})^{-1}$.

Temperature dependence of the density of liquid alloy at various chromium concentrations is shown in Fig. 11. It can be described as follows:

$$\rho/\text{Mg} \cdot \text{m}^{-3} = 7.91 - 1.43 \times 10^{-3}(T - 1728)$$

(23)

$$\beta/\text{K}^{-1} = 1.81 \times 10^{-4}, \quad C_Cr(\text{mass%}) = 0.00$$

(24)

$$\rho/\text{Mg} \cdot \text{m}^{-3} = 7.76 - 1.46 \times 10^{-3}(T - 1725)$$

$$\beta/\text{K}^{-1} = 1.88 \times 10^{-4}, \quad C_Cr(\text{mass%}) = 5.00$$

(25)

$$\rho/\text{Mg} \cdot \text{m}^{-3} = 7.61 - 0.99 \times 10^{-3}(T - 1719)$$

where $r$ is the correlation coefficient of regression equation.

Fig. 10 Effect of chromium concentration on the density of liquid nickel-chromium alloy.

Fig. 11 Temperature dependence of the density of liquid nickel-chromium alloy.

Fig. 12 Relationship between temperature coefficient for density of nickel-chromium alloy and chromium concentration.
The calculated values from eq. (31) and (39) show good agreement with the measured results in present work and the maximum error is about 0.9%.

4. Conclusions

(1) A modified sessile drop method was developed to obtain the precise density value of liquid nickel and nickel-chromium alloy in liquid and solid-liquid coexistence state. The total maximum relative error of the method is estimated as ±0.75%. Experimental result indicates that, besides the density of liquid alloy, the density of alloy in solid-liquid coexistence state can also be measured by using the modified sessile drop method.

(2) By the observation of drop profile in experiment and the analysis of density value, the solidus temperature and liquidus temperature of alloy can be determined by modified sessile drop method.

(3) The density of liquid nickel decreases linearly with increasing temperature in the range from the melting point to 1923 K. The density at the melting point and the thermal expansion coefficient of liquid nickel are 7.91 Mg m⁻³ and 1.81 × 10⁻⁴ K⁻¹, respectively.

(4) The density of nickel-chromium alloy in liquid or solid-liquid coexistence state decreases linearly with increasing temperature and chromium concentration in the alloy. The temperature coefficient of density of nickel-chromium alloy changes at the liquidus temperature. The absolute value of temperature coefficient of density in solid-liquid coexistence state is larger than that in liquid state.

(5) The density of liquid nickel and nickel-chromium alloy in liquid and solid-liquid coexistence states as a function of temperature and chromium concentration was expressed and the calculated values show good agreement with the measured value and the maximum error is estimated as about 0.9%.

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