Measurement of the Density of Ni-Cr Alloy by a Modified Pycnometric Method

Kusuhiro Mukai¹, Feng Xiao¹, Kiyoshi Nogi² and Zushu Li³

¹Department of Materials Science and Engineering, Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan

²Joining and Welding Research Institute, Osaka University, Ibaraki 567-0047, Japan

³Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK

A modified pycnometric method has been developed to obtain the accurate density value of liquid nickel and Ni-Cr alloy in the liquid and solid-liquid coexistence states. The density of liquid nickel decreases linearly with increasing temperature in the range from the melting point to 1873 K. The density at the melting point and the volume thermal expansion coefficient of liquid nickel are $7.91 \text{ Mg}\cdot\text{m}^{-3}$ and $1.87 \times 10^{-4} \text{ K}^{-1}$, respectively. The density of Ni-Cr alloys in the liquid and solid-liquid coexistence states was found to decrease linearly with increasing temperature and chromium concentration in the alloy. The temperature coefficient of density of Ni-Cr alloys was found to change at the liquidus temperature. The absolute value of temperature coefficient of density in the solid-liquid coexistence state is larger than that of the liquid alloy.

(Received November 17, 2003; Accepted May 7, 2004)

Keywords: liquid nickel, nickel-chromium alloy, density, modified pycnometric method

1. Introduction

In order to model shrinkage, transport phenomena and macro-segregation during dendritic solidification of alloys, the densities of the alloy in the liquid and solid-liquid coexistence states are needed. In the solidification process, the temperature and element concentrations in both phases vary. Consequently, we have devised the methods to measure and estimate the densities. We are particularly interested in simulating the solidification of nickel-chromium super-alloy because of their use in castings of critical components in gas-turbine engines.

The density of liquid nickel has been measured by a variety of techniques: the gamma radiation attenuation method,¹⁾ the maximum bubble pressure method,^{2,5,7-10)} the levitated drop method,^{3-5,13)} the direct Archimedean method,⁷⁾ the modified Archimedean method¹⁷⁾ and the large drop method,^{6,12)} etc. However, there is a large scatter in the reported density values for liquid nickel and its temperature dependence because of the experimental uncertainties associated with the above methods.

The data for the density of Ni-Cr alloy in the liquid and solid-liquid coexistence states are sparse since it was only measured by Eremenko *et al.*¹⁸⁾ for chromium concentrations between 8.96 and 57.06 mass% using the large drop method.

The authors have proposed a new method named of a modified sessile drop method, whose measurement error is estimated as $\pm 0.75\%$, to measure the density of Ni-Cr alloy in the liquid and solid-liquid coexistence states.¹⁹⁾ In order to decrease the measurement error further and to obtain more accurate density for liquid nickel and Ni-Cr alloys in the liquid and solid-liquid coexistence states, the authors modified the traditional pycnometric method and applied it to the density measurement of the same Ni-Cr alloy. In order to minimize the influence of the systematic errors of the two methods on the measured value of density, the recommended equation was obtained by regressing the density data measured by the modified sessile drop method and the modified pycnometric method.

The principle of the traditional pycnometric method is to determine the mass of metal that fills a known volume. The only source of systematic error lies in the calculated pycnometric volume and the only source of random error lies in temperature measurement. Therefore, the pycnometric method has the potential to be the most accurate of all methods.²⁰⁾ However, since density values at only one temperature can be measured at any one time, efficiency in the performance of the experiment tends to be low, which results in a large scatter of measured values. Sato *et al.*²¹⁾ modified the traditional pycnometric method and measured the density of silicon. The experimental efficiency was increased.

In the modified pycnometric method of present work, the disadvantages of the traditional pycnometric method have been overcome and the density of the alloy can be measured at wide temperature range in a single experiment.

2. Experimental

2.1 Principle of measurement

The principle of the modified pycnometric method is shown in Fig. 1. A pycnometer is an alumina crucible made up of upper and lower parts machined with high precision. A sample is charged into a horizontal lower crucible, and the upper one is placed on the solid sample and fabricated into the lower one. After the alloy sample melted down, the upper crucible is pressed to intimately contact with the edge of the lower one. The volume of liquid sample is larger than the sum of the inner volume of cylinder in the lower crucible at experiment temperature (V_1) and that of the inner volume of the cone in the upper crucible at experiment temperature (V_2). Consequently, the surplus liquid alloy is forced into the cylindrical hole machined in the center of upper crucible. A liquid column with a smooth meniscus is formed in the aperture with a volume of $V_3 + V_4$. The shape of the liquid column in the hole was recorded on an X-ray film by X-ray emission. From the film, the height of liquid column, h_3 , and the height of the crown at the upper end of liquid column, h_4 ,

Fig. 1 Principle of the modified pycnometric method for measurement of the density.

can be measured. Then, the volume of $V_3 + V_4$ can be calculated. The total volume of sample is the sum of V_1 , V_2 , V_3 and V_4 . The sample mass, m , is calculated from the change of the sample mass before and after the experiment and the experimental time. This is discussed further in section 3.1.1. The density ρ can be obtained from the following equations:

$$\rho = \frac{m}{V} \quad (1)$$

$$V = V_1 + V_2 + V_3 + V_4 \quad (2)$$

$$V_3 = \frac{\pi}{4} [d_2(1 + \alpha_L)]^2 h_3 \quad (3)$$

$$V_4 = \frac{\pi h_4}{6} \left[3 \left(\frac{d_2}{2} \right)^2 (1 + \alpha_L)^2 + h_4^2 \right] \quad (4)$$

where, the value of $V_1 + V_2$ at experimental temperature (eq. (2)) is obtained by calibrating the value of $V_1 + V_2$ at room temperature measured by high purity mercury as described further in section 3.1.3 with the volume expansion of pycnometer, d_2 is the inner diameter of hole in the upper crucible, and α_L is the linear expansion of pycnometer.

2.2 Experimental procedure

The experimental apparatus has been described previously in detail.²⁵⁾ The atmosphere in the apparatus was purified argon and a flow rate of 0.80 l/min was maintained.

The following procedure was adopted to prevent the formation of bubbles and gaps in the contacting area between the liquid alloy and the inner wall of the pycnometer. Before the experimental temperature has exceeded the melting point of nickel or the solidus temperature of alloy, the furnace tube was evacuated. When the sample had melted and the liquid column had a smooth surface in the upper crucible and was in stable state, then purified argon gas was re-introduced into furnace. The lower part of upper crucible was machined to be like a inverse funnel to prevent the gas bubble in pycnometer from attaching and stagnating on the wall of pycnometer. The gap between the internal wall of lower crucible and the external wall of upper one was machined precisely so as be small enough to prevent the liquid alloy from being pressed

out of the pycnometer.

After holding at a given temperature for 0.6 ks, the photographs of liquid alloy were taken by the X-ray emission.

3. Results and Discussion

3.1 Measurement error of the modified pycnometric method

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

$$d\rho = (\partial\rho/\partial m)dm + (\partial\rho/\partial V)dV \quad (5)$$

$$d\rho/\rho = dm/m + dV/V \quad (6)$$

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

The measurement error for volume includes the errors arising from the following sources: the measurement of the heights of the liquid column and the crown in the aperture of the upper crucible, from the machining accuracy of the pycnometer and from the thermal expansion of the alumina pycnometer. In addition, the temperature distribution in the temperature zone of the furnace tube also gave rise to errors in the density measurement.

3.1.1 Measurement error of sample mass (dm/m)

In the modified pycnometric method, it is very important to take an optimum sample mass for the determination of the precise volume of a liquid alloy. If the alloy mass is too small, the upper part of the liquid alloy can not be forced into the aperture in the upper crucible when the latter is pressed to contact with the edge of the lower one. Alternatively, if the alloy mass is too much, the upper part of the alloy will be pressed completely out from the pycnometer through the hole of upper crucible. In preliminary experiments, it was established that the optimum sample mass for the measurements of each alloy with various chromium concentrations was determined to be between 27 and 30 g.

The sample mass was measured using a high accuracy electronic balance (0.1 mg of the resolution) before and after the experiment. If it is assumed that the mass loss due to evaporation at the temperature below the solidus is negligible and the sample mass decreases linearly with experimental time at the temperature above the solidus, the maximum error of density arisen from the mass loss of sample can be expressed by the following equation:

$$\frac{dm}{m} = \frac{m_0 - m_f}{m_0} \times \frac{t}{t_f} \times 100\% < \pm 0.04\% \quad (7)$$

where, m_0 is the mass of sample before experiment, m_f is the mass of sample after experiment, t is the time from the beginning of density measurements to the taking of the photograph and t_f is the total time of density measurements at temperatures above the solidus.

Experimental result indicates that the mass loss of the sample in the method is smaller than that in the modified sessile drop method, reported by Mukai and Xiao,¹⁹⁾ as

$\pm 0.06\%$. The reason is that the surface of sample exposed to gas in the pycnometer ($\approx 28 \text{ mm}^2$) is much smaller than that in the modified sessile drop method ($\approx 154 \text{ mm}^2$).

3.1.2 Error arising from the measurement of the heights of liquid column and the crown in the upper crucible (dV/V_h)

The heights of liquid column and the crown are obtained by measurements carried out on the photographed image. The error arising from measurements of the photographed image can be less than $\pm 1.00 \text{ mm}$. The magnification between the photographic image of the alloy sample and the actual sample was about 6 times. Therefore, the measurement error arising from the measurement of the heights of liquid column and crown in upper crucible is less than $\pm 0.17 \text{ mm}$. The density error arising from the measurement in the height is calculated to be less than $\pm 0.11\%$ according to eqs. (3) and (4).

3.1.3 Error arisen from the machining accuracy of pycnometer (dV/V_m)

As shown in Fig. 1, the corner of the inner wall of the lower crucible of pycnometer was machined to have a circular cross section in order to ensure that there was no gap in the contacting area between liquid sample and inner wall. In order to observe any small volume variations with temperature, an aperture of small diameter was machined in the center of upper crucible. The error caused by any machining accuracies can be eliminated by the following method. Before an experiment, high purity mercury of well known density is charged into the pycnometer used to measure the density of alloy. In order to ensure the inner volume of pycnometer is occupied completely by mercury, an alumina plate with a flat and smooth surface is set on the surface of mercury and forced into the upper surface of the upper crucible. The surplus mass of mercury was forced from the upper crucible. From the mass of mercury left in the pycnometer and its density, the real inner volume of pycnometer at room temperature can be calculated. The accurate value of $V_1 + V_2$ at room temperature is the difference between the real inner volume of pycnometer and the volume of the hole in the upper crucible. Any errors caused by the machining accuracies can be neglected.

3.1.4 Errors arising from the thermal expansion of the alumina pycnometer (dV/V_t)

The linear thermal expansion of alumina materials used in this work is from 0.93% to 2.09% in the temperature range from 1439 to 1923 K , and the volume expansion is from 2.82% to 6.40% . The maximum difference of thermal expansion between the heating and cooling cycles is about $\pm 1.91\%$.¹⁹⁾

The relative error of volume arising from the measurement error of the thermal expansion of the pycnometer ($\Delta\alpha_V$) is estimated as

$$\Delta V/V_0 \approx (3.1 \times 10^{-2} \Delta\alpha_V + 1.04 \times 10^{-5} \Delta\alpha_V^2) \times 100\% \quad (8)$$

In eq. (8), the second term is much smaller than the first term. Therefore, the error in volume measurement approximates to a linear function of that of thermal expansion of the alumina pycnometer. This is shown in Fig. 2 together with that for the modified sessile drop method.¹⁹⁾

Fig. 2 The relationship between the error in volume measurement of the sample and that of the thermal expansion of crucible.

The maximum difference of the thermal expansion resulting from the measurements obtained in heating and cooling cycle is $\pm 1.91\%$. Thus the maximum measurement error of density arising from thermal expansion in the present work is calculated to be $\pm 0.06\%$ which is larger than that of the modified sessile drop method, $\pm 0.04\%$, reported by Mukai and Xiao.¹⁹⁾

3.1.5 Errors arising from the temperature distribution in the temperature zone of furnace tube ($d\rho/\rho_T$)

The temperature difference ΔT in the temperature zone in which pycnometer is located is $\pm 5 \text{ K}$. The density error arisen from the temperature distribution in furnace tube can be expressed by the following equation:

$$\frac{d\rho}{dT} \cdot \frac{\Delta T}{\rho} \times 100\% < \pm 0.09\% \quad (9)$$

3.1.6 Measurement error for density measurement ($d\rho/\rho$)

On the basis of the above analysis of measurement error, the relative measurement error in density can also be derived from the following equation:

$$\begin{aligned} \frac{d\rho}{\rho} &= \frac{dm}{m} + \left(\frac{dV}{V}\right)_h + \left(\frac{dV}{V}\right)_m + \left(\frac{dV}{V}\right)_t + \left(\frac{d\rho}{\rho}\right)_T \\ &= \pm 0.04\% \pm 0.11\% \pm 0.00\% \\ &\quad \pm 0.06\% \pm 0.09\% = \pm 0.30\% \end{aligned} \quad (10)$$

Thus the total maximum relative error for the method is estimated as $\pm 0.30\%$ in this study.

3.2 Advantages of the modified pycnometric method

Compared with the traditional pycnometric method, the major advantage of the present technique is that the modified pycnometric method allows a continuous measurement of density over a wide temperature range in a single experiment. Therefore, the efficiency for performance of experiments is much greater.

Furthermore, in the solid-liquid coexistence state, the solid particles trend to sink to the bottom of lower part of the crucible of pycnometer and the surface of the liquid column

remains smooth. Therefore, the measurement accuracy of sample volume in the solid-liquid coexistence state was not influenced by the solid particle precipitated in the liquid sample. This was verified in the density measurements on Ni-Cr alloys in the solid-liquid coexistence state using the method. In other words, in addition to the density of liquid alloy, the density of alloy in the solid-liquid coexistence state can also be measured using the modified pycnometric method.

The total maximum relative error of the modified pycnometric method is estimated to be $\pm 0.30\%$. It is smaller than that of the modified sessile drop method, $\pm 0.75\%$.¹⁹⁾

Furthermore, the scatter of measured density values for an identical condition for the modified pycnometric method, $\pm 0.11\%$, is smaller than that for the modified sessile drop method, $\pm 0.40\%$. The standard deviation $\sigma = (\sum \varepsilon_i^2/n)^{1/2}$ (ε_i : the deviation of a measured value from the mean value of all the measured values, n : the number of measurements) among density values measured at a constant temperature for the modified pycnometric method was $5.20 \times 10^{-3} \text{ Mg}\cdot\text{m}^{-3}$, which is also smaller than that for the modified sessile drop method, $2.60 \times 10^{-2} \text{ Mg}\cdot\text{m}^{-3}$. The reason is that the alloy volume in the upper crucible compared with the total volume for the modified pycnometric method (about 11%) is less than that for an alloy drop formed above the upper edge of the crucible for total volume in the modified sessile drop method (about 30%).

Finally, only the heights of the liquid column and the crown in the hole of the upper crucible are measured on the X-ray film in the modified pycnometric method, thus the influence of the solid particle precipitated in alloy sample on the measurement accuracy is pretty little even though at the temperature approach the solidus temperature of the alloy. But in the modified sessile drop method, the profile of alloy above the upper end of the crucible, which is numerically input to calculate the sample volume, may be influenced by the solid particle precipitated in alloy sample, especially at the temperature approach the solidus temperature of the alloy, although it is difficult to distinguish clearly the precipitated solid particle from the smooth profile on the photograph of the drop. At the point, the modified pycnometric method is also better than the modified sessile drop method.

Although the modified pycnometric method has above advantages compared with the modified sessile drop method, the modified sessile drop method can not be substituted by the former because of its following advantages: 1. The solidus temperature of alloy can be measured by observing the drop profile in the course of decreasing temperature. 2. The atmosphere in the furnace can be controlled precisely. 3. The density of alloy can be measured both in the courses of temperature rising and temperature falling.

3.3 Temperature dependence of density of liquid nickel

It was found experimentally that the temperature dependence of density for liquid metals and alloys is linear.¹⁹⁾ Using Steinberg's formula,²²⁾ the density data for liquid nickel can be represented by the following equation:

$$\rho = \rho_m + k(T - T_m) \quad (11)$$

1. Makeev ¹⁾	2. Saito ²⁾	3. Shiraishi ³⁾	4. Saito ⁴⁾	5. Saito ⁵⁾
6. Saito ⁵⁾	7. Popel ⁶⁾	8. Kirshenbaum ⁷⁾	9. Lucas ^{8,9)}	
10. Lucas ¹⁰⁾	11. Benedicks ¹¹⁾	12. Vertmann ¹²⁾		
13. Saito ¹³⁾	14. Kozakevitch ¹⁴⁾	15. Geld ¹⁵⁾	16. Allen ¹⁶⁾	
17. Morita ¹⁷⁾	18. Mukai ¹⁹⁾	and Present work		

Fig. 3 The density of molten nickel measured by various investigators.

where ρ_m stands for the density at the melting point T_m and the temperature coefficient at constant pressure, k , can be expressed as follows:²²⁾

$$k = (\partial\rho/\partial T)_P = -\beta\rho_m \quad (12)$$

where β is the volume thermal expansion coefficient of nickel.

The density of liquid nickel measured in this study is given in Fig. 3 together with the literature values and is expressed as follows:

$$\begin{aligned} \rho/\text{Mg}\cdot\text{m}^{-3} &= 7.90 - 1.52 \times 10^{-3} (T - 1728) \\ \beta/\text{K}^{-1} &= 1.92 \times 10^{-4}, \quad 1728 \sim 1873 \text{ K} \end{aligned} \quad (13)$$

It shows a good agreement with that measured with the modified sessile drop method.¹⁹⁾ The difference between the density values measured with the two methods is smaller than 0.16% which can be regarded as the result from the systematic errors of the two methods. Then, in order to offset the influence of the systematic error of the two methods on the measured value of density, the data on the density of liquid nickel obtained in the two methods were regressed in an equation as follows using a least-squares analysis and were recommended.

$$\begin{aligned} \rho/\text{Mg}\cdot\text{m}^{-3} &= 7.91 - 1.48 \times 10^{-3} (T - 1728) \\ \beta/\text{K}^{-1} &= 1.87 \times 10^{-4}, \quad 1728 \sim 1873 \text{ K} \end{aligned} \quad (14)$$

Figure 3 also showed that there is a large scatter in the density at melting point ρ_m and the volume thermal expansion coefficient of liquid nickel β . The density at the melting point measured in the present work shows good agreement with the values reported by Shiraishi and Ward,³⁾ Kirshenbaum and Cahill,⁷⁾ Saito and Sakuma.¹³⁾ The thermal expansion coefficient β of liquid nickel obtained in the present work is larger than the values obtained by other

researchers with the exception of values reported by Benedicks *et al.*,¹¹⁾ Geld and Gertman,¹⁵⁾ and is in good agreement with values reported by Allen and Kingery,¹⁶⁾ and Morita *et al.*¹⁷⁾

3.4 Density of Ni-Cr alloy

The solidus temperature and liquidus temperature of the alloys are necessary to distinguish the state of alloy. The solidus temperature of the four Ni-Cr alloys studied in present work was evaluated in the modified sessile drop method by observing the drop profile in the course of temperature falling.¹⁹⁾ They are 1718 K for Ni-5 mass%Cr alloy, 1696 K for Ni-11.45 mass%Cr alloy, 1689 K for Ni-15 mass%Cr alloy, and 1679 K for Ni-20 mass%Cr alloy, respectively.

For the liquidus temperature of the alloys, the temperature coefficient of density of alloy changes possibly at the liquidus temperature. The inflexion of the density-temperature curve is corresponding to the liquidus temperature. In our experiment, one inflexion of density-temperature curve did exist. The solidus temperature evaluated with the modified sessile drop method and the temperature corresponding to the inflexion of density-temperature curve of the alloys measured with the modified pycnometric method and the modified sessile drop method are shown in Fig. 4. The temperature corresponding to the inflexion of density-temperature curve of the alloy is close to the liquidus temperature of alloy in the phase diagram of the alloy.^{23,24)} Thus, the temperature at the inflexion of density-temperature curve of alloy can be regarded as the liquidus temperature of alloy. They are 1722 K for Ni-5 mass%Cr alloy, 1715 K for Ni-11.45 mass%Cr alloy, 1708 K for Ni-15 mass%Cr alloy and 1707 K for Ni-20 mass%Cr alloy, respectively.

The density of four Ni-Cr alloys with chromium concentration between 0 and 20 mass% was measured by the modified pycnometric method in the temperature range from the solidus temperature to 1923 K. The results are shown in Fig. 5 together with the results by Eremenko *et al.*¹⁸⁾ According to the results measured by Eremenko *et al.* with

Fig. 4 Comparison of the liquidus temperature and solidus temperature of alloy measured by a modified sessile drop method and a modified pycnometric method with that from the phase diagram.

Fig. 5 The density of Ni-Cr alloys measured by various investigators.

large drop method, the density of Ni-Cr alloy in the temperature range from 1673 to 1950 K is represented by straight lines, and the temperature coefficient of density is a constant over the above temperature range. Furthermore, the density of alloy did not decrease with increasing chromium concentration in alloy. In the present work, the relationship between the density of individual Ni-Cr alloys and the temperature can be represented by two straight lines over the temperature range above the solidus temperature of the alloy. The temperature coefficient of density changes at the liquidus temperature which is corresponding to the intersection point of two density-temperature straight lines. The density of the alloy decreases with increasing chromium concentration in the alloy. The anomalous chromium concentration dependence of the density obtained by Eremenko *et al.* was not observed in this study.

3.4.1 Density of liquid Ni-Cr alloy

The temperature dependence of the density of the liquid alloy at various chromium concentrations is shown in Fig. 5 and Table 1. The volume thermal expansion coefficient for the liquid alloy lies in the range of 1.62×10^{-4} to $1.95 \times 10^{-4} \text{ K}^{-1}$ for the various chromium concentration in the alloys studied.

An extensive amount of work has been carried out to determine k (eq. (12)) for liquid alloys. The temperature coefficient for the density of liquid Ni-Cr alloys in Table 1 changes with increasing chromium concentration, as shown

Table 1 Densities of liquid Ni-Cr alloys as a function of temperature measured by the modified pycnometric method.

C_{Cr} (mass%)	Equation	β/K^{-1}
0	$\rho/\text{Mg}\cdot\text{m}^{-3} = 7.90 - 1.52 \times 10^{-3} (T - 1728)$	1.92×10^{-4}
5.00	$\rho/\text{Mg}\cdot\text{m}^{-3} = 7.73 - 1.51 \times 10^{-3} (T - 1722)$	1.95×10^{-4}
11.45	$\rho/\text{Mg}\cdot\text{m}^{-3} = 7.53 - 1.22 \times 10^{-3} (T - 1715)$	1.62×10^{-4}
15.00	$\rho/\text{Mg}\cdot\text{m}^{-3} = 7.43 - 1.25 \times 10^{-3} (T - 1708)$	1.68×10^{-4}
20.00	$\rho/\text{Mg}\cdot\text{m}^{-3} = 7.28 - 1.27 \times 10^{-3} (T - 1707)$	1.74×10^{-4}

Fig. 6 The relationship between the temperature coefficient for density of Ni-Cr alloy and chromium concentration.

in Fig. 6 and eq. (15), which is similar to that determined by the modified sessile drop method.¹⁹⁾

$$k \times 10^2 / \text{Mg} \cdot \text{m}^{-3} \cdot \text{K}^{-1} = -0.15 + 1.59 \times 10^{-3} C_{\text{Cr}}(\text{mass}\%) \quad (15)$$

Therefore, a least-squares analysis of our data in the modified pycnometric method gives an equation for the density of liquid Ni-Cr alloy as a function of both temperature and chromium concentration, as follows,

$$\begin{aligned} \rho / \text{Mg} \cdot \text{m}^{-3} = & (7.89 - 3.08 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)) \\ & - (0.15 - 1.59 \times 10^{-3} C_{\text{Cr}}(\text{mass}\%)) \\ & \times 10^{-2} (T - T_L) \\ & (T_L \leq T \leq 1913 \text{ K}) \end{aligned} \quad (16)$$

where, T_L is the liquidus temperature of Ni-Cr alloy.

The above relationship between the density and chromium concentration and temperature determined with the modified pycnometric method shows good agreement with that by the modified sessile drop method.¹⁹⁾ The difference between the density values measured with the two methods is smaller than 0.25% which can be regarded as the result from the systematic errors of the two methods. Then, in order to offset the influence of the systematic error of the two methods

Table 2 Densities of liquid Ni-Cr alloys as a function of Cr concentration measured by the modified pycnometric method.

T/K	Equation
1733	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.90 - 3.06 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)$
1753	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.85 - 3.22 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)$
1773	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.83 - 3.21 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)$
1793	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.79 - 3.12 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)$
1813	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.77 - 3.14 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)$
1833	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.73 - 3.07 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)$
1873	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.68 - 3.07 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)$
1913	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.62 - 3.04 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)$

Table 3 Densities of Ni-Cr alloys in the liquid-solid coexistence state as a function of temperature measured by the modified pycnometric method.

$C_{\text{Cr}}(\text{mass}\%)$	Equation	β / K^{-1}
5.00	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.80 - 1.10 \times 10^{-2} (T - 1718)$	1.41×10^{-3}
11.45	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.65 - 6.45 \times 10^{-3} (T - 1696)$	8.43×10^{-4}
15.00	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.51 - 4.25 \times 10^{-3} (T - 1689)$	5.66×10^{-4}
20.00	$\rho / \text{Mg} \cdot \text{m}^{-3} = 7.36 - 2.99 \times 10^{-3} (T - 1679)$	4.06×10^{-4}

on the measured value of density, the data on the density of liquid Ni-Cr alloys obtained in the two methods were regressed in an equation as follows using a least-squares analysis and was recommended.

$$\begin{aligned} \rho / \text{Mg} \cdot \text{m}^{-3} = & (7.90 - 3.09 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)) \\ & - (0.15 - 1.66 \times 10^{-3} C_{\text{Cr}}(\text{mass}\%)) \\ & \times 10^{-2} (T - T_L) \\ & (T_L \leq T \leq 1833 \text{ K}) \end{aligned} \quad (17)$$

As shown in Fig. 5 and Table 2, the density decreases linearly with increasing chromium concentration in the alloy in the temperature range of 1733 ~ 1913 K. At different temperature, $\partial \rho / \partial C_{\text{Cr}}$ lies between -3.04×10^{-2} and $-3.22 \times 10^{-2} \text{ Mg} \cdot \text{m}^{-3} \cdot (\text{mass}\%)^{-1}$.

3.4.2 Density of Ni-Cr alloy in the solid-liquid coexistence state

The temperature dependence of the density of an alloy in the solid-liquid coexistence state is shown in Fig. 5 and Table 3.

The absolute value of the temperature coefficient of density in the solid-liquid coexistence state is larger than that for the liquid alloy as shown in Fig. 6. Temperature coefficient for density of Ni-Cr alloy in the solid-liquid coexistence state in Table 3 increases with increasing chromium concentration, which is little larger than that for the values obtained with the modified sessile drop method.¹⁹⁾ The temperature coefficient difference between the two methods may be arisen from the error caused by the solid particles in the sample in the solid-liquid coexistence state. The temperature coefficient of the density of Ni-Cr alloys with the modified pycnometric method was obtained as follows:

$$k \times 10^2 / \text{Mg} \cdot \text{m}^{-3} \cdot \text{K}^{-1} = -1.32 + 5.46 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%) \quad (18)$$

Therefore, least-squares analysis of our data in modified pycnometric method gives eq. (19) for the density of Ni-Cr alloy in the solid-liquid coexistence state as a function of both temperature and chromium concentration which is similar to that determined with the modified sessile drop method.¹⁹⁾

$$\begin{aligned} \rho / \text{Mg} \cdot \text{m}^{-3} = & (7.96 - 2.97 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)) \\ & - (1.32 - 5.46 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)) \\ & \times 10^{-2} (T - T_S) \\ & (T_S \leq T \leq T_L) \end{aligned} \quad (19)$$

where, T_S is the solidus temperature of Ni-Cr alloy.

The data determined by the two methods show good agreement. Because the measurement accuracy of the

modified pycnometric method is higher than that of the modified sessile drop method in the solid-liquid coexistence state of alloy, in order to offset the influence of the systematic error of the two methods on the measured value of density, the data obtained in the modified pycnometric method can be treated as follows. At first, the difference between the density value at the liquidus temperature measured in the modified pycnometric method and that calculated by eq. (17) was calculated and was defined as $\Delta\rho_d$. Then, the density-temperature curve obtained in the modified pycnometric method was moved parallelly from the original place in the direction of density axle. The moving distance is $\Delta\rho_d$.

The new density-temperature curve was regressed in an equation as follows using a least-squares analysis and was recommended.

$$\begin{aligned} \rho/\text{Mg}\cdot\text{m}^{-3} = & (7.94 - 2.67 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)) \\ & - (1.32 - 5.46 \times 10^{-2} C_{\text{Cr}}(\text{mass}\%)) \\ & \times 10^{-2} (T - T_S) \\ & (T_S \leq T \leq T_L) \end{aligned} \quad (20)$$

The values of density measured in present work and those calculated from eqs. (17) and (20) show good agreement and the maximum error is about 0.68%.

4. Conclusions

(1) A modified pycnometric method has been developed to obtain precise density values for liquid nickel and Ni-Cr alloys in the liquid and solid-liquid coexistence states. The modified pycnometric method allows a continuous measurement of density over a wide temperature range in a single experiment. The maximum relative error of the method was estimated as $\pm 0.30\%$.

(2) The density of liquid nickel decreases linearly with increasing temperature in the range from the melting point to 1873 K. The density at the melting point and the thermal expansion coefficient of liquid nickel are $7.91 \text{ Mg}\cdot\text{m}^{-3}$ and $1.87 \times 10^{-4} \text{ K}^{-1}$, respectively.

(3) The density of Ni-Cr alloys in the liquid or solid-liquid coexistence state decreases linearly with increasing temperature. The temperature coefficient for the density of Ni-Cr alloys changes at the liquidus temperature. The absolute value of temperature coefficient of density in solid-liquid coexistence state is larger than that of liquid alloy.

(4) In the temperature range of 1733 ~ 1913 K, the density of liquid Ni-Cr alloy decreases linearly with increasing the chromium concentration in the alloy, and $\partial\rho/\partial C_{\text{Cr}}$ has value between -3.04×10^{-2} and $-3.22 \times 10^{-2} \text{ Mg}\cdot\text{m}^{-3}(\text{mass}\%)^{-1}$.

(5) The density of liquid nickel and Ni-Cr alloy in the liquid and solid-liquid coexistence states as a functions of both temperature and chromium concentration was ex-

pressed; the calculated values show good agreement with the measured value; the maximum deviation is estimated as 0.68%.

Acknowledgments

This work was performed as a part of Research and Development of Innovative Casting Simulation supported by New Energy and Industrial Technology Development Organization, Japan. The authors are indebted to Prof. Kenneth C. Mills of Imperial College London for his kind suggestion on the measurement of density and the modification of the paper. The authors also wish to thank Ms. Rika Umegane and the center for instrumental analysis of Kyushu Institute of Technology for advice, comment and help.

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