1. Introduction

Density is one of the fundamental order parameters that are used to explain phase transformations, such as solidification, vitrification, and crystal–crystal, liquid–liquid and glass–glass transitions. In addition, successful detection of liquid–liquid and glass transitions can often be appeared in thermal expansion coefficient deduced by precise density. Density measurements of supercooled liquids is especially important because it plays a key role in controlling detailed paths of phase transformations, and thus often carries crucial information necessary for finding new materials. Despite the simple definition of density ($\rho = \text{mass}/\text{volume}$), the density measurement of molten metals with high melting temperatures is still non-trivial because of contamination and high reactivity from sample containers. In order to overcome such challenges, various levitation methods [1–8] have been developed. In particular, the containerless techniques allow measuring the density of deeply supercooled liquids, which are extremely difficult to obtain via conventional contact-based methods.

Electrostatic (ESL) [1–6], aerodynamic (ADL) [7, 8], and electromagnetic (EML) [9] levitation methods can provide a high temperature environment and have been used to measure...
the densities of liquid metals. Among the above containerless approaches, ESL carries distinctive advantages over other methods for measuring densities of a levitated liquid droplet, e.g. a quiescent condition, and an almost spherical shape of the melts under high vacuum. Those advantages make simple image analysis possible for density, viscosity, and surface tension measurements while assuring accuracies of the results. However, there have been discrepancies between several reported density values, in particular on Fe [5], Ti [10], Zr [12, 13], and Nb [12, 13], which have all been obtained via ESL experiments. Ultimately, inaccurate liquid density values could lead to a misinterpretation in understanding phase transition and liquid structure as well as predicting other physical quantities via numerical simulation. Therefore, it is very important to establish uncertainty criteria and its evaluation procedure for the high temperature liquid density measurement.

Here, we evaluate the uncertainty of density measurement using the ESL, which has been built in KRISS (Korea Research Institute of Standards and Science). The present study is comprised of the following sections. First, an electrostatic levitation device will be described, and the details, i.e. how to measure the density of liquid metals and how to analyze the measurement, will be given in section 2. In section 3, density data of high temperature molten liquid metals (Ni, Zr, Nb, and Hf) will be provided. Finally in section 4, the uncertainty budget for our density measurement will be evaluated.

2. Instrument and experiment

2.1. Electrostatic levitation

Figure 1 shows schematics of the electrostatic levitation system, which has been recently developed in KRISS for the first time in Korea. Basic configurations of the present ESL system are similar to previously developed ESL devices [1–4]. Recent status and history of the ESL development are well elaborated elsewhere [6]. Our ESL unit consists of five main parts, i.e. a vacuum chamber, electrodes and high voltage systems, position and rotation controls, charging and heating systems, and measurement system for physical properties.

2.1.1. Levitation process: levitation and positioning. An as-casted metallic sample (Ni, (99.995%), Zr (99.95%), Nb (99.95%), and Hf (99.9% with nominal 2 wt% of Zr)) with masses ranging between 20 and 40 mg are prepared by an arc-melter under argon atmosphere (99.9999%). Subsequently it is placed at a bottom electrode that is grounded positively in a vacuum chamber (10⁻⁶ ~ 10⁻⁷ Torr, stainless steel 304). At the center of the chamber, a pair of electrodes is located; top and bottom electrodes adjust the z-position of the levitated sample, and two-pair side electrodes control the x- and y-positions. Electrodes were designed to have a restoring force toward the center and to give position stability by using a smaller size top electrode with a convex shape than the bottom electrode.

The initial set-position of the sample is given by two He–Ne lasers beams (632 nm). The two He–Ne lasers are aligned perpendicular to each other as shown in figure 1. The laser beams are detected by two position sensitive detectors (PSD) (Hamamatsu Photonics, C10443-03) which are located at opposite sides of the positioning lasers. Then, the positively charged sample on the bottom electrode is lifted to the set-position while negative high voltage (HV) is applied to the top electrode. As the sample approaches the set-position, the applied voltage is automatically modulated to keep the sample at the set-position by counter-balancing the gravitational force, using automatic PID feedback control of position to voltage with 2 ms response time interval. A schematic description of ESL is given in figure 1.

2.1.2. Heating, charging, and temperature measurement. The sample is heated and melted using two CO₂ heating lasers (a 50 W laser and a 100 W laser). The laser beam with 100 W is divided into two 50 W beams by a beam splitter. The laser beams incident on the sample with 120 degrees for symmetrical heating. This gives a better homogeneity of temperature and position stability of the sample at high temperature, as seen in figure 1(b).

On heating, charge on the sample surface can be lost by out-gassing from the sample, which causes the sample to fall. Therefore, we should provide the charge on the sample surface by using an UV (ultraviolet) lamp (Hamamatsu, L2D2) via a photoemission process. Once the sample temperature increases over 900 °C typically, but depending on samples, thermionic emission occurs so that the sample is positively charged itself. Temperature measurement is carried out using three infrared pyrometers with Si (0.9 μm, Chino (IR-CAS8CS3)) and InGaAs (1.55 μm, Chino (IR-CA13CS3)), and 1.6 μm, Metis (MI16)) detectors, depending on temperature ranges. The temperature is recorded in 6 ms time intervals.

2.2. Density measurement: calibration and image analysis

For the density measurement, we employed an imaging method which had been well implemented in previous ESL experiments [3, 14]. The levitated samples were illuminated by an UV-backlight (365 nm, 100 W, LICHTZEN CO.). The sample images were recorded by a long distance black/white (B/W) CCD camera (BASLER, 210 frame per second, 7.4 μm × 7.4 μm pixel size, high resolution (648 × 488)) (see figure 2). The UV-backlight and fast recording speed (210 frame s⁻¹) prevent image-blurring that can be caused by white-backlight and sample motion. As well as the smaller pixel size and high resolution, this is particularly helpful, when the liquids are held at very high temperatures and thus susceptible to instability of the sample position. As temperature increases, the sample may emit UV light, depending on temperature. Ishikawa described the effect of UV light from a heated sample, which the Wien’s wavelength is 827 nm at 3500 K [12]. Since we used the 365 nm band pass filter for the UN-backlight, we believed that the image negligibly interfered by UV light from the glowing sample. Here, we describe the process of calibration and image analysis as follows.
2.2.1. Calibration. The calibration process is necessary for the density measurement since we acquire a 2D image of the sample from the CCD camera. We used two tungsten carbide (WC) balls (Industrial Tectonics Inc.) as standard-reference balls, with different diameters 2.3813 mm, 1.984 mm ($\pm$254 nm), respectively. The image of the large WC ball was used for the calibration of a pixel-to-meter conversion factor. The diameter of the small WC ball was measured to check the accuracy of the calibration factor.

2.2.2. Image analysis. In the present study, the image analysis to calculate sample volume is basically similar to that used in the early studies [3, 10, 11, 14]. The captured images were analyzed by using the following process.

2.2.2.1. Edge detection. Edge detection is the first step to obtain the sample volume from the UV image. The edge of the image is determined by finding maximum differential values of brightness intensity of pixels along radial direction from an arbitrarily chosen center of the sample image [3, 10]. Compared with a mask method [15], this method does not depend on the shape of the boundary image, provides fast calculation, and determines a single value from the differential. Figure 3 gives a temporary boundary of the sample that is obtained by using this method.

Searching direction for maximum differential value is fixed with specific polar angle, $\theta_i$, when $i$ varies from 1 to $N = 800$. The edge detection is performed along the radial direction for each polar angle (figure 3(b)), and pixel intensity and the differential values are found at the pixel coordinate satisfying the following equations.

$$\theta_i = \frac{2\pi i}{N}$$  

$$x_i = r_i \sin \theta_i + x_0$$
Here $x_i$ and $y_i$ are the horizontal and vertical coordinates of $i$th pixel along the radial direction from center $x_0$ and $y_0$ in figure 3(b), respectively. $Y_j$ expresses a $j$th line along the radial direction.

After the center of the image is recalculated from the previously determined boundary, the process is repeated to determine the boundary again. However, with equation (4), two singular points occur at zero or 180 degrees (figure 4). To avoid this divergence, we divided the image into four different areas in figure 5. Then we used equation (5) for areas 1 and 3 and equation (6) for areas 2 and 4. This simple method removes the divergence of edge detection, resulting in better edge determination as shown in figure 5.

Where $i = 100 \sim 300$, and $i = 500 \sim 700$.

2.2.2.2. Volume calculation. After the coordinates of the sample boundary is determined, it is fitted with 6-order Legendre polynomial using the least square method. The radial coordinate of the boundary ($R(\theta)$) is represented as a function of polar angle (figure 6). The volume is calculated by putting the Legendre polynomial $R(\theta)$ into equation (7). Then, the density is obtained with the volume and the given mass.

$V = \frac{2\pi}{3} \int_{0}^{\pi} R(\theta)^3 \sin \theta \ d\theta \quad (7)$

3. Results: densities of supercooled and stable liquids of Ni, Zr, Nb, and Hf

Figure 7 shows the density of liquid Ni in supercooled and stable liquid state. The present data are close to [16] at melting temperature, but deviate by 1.4% at melting temperature from the values obtained by containerless methods [14, 17, 18]. On the other hand, the temperature dependence of the liquid and supercooled liquid of Ni is consistent with other ESL results, but differs from the remaining one. Since the density difference of 0.19 g cm$^{-3}$ is comparable to the density difference between liquid and crystal, the density difference in figure 7 requires uncertainty evaluation. We will present the uncertainty evaluation of the density measurement for liquids later.

Figure 8 shows the density of liquid Zr in supercooled and stable phases. Density of liquid Zr in this study is in agreement with [12, 19, 21], but is different from [13, 20, 22] by 2.1%, 4.9%, and 2.5%, respectively. The density of liquid Nb in the present study is consistent with Ishikawa’s result [13] within 0.8% (figure 9). However, it differs by 1 ~ 2% from other methods [20, 22, 23].

In case of Hf (figure 10), the density obtained in this study is close to previous work [20, 22, 25].

4. Evaluation of the uncertainty

Here, we evaluate the uncertainties (both A and B type) in our density measurement. Main uncertainty contributions are
Mass (m), calibration factor (q) for converting pixel volume (Vp) to real volume (V), temperature (T), and aspect ratio (R) due to the sample shape. Density determined by the imaging method is given by equation (8).

\[ \rho(T) = \frac{m}{V} = \frac{m(T)}{qV_p(T)} \]  

Therefore the uncertainty of the density measurement is as follows,

\[ (\Delta \rho)^2 = \left( \frac{\partial \rho}{\partial m} \Delta m \right)^2 + \left( \frac{\partial \rho}{\partial q} \Delta q \right)^2 + \left( \frac{\partial \rho}{\partial V_p} \Delta V_p \right)^2 + \left( \frac{\partial \rho}{\partial T} \Delta T \right)^2 \]  

\[ (\Delta \rho/\rho)^2 = \left( \frac{\Delta m}{m} \right)^2 + \left( \frac{3 \Delta q}{q} \right)^2 + \left( \frac{\Delta V_p}{V_p} \right)^2 + \left( \frac{\Delta T}{T} \right)^2 \]  

4.1 Mass

Mass measurement directly affects the uncertainty of the density. The uncertainty of the mass can be evaluated when we measure the mass after the experiment. Here, we did not account for the mass loss during the experiment, which can occur during evaporation of the levitated sample. Unfortunately, we cannot measure the mass loss during the experiment because the evaporation rate cannot be given with temperature and pressure. Therefore, the uncertainty of mass was evaluated with balance resolution and sample mass after the experiments, and we used the sample volume measured at the last cycle on cooling. The precision of the mass balance is ±0.02 mg. Typical mass of sample, 35 mg gives a type B uncertainty of ±0.06%.

4.2. Calibration

Since the position of levitating samples, optical alignment and experimental environment is not exactly the same for
each measurement, the density measurement should be performed after the image calibration procedure. This is an important procedure to determine accurate density measurement. A calibration factor, the ratio of centimeter to pixel in CCD camera, was obtained by a calibration sphere ball (precision tungsten carbide ball with diameter 2.3813 ± (254 nm) mm (Industrial Tectonics)). This results in ±0.032% volume uncertainty. Using this calibration ball, the measured volume showed 7.07062 × 10⁻⁹ (m³) ± 0.14% in figure 11. Therefore, the total uncertainty of volume of the calibration ball is ±0.172%. Subsequently, the calibration factor q is obtained by the ratio of the known radius of the sample to the pixel radius of the image. The obtained uncertainty of calibration factor q is given in table 1. We note that images of liquid samples at their melting temperature were used to evaluate the associated uncertainties of volume measurement.

### 4.3. Aspect ratio of the asymmetric shape

When sample size is large, the 2D image of the liquid droplet cannot be perfectly circular, but slightly elongated along the z-axis, due to the gravity or small surface tension. This may lead to an inaccurate volume calculation, since the curve fitting depends on the order of the Legendre polynomial. Here, we tested azimuthally the asymmetric shape of a sample with 4th to 6th order Legendre fitted radius from the edge detected radius. Figure 12 shows the radius error ΔR, when the radius of the sample image deviates from a perfect circle, i.e. aspect ratio, \( R_z / R_x \neq 1 \). The radius error \( \Delta R \) is given by

\[
\Delta R = \frac{1}{N} \sum_{k=1}^{N} \sqrt{(R(\theta_k) - R_k)^2},
\]

where \( N \) is the total pixel number that is detected at the boundary, \( R(\theta_k) \) is the radius of the curve fitting at \( \theta_k \) by the Legendre polynomial, \( R_k \) is the radius of kth pixel. It shows that the deviation is negligible up to aspect ratio 1.4, but rapidly increases after aspect ratio 1.4. In this experiment, the typical aspect ratio of the sample image was less than 1.017. Therefore the uncertainty caused by the aspect ratio is negligible.
Temperature is one of the main contributing factors for the uncertainty in the density measurement. The pyrometers should be calibrated with a standard blackbody radiation. The uncertainty of the temperature measurement using pyrometers depends on the accuracy of the pyrometers. In this experiment, the uncertainty of temperature measurement is 0.5% for a low temperature (600 K ~ 2800 K) pyrometer, and 2% for a high temperature (1000 K ~ 3800 K) pyrometer, indicated by makers, i.e. B type of evaluation. The uncertainty in the temperature measurement also affects values of the thermal expansion coefficient.

4.5. Uncertainty evaluation

Table 1 shows the dominant criteria for uncertainties and their evaluation in the density measurement of high temperature liquids. We can readily recognize that temperature measurement brings the most dominant uncertainty contribution in the measurement. Since we use infrared pyrometers, the uncertainty of the temperature measurement of the sample relies on emissivity properties, such as the dependence of wavelength and temperature, and surface condition of the sample. However, ESL measurement system itself has a marginally small uncertainty of about 0.7% using a pyrometer with 1.6 μm for relatively low temperature, but 2.1% using a pyrometer with 0.9 μm for high temperature (see table 1).

Meanwhile, the levitated liquid droplets cannot be held at the exact same position for different sets of the experiment, due to the change in the device alignment required during physical cleaning of electrodes, the degree of evaporation affecting charge stability, laser alignment causing rotation or shifting position, and so on. Such factors depend on samples and operators. Therefore, random error should be considered and

| Factors (x) | Evolution type | ΔX/X | Ni | Zr | Nb | Hf |
|------------|----------------|------|----|----|----|----|
| Mass (m)   | B              | Δm/m | 0.0006 | 0.0006 | 0.0006 | 0.0006 | 0.0006 |
| Calibration factor (g) | A | Δg/g | 0.002 98 | 0.002 98 | 0.002 98 | 0.002 98 | 0.002 98 |
| Pixel volume (Vₚ) | A | ΔVₑ/Vₚ | 0.001 72 | 0.001 72 | 0.004 | 0.004 06 | 0.007 12 |
| Aspect ratio (R) | A | ΔR/R | N.S. a | N.S. a | N.S. a | N.S. a | N.S. a |
| Temperature (T) (1.6 μm/0.9 μm)b | B | ΔT/T | 0.005/0.02 b | 0.005 | 0.005 | 0.005/0.02 b | 0.005 |

Combined uncertainty of measurement system: 0.005/0.021 b 0.005 0.007 0.007/0.022 b 0.009

Volume expansion at Tₘ (ΔV) A

\[ \left( \frac{\partial V_p}{\partial T} \right) \left( \frac{\Delta T}{V_p} \right) \]

3.83 × 10⁻⁴ 4.72 × 10⁻⁴ 6.88 × 10⁻⁴ +/- 2.755 × 10⁻³ 5.55 × 10⁻⁴

Density measurement at Tₘ (ρ) (random error) A

Δρ/ρ 0.0127 0.0008 0.0074 0.0047

Combined uncertainty of density measurement at Tₘ 0.014 0.011 0.01/0.022 b 0.01

a N.S. means negligibly small.
b Temperature was measured by different pyrometers with spectral wavelength 1.6 μm for low temperature (600 K ~ 2800 K) and 0.9 μm for high temperature (1000 K ~ 3800 K) ranges, respectively.
becomes one of the main factors contributing to the uncertainty. In the present work, the combined uncertainty of density measurement at melting temperatures is less than ±1.4% for low temperature (~2800 K) and ±2.2% for high temperature (~3800 K).

5. Summary

In the present work, a newly developed electrostatic levitation in KRISS was described. Using the ESL, the densities of Ni, Zr, Nb, and Hf were successfully measured in supercooled and stable liquid phases. Since the levitation techniques have previously reported different results for the density measurement, in particular, for high melting temperature materials, we conducted the uncertainty evaluation of the density with ESL for the first time. We concluded that the combined uncertainties in our present measurement system are less than 0.5% and 2.1% with low temperature pyrometer (1.6 μm) and high temperature pyrometer (0.9 μm), respectively. The combined uncertainty of density measurement of the liquid metals at melting temperatures is about ±1.4% for liquid Ni, ±1.1% for liquid Zr, less than ±2.2% for liquid Nb, and ±1.0% for liquid Hf. In the near future, we expect to expand the density evaluation for different elements that have even higher melting temperatures such as Tungsten as well as various alloys.

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