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Successful melting and density measurements of Cu and Ag single crystals with an electrostatic levitation (ESL) system

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We report the successful melting and high-temperature liquid density measurements of grain-free single copper and silver crystals using electrostatic levitation (ESL) for the first time. The melting of Cu and Ag using ESL has not been reported to date because of unusual charge instability of the samples at high temperatures. We report here improved levitation stability during heating by using single-crystal specimens. These results will aid the development and further study of industrially important Cu- and Ag-based materials by providing key physical properties of their liquid phases.

Introduction

Silver (Ag) and copper (Cu) are metallic elements with very high electrical conductivities belonging to group 11 in the periodic table. Owing to their low electrical resistivities (Cu, 1.678×10^{-6} and Ag, 1.587×10^{-6} Ωcm), which have been thought as almost intrinsic material constants, Ag and Cu are the most commonly used metals for electronic and electrical applications in the world. However, compared to their great heritage for the high electrical conductivity, there have been few intensive investigations to further improve their electrical conductivities through modification of their crystal lattices by dilute doping of metal single crystals. Most metallurgical studies of the $Ag_{1-x}Cu_x$ alloy system have focused on enhancing mechanical strength while sacrificing conductivity.[1–3]

Over the last 100 years, the great developments in technology for the processing of conducting copper wire have only enhanced the electrical conductivity by about 3%. Our recent study of the electrical conductivity of grain-free Cu single crystals demonstrated that the accepted bulk conductivity of Cu has been underestimated by 9 - 14% because of hidden grain boundary scattering[4,5]. The unintentional grain boundaries of highly conducting metals result in a distortion and an attenuation of electronic signals[6]. Contrary to metallurgical expectations, we found an unusual decrease in the electrical resistivity in Cu (≤ 3 mol%)-doped Ag single crystals[7]. This result suggested that the electrical conductivity of metals could still be enhanced by modification of the electron-phonon interaction and grain boundary effect even for the highly conducting Ag and Cu.

Verification of thermophysical characteristics is essential to better understand any changes in the conductivity behavior of metal crystals. Herein, we used electrostatic levitation (ESL) to provide a contactless synthesis and characterization technique that enabled experiments not possible by conventional means. Because ESL provides a containerless environment under high vacuum (ca. 10^{-7} Torr), the possibility of contamination from a crucible during synthesis and characterization is removed. Additionally, measuring the liquid density using ESL is somewhat simpler than using other levitation techniques. ESL provides quiescent liquids on melting and employs spherical liquid drops, which simplify analyses. These features enable ESL to be used for material characterization and solidification studies at extremely high temperatures, e.g., Zr (2158 K),[8-10] Fe (1811 K),[11] Ti (1941 K),[12] Nb (2750 K),[10] Rh (2236 K),[10] Hf (2604K),[10] Mo (2896 K),[13] W (3695 K),[14] and Os (3306 K).[15]

Cu, Ag, and Au are the most difficult materials to melt using ESL. There have been no reports using this technique with Cu and Ag and just one report with Au[16]. The challenge is mainly due to unpredictable charge emission of the sample, which results in levitation instability during the heating process. With ESL systems, the sample is levitated through a stable balance between the electrostatic force and the sample weight. Generally, ultraviolet (UV) irradiation is used to increase electrical charging on the sample surface by the photoelectric effect, which opposes the influence of gravity. Interestingly, compared with the other metallic elements mentioned above, the unpredictable charge loss is particularly serious with Ag and Cu, which have the highest electrical conductivities. The charge loss with these metals results in the sample falling, which terminates the ESL experiment. ESL typically uses high-purity polycrystalline specimens. We speculate that the difficulties with Ag and Cu may lie with out-gassing or abrupt formation of vacancies in the polycrystalline structures.

In this research, we used grain-free single crystals grown by the Czochralski method and successfully melted them with an ESL system. The origin of the levitation stability of single crystal samples in ESL experiments is discussed.

Experimental

Fig. 1(a) shows a schematic diagram of the crystal growth system and specifically Ag single-crystal growth by the Czochralski method. Cu and Ag beads having 4N purities (Sigma-Aldrich) were used as starting materials. A graphite crucible was used for the crystal growth. The growth chamber was evacuated and then filled with Ar gas of 5N purity to avoid oxidation of the crucible and starting materials. Heating was carried out by radio frequency (RF) induction (40 kHz, 20 kW). Fig. 1(b) and (c) show the as-grown Ag and Cu single crystals grown along the (100) direction. The bulk metal ingots were cut with a wire-electrical-discharge machine by applying a rapid series of repetitive electrical discharges with a very thin wire that served as the electrode. X-ray pole figure measurements were used to structurally characterize the crystals. A sample must have a spherical shape for levitation experiments to stabilize the position in the static electric field of the ESL system. The cut single-crystal samples were spherically ground with sandpaper and polished with a polishing pad in a small cylindrical chamber. The cut cubic Cu and Ag crystals were ground and polished in flowing high-purity Ar gas (Fig. 1(d)). The fabricated spherical samples were cleaned with dilute acid prior to use in experiments.

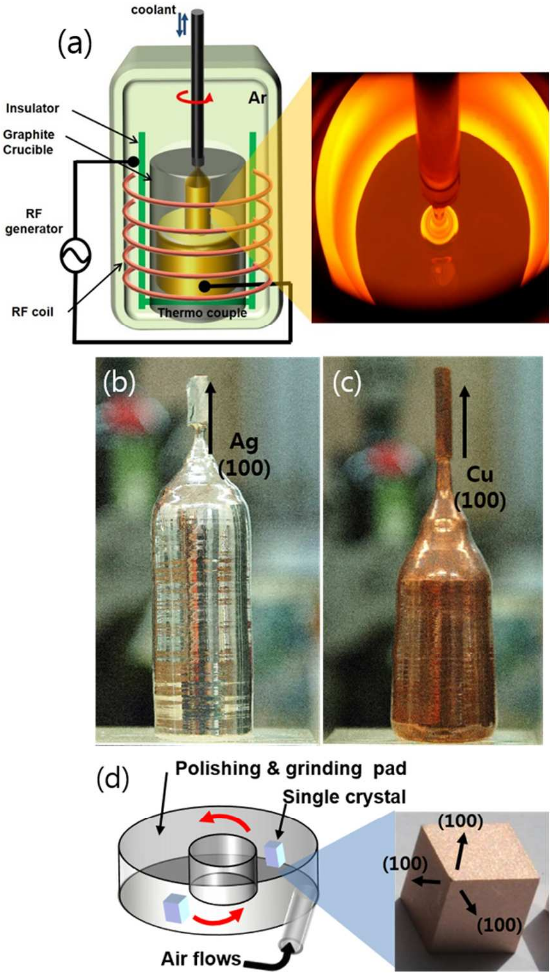

Fig. 1 (a) A schematic diagram of the single-crystal growth system and a photograph of Ag growth using the Czochralski method. Photographs of as-grown Ag (b) and Cu (c) bulk single crystals. (d) A schematic diagram detailing the fabrication of spherical single crystals and cubic Cu single crystals cut by wire-electrical-discharge machining.

Fig. 2(a) and (c) show a photograph and a schematic diagram of the ESL system at the Korean Research Institute of Standards and Science (KRISS). This ESL system has been extensively described in previous publications.[12-17] It is composed of a high-vacuum chamber, high- voltage system, an electrode pair for levitation, a UV lamp for sample charging, and a high-power laser and measurement system. All experiments were carried out under high vacuum (ca. 10^{-7} Torr) to facilitate high-temperature removal of any contamination from the environment. Levitation was accomplished by balancing the electrostatic force from the high voltage of the top electrode with the gravitational force on the sample (Fig. 2(b)). Two He-Ne lasers (632 nm) and two position sensitive detectors (PSD, Hamamatsu Photonics, C10443-03) were used to detect the sample position (Fig. 2(c)). The top electrode voltage was controlled through PID position-voltage feedback with a 2-ms time interval. For homogeneous heating, high-power CO_2 lasers with a total of 150 W were focused on the sample at 120^{o}. Measurement of the heating and cooling was performed in situ every 6 ms using Si (0.9 μm) and InGaAs (1.55 and 1.6 μm) infrared pyrometers depending on the temperature region.

During cooling, the density of the levitated liquid Cu or Ag was measured using an image analysis method using a UV black-light lamp and a black-and-white camera equipped with a charge-coupled detector[12]. The detected edge of the samples at high temperature was fitted by the sixth-order Legendre polynomial and used to estimate the sample volume.[12] The sample mass and volume were then used to calculate the density of the material.

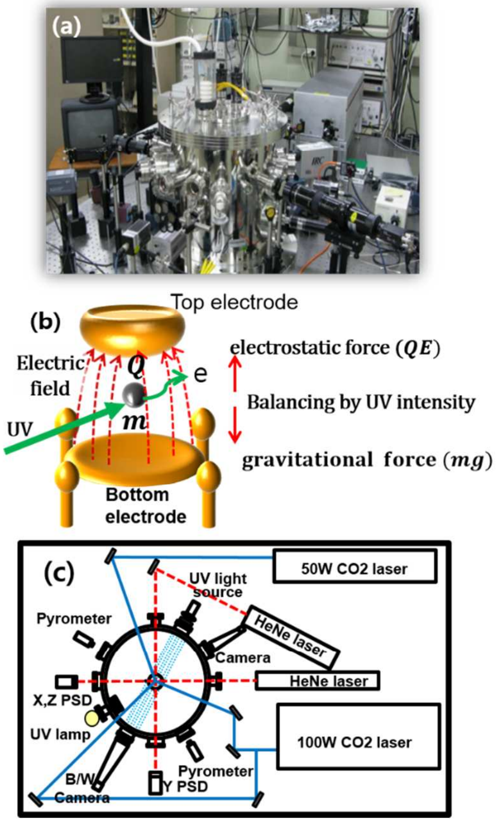

Fig. 2 (a) A photograph of the ESL system at the Korean Research Institute of Standards and Science. (b) A schematic diagram showing the principles of ESL. (c) A schematic diagram of the ESL system.

Results and Discussion

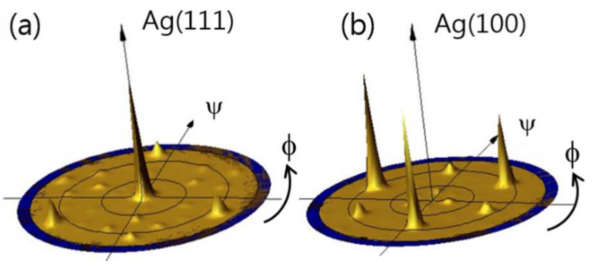

Fig. 3 The (111) pole figure for the Ag single crystal disk. (a) The scan with d(111) spacing and (b) the scan with d(100) spacing.

To verify the crystallinity of the as-grown crystals, X-ray pole figure measurements were taken perpendicular to the growth direction (Fig. 3(a) and (b)). The crystallinity of Cu single crystals has been previously reported.[4,5] After fixing θ and 2θ for (111) diffraction conditions, we obtained the (111) plane distribution through Ψ and ϕ scans (Fig. 3(a)). The central (111) peak in Fig. 3(a) corresponds to the crystal plane of the fabricated disk. The surrounding three peaks with three-fold symmetry correspond to the (-111), (1-11) and (11-1) planes. Fig. 3(b) shows the d-spacing distribution of the (100) plane for the same specimen. In this configuration, three peaks having three-fold symmetry were also observed.

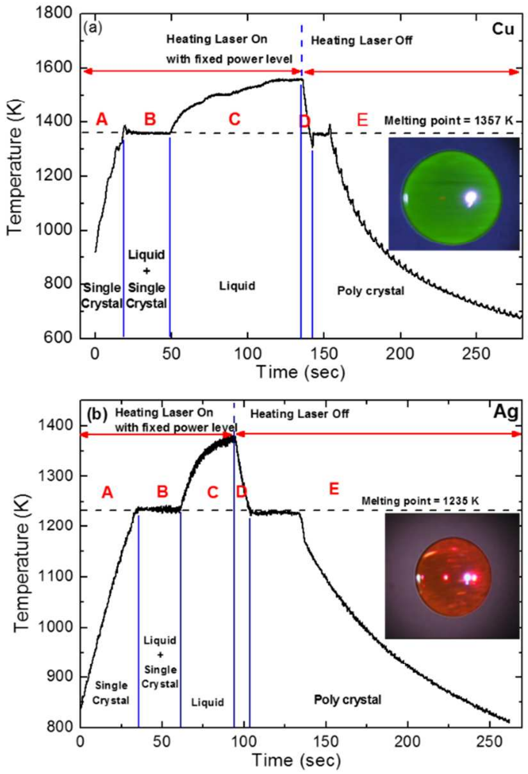

Fig. 4 The cooling curves from the high-temperature liquid phases of the (a) Cu single crystal and (b) Ag single crystal. The inset images of (a) and (b) show levitating spherical droplets of liquid Cu and Ag above their melting temperatures, respectively. The images were obtained by color and neutral filtering.

No traces of grains having different orientation states were detected with X-ray pole figure measurements of other specimens at various locations. These results indicated that the fabricated Ag single crystal disk was oriented only in the (111) direction.

Fig. 2(b) shows how the sample is levitated in the ESL system by balancing the electrostatic force from a high voltage on the top electrode and the gravitational force from below. Successful melting requires stability of the sample position from sample loading at room temperature through to the melting temperature. ESL systems typically use UV light irradiation to render the sample surface positively charged by the photoelectric effect. However, the positive charge of the sample is also irregularly released during the heating process, which induces instability in the levitation state. If the charge loss by the sample is faster than the supply from photoemission or photoelectric processes, then the levitated sample will fall. A smooth and homogeneous sample surface is important for successful levitation, too. We considered that out-gassing and vacancy formation may be more severe in polycrystalline materials because of the many grain boundaries and crystal imperfections. We used single-crystal Cu and Ag samples for melting in ESL for these reasons. Fig. 4 (a) and (b) present the temperature-time curves of Cu and Ag single crystals, respectively, in the ESL experiment. To our knowledge, this is the first successful report of melting both Cu and Ag in an ESL system.

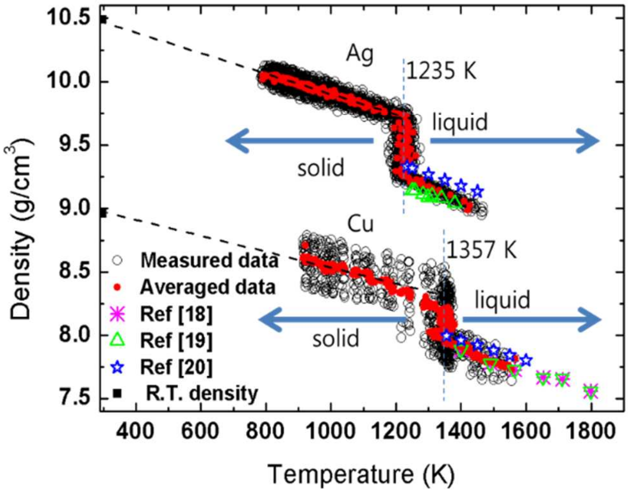

Fig. 5 The densities of liquid and solid Cu and Ag derived from ESL data. The ESL results are compared with literature data obtained using different methods. The scarlet asterisk (✱) and green triangles (△ and ▽) symbols represent EML data for Cu and Ag, respectively. The blue open star (☆) symbol indicates data measured by the sessile drop method. The solid black square symbols represent the densities at room temperature. The solid dashed line extrapolates the density to room temperature. The vertical dashed lines indicate the melting temperatures of Ag and Cu.

A detailed description of the ESL melting and crystallization process is as follows. In Fig. 4(a), a single Cu crystal is heated to its melting temperature of 1357 K by a CO_2 laser (region A). In region B, the solid Cu crystal starts melting at constant temperature by absorbing the latent heat. Region C is that of Cu liquid overheated by the laser. The laser is turned off at the start of region D, causing the liquid Cu to cool; it supercools slightly below the melting temperature by radiation. At the end of region D, the supercooled temperature instantly increases to the melting temperature because of the release of the latent heat (recalescence) for crystallization.

Table 1. ρ and ρ_T in this study and the literature data reported in the past 100 years for both Cu and Ag.

material	ρ at melting temperature [gcm^{-3}]	ρ_T of liquid phase [gcm^{-3}K^{-1}]	Method	Ref.
Ag	9.24	-6.5×10^{-4}	Buoyancy	22
	9.28	-9.0×10^{-4}	Buoyancy	23
	9.32	-9.78×10^{-4}	Buoyancy	24
	9.346	-9.11×10^{-4}	Bubble pressure	25
	9.304	-7.1×10^{-4}	Sessile drop	26
	9.15	-7.4×10^{-4}	EML	19
	9.29	-11.75×10^{-4}	Sessile drop	21
	9.23 ± 0.03	$-(10.5 \pm 0.1) \times 10^{-4}$	ESL	This work
Cu	7.98	-15×10^{-4}	Buoyancy	22
	7.9	-7.65×10^{-4}	EML	18
	7.9	-7.7×10^{-4}	EML	19
	7.90 ± 0.11	$-(7.8 \pm 0.4) \times 10^{-4}$	ESL	This work

After crystallization along the plateau period, the temperature cools down again. The spiky feature after crystallization (region E) is attributed to the surface roughness of the crystal. The inset image of Fig. 4(a) shows a levitating spherical drop of liquid Cu above the melting temperature. Fig. 4(b) presents the temperature-time curve for the high-temperature liquid phases of the Ag single crystal, which is similarly classified into several regions for the cooling curve from the liquid. Although the samples were carefully prepared, the near absence of undercooling of the Cu and Ag liquids implies the existence of heterogeneous nucleation sites. This is attributed to a partial oxide layer on the sample surfaces (inset of Fig. 4 (b)).

The measured densities of Ag and Cu for the liquid and solid phases during levitation are shown in Fig. 5 and Table 1. The density data for the solids are more scattered than those of the liquids because of the rough surface of the samples caused by crystallization. The black dashed line extrapolates the solid Ag density to room temperature. The measured density (ρ) and the thermal coefficient of the density (ρ_T) of liquid Cu at the melting temperature 1357 K were 7.90 ± 0.11 gcm^{-3} and $-(7.8 \pm 0.4) \times 10^{-4}$ gcm^{-3}K^{-1}, respectively. Although the Cu density data are more scattered than those of Ag, the average ρ and the ρ_T of liquid Cu from the ESL experiments are in good agreement with reported values[18,19] using the electromagnetic levitation (EML) method.

The measured ρ and the ρ_T of liquid Ag at its melting temperature 1235 K were 9.23 ± 0.03 gcm^{-3} and $-(10.5 \pm 0.1) \times 10^{-3}$ gcm^{-3}K^{-1}, respectively. The ρ of liquid Ag at its melting temperature is in good agreement (within 1.5 %) with previous reports using EML[19] and other methods.[20–26] Although the ρ_T of Ag liquid at the melting temperature in the ESL experiments is close to the reference value[24] derived from the buoyancy method, it differs from the EML result.[19] Table 1 indicates that most methods give nearly the same densities for Cu and Ag liquids at their melting temperatures, while the thermal coefficients of the liquids significantly differ from the values of this study.

Although we succeeded in using ESL to melt grain-free Cu and Ag single crystals, the effect of grains needs still further investigation. Careful sample preparation (e.g., removal of the oxide layer) will be required for more accurate measurements of the thermophysical properties of Cu and Ag by the ESL technique.

Conclusions

Melting Cu and Ag using ESL and obtaining their high temperature densities were accomplished for the first time. The hitherto unstable levitation attributed to the occurrence of charge emission and imperfections of the levitated sample during the heating process was reduced by using grain-free single crystals in the ESL experiments. The measured densities of Cu and Ag liquids are in good agreement with previous measurements. These results will be useful to the development of Cu- and Ag-based industrial materials and will contribute to a better understanding of the unusual electrical conductivity changes that can occur with lattice-modified mixed crystals.

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Notes and references

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Title: "**Successful melting and density measurement of Cu and Ag single crystals with an electrostatic levitation (ESL) system**"

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Geun Woo Lee and Se-Young Jeong

Graphical Abstract

With grain-free single crystal specimens, melting Cu and Ag using electrostatic levitation (ESL) and obtaining their high-temperature densities were accomplished for the first time.