Application of the Levitation Technique for Investigation of Metal Alloys and Phase Equilibria in Slags

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Abstract. Experimental methods, based on electromagnetic levitation, have been developed for preparation and investigation of copper-rich alloys, and for the determination of oxide-metal phase equilibria. These techniques involve high-temperature equilibration, rapid quenching and chemical analysis of the phases using electron probe X-ray microanalysis. The experiments can be carried out in the temperature range 1373–1873 K (= 1100 °C–1600 °C). A developed calibration method, using phase equilibria data in known oxide systems, was applied for pyrometric temperature measurements. Described methods of the application of the electro-magnetic levitations were used for in-situ formation of Cu-based alloys and for formation of Ca-ferrite slags equilibrated with metallic copper.

1 Introduction

Electromagnetic levitation of liquid metal and alloys, sometimes referred to as containerless melting, has practical advantages in the investigation of metal alloy properties. Since there is no contact with any other condensed phases, possible metal- container reactions and the resultant contamination of melts are avoided. This property is particularly important for alloys containing metals that are readily oxidised. Zr and Zr-based alloys are known as excellent oxygen getter materials. For example, Zr-based amorphous alloys were found [1] to contain dissolved oxygen, which has been dissolved in the melt from the crucible during the melting.

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It was found that alloys prepared using an arc furnace had to be re-melted several times and homogenised in a vacuum heat-treated furnace in order to avoid possible compositional inhomogeneities in a vacuum heat-treatment furnace [2]. The use of electro-magnetic levitation also enables the single stage preparation of homogeneous alloys and faster alloying due to electro-magnetic stirring.

Electro-magnetic levitation of metal alloys has been used in the measurements of a range of thermo-physical properties, such as surface tension, density, viscosity, thermal expansion and electrical conductivity [3, 4]. This technique has been also used in the preparation of highly undercooled and metastable microstructures [2, 4–6]; in extreme, high cooling rates of the melts can lead to the formation of amorphous alloys [7].

Electro-magnetic levitation and melting can also be used for the investigation of slag properties, particularly for phase equilibria studies of slag systems that cannot be investigated using conventional equilibration techniques [8]. It was shown that slags can be equilibrated and attached by interfacial forces to the surface of a molten metal droplet levitated in an electromagnetic field. One of the attractions of this latter method is the ability to achieve the rapid cooling necessary to quench even silica-free slags into the amorphous state, due to the direct contact between the slag and the cooling medium.

In the present paper several methods are described, which demonstrate ways in which electromagnetic levitation can be used to overcome a number of experimental problems, associated with i) the alloying and ii) the determination of phase equilibria between metals and slags. The methods are applied for the i) in-situ alloying and homogenization of copper-rich alloys, and ii) for the preparation of the molten calcium ferrite slags equilibrated with metallic copper. Microstructural and compositional characterisation of alloys and slags is presented in order to validate the methods.

2 Experimental Methods

2.1 Methodology

The methodology essentially involves i) electromagnetic levitation and heating of metals until it becomes liquid, ii) the rapid quenching of the metal (alloy), and any associated materials, iii) the examination of the microstructures and measurements of the phase compositions in the resulting materials.

3 Sample Preparation

The examples used in the present paper involve the use of copper but the principles could be equally applied to other metal systems. The materials to be melted in experiment can consist of metals or mixture of metals and pure oxides. In either case the major metal making up the alloy is machined into a crucible or capsule, which enables to levitate in electromagnetic field. The alloying elements or oxide mixtures are pressed into the crucible. The samples of carefully controlled mass are introduced into the electromagnetic field. The sequences of stages occurring during heating of the samples are shown in Figure 1a and Figure 1b. In each case, interaction between the electromagnetic field and the metal create levitation forces and regions of high electrical current, which heat the sample. In both cases, the copper capsule is levitated while solid. Subsequent heating past the melting point of the containing metal only induced after sample is levitated in a stable manner. For alloy preparation, the temperature at which alloying commences is dictated by the melting points of the alloying elements relative to copper. If the alloying metals inside of the copper capsule have lower melting points than copper, alloying commences inside the capsule gradually dissolving the copper crucible. If the alloying metals have higher melting points than copper, alloying proceeds following the melting of the copper container. Finally, as the liquid alloy held at temperature at the levitation conditions, electromagnetic stirring of the melt occurs, leading to homogenisation of the melt (Figure 1a).

For oxide-copper phase equilibria samples, solid oxides appear on the surface of molten droplet as the temperature exceeds the copper melting point. With further heating, these oxides melt to form a slag film on the copper surface (Figure 1b). The oxide film is held on the outer surface of the metal by surface tension forces.

i)   ii   iii

i)   ii   iii)
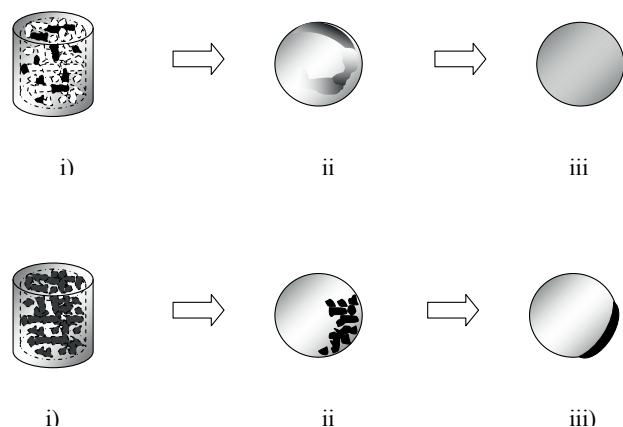
Figure 1. Schematic illustration of in-situ alloying (a) and slag forming (b).

3.1 Heating and Levitation Apparatus

Levitation and heating of the metal droplets is achieved by applying a high frequency electro-magnetic field through the sample. Eddy currents induced in the metal interact with the electromagnetic field, the resultant forces stabilise the metal position within the coil and heat the metal sample.

Experiments were conducted using an InductoTherm (Melbourne, Australia) RF power source, with a maximum output of 15 kW at 200 kHz. A water-cooled levitation coil, consisting of upper and lower sections, was prepared from 4.76 mm OD copper tubing. The upper section had two complete 13 mm external diameter turns spiralling clockwise from the top. The lower section had five counterclockwise spiralling turns with the external diameters of (from top down) 18, 13, 16, 19 and 23 mm. The bottom section provided the levitation forces, while the upper section stabilised the position of the levitated sample in the electromagnetic field. The coil was placed inside a gas-tight glass chamber fitted with several entry ports, as shown in Figure 2. Polyethylene film was placed across the lower port to seal the chamber.

In present experiments high purity CO_2-H_2 gas mixtures, flowing at 200–300 ml/min, were used to control the oxygen partial pressure.
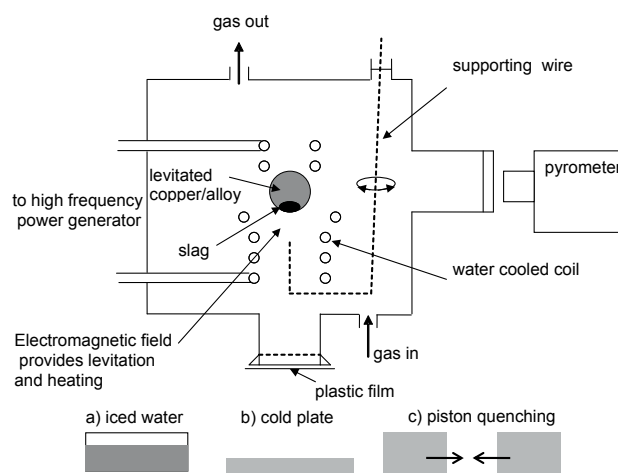
Figure 2. Schematic of levitation apparatus experiments.

3.2 Quenching Techniques

After the desired equilibration time had elapsed, HF power was cut, causing the molten sample to drop from the coil under gravity, through the sealed plastic film. One of three methods can then applied to quench the molten sample.

Copper-slag samples were quenched allowing the samples fall under gravity into an iced-water reservoir (a), placed below the centre of the coil, which provided a spherical sample and allowed rapid surface cooling, but with slower cooling in the centre of the droplet. Alloy samples

were quenched onto a steel plate (b), placed below the centre port, which provided rapid quenching to one side of the resulting solid sample. Alternatively, for fast alloy solidification, a piston quenching system (c) was employed, in which the falling droplet was captured and quenched between two plates activated by a pneumatic piston [9]. This created metal films approximately 100–500 μm in thickness.

3.3 Sample Characterisation

The sample microstructures were characterised using a JEOL 6400 Scanning Electron Microscope (SEM) equipped with energy dispersive spectrometer (EDS). The phase compositions in the samples were determined using a JEOL 8800L Electron Probe X-Ray Microanalyser (EPMA) operating with wavelength dispersive spectrometers (WDS); an accelerating voltage was 15 kV and a probe current was 15 nA. Alloy phase composition was also determined by X-ray diffraction (Siemens D5000 with Cu Kα radiation).

3.4 Temperature Measurements and Temperature Calibration

For temperature measurements during levitation, a two-colour radiation pyrometer (MODLINE PLUS$^{®}$ – R series, IRCON) was used. The pyrometer was focused on the centre of the levitated Cu droplet through the quartz window (see Figure 2). The pyrometer was initially calibrated against the melting point of copper 1359 K (= 1086 °C) (confirmed by DTA) under low oxygen partial pressure conditions such that copper oxide is not formed. However, one calibration point is not sufficient to conduct experiments at variable temperature range. Potential errors in temperature measurements associated with the use of electro-magnetic levitation technique may occur due to geometry/spot size of the body (which is also not a "black body"), as well as emissivity changes with alloy composition. For temperature measurements of levitated liquid droplets, special emissivity data are required to derive true temperatures from radiance measurements. If these data are unknown for the materials in question, emissivity values are selected based on the radiance temperatures observed at the melting point, and then combined with the known melting or liquidus temperature, and using the assumption that the spectral emissivity is independent of temperature [10].

The method of the temperature control, used in this work is based on the knowledge of phase equilibria in known oxide system, and the comparison of that data with that one obtained when the oxide system (in slag form) is attached on the levitated droplet. If the true temperatures of the slags attached on the surface of molten metals and alloys are known, we can estimate temperature deviations and apply these values for the temperature measurements of levitated liquids with unknown emissivity.

A series of phase equilibria experiments in the CaO-SiO$_2$-Al$_2$O$_3$ system were carried out to calibrate pyrometer reading obtained from the metal surfaces in the levitation technique. This well-known system was selected for levitation of the copper metals because phase equilibria in the system is well characterised and is not affected by partial oxygen pressure, p_{O2}.

In this test program the results from the levitation experiments were compared with results obtained using a well-established tube furnace equilibration/quenching/EPMA technique [11–13]. The univariant equilibria between anorthite (CaO·Al$_2$O$_3$·2 SiO$_2$), pseudo-wollastonite (CaO·SiO$_2$) and liquid phase was selected for this comparison since the temperatures along this line strongly depend on the SiO$_2$ concentration [14, 15].

Master slags of selected compositions were prepared first by melting in air. Their bulk compositions were selected a) to be in the anorthite and pseudo-wollastonite primary phase fields – to approach equilibria from two directions; and b) to have high proportions of solids in the temperature range of 1463–1563 K (= 1190–1290 °C) – which ensures achievement of chemical equilibrium in these high silica slags. The master slags were equilibrated at controlled temperatures, either in a vertical tube furnace using platinum crucibles, or suspended on copper droplets levitated in a highly reducing atmosphere. The slags were then quenched, mounted, polished and the compositions of the glass (liquid) and solid phases in the samples were measured using EPMA.

A microstructure typical of quenched samples in the CaO-SiO$_2$-Al$_2$O$_3$ system is shown in Figure 3. The sample consists of anorthite and wollastonite phases, and a for-
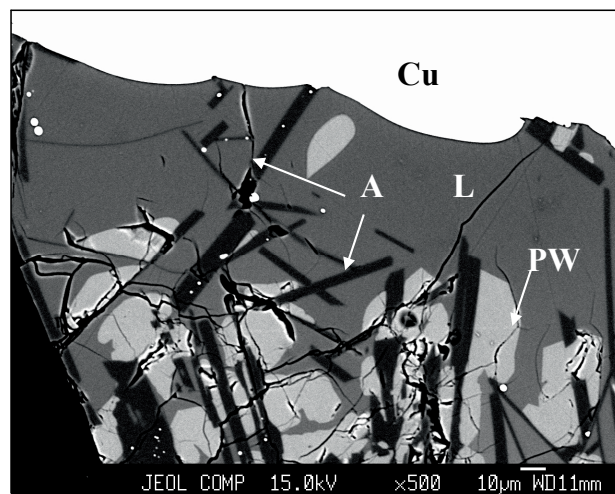
Figure 3. Typical microstructure of quenched CaO-SiO$_2$-Al$_2$O$_3$ samples equilibrated with metallic copper. Composition of liquid phase was used for temperature determination. Legend: Cu-metallic copper, L-former liquid phase, A-anorthite, PW-pseudo-wollastonite.
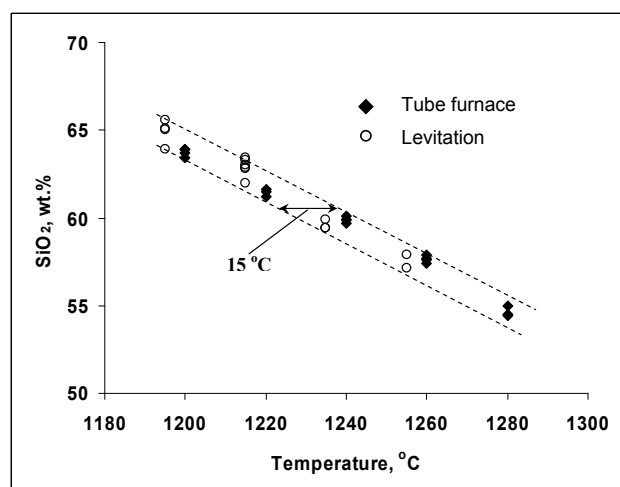
Figure 4. Comparison of the SiO_2 content in the liquids on the univariant line between the anorthite and pseudowollastonite phases in the CaO-SiO_2-Al_2O_3 system.

mer liquid phase which has been concentrated near the surface of copper. The composition of liquid phase on the univariant line between the anorthite and pseudowollastonite phases is variable, particularly in SiO_2 content.

Figure 4 shows the measured liquid phase SiO_2 concentrations versus the equilibration temperatures from tube furnace and levitation experiments. The uncertainties reflected in the standard deviations of the EPMA measurements are ± 0.3 mass pct and ± 0.8 mass pct for tube furnace and levitation experiments, respectively. Viewed in terms of the temperature uncertainty the results obtained from the levitation technique can be regarded as accurate to within 15 K.

4 Results and Discussion

Described methods of the application of the electromagnetic levitations are illustrated below by two examples: i) in-situ formation of Cu-based alloys and ii) formation of Ca-ferrite slags equilibrated with metallic copper.

4.1 Cu-Based Alloys Formed In-Situ by Electromagnetic Levitation

Al/Zr and Ti/Zr mixtures (Aldrich, $\geq$ 99.9 wt% purity), were placed into a Cu capsule with total weight between 0.5–1.3 g. As with the procedure described above, the capsule was placed in the chamber, which was sealed and flushed with a CO_2-H_2 (ratio 9 : 1) gas mixture. The sample was levitated while solid, and the HF power was gradually increased until the Cu melted and alloyed the other components. HF powder was adjusted in order to keep alloy levitated at the desired equilibration temperature for 1–10 min, after which the alloy droplet was quenched.

Composition, mole %	Cu	Zr	Ti
Starting mixture 1	55	10	35
Bulk	58.6 ± 0.6	8.9 ± 0.7	32.5 ± 0.9
Amorphous phase	58.4 ± 0.5	9.2 ± 0.5	32.4 ± 0.3

Composition, mole %	Cu	Zr	Al
Starting mixture 2	40	13.8	46.2
Bulk	39.9 ± 0.7	13.9 ± 0.8	46.2 ± 0.8
Amorphous phase	40.9 ± 0.9	13.5 ± 0.3	45.6 ± 0.7

Table 1. Compositions of alloys, obtained in-situ during electromagnetic levitation.

In-situ formation of Cu-Zr-Al and Cu-Zr-Ti alloys was achieved in the temperature range 1273–1473 K (= 1000–1200 °C). After homogenization, the alloys were quenched and their microstructures were investigated. Backscattering electron images and EDS of different regions indicate that no unreacted starting metals (Cu, Zr and Al or Ti) are present in the alloys.

Initial and bulk compositions of alloys are listed in Table 1. The results confirm that in-situ alloying of Cu-rich mixtures produced bulk compositions, which are close to their respective initial compositions.

Figure 5a shows the microstructure of a Cu-Zr-Ti alloy, quenched on a fixed steel plate. The bulk microstructure consists of lamellar structure resulted from a eutectic reaction. EPMA indicates that the two major solid phases are CuTi (dark colour phase) and $Cu_{51}Zr_{14}$ (light colour phase). Furthermore, the results showed that the solubility of Zr in the CuTi phase, and Ti in the $Cu_{51}Zr_{14}$ phase, were up to 1.5 and 2.2 mole % respectively.

In order to produce an amorphous phase in Cu-Zr-Ti alloy, the piston quenching was used. The resulting alloy was 350–400 μm thick, and contained amorphous surface regions 40–50 μm thick (Figure 5b). Amorphous scattering in an X-ray diffraction measurement of the alloy surface supports the presence of amorphous regions. The composition of the amorphous phases as determined by EPMA was the same as the bulk composition of alloy (as shown in Table 1). The bulk region of the quenched alloy featured large dispersed mixed phases with an overall composition ($Cu_{57.9}Zr_{8.0}Ti_{34.1}$) very close to bulk composition ($Cu_{58.6}Zr_{8.9}Ti_{32.5}$). According to the calculated phase diagram in Cu-Ti-Zr system [16], it could be mixture of Cu_2TiZr and $Cu_{51}Zr_{14}$ phases. Another observed phases, CuTi and $Cu_{51}Zr_{14}$, represented dendrite structure, are within compositional range of Cu-Ti-Zr phase diagram corresponded to fabricated alloy system.

An amorphous phase is also formed if piston quenching is applied in the cooling of the Cu-Zr-Al alloy. Figure 6 shows a typical microstructure of Cu-Zr-Al quenched alloy, where the amorphous phase is locally detected in the first 10–15μm of the surface. The inner part of alloy contains numerous sub-micron precipitated phases, which are too small for EPMA measurements.
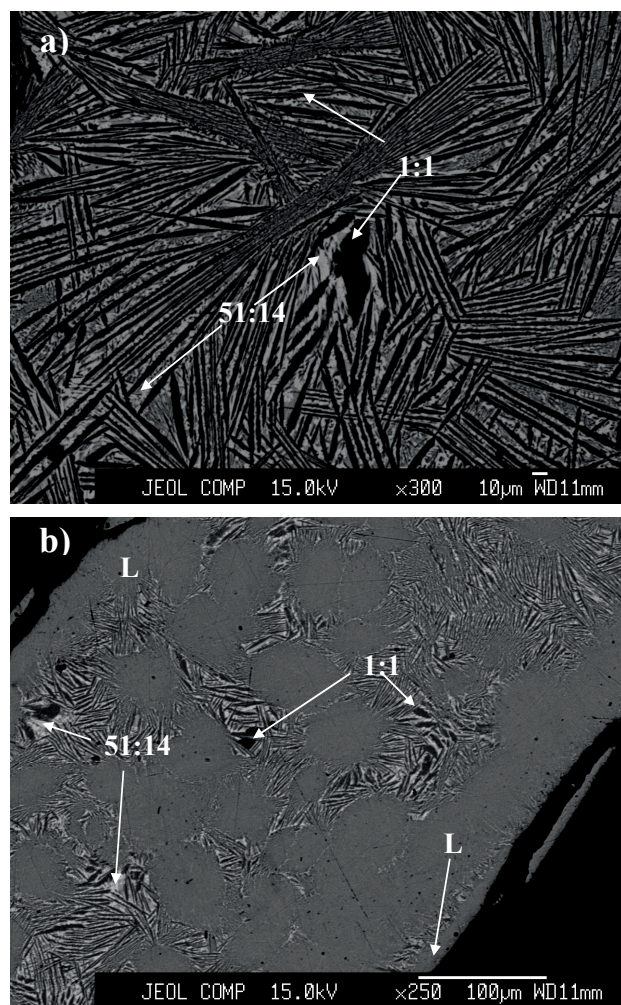
Figure 5. Microstructure of Cu-Zr-Ti alloy quenched on a cold plate (a) and using piston quenching (b). Legend: L-amorphous phase, 1 : 1-CuTi phase and 51 : 14-$Cu_{51}Zr_{14}$ phase.
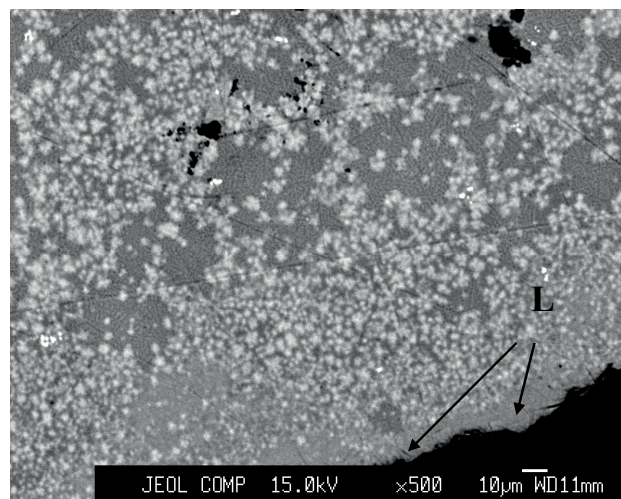
Figure 6. Microstructure of quenched Cu-Zr-Al alloy. Arrows show amorphous phase.

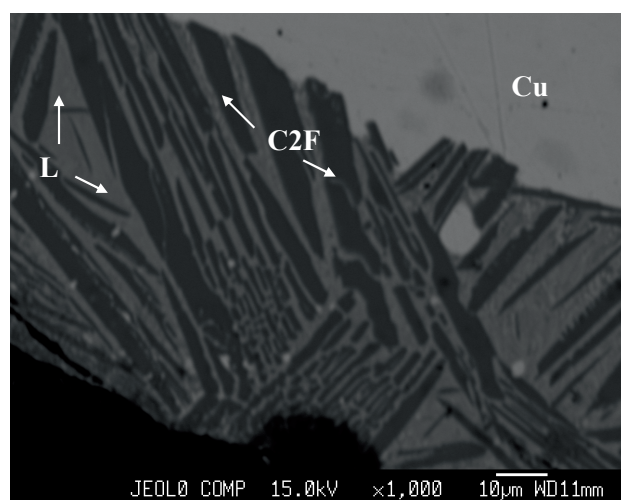## 4.2 Ca-Ferrite Slags Equilibrated with Metallic Copper

5–15 mg of pelletised oxide powder was placed into a 1.3 g Cu capsule made from rectangular pieces of Cu sheet (Aldrich, 99.98 wt% purity, 1.0 mm thickness). Before levitation, the capsule was supported on plastic film placed across the upper opening of the lower part of the levitation coil. The chamber was flushed with CO_2 and H_2 gas mixtures for 20–30 minutes before the experiment. After levitation and melting of the copper capsule, the temperature of the Cu-metal/slag sample was gradually increased to 1623–1473 K (= 1350–1400 °C) to melt the oxide mixture. The non-conducting slag film flowed under gravity to the lower part of the copper droplet. The thickness of the slag film was kept to a minimum (50–100 µm) in order to maximize the rate at which equilibrium was attained and to increase quenching rates. The sample was then equilibrated at the desired temperature for 0.5 to 2 hours. Finally, the sample was quenched directly into an iced-water reservoir by cutting the electrical power to the coil.

In order to obtain accurate high-temperature phase equilibria data, any liquid phases present at the temperature of interest must be quenched to the glassy state. With conventional crucible-based techniques, only silica-rich slags can be quenched to glass. Quenching rates achieved in the present study, approximately 10^7 K s^{-1} are very much greater than in previous practice, due to the direct exposure of the thin slag film to the quenching medium. The cooling rates of the slag regions in direct contact with the quenching medium are not limited by thermal diffusion through the walls of container materials. Examination of the microstructures produced in the present study has shown that it is possible to quench silica-free slags to produce amorphous or microcrystalline materials. For example, the microstructure obtained from a slag in the Ca-Cu-Fe-O system is shown in Figure 7. The slag films on the supported substrates in these cases are of the order 100–300 µm in thickness. The figure shows the coexistence of copper metal, dicalcium ferrite ($2CaO \cdot Fe_2O_3$) and glassy slag. A variety of microstructures obtained in this system using levitation techniques, are also shown in [9], which include liquid-solid phases, equilibrated with copper, from spinel (Fe_3O_4) and dicalcium ferrite primary phase fields.

Table 2 shows a range of former liquid phase compositions obtained from phase equilibria studies of the Ca-Cu-Fe-O system. The compositions, calculated on average results for 20 EPMA measurements, represent isotherms in temperature range 1473–1523 K (= 1200–1250 °C). The homogeneity of the liquid phase in the slag samples is within 0.8 wt%. Further details on the phase equilibria of calcium ferrite slags are presented in work [8], which shows some silica-free amorphous compositions that can be obtained using the levitation technique. The range of chemical systems that can be investigated has been considerably extended by using the described above method.

	Temperature, K/°C	Liquid phase, mass %			Solid phases
		CaO	Cu₂O	Fe₂O₃	
1	1473/1200	20.6 ± 0.3	15.5 ± 0.4	63.9 ± 0.7	dicalcium ferrite
2	1473/1200	21.8 ± 0.2	9.1 ± 0.5	69.1 ± 0.8	dicalcium ferrite
3	1473/1200	21.0 ± 0.3	5.8 ± 0.4	73.2 ± 0.6	dicalcium ferrite, spinel
4	1508/1235	21.0 ± 0.4	3.9 ± 0.6	75.1 ± 0.8	spinel
5	1508/1235	12.6 ± 0.3	30.3 ± 0.6	57.1 ± 0.8	spinel
6	1508/1235	21.2 ± 0.2	19.4 ± 0.5	59.4 ± 0.7	dicalcium ferrite
7	1623/1250	18.5 ± 0.2	7.2 ± 0.3	74.3 ± 0.7	spinel
8	1623/1250	24.2 ± 0.3	11.9 ± 0.6	63.9 ± 0.6	dicalcium ferrite
9	1623/1250	23.1 ± 0.5	9.1 ± 0.5	67.8 ± 0.8	dicalcium ferrite

Table 2. Phase compositions in the Cu-Ca-Fe-O system, obtained by levitation technique.

Figure 7. Microstructure of quenched slags in Ca-Cu-Fe-O system equilibrated with metallic copper. Legend: Cu-metallic copper, L-former liquid phase, C2F-dicalcium ferrite.

5   Summary

Based on the electromagnetic levitation of copper, methods have been developed for the in-situ preparation of copper-based alloys and for the formation of silica-free melts equilibrated with metallic copper. In both cases, a similar experimental procedure has been applied whereby oxides or metals were contained within a levitating copper capsule. First method enables preparation of ternary Cu-Zr-Ti and Cu-Zr-Al alloys. These alloys were uniform on the bulk composition and were similar in composition to the sum of the component metals. Amorphous phase can also be formed through application of piston quenching. The second method enables the preparation of silica-free slags supported on a levitated copper droplet in reduced conditions. In combination with rapid quenching, amorphous non-silica glasses can be obtained, and the composition of these can be

measured by EPMA with ~0.8 % accuracy. In both types of experiments, pyrometric temperature measurement was employed, which was calibrated using phase equilibria in known oxide systems. This method enabled accurate temperature measurements in levitated liquids with unknown emissivity.

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