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Process methodology for the small scale production of m6N5 purity zinc using a resistance heated vacuum distillation system

Anil Gopala, Heinrich Kipphardt*, Ralf Matschat, Ulrich Panne

BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Strasse 11, 12489 Berlin, Germany

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ABSTRACT

Ultra high purity Zn (m6N5) was obtained through triple vacuum distillation using an m4N5 Zn as input material. High-volatile impurities were removed from the zinc matrix by vacuum evaporation, while traces having lower volatility than the matrix remained in the residual material after finishing of the entire purification process. The time required for the removal of the main high-volatile impurity (Cd) was monitored using a connected gas source mass spectrometer. During distillation the Zn vapor of the distillate was condensed on the cap of a glassy carbon crucible which was water cooled by a movable copper block. The temperatures were optimized for the removal of the volatiles and for the distillation process using vapor pressure data. High resolution glow discharge mass spectrometry was applied for the analysis and purity evaluation of the distilled and input zinc. The analysis confirmed the reduction of the metallic impurities from 43 mg kg^{-1} to 0.5 mg kg^{-1} (m6N5) after three consecutive vacuum distillations. An increase in the grain size and a decrease in the micro-hardness were observed for the purified Zn material.

1. Introduction

The demand for the preparation of ultra high purity (UHP) Zn has been primarily promoted by the recent developments in semiconductor industry [1]. One of the expanding applications is the production of zinc selenide single crystals used as wide-gap semiconducting compound, for blue light emitting diodes. Other important areas where the purity of zinc matters are for the definition of the International Temperature Scale ITS90, the use of zinc as a standard in high precision coulometric titration and for the establishment of a primary reference materials system to meet the demands of metrological traceability in chemical analysis [2]. UHP metals are frequently required during atomic spectrometric analysis to distinguish between low real impurity contents and apparent contents arising from unspecific matrix signals. To distinguish the ambiguous signals and to rightly accord the determined values, UHP metals with a well defined impurity profile are indispensable. The preparation of UHP metals requires first to get a basic knowledge of the identity and the concentrations of impurities present in the starting material, which is normally a commercial grade material. Subsequently, schemes for purification by multistage processes need to be worked out, such as hydro-chemical processing, electrolysis, ion-exchange, solvent extraction, vacuum refining, zone refining, electron migration, etc. Vacuum distillation followed by zone refining process techniques, is normally applied for the purification of zinc [3]. Both vacuum distillation and zone refining processes have distinct purification roles. Vacuum distillation is more viable than the time consuming zone refining, because a higher purification yield is reached in less time. In this work, a resistance heated vacuum distillation system connected with a gas source mass spectrometer was used to investigate the purification of Zn from a purity of 99.995% to 99.99995%. The impurities were determined in the input and the distilled materials using high resolution glow discharge mass spectrometry (HR-GDMS), additionally the hardness was measured using a micro-hardness tester and the surface topography was investigated using optical microscopy.

2. Experimental

The schematic diagram of the vacuum distillation system is shown in Fig. 1. Via a vacuum valve a turbo pump (PFEIFFER TCP-121) backed by a membrane pump is connected to the recipient and the vacuum achieved was ~2.0×10^{-7} mbar measured using a Pirani and cold cathode gauge. A high current/low voltage supply is connected to two copper electrodes mounted side by side and carrying a crucible support made out of tantalum, which has a high thermal resistance for heating. The cylindrical glassy carbon SIGRADUR® crucible (12.5 mm OD × 10.2 mm ID × 20 mm Ht) which is high temperature resistant up to 3000 °C in inert gas and vacuum was kept in the tantalum crucible support. About 2 g of Zn metal (Alfa Aesar – nominal metallic purity 99.995%) was loaded into the glassy carbon crucible and it was closed by a lid which has an exit orifice of about 1 mm diameter. The cooling system (fed by a PERKIN ELMER HGA cooling system) is a movable water cooled copper block (27 mm OD × 16 mm Ht) cooled by water circulated with an inlet temperature of 5 °C through the jacket which is swiveled during the removal of the volatile impu-

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* Corresponding author. Tel.: +49 30 8104 1116; fax: +49 30 8104 1117.
E-mail address: heinrich.kipphardt@bam.de (H. Kipphardt).

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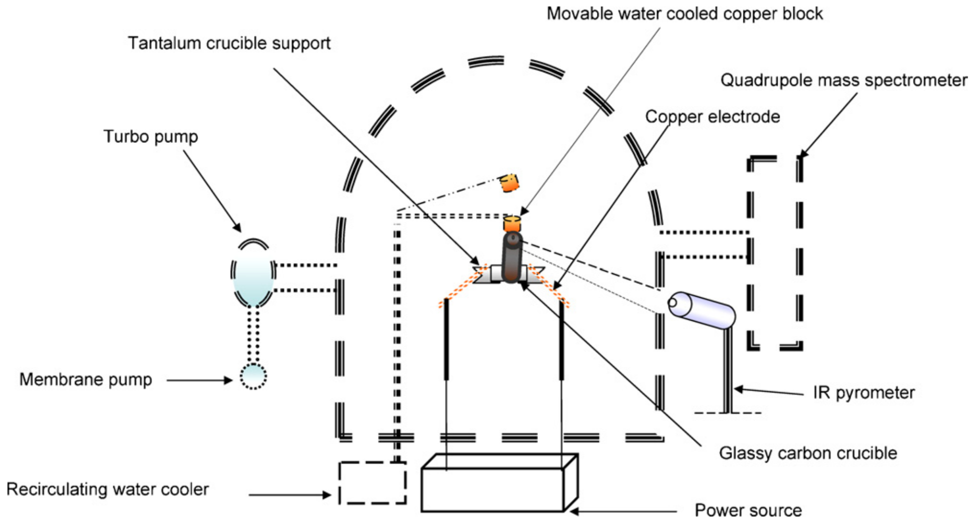

Fig. 1. Schematic diagram of resistance heated vacuum distillation system with connected gas source mass spectrometer. The volume of the recipient is 55 L. The system was built by EMPA, Switzerland.

rities. The temperature of the crucible was maintained by varying the current and voltage to the Cu electrodes using a Power Station pe2050 power source and the temperature was monitored by a laser (infra-red) pyrometer, Quantum Logic 3600 through one of the optically transparent quartz windows. The VD system includes an electron ionization (thoriated iridium filament) quadrupole mass spectrometer (QMS) Pfeiffer Prisma$^{\mathrm{TM}}$ QMS 200. The software used for collecting/monitoring the data of the evolved volatile metals is Balzers Quadstar$^{\mathrm{TM}}$ 422 V 5.0. After each distillation, the distilled Zn material was analyzed using HR–GDMS, Finnigan Element GD$^{\mathrm{TM}}$. The micro-hardness tests were performed using a Vickers hardness tester (Leitz, RZD-DO, Germany). A load of 50 g was applied on the Zn samples and a hardness value has been reported by taking average of three readings in each case. The surface topography of the input and the purified sample was scanned using optical microscopy (Leitz Dialux 20, Germany).

3. Results and discussions

Zn metal has a melting point of 693 K and a boiling point of 1180 K at standard pressure. Purification of the zinc is possible by vacuum refining for impurity elements with higher vapor pressure (p_{v}) than that of Zn and by vacuum distillation for impurities with lower vapor pressure.

The vacuum distillation has been carried out for the removal of impurities from the zinc material. This was achieved in two steps, firstly the removal of the high-volatile elements (mainly Cd) from the Zn material and secondly the distillation of the Zn from the residuum of low volatile elements. These steps were repeated three times consecutively. Zhan and Xu have carried out vacuum distillation on technical scale for the separation of Zn from other metals for recycling electronic waste [4].

3.1. Removal of volatile elements

The removal of volatiles, prior to a distillation is defined as first fraction distillation (FFD) [5]. The FFD distillation temperature in this work was set to 743 K, as the low volatile elements have a lower molar heat of vaporization which is in first approximation proportional to the normal boiling point as per Trouton's law [6]. The removal of the volatile element Cd from the Zn material in the crucible can be related to the effusion, as in this experiment the Zn sample was held in a closed crucible of a volume of 2.55 mL with a 1.0 mm hole diameter. The sample was assumed to maintain its equilibrium p_{v} inside the crucible. The p_{v} calculated for the removal of the volatile impurity element Cd at 743 K (9.6 mbar), was one order of magnitude higher than that of Zn (0.9 mbar), hence the FFD temperature was optimized to carry out the experiment [7]. The rate of volatile Cd escaping through the crucible hole equals to the rate at which it would strike an area of the wall equal to the hole area, under the condition that the mean free path length λ of the volatile molecules is long compared to the diameter of the hole. Under these conditions, the value for the mean free path length for Cd is $\lambda = 0.029$ mm which was calculated using the Sutherland formula:

$$\lambda\,(\mathrm{cm}) = \frac{2.33\times10^{-20}\times T}{\xi^{2}P}$$

T is the soaking temperature (743 K), ξ is diameter of the atom (Cd – 2.88×10^{-8} cm) and P is the initial vacuum in the crucible taken as the p_{v} of the Cd i.e., 7.2 Torr [9]. At this pressure the removal process flow can be termed as 'viscous' type where the molecules undergo many inter collisions. However, already in the 1st FFD the total Cd amount $n(\mathrm{Cd}) = 1.1\times10^{-8}$ mol present is 40 times less than the amount of Cd that would be needed (4.0×10^{-7} mol) to fill the crucible volume to the Cd equilibrium vapor pressure, hence the flow conditions must be more of molecular type.

When the Zn metal starts to melt the element Cd volatilizes and leaves through the hole in the cap of the glassy carbon crucible into the vacuum chamber from where the Cd atoms reach the gas source mass spectrometer where they are ionized and measured [8]. The Cd mass fraction in the input material as determined by GDMS was 620 μg kg^{-1}, which is rather high and at a temperature of 743 K Cd has a p_{v} only one order of magnitude higher than that of Zn, this makes it difficult to separate Cd from Zn. The online profile of the Cd removal monitored during the subsequent FFD steps by quadrupole mass spectrometry is shown in Fig. 2. The 1st FFD shows a sharp increase in the ion current (IC) of Cd from 5 min to 15 min. This indicates that the Zn starts to melt and this initiates the volatilization of Cd. It was observed, that the IC decreased to a minimum for a period of 25 min and there was an increase between 40 min and 50 min and again it decreased to a minimum. Hence the time for the removal of Cd was set for 1 h prior to each distillation. The Cd mass fraction present in the Zn material was determined using GDMS and after 1st FFD its mass fraction was found to be 257 μg kg^{-1}. The 2nd and 3rd FFD QMS profiles were similar and the analysis of the material showed Cd mass fractions of 19 μg kg^{-1} and 4.5 μg kg^{-1} respectively. After three FFD's the total removal efficiency of Cd was found to be 99.2%.