

# Mass Spectrometric Study of the Impurity Profile in Zn During Reduction-Distillation of ZnO with Activated and Inactivated Al

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In this work, we report on the application of hyphenated gas source mass spectrometry to study and understand the mechanism of the reduction-distillation of ZnO using Al powder as reductant in its activated and inactivated form. The experiments revealed that the purity of the Zn metal produced were superior using activated Al with respect to inactivated Al, i.e., m5N8 (99.9998% metallic based) versus m5N3. The achieved purity levels of Zn and the absence of high volatile Cd, Mg, and Sb impurities in the gas phase and the material collected were explained with respect to the impurity elements free-energy values, vapor pressure data, and an observed scavenging effect of the Ta crucible, which was supported by the on-line observed mass spectrometric profiles of the residual gas. (J Am Soc Mass Spectrom 2010, 21, 1620–1623) © 2010 American Society for Mass Spectrometry

In recent years, increasing attention has been paid for the aluminothermic reduction of MgO, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> [1, 2]. Several researchers have carried out work on the aluminothermic reduction of ZnO using activated and inactivated Al for the preparation of Al<sub>2</sub>O<sub>3</sub>. However, the reduction was seldom utilized for the purification of zinc [3–5]. The present study focuses on the behavior of impurities during the purification of Zn by reduction-distillation of zinc oxide with activated and inactivated Al powder in vacuum. The experiments were conducted at different temperatures and the evolving metal atoms were monitored in real-time to investigate the impurity element's oxide reduction ability and the impurity element's ability for co-distillation. All experiments were performed in a resistance heated vacuum reduction distillation system connected to a gas source mass spectrometer.

The activation process of Al is discussed in detail in [6]. The mechanical treatment of Al with added carbon powder as surfactant in vibration milling results in an extremely high chemical activated Al with the removal of inhibiting alumina layer. The addition of graphite also allows one to conserve the powder state of the material without getting oxidized after mechanical milling. The Al powder without pretreatment inherently contains an alumina film at its surface, and is usually denoted as inactivated Al [1]. A smaller particle size presents, in general, a faster reaction rate in the reduction process because of the greater contact area between the reactants; however, in the

case of Al, more than particle size, the surface coating matters.

## Experimental

The vacuum reduction distillation system consists of a cylindrically shaped recipient ( $V \sim 55$  L) on a base plate connected to the mass spectrometer [7]. The schematic of the set-up, originally developed by EMPA, Switzerland, is given in Supplemental Figure S1, which can be found in the electronic version of this article. A turbo pump (PFEIFFER TCP-121) backed by a membrane pump is connected via a vacuum valve. The vacuum achieved was  $\sim 2.0 \times 10^{-7}$  mbar measured using a Pirani and a cold cathode gauge. The two copper electrodes mounted side by side to carry the crucible assembly are connected to a high current/low voltage supply. The crucible used for the reduction is made out of tantalum (9.0 mm o.d.  $\times$  7.0 mm i.d.  $\times$  8 mm Ht) with a glassy carbon SIGRADUR cylinder (12.0 mm o.d.  $\times$  8.0 mm i.d.  $\times$  12 mm Ht, HTW high-temperature Materials GmbH, Germany) on top, both high-temperature resistant up to 3000 °C in inert gas and vacuum. About  $\sim 0.5$  g of ZnO (99.9%, Alfa Aesar) and 25% Al (99%, Alfa Aesar, Karlsruhe, Germany), in excess to stoichiometry, was loaded into the crucible. Then, the cylinder was placed on top of it and closed by a lid (with an exit orifice of  $\sim 1$  mm diameter) also made out of glassy carbon. The cooling system (fed by a CETAC model 2050 cooling system, Omaha, NE, USA) is a movable water cooled copper block (27.0 mm o.d.  $\times$  16 mm Ht) cooled by water circulated with an inlet temperature of 0 °C. The cooling block was swiveled during the mon-

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itoring of the evolved elements by the mass spectrometer and during the deposition of Zn to about 1 mm above the crucible lid. The temperature of the crucible was maintained by varying the current to the Cu electrodes using a Power Station pe2050 power source and the temperature of the Ta crucible wall was monitored at an area of 9 mm diameter by a laser (infra-red) pyrometer, INFRATHERM IGA 120 (Impac Infrared, Frankfurt, Germany) through one of the optically transparent quartz windows. The temperature gradient between the lid and the tantalum crucible bottom was estimated to be in the order of magnitude of 300 °C, the gradient within the Ta crucible itself was considered to be small. The distilled Zn is collected on the bottom of the glassy carbon crucible lid and could be easily removed without applying any mechanical force. The evolution of volatile compounds during the reduction and the apparent start of the zinc deposition were monitored with the hyphenated mass spectrometer, which includes an electron impact (thoriated iridium filament) quadrupole mass spectrometer (QMS) Pfeiffer Prisma TM QMS 200 (Asslar, Germany). The software used for collecting/monitoring the data of the evolved volatile metals is Balzers Quadstar 422 V 5.0 (Balzers, Liechtenstein).

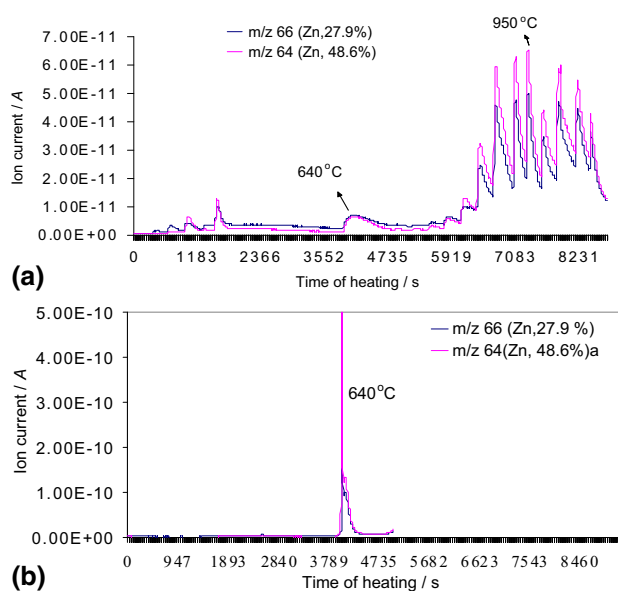
For preparation of activated aluminium, Al/C (10:1; 5.5 g) mixture, a mixer mill MM 301, Retsch GmbH, Haan, Germany, with the grinding jar of 25 mL capacity and a single ball of 20 mm diameter, made out of zirconia, was used. The mixture was milled for 1 h at 20 Hz frequency, similar to the experiment performed by Streletskii et al. [8]. For the mixture, high purity carbon in the form of spectral coal (Ringsdorff, Germany) as used for the preparation of electrodes for dc-arc spectrometry was used.

For the ICP-OES measurements 0.5 g of the material was dissolved in 9 mL aqua regia and filled-up with water to 100 mL. The analytes were determined using at least three different wave lengths each after external calibration with inductively coupled plasma optical emission spectrometry (Varian 725, Palo Alto, CA, USA).

## Results and Discussion

The aluminothermic reduction of ZnO was carried out using inactivated and activated aluminum following:  $3 \text{ZnO} + 2 \text{Al} \rightarrow 3 \text{Zn} + \text{Al}_2\text{O}_3$  with  $\Delta_r G^\circ = -627 \text{ kJ} \cdot \text{mol}^{-1}$  [9]. The reaction is possible even at ambient temperature. Zn metal has a melting point of 420 °C and a boiling point of 907 °C at standard pressure.

The reduction of ZnO with inactivated Al in vacuum takes place with sufficient speed at ~950 °C as observed with the hyphenated mass spectrometer (Figure 1a). At temperatures below the melting point of Al, the passivating alumina coating inhibits the reaction completely. The reduction distillation of ZnO was confirmed with the appearance of an ion current ratio  $I(m/z 64)/I(m/z 66)$  identical to the ion current ratio from pure Zn as observed with this equipment. By comparing with a



**Figure 1.** Observed ion currents of Zn ( $m/z$  66 and 64) using gas source QMS by stepwise heating. (a) Reduction of ZnO with inactivated Al. (b) Reduction of ZnO with activated Al.

pure material fractionation effects cancel to a wide extent, although the individual absolute isotopic abundance ratios of Zn  $f(^{64}\text{Zn})/f(^{66}\text{Zn}) = 48.6\%/27.9\% = 1.74$  are not perfectly matched by the observed ion current ratio. At 950 °C the Zn vapor pressure is  $p_v = 2.5 \cdot 10^5 \text{ Pa}$  calculated using the relationship  $\log(p_v) = A - B/T$  between  $p_v$  and temperature  $T$  with the constants  $A$  and  $B$  given by Dushman [10]. The Zn evaporates and is deposited on the bottom of the crucible lid due to the thermal gradient along the glassy carbon cylinder. The temperature at the collector is ~650 °C and was even further decreased through the water cooled copper block.

A similar reduction distillation experiment was carried out with activated Al, where the crystalline size of Al decreased from 77 to 55 nm after milling with carbon. It was observed that the reduction already took place at a much lower temperature (i.e., 640 °C) as confirmed through the appearance of the Zn ion currents (Figure 1b) [4]. The reduction observed was still due to Al and not due to the presence of carbon, as a separately heated mixture of carbon and ZnO did not realize Zn in this temperature range. The ZnO reduction with carbon is known to occur between 970 °C and 1170 °C, which is above the temperatures of the aluminothermic reduction and also the formations of carbides were negligible owing to very high-temperature requirements [11]. At 640 °C the  $p_v$  of the Zn was  $3.7 \cdot 10^3 \text{ Pa}$  and the Zn gets collected on the bottom of the crucible lid.

The deposited zinc samples were analyzed by ICP-OES (Table 1) for the concentration of 14 metallic impurities. The measurements of the input material and the reduction-distilled Zn (activated and inactivated Al) by ICP-OES revealed that for almost all impurity elements (except Bi and Pb) a removal efficiency of ~99% was found. The mass spectrometry

**Table 1.** Calculated free energy  $\Delta_r G^\circ$  for the reduction of the oxides to the corresponding metal using Al, mass fractions  $w$  of the metals in the Zn materials as obtained by ICP-OES and vapor pressures  $p_v$  of the metals.

$\Delta_r G^\circ/\text{kJ/mol}$ for reduction of metal oxide to metal with Al	Metal	$w/\text{mg/kg}$ metal in input material (ZnO + Al)	$w/\text{mg/kg}$ metal in output material (Al reduced Zn)		metal $p_v/\text{Pa}$	
			Inactive	Active	Inactive	Active
—	Al	20%	0.21	0.11	950 °C	640 °C
−1088 (Bi <sub>2</sub> O <sub>3</sub> )	Bi	6.5	4.7	0.024	$8.1 \cdot 10^{-3}$	$2.0 \cdot 10^{-7}$
−895 (CdO)	Cd	9.0	<0.025	0.067	$3.3 \cdot 10^2$	0.8
−4004 (Co <sub>3</sub> O <sub>4</sub> )	Co	0.9	0.038	0.001	$1.0 \cdot 10^6$	$2.5 \cdot 10^4$
−523 (Cr <sub>2</sub> O <sub>3</sub> )	Cr	5.5	0.12	0.001	$3.3 \cdot 10^{-6}$	$5.3 \cdot 10^{-12}$
−1144 (Cu <sub>2</sub> O)	Cu	71	<0.005	0.007	$4.6 \cdot 10^{-5}$	$1.4 \cdot 10^{-10}$
−3283 (Fe <sub>3</sub> O <sub>4</sub> )	Fe	217	<0.025	0.098	$1.8 \cdot 10^{-3}$	$3.8 \cdot 10^{-8}$
+126 (MgO)	Mg	21	<0.005	<0.005	$1.8 \cdot 10^{-5}$	$4.6 \cdot 10^{-11}$
−493 (MnO)	Mn	2.9	<0.025	<0.025	$3.1 \cdot 10^4$	$2.3 \cdot 10^2$
−946 (NiO)	Ni	11	<0.087	<0.087	1.1	$3.3 \cdot 10^{-5}$
−1018 (PbO)	Pb	11	1.8	1.14	$5.9 \cdot 10^{-6}$	$7.4 \cdot 10^{-12}$
−5421 (Sb <sub>2</sub> O <sub>5</sub> )	Sb	10	<0.05	<0.05	$9.0 \cdot 10^1$	$2.0 \cdot 10^{-1}$
−217 (Ta <sub>2</sub> O <sub>5</sub> )	Ta	1.8	<0.025	<0.025	$1.5 \cdot 10^3$	$2.2 \cdot 10^{-1}$
−509 (TiO <sub>2</sub> )	Ti	9.3	<0.025	<0.025	$1.8 \cdot 10^{-21}$	$1.4 \cdot 10^{-32}$
					$4.2 \cdot 10^{-8}$	$1.7 \cdot 10^{-14}$

ter hyphenated to the system was used to probe the mechanism by which the impurity removal takes place during the deposition of Zn.

Due to the general principle and technical restriction of the mass spectrometer, only those elements with high  $p_v$  and mass  $m/z < 200$  (i.e., Cd, Mg, and Sb) were studied. Elements with low  $p_v$  (i.e., Al, Co, Cr, Cu, Fe, Mn, Ni, Ta, and Ti) tend to remain in the residue and could not be monitored on-line, although the free-energy for the reduction of their oxides is negative. Especially, the high impurity contents of Cd, Mg, and Sb in the input material were not found in both types of reduced Zn material (Table 1). The justification for their absence was probed initially with respect to their free-energy values. MgO had a positive free-energy value, indicating that the reduction reaction is not favorable, whereas CdO and Sb<sub>2</sub>O<sub>5</sub> were found to have negative free-energy values. Hence, they are favorably reduced at STP (Table 1). The products formed, Cd and Sb, have a sufficiently high  $p_v$  at the reduction temperatures to be detected by the mass spectrometer, however they were not observed.

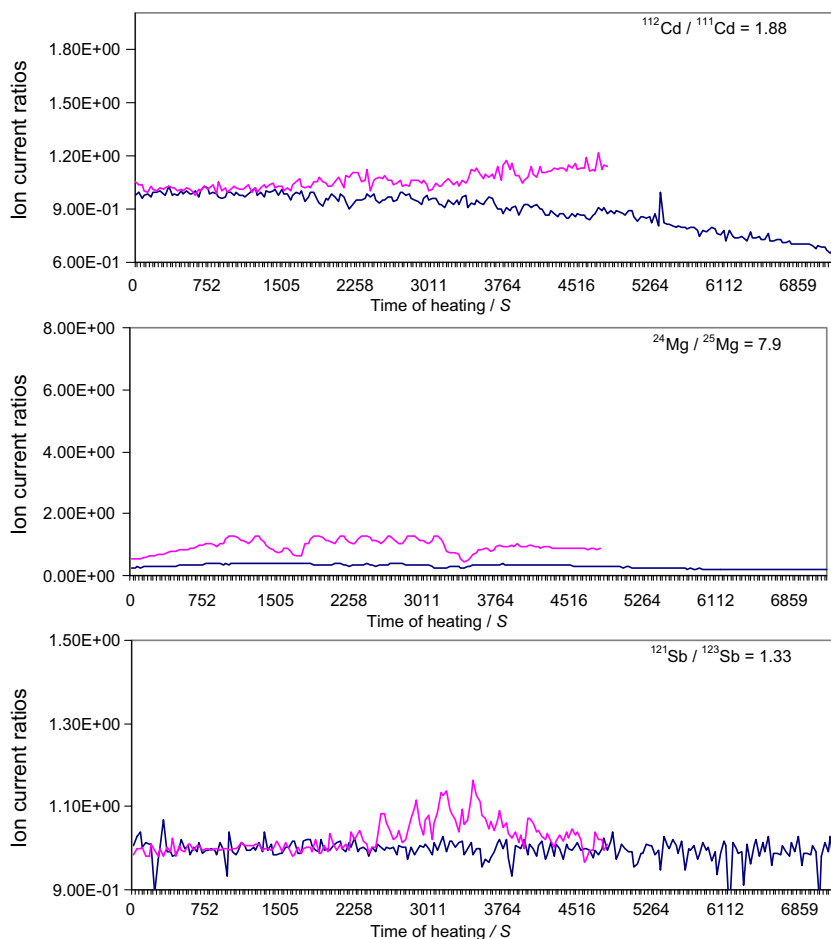
The absence of these impurities was further confirmed by the mass spectral profiles of their isotopes observed in real-time. In Figure 2 it can be seen, that the ion current ratio  $I(m/z 112)/I(m/z 111) \sim 0.9$  does not match the isotope ratio  $f(^{112}\text{Cd})/f(^{111}\text{Cd}) = 24.13\%/12.80\% = 1.88$ , indicating the absence of Cd, and similarly for Sb  $I(m/z 121)/I(m/z 123) \sim 1.0$ , which does not correspond to the isotopic ratio of  $f(^{121}\text{Sb})/f(^{123}\text{Sb}) = 57.36\%/42.64\% = 1.33$ . The unexpected absence of Cd and Sb in the vapor phase during distillation and in the reduction distilled Zn were experimentally probed by reducing their oxides ( $\sim 0.1$  g) individually with Al similar to the conditions used for Al/ZnO reduction. It was again observed that the mass spectral profiles were similar to Figure 2, indicating the absence of sufficiently volatile Sb and Cd. Therefore, the crucible was further

examined using X-ray spectrometry (Niton XL3t XRF analyzer, Thermo Scientific, Munich, Germany) and it was found that Sb and Cd were attached to the Ta crucible as a globule.

The XRF results confirmed that Ta metal acts as a scavenger for Sb and Cd even for a higher concentration. This phenomenological observation is in line with the recommendation of a major Ta producer ([www.plansee.com/lib/dl\\_Tantal-Niob.pdf](http://www.plansee.com/lib/dl_Tantal-Niob.pdf)) to restrict the use of Cd with Ta at temperatures above 500 °C. In the frame of this work, we did not further investigate the scavenging mechanism. Bi and Pb impurities, which had negative free-energy values, were found to be present in lower concentrations in the activated Al reduced Zn material owing to the decrease in temperature of the reduction reaction from 950 °C to 640 °C. This lowered the  $p_v$  by almost three orders for Bi and two orders of magnitude for Cd, respectively. The marked decrease in the  $p_v$  is translated also into the purity of Zn, with an increase in the purification efficiency of Bi from 27% to 99% and of Pb from 83% to 89%. Accordingly, the temperature difference in reduction varied the purity of the deposited Zn in relation to the total metal impurities (reductant Al 20% and other metallic impurities  $\sim 400$  mg/kg) reduced to 6.9 mg/kg (i.e., m5N3; where the m stands for investigated metallic based impurities, 5N3 for five nines followed by a 3, i.e., 99.9993% based on the investigated metallic impurities) for inactivated Al reduction and to 1.4 mg/kg (m5N8) for activated Al reduction.

## Conclusions

The in situ observations of the isotopic ratio pattern revealed that the reduction of ZnO with activated Al took place 310 °C lower than with inactivated Al. Oxides that can in principle be reduced by Al and that



**Figure 2.** Observed ion currents ratios corresponding to the isotopes of Cd (111 and 112), Mg (24 and 25), and Sb (121 and 123) using mass spectrometry during reduction-distillation of ZnO with (red dashed line) activated (up to 640°C) and (black dashed line) inactivated Al (up to 950 °C).

form elements of high volatility (Sb and Cd) did not distil along with the Zn. It was confirmed, that these metals stuck to the crucible, forming a high boiling mixture with Ta. On-line gas source mass spectrometry has demonstrated to be a valuable technique in probing and understanding the achieved purity of Zn during the reduction distillation of ZnO with Al.

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## Appendix A Supplementary Material

Supplementary material associated with this article may be found in the online version at [doi:10.1016/j.jasms.2010.04.009](https://doi.org/10.1016/j.jasms.2010.04.009).

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