The Effect of Lead on the Activity of Sodium in Liquid Zinc

X.Y. YAN, D.E. LANGBERG, and W.J. RANKIN

The zinc produced by smelting contains many impurities, mainly lead, cadmium, iron, copper, tin, bismuth, cobalt, arsenic, and antimony. The zinc produced from the Imperial Smelting Furnace (ISF) process contains on average 1.0 to 1.3 pct lead and 0.03 to 0.05 pct arsenic. The arsenic content can be readily reduced to below 0.003 pct by treatment with sodium. A knowledge of the thermodynamic activity data of sodium in zinc and how it is affected by the major contaminant lead is required to determine the end point of the sodium additions.

Thermodynamic properties of liquid binary Zn-Na alloys have been studied by several investigators [1-3] but the effect of lead on the activity of sodium in molten zinc has not been determined experimentally. This work was aimed at determining the activities of sodium in zinc-rich Zn-Pb-Na melts and investigating experimentally the thermodynamic interaction between sodium and lead in liquid zinc at 465 °C. The electromotive force (emf) method was used to determine the activities of sodium in zinc-rich Zn-Na melts [5] employed. The same materials as used previously were used in the present work. The lead was 99.999 pct pure.

The solid electrolyte cell used, as shown in Figure 1, had the configuration

$$Ta, Bi (l) + Na \text{Bi} (s) | Na^+ \beta - \text{alumina} | Bi-Na (l) | Na^+ \beta - \text{alumina} | Zn-Na (l) or Zn-Pb-Na (l), Ta.$$  

Details of the configuration were provided previously. [5]

The Bi-Na alloy bath and Zn-Pb alloy were prepared by melting the required amounts of the metals in a graphite crucible under a cover of dry and deoxidized high purity argon. The melt was held for 3 days at 320 °C for Bi-Na alloys and 450 °C for Zn-Pb alloys. The furnace power was then switched off, allowing the melt to cool under a dry and deoxidized high purity argon atmosphere. The solidified alloy was stored in an evacuated desiccator. Approximately 1.5 g of zinc (or alloy of zinc with lead or bismuth) was taken for each experiment. The metals were added to the electrolyte tubes and sealed under a nitrogen atmosphere in a glovebox to prevent contamination by air and moisture.

In this work, the zinc-lead alloy as prepared initially contained 0.96 pct lead, which is very close to the average concentration of lead in zinc produced from the ISF process. Thus, the ratio for the numbers of moles of zinc and lead was essentially kept constant in Zn-Pb-Na melts as sodium contents of the melts were varied in the working electrode during each experiment.

Each half-cell was arranged as shown in Figure 1 and then loaded into the stainless steel reactor tube after the graphite crucible holding the Bi-Na alloy was placed on the bottom of the reactor tube. The procedure for the experiments was as described previously. [5] Coulometric titration was
used to vary the alloy compositions in situ in the working electrode and to prepare the reference electrodes. After each experiment, the used electrolytes were examined for any possible reactions using a PHILIPS* XL 30 scanning electron microscope with an Oxford Instruments ISIS energy dispersive system.

Figure 2 shows a typical variation of the cell emf with time for the composition of $2.09 \times 10^{-3}$ atom fraction of sodium in zinc-rich Zn-Pb-Na melts during the temperature cycle. The emf measured was the potential difference between the working and counterelectrodes rather than the reference electrode. This was done to avoid the effect of chemical association and dissociation of solid Na$_3$Bi in the reference electrode during the temperature cycling, which could require a longer period of time for the electrode to come to equilibrium. It was observed that the cell emf returned to its original value within ±1.5 mV after cycling the cell temperature, demonstrating that the working electrode half-cell was reversible with respect to molten sodium.

The titration curves relative to pure liquid sodium are shown in Figure 3 for Zn-Pb-Na melts at 465 °C and 480 °C. The corresponding curve for the lead-free system is shown for comparison.$^5$ The emfs measured from the preceding cell were calibrated using the same method as described previously.$^5$ It can be seen from Figure 3 that the emf of each cell decreased with increasing content of sodium until the melts became saturated with solid Na$_3$Zn$_{13}$, after which the emfs measured were independent of alloy composition. The titration curve for the zinc-rich Zn-Pb-Na melts at 465 °C as shown by the dashed line indicates that the alloys were metastable at the compositions from $4.68 \times 10^{-3}$ to $1 \times 10^{-2}$ atom fraction of sodium after which the alloys fell within the two-phase region of Zn (l) + Na$_3$Zn$_{13}$ (s) with the same chemical potential as that for the lead-free binary melts. The observed metastable region almost disappeared for the zinc-rich Zn-Pb-Na melts at 480 °C.