A TECHNIQUE FOR PURIFICATION OF ZINC USED AS TEMPERATURE STANDARD

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Abstract

The present investigation describes a technique for purification of zinc by vacuum distillation. By this technique it is possible to obtain zinc with purity better than 99.999% which is necessary for a thermometric fixed point. For the assessment of purity of the purified zinc, thermal analysis technique was used. This technique was found by many authors to be simple and very useful for discrimination between high purity samples.

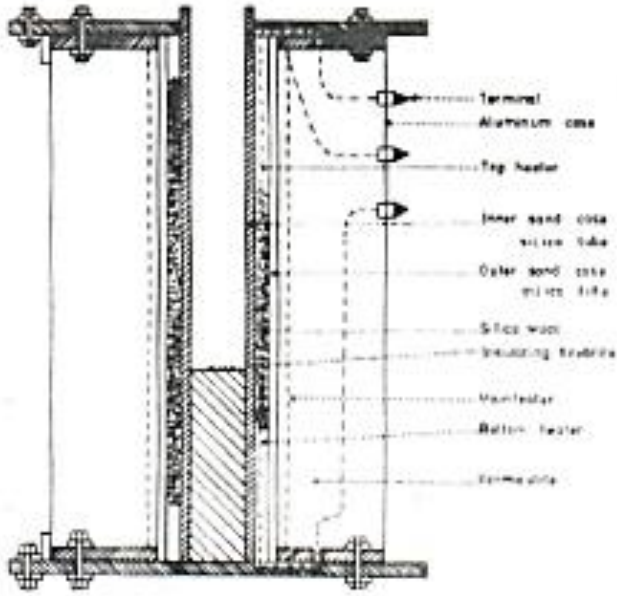
Introduction

To provide adequate calibration service, the various national standardizing laboratories have developed resistance thermometry techniques of high accuracy. Measurements to a precision of 10^{-4} degree in the range 0 to 450°C have been current practice.

To realize the full capability of these techniques a need has arisen for corresponding advances in the quality and usefulness of fixed temperature points. A precision thermometric fixed point must realize a unique temperature state with an experimental reproducibility that is comparable with the stability of the temperature detector and its associated measuring apparatus. These temperatures are obtained from the controlled freezing of metallic elements which are of purity better than 99.999%.

In the temperature range 0-630°C the freezing point of high purity zinc[1] (419.58°C) has been recognized by the International Practical Temperature Scale (IPTS) 1968 as a fixed point for calibration of platinium resistance thermometer. For this reason it is essential to get zinc of very high purity, to satisfy the above mentioned requirements.

This paper describes a technique for purification of zinc by vacuum distillation, since the vapour pressure of zinc (10^{-1} mmHg at its melting point), is far higher than that of the most likely impurities (except cadmium, 10^{-1} mmHg at 321°C) which are Pb (10^{-7} mmHg at 450°C), Fe (1.5×10^{-2} mmHg at 1536°C), and Cu (1.5×10^{-3} mmHg at 1083°C), the metal should therefore be refined easily by this technique.



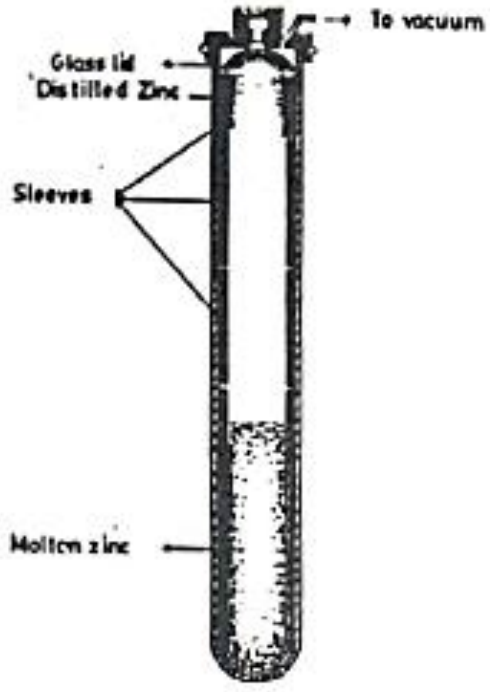


Fig.(1B). Vacuum Still assembly.

Results and Discussion

Thermal analysis of a high purity metal by a careful intercomparison of the plateau freezing temperature using the technique outlined before can give a good measure for discrimination between samples[4] of different purity. For that purpose interest lies primarily on the form of the thermal curves and not on the freezing temperature. Fig. (3) gives typical freezing curves for 3 different zinc samples, curve (1) for the commercial zinc after distillation (one time), curve (2) for cominco 99.999% purity zinc, (curve (3) for zinc twice distilled.

From these curves, it can be seen the following:

a) The twice distilled zinc sample has the highest liquidus (freezing) point as is clear srom Fig. (3) and Table (1).

Table (1): Intercomparison of plateau temperatures

	No. of freezes	Mean $(\frac{R_{Zn}}{R_{T_p}})$	plateau Temp. rel. to Cominco
Zinc twice distilled	15	2.568449	+ 0.0001
Cominco 59 grade	3	2.568446	0.00
Zinc once distilled	8	2.568436	- 0.004

It is known that when the sample contains no solutes that raise the liquidus point on solution, then the highest liquidus point found among the group is necessarily closest to that of the pure metal (solvent).

In case of zinc the most probable impurities are Cd, Cu, Fe and Pb all of these solutes depress the freezing point except Cu, but the common effect of all impurities is to depress the liquidus temperature on solution. Hence the twice distilled zinc sample must be purer than the 99.999% purity cominco sample.

b) The twice distilled sample has the lowest freezing range* and the most steady freezing plateau. The existance of a plateau of constant temperature on the cooling curves is due to the finite limit of about 0.0001°C in temperature resolution that is usually obtainable in precision, platinum resistance thermometers.

On overcoming the supercooling, the temperature at the advancing freezing interface (and hence at the resistance thermometer) is determined by the concentration of solute in the newly frozen solid. When the change in the liquidus temperature

* The freezing range is the difference in the temperature at which freezing begins and ends.

associated with the solute concentration gradient in this solid becomes less than 0.0001°C, a plateau feature appears. The concentration changes to produce a depression of 0.0001 degree can be calculated from the phase diagram for the likely impurities. In most cases it is about 0.1 ppm.

(c) The rounding at the end of the freezing curve in case of once distilled sample is less sharp than that of Cominco and the most sharp rounding is in the case of the twice distilled zinc, which is also a criterion of its higher purity than Cominco 59 grade. This change in the slope near the end of the freezing curve is due to the fact that near the end of the freez most of the impurity has been radialy swept to the central region of the ingot, which is close to the thermometer and start to depress the temperature more rapidly. Hence the rate of change of the slope of the freezing curve near the end of the freez is a good measure of the impurity concentration in the original sample.
The above analysis of the freezing curves shows that the twice distilled zinc sample is of higher purity than Cominco 59 grade sample.

Conclusions

The purification of zinc by using the freezing point assemblies, is proved to be successful. The method is simple and requires little attention.

From the point of view of laboratory doing temperature measurements of the type described in this work, the vacuum distillation technique for production of high purity zinc seems to be very useful as it requires little extra equipment and can be carried out when the furnace is not occupied in calibration work, ensuring that full use is made of the melting furnace.

Concerning the method of thermal analysis used in this work for assessment of purity, it is sensitive to many impurities to less than 1 ppm. The method however, cannot give information on which impurities are present, but only on their overall effect which is sufficient for the present work. Spectrographic analysis is usually not reliable below about 5 ppm and the method depends on comparison with standards for calibration, these standards are not known to better than 1 in 10^6. Thermal analysis technique has also the advantage, that the 1 kg ingots required for precision resistance thermometry, allow freezing point and the melting range determinations to be made on fairly representative samples which help to eliminate sampling errors frequently found in spectrochemical analysis.

References

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