

ON THE BEHAVIOUR OF METALLIC IMPURITIES IN TIN DURING ZONE MELTING PROCESS

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ABSTRACT

Zone melting process is considered as an important development in purification of semi-conductors and metals. Several charges were prepared by alloying spec-pure tin with 0.1514% Cu. A comprehensive study including the application of wide range variation of molten speed, spectroscopic analysis, scanning electron microscopy as well as mechanical measurements on these charges are performed. The results of these investigations are as follows: i) To give quite satisfactory results, the molten speed lower than 2 cm/hr must be used. ii) Equations representing the distribution of impurity concentration along the ingot length such as Tiller and Pfann equations are Unrealistic to experimental results. iii) A semi empirical formula is suggested to give satisfactory results for the degree of purification along the ingot length. This formula is also applicable for different ingot lengths. iv) The purification along the cross sectional area may be of a good homogeneity. v) There is a difference in mechanical properties along the entire length of the ingot.

Keywords: Zone melting, Tin, Impurities, Spectroscopic analysis Purification of metals, Semiconductors

INTRODUCTION

There have been several important developments in purifications of semi-conductors and metals by zone melting process in the past few years [1]. This process is based on the fact that, the concentration of impurities in a liquid phase differs as a rule from that in a solid phase formed after solid crystals precipitate from the molten ingot on cooling. The impurity distribution coefficient is very sensitive to the rate of crystallization or the temperature drop and consequently depends on the velocity of the molten zone. Although it was mentioned that the process can be successfully used at a speed varying from 1.8 cm/hr to 72 cm/hr [1], it appears that this wide range of variation has unrealistic meaning on the basis of interaction of solute and solvent during zone melting process.

In discussing the phenomena of solute transfer in the molten zone, Tiller et al [2] have pointed out that it is a diffusion -dominated, while Pfann [3] has assumed a complete mixing to be the case in the molten zone. Abol-Hassan et al [4] showed that neither the equation used by Tiller nor Pfann equation could be regarded as suitable mean for

analysis the experimental distribution curves of the solutes along the purified parts of the charge.

In this article, we presented the results of a comprehensive study of:

- (i) the effect of speed of the molten zone on the degree of purification,
- (ii) scanning electron microscopy for the cross-sectional distribution of impurities of the purified ingot,
- (iii) mechanical properties of the purified charge, and
- (iv) deducing an empirical formula for evaluating and analysing the experimental distribution curves.

2. EXPERIMENTAL

2.1 Preparation of the charge

Several charges were prepared by alloying spec-pure tin with 0.1514% Cu. Each charge was introduced into a pyrex tube of inner radius and

length approximately the same as those of the charge. The tube with the charge was introduced into a wider pyrex tube fixed along the axis of a resistance ring heater. Horizontal single-pass zone melting was made in a reducing agent atmosphere [5]. The zone speed was changed from 1.0 cm/hr to 14 cm/hr.

2.2 Preparation of charges for scanning electron microscopy (SEM) and for mechanical testing

Zone melted sample were marked and then cut into small segments about 2 cm long each. These segments were prepared for SEM through application of a series of grinding paper, AlO₂ and the diamond until become optically flat. Other samples were prepared with suitable form to be used for the stress-strain measurements.

3. RESULTS AND DISCUSSIONS

3.1. Spectrographic evaluation [5] of the quantity of copper along the entire length of a charge leads to the construction of the experimental distribution curves of copper after each single pass zone melting. The value of the distribution coefficient of the solute was determined for each speed. Figure (1) gives an example of the experimental distribution curves along two different ingot lengths (9, 16 cm) at a zone speed ≈ 3.2 cm/hr and zone length of 3 cm, while Figure (2) shows a typical sequence of distribution coefficients recorded after successive single-pass zone melting at zone speeds in the range from 1 cm/hr to 14 cm/hr.

Analysis of Figure (2), indicates that, the best purification is achieved under normal conditions at zone speed less than 5 cm/hr. On the other hand, it was impossible to achieve a good purification by raising the zone speed up to about 10 cm/hr. There is nothing surprising in this fact since solid and liquid phases are practically at equilibrium in the case of a very slow crystallization (as result of a very slow temperature drop). With the rise in the crystallization rate, however, equilibrium is disturbed.

It is evident from Figure (1) that, neither the concentrations calculated by Tiller equation (T_d) nor that calculated by Pfann equation (T_c) represent

accurately the experimental distribution along the entire length of the ingot. Moreover, the use of these equations can't explain the dependence of purification on the ingot length.

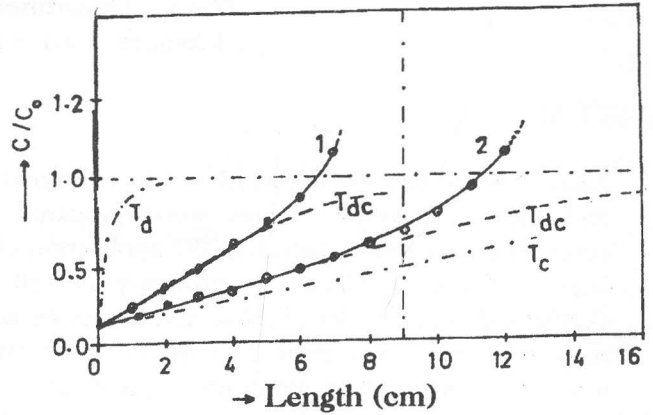


Figure 1. Distribution of Copper along the charge after a singlepass zone melting. (1 and 2) represent the experimental curves for two samples of 9 and 16 m long respectively, T_{dc} represents the values calculated by equation (2) for two ingot lengths, (T_d and T_c) represent the values calculated by Tiller and Pfann equations respectively.

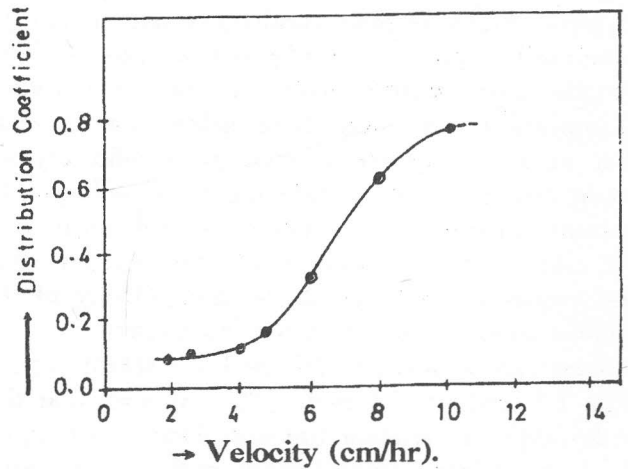


Figure 2. The distribution coefficient as a function of the speed of the molten zone.

The solution of this problem, however, has certainly lead us to remember the concepts of the others [4] corresponding to the transfer mixed diffusion- convection regimes. It is convenient

therefore, to alter the functional form of Tiller and Pfann equation to be in the form:

$$C/C_0 = [K] \exp\left(\frac{-KRx}{D}\right) \quad (1)$$

where K is the distribution coefficient of the solute, D is the diffusion coefficient of the solute in the molten tin, R is the zone speed, and x is the distance from the start of the ingot. However, even with this latter configuration, there is still "the ingot total length error". The procedure for correcting this error was based on introducing the factor (L-ℓ). Thus Eqn (1) becomes:

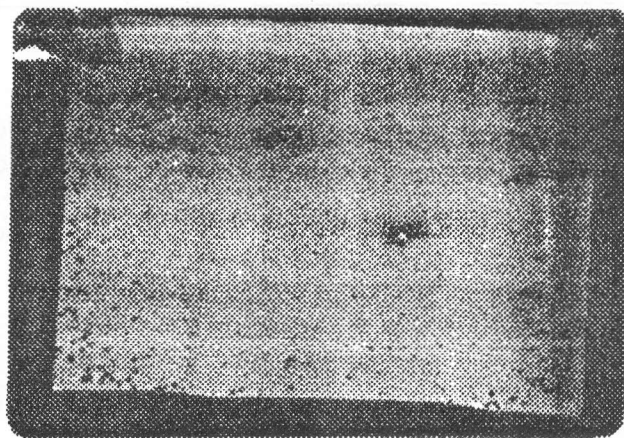
$$C/C_0 = [K] \exp\left(\frac{-KRtx}{mD(L-\ell)}\right) \quad (2)$$

where L is the total length of the ingot and m is a dimensionless parameter having the numerical value of the zone length ℓ.

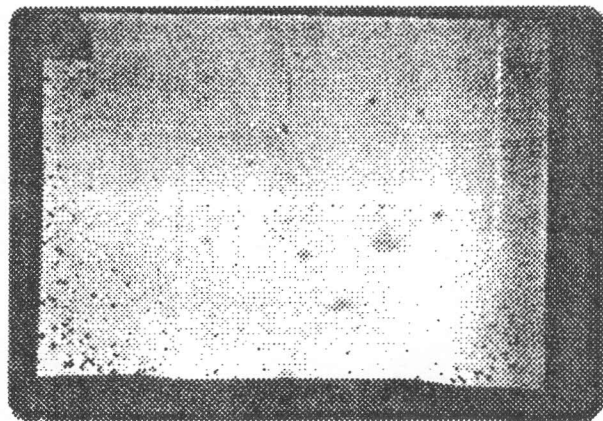
The value of K for copper used in this calculation was 0.12 (from Figure (1)). For D, the value assumed for copper is 5×10^{-5} cm²/sec. [6]. The calculated distribution curves (T_{dc}) are shown in Figure (1) for comparison. These curves indicate that the calculated concentration using Eqn(2) is in good agreement with that determined experimentally especially at the first parts whatever may be the length of the ingot.

3.2. To get more insight into the way in which impurities are distributed along the cross-section of the ingot, we present a photograph taken by the scanning electron microscope for a cross sectional area of an ingot after a single pass at zone speed ~ 3,2 cm/hr. Analysis of the photograph given in Figure (3) indicates that the distribution of impurities is symmetrical along the cross-sectional area, yet it is expected to be dependent on the rate of crystallization. This was also verified by spectrographic analysis. At higher crystallization rates, the impurity distribution in the solid phase depends entirely upon the actual conditions of the metallurgical process.

3.3. Analysis of the curves in Fig. 4 clarify that there is a difference in the mechanical properties along the entire length of the sample. curves b's in these figures corroborate the presence of an increase in the stress at the end of the ingot, while curves a's emphasize that the strain is the same along the total length of the purified sample. There is nothing surprising in this fact, since accumulation of the impurity atoms at the end of the sample must alter the physical properties of the solid crystal.



Central image



Peripheral image

Figure 3. A photograph of the cross-sectional area of a purified zone sample. taken by scanning electron microscope.

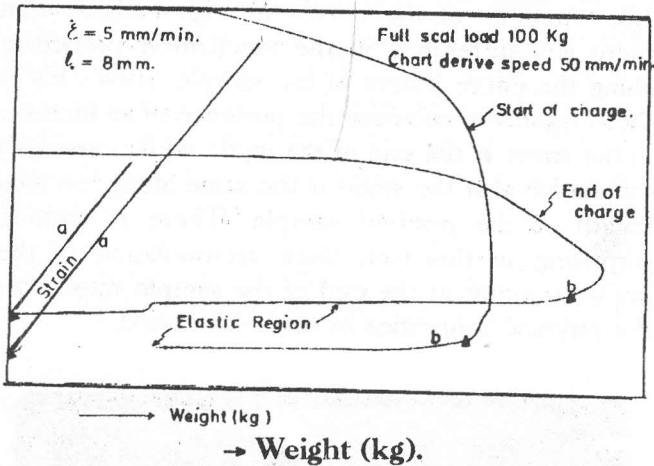


Figure 4. Mechanical testing of a zone melted sample at the start and at the end of a purified sample. Curves a's represent the strain while curves b's represent the stress and Δ - Δ represents the elastic range.

4. CONCLUSION

From the foregoing discussions we conclude the following:

- (i) it is important to use a zone speed lower than 2 cm/hr. These lower speeds do not only give quite satisfactory results, but also make the solid and liquid phases, practically, in equilibrium.
- (ii) Tiller equation is only applied for too short ingot lengths, while Pfann equation is only applied for too long lengths. The distribution of

concentration given by these equations are independent of the ingot lengths, which are unrealistic to the experimental results.

- (iii) equation (2) can be applied successfully for all different ingot lengths.
- (iv) the purification along the cross-sectional area may be of a good homogeneity.
- (v) generally, for saving time, speeds up to 4 cm/hr are recommended. The corresponding decrease in sensitivity can be balanced by using more than one successive zone.
- (vi) there is a difference in the mechanical properties along the entire length of the ingot. This work will be continued with other impurities to show the effect of the different parameters on the purification process.

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