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Abstract

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PURIFICATION OF INDIUM FROM TIN AND LEAD IMPURITIES BY ZONE MELTING OF ITS CHLORIDE

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In recent years, the use of indium in semiconductor technology has become widespread, and therefore the requirements for the purity of the metal obtained have increased. According to established technical requirements, the content in especially pure indium of such impurities as As, Sn, Hg, Tl, Fe, Zn must be $1 \cdot 10^{-5}$%; Pb, Fe, Cd, Ag, Ni $1 \cdot 10^{-5}$–$1 \cdot 10^{-6}$%, and Cu $1 \cdot 10^{-6}$–$1 \cdot 10^{-7}$%. One of the most effective methods for fine purification of metals is zone melting ([1–3]). However, in zone melting of metallic indium, purification does not occur from all impurities, since some of them (for example, tin and lead) have distribution coefficients close to unity.

In such cases it is possible to change the distribution coefficient by subjecting not the metal to zone melting, but a suitably selected compound of it, so that pure metal can be obtained from the purified compound. The selection of a suitable compound for the purification of indium causes difficulties, since ordinary indium salts (sulfate, nitrate, etc.) decompose without melting, while indium chloride sublimes below its melting point.

In 1960 we proposed a method for purifying indium from impurities by zone melting of eutectic alloys of indium chloride with alkali-metal chlorides, in particular sodium ([4]).

In the present article, results are reported from a study of the behavior of tin and lead during zone melting of the eutectic of indium chloride with sodium chloride. The eutectic alloy contains 21.5 wt.% sodium chloride and melts at a temperature of 272°.

As starting materials we used indium chloride, obtained by chlorination of metallic indium, and "chemically pure" sodium chloride, recrystallized. A mixture of the specified composition was introduced into an ampoule of molybdenum glass 15–20 cm long. To obtain a homogeneous melt, the ampoule was kept in

Figure 1. Distribution of lead along the length of the ingot after one zone pass at different initial lead concentrations: 1 $-C_0 = 1.65 \cdot 10^{-4}\%$; 2 $-C_0 = 6.57 \cdot 10^{-4}\%$, 3 $-C_0 = 3.66 \cdot 10^{-3}\%$; 4 $-C_0 = 1.75 \cdot 10^{-2}\%$

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a muffle furnace at 400° for two—three hours. In studying the dependence of the effective distribution coefficients on the initial concentration of the impurity, stannous chloride or, respectively, lead chloride was additionally introduced into the initial mixture of chlorides.

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1 $-C_0 = 1.65 \cdot 10^{-4}\%$; 2 $-C_0 = 6.57 \cdot 10^{-4}\%$, 3 $-C_0 = 3.66 \cdot 10^{-3}\%$;
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The experiments were carried out on a horizontal apparatus for zone melting. The molten zone was created by moving an annular heater

resistance. Zone melting was carried out with a zone-travel rate of 2 cm/h, a zone width of 20 mm, and a temperature of 350°. When the zone-travel rate was increased above the indicated value, a considerable deterioration in the efficiency of purification was observed.

Since, during the process of zone melting, strong transfer of material was observed in the direction opposite to the motion of the zone, the samples were placed at an angle of 2° to the horizontal.

After zone melting, the distribution of impurity along the length of the sample was investigated. Tin was determined colorimetrically with the aid of paranitrophenylfluorone (method sensitivity $5 \cdot 10^{-5}\%$); lead, by a spectral method after its separation from indium by coprecipitation with strontium sulfate (method sensitivity $1 \cdot 10^{-5}\%$) ([5]). The effective distribution coefficients were determined by approximate graphical methods described in ([6],[7]).

The dependence of the effective distribution coefficients on the concentration of tin and lead in the starting product was studied over the impurity-concentration range from 10^{-4} to 10^{-2} wt. %. Figure 1 shows the distribution of lead along the length of the ingot after one zone pass at different initial lead concentrations. The tin distribution curves are analogous. The character of the curves is preserved for all the initial impurity concentrations studied. Both in the case of tin and in the case of lead, in the very initial part of the ingot a higher impurity concentration is observed than could have been expected from theoretical considerations ([8]).

This is probably explained by the formation of a supercooled melt and by a delay in crystallization owing to the absence of a seed at the initial moment of

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

the process.

Figure 2 shows the dependence of the effective distribution coefficient of tin on the initial impurity concentration.

Fig. 2. Dependence of the effective distribution coefficient of tin on the initial impurity concentration

Fig. 3. Distribution of tin along the length of the ingot after 5 (1), 10 (2), and 15 (3) zone passes. Initial tin concentration $1.5 \cdot 10^{-4}\%$

Consequently, in the indicated concentration range the effective distribution coefficient increases with increasing initial impurity concentration; i.e., purification proceeds most effectively at low initial tin concentrations.

Unlike tin, the effective distribution coefficient of lead does not depend on the concentration of lead in the initial indium chloride (in the same concentration range from 10^{-4} to 10^{-2} wt.%) and is equal to 0.21. To determine the required number of passes, ensuring the practically attainable degree of purification, a series of experiments was carried out with different numbers of passes of the molten zone.

The distribution of tin along the length of the ingot was determined after 5, 10, and 15 zone passes (Fig. 3), and the distribution of lead after 5, 12, and 18 passes.

As follows from the results of these experiments, purification may be considered sufficient only after 15 zone passes. In this case, about 81% of the ingot by weight contains tin in amounts below the sensitivity of the analytical method.

Similarly, after 18 zone passes, about 85% of the ingot by weight contains lead in concentrations lying at the threshold of sensitivity of the analytical method.

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Note: Figure translations are in progress. See original paper for figures.