EVALUATION OF THE EFFECTIVENESS OF LIQUATION REFINING
OF ZINC MELTS FROM IRON IMPURITY

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ABSTRACT

The methodology of selection of additive elements for purification of zinc melts from iron impurity by liquation refining is proposed. Calculations of the effectiveness assessing the possibility of application of the formula of the periodic process of extracting to a single stage of extraction are performed. The extracting ability of the additives chosen is established. The experimental results show that the highest efficiency of unalloyed zinc purification from iron impurity is achieved by using silicon as an extraction additive. Aluminum and manganese are recommended to be used as extracting additives in zinc alloys refining from iron.

Keywords: zinc melts, liquation refining, effectiveness, additive elements, iron impurity.

INTRODUCTION

Zinc is widely used in various industries for production of casting and wrought alloys for structural and functional purposes including antifriction, sacrificial, high-damping and other materials [1 - 4].

Modern requirements to the purity of primary zinc used for alloys production are very high. The main impurities in zinc produced by electrolysis refer to iron, lead, cadmium, copper, tin and arsenic [5]. Concentrations of these impurities determine the grade of primary zinc in accord with ASTM B6-13 or other standards. The production of zinc of decreased iron content is an especially actual problem. Due to its low solid solubility in zinc (≈ 0.001 %) the iron impurity forms brittle intermetallic compounds (FeZn, FeZn₃, etc.), which significantly decrease the corrosion resistance and deteriorate the mechanical and casting properties of zinc and its alloys [5 - 7].

Many of the known physical and physicochemical methods of zinc melts refining from metallic impurities (Fe, Pb, Cu, etc.) are low productive and difficult from the point of view of constructive-technological realization [8-14]. The method of liquation refining draws the greatest interest towards production of zinc melts of a low content of iron and other metallic impurities as it is easily adapted to the conditions of the acting industrial enterprises. This method is based on the use as refining additives of various metals, which form high-melting phases at interaction with the impurities [15]. These phases segregate due density difference of the newly formed phases and the zinc melt. Subsequent separation of the phases can be carried out by standing, centrifugation or filtration of zinc melts.

The main objective of the present work is to evaluate the effectiveness of liquation refining of zinc melts from metallic impurities (iron for an example) by additives introduction.

THEORETICAL CONSIDERATIONS

Selection of refining additives for purification of zinc melts from iron impurity

The selection of additives in case of production of metal melts of low impurities content by the liquation refining method is based on the assessment of the nature
of interaction of the elements of the periodic system with the impurities present and the base metal. The possibility of application of various elements as extractive additives to zinc melts purification is determined by their solubility in zinc and the efficiency of their interaction with the impurities present. The analysis of the metal-chemical properties of the elements in the course of their interaction with the zinc melts and the iron impurity shows that various types of bonding are formed [5, 16]. The selection of the elements retained for further consideration as potential refining additives is carried out taking into account the nature of their interaction with zinc and iron, and also their cost and toxicity. The elements of the periodic system are screened on the ground of these requirements aiming to allocate the potential additives. The characteristics of their interaction with zinc and iron are presented in Table 1.

The analysis of the data in Table 1 shows a possibility to use C, Si, S (group A) as refining additives for purification of unalloyed zinc from iron impurity. These elements practically do not interact with zinc or have very small solubility in it, but form chemical compounds and solid solutions with iron. Elements Al, Mn, Ti (group B) may be used in zinc alloys production as they act as alloying elements and refining additives as well.

Table 2 presents the characteristics of the phases formed in system “zinc-iron-additive” for the chosen potential extraction additives in liquation refining of zinc melts [16, 23].

The analysis of the data in Table 2 shows that the additive elements of group A, having low solubility in zinc, and elements of group B, dissolving in zinc, form on high-melting chemical compounds with iron whose melting point is above 1000°C.

Theoretical evaluation of the effectiveness of zinc liquation refining from an iron impurity

The extraction theory fundamentals [24] are used to evaluate the effectiveness of zinc purification from metallic impurities. In relation to the technological processes of zinc melts purification from iron the formula of the periodic process is applied to a single stage extraction on the ground of the analogy with the metallurgical processes of extracting [25]:

\[
X = X_0 \frac{K \cdot m}{K \cdot m + L}
\]

where \(X_0\) is the initial concentration of the impurity in the metal (zinc) in mass % (in this case and hereinafter), \(X\) is the concentration of the impurity after the extraction operation (mass %), \(K\) is the equilibrium coefficient of distribution of the impurity between the phases of the segregating system, \(m\) is the mass of the solvent (zinc) in g, while \(L\) is the mass consumption of the extracting additive (g).

The impurity distribution between two phases at a temperature set in advance is determined by the value of the equilibrium coefficient of distribution, \(K\), which

<table>
<thead>
<tr>
<th>Element (X)</th>
<th>System Zn-Fe-X</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>CC</td>
<td>0.019</td>
</tr>
<tr>
<td>Mn</td>
<td>CC + PSS</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.017</td>
</tr>
<tr>
<td>Al</td>
<td>CC + PSS</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>C</td>
<td>CC + PSS</td>
<td>none</td>
</tr>
<tr>
<td>Si</td>
<td>CC + PSS</td>
<td>none</td>
</tr>
<tr>
<td>S</td>
<td>CC + PSS</td>
<td>partial miscibility in the melt</td>
</tr>
</tbody>
</table>

* PSS – a partial solid solution; CC – a chemical compound.
is approximately equal to the ratio of iron solubility in molten zinc and iron solubility in the solid solution or its content in the new phase formed with the additive participation:

\[ K = \frac{C_{Fe}}{C_{CC}} \tag{2} \]

where \( C_{Zn}^{Fe} \) is the solubility of iron in molten zinc at the process temperature (%), while \( C_{CC}^{Fe} \) is the iron content in the solid solution or the chemical compound formed with the additive (%).

The consumption of the additive element is calculated taking into account its solubility in solid zinc. It is necessary to consider two cases aiming this. In the first one the extracting additive is insoluble in the base metal. Its consumption is designated by \( L \). In the second case the additive has a known solubility determined by the system phase diagram. Its consumption is presented by \( L = L_1 - L_0 \), where \( L_1 \) is the amount of the additive element required to obtain the final concentration of the impurity, while \( L_0 \) is the amount of the additive element dissolved in the base metal (determined by the additive element solubility at the temperature of extraction).

As the equilibrium state between the liquid and solid phases is not attained under the real conditions of crystallization and phase separation presence, the experimental value of the impurity content after refining must be somewhat greater than the calculated one.

Calculations of the efficiency of extraction of iron impurity from zinc melt are executed for system Zn-Fe-X (where \( X = C, Si, S, Al, Mn, Ti \)). The following input data are accepted: iron initial concentration \( X_0 = 0.015 \% \), base metal mass \( m_{Zn} = 100 \) g, temperature of impurity extraction - 500°C. Iron solubility in the zinc melt is 0.02 % [5] at this temperature. Averaged values of the concentrations of iron in the formed solid solutions or compounds with the extracting additive are assumed on the ground of the phase diagrams of iron and the additives selected. The extracting additive consumption is accepted to 10 times higher than impurity element concentration, i.e. \( L_1 = 0.15 \% \) on the ground of the base metal mass.

For an example, consider the principle of calculating the final iron content in molten zinc in case of Zn-Fe-Ti system according to the formula of the periodic process of extracting (1). The equilibrium coefficient of iron distribution will be \( K = C_{Zn}^{Fe} / C_{CC}^{Fe} = 0.02 / 50 = 4.0 \cdot 10^{-4} \). The solubility of titanium in molten zinc is accepted equal to 0.04 % at 500°C. Thus it follows that the extracting additive consumption per 100 g of base metal will be \( L_{Ti} = 0.15 - 0.04 = 0.11 \) g, while the final concentration of the iron impurity will reach:

\[ X = X_0^{Fe} \frac{K \cdot m_{Fe}}{K \cdot m_{Zn} + L_{Ti}} = 0.015 \cdot \frac{4.0 \cdot 10^{-4} \cdot 100}{4.0 \cdot 10^{-4} \cdot 100 + 0.11} = 0.004\% \tag{3} \]
The calculations carried out in accord with the procedure described above show that the selected 10-fold increase of the consumption of titanium as an extracting additive leads to 3.75 times iron content decrease in the zinc melt.

Similar calculations are performed for other elements considered as potential extracting additives. Intermediate data and calculations results are listed in Table 3.

The efficiency of zinc purification, \( \eta \) (%), from iron impurity is evaluated in correspondence with:

\[
\eta = \frac{F_{e_0} - F_{e_1}}{F_{e_0}} \times 100 \%
\]

where \( F_{e_0} \) and \( F_{e_1} \) are the initial and final concentrations of iron impurity in the zinc melt, correspondingly.

Table 3 shows that in case of initial iron content in zinc of 0.015 % and 10-fold increase of the consumption of the extracting additive the additive elements line in respect to their extracting ability decrease is as follows: Si → S → C → Ti → Al (Mn).

The efficiency estimation of zinc purification from iron at the accepted 10-fold increase of the extracting additive consumption shows that \( \eta = 81.2 - 83.3 \) % if elements of group A are used. Only titanium among the elements of group B provides refining with \( \eta = 78.3 \) %.

Fig. 1 illustrates the results obtained in calculating the iron content change in a zinc melt in case of a various consumption of the additive elements referred to the iron content in zinc. It is seen that while C, Si, S, Ti provide iron content decrease from 0.015 % to 0.002 - 0.004 % at their 10-fold excess, 30-fold excess of manganese and 50-fold excess of aluminum are required to obtain the same purification effect. Obviously, the use of manganese and aluminum will be possible in production of zinc alloys of low iron content only in case they are present as basic alloying elements.

The efficiency assessment of zinc purification at different initial content of iron impurity and 10-fold excess of the extracting additive (Fig. 2) shows that it grows up to 85 % - 90 % with iron content increase in initial zinc (0.003 % - 0.030 %) excluding aluminum and manganese. Purification in the presence of the latter in fact does not proceed under the conditions pointed above. It is also seen, that the liquidation refining method is not suitable for technologies of deep purification of unalloyed zinc with initial iron content up to 0.003 %.

### EXPERIMENTAL VERIFICATION

**Materials and methods**

Melting of high grade (99.95 % Zn) zinc was performed in an alundum crucible in an electric resistance furnace. The iron content of the zinc melt prior the refining was 0.014 % - 0.016 %. Carbonyl iron was added to zinc at 500 °C, Al and S were introduced to the melt as refining additives at 490 °C, while Ti, Si, Mn and C - at 600°C. The purity of all materials used was higher than

<table>
<thead>
<tr>
<th>Additive element</th>
<th>Averaged iron content in the solid phase formed by the additive ( C_{CC}^{Fe} ) / %</th>
<th>( K \cdot 10^4 )</th>
<th>Solubility of the additive element ( L_0 ) / %</th>
<th>Additive element consumption ( L ) / %</th>
<th>Final impurity concentration ( F_{e_1} ) / %</th>
<th>Purification efficiency ( \eta ) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>57</td>
<td>3.5</td>
<td>0</td>
<td>0.15</td>
<td>0.0028</td>
<td>81.2</td>
</tr>
<tr>
<td>Si</td>
<td>66</td>
<td>3.0</td>
<td>0</td>
<td>0.15</td>
<td>0.0025</td>
<td>83.3</td>
</tr>
<tr>
<td>S</td>
<td>63</td>
<td>3.2</td>
<td>0</td>
<td>0.15</td>
<td>0.0026</td>
<td>82.6</td>
</tr>
<tr>
<td>Al</td>
<td>36</td>
<td>5.6</td>
<td>0.5</td>
<td>0</td>
<td>0.015</td>
<td>0</td>
</tr>
<tr>
<td>Mn</td>
<td>100</td>
<td>2.0</td>
<td>0.3</td>
<td>0</td>
<td>0.015</td>
<td>0</td>
</tr>
<tr>
<td>Ti</td>
<td>50</td>
<td>4.0</td>
<td>0.04</td>
<td>0.11</td>
<td>0.004</td>
<td>78.3</td>
</tr>
</tbody>
</table>
Fig. 1. Theoretical changes of iron content in zinc melt depending on consumption of extracting additive.

Fig. 2. Theoretical efficiency of purification of zinc with different iron content at 10-fold excess of extracting additive.
99.5%. The melt was stirred with a graphite rod within 8-10 min during the additives introduction. Then it was cooled at a speed of 40°C/h-60°C/h down to the temperature of crystallization (~ 420°C). Then the mixture was quickly heated to 480°C and a sample for chemical analysis was taken from the crucible bulk using a quartz tube. The chemical composition of the samples was determined by X-ray fluorescence spectrometer ARL Advant’X (Thermo Scientific, USA). Refining additives were introduced to the melt in various ratios in respect to the iron impurity ranging from 0.1 to 1.3 %.

**Experimental results on purification of zinc melt from iron using additive elements**

The results of the experimental investigation of zinc purification from iron impurity using additive elements (Fig. 3) shows the different refining capacity of the additives used. The discrepancy between the calculated and experimental data referring to the efficiency of purification of zinc from iron impurity can be explained with some of the assumptions made (complete interaction of the extracting additives with iron impurity used, selected phases of only one stoichiometric composition taken into consideration in equilibrium phase diagrams preparation, complete removal of the reaction products from the melt, etc.), as well as with possible losses of the extractive additives and their incomplete recovery at entering the melt. Fig. 3 shows that only silicon should be considered as an effective extracting additive in relation to iron in case of unalloyed zinc production. As expected, aluminum and magnesium are partially dissolved when introduced to the zinc melt and stay there after purification. In case of large consumption of additives their content in zinc reaches high values as expected from the nature of their interaction with zinc in correspondence with the phase diagrams considered. Obviously, the process of purification of unalloyed zinc from iron using the additives studied will be difficult under conditions of large-scale production due to their high consumption. At the same time, the use of aluminum and magnesium as alloying and extracting additive elements in production of zinc alloys provides neutralizing the negative effect of iron because of the formation of complex products of interaction. In this case the refining is simultaneously combined with alloying of the base metal with aluminum or manganese.

Thus, it is recommended to use silicon as an extracting additive in the production of unalloyed zinc of a low iron content, while aluminum and manganese - in case of zinc alloys production.

![Fig. 3. Experimental data on efficiency of purification of zinc from iron by extracting additives.](image-url)
CONCLUSIONS

The principle of selection of additive elements for purification of zinc melts from iron impurity by liquation refining is theoretically motivated. The possibility of application of the formula of the periodic process of extracting to the single stage extraction is verified. The effectiveness of liquation refining and the extracting ability of the additives chosen are determined. It is recommended to use silicon as an extracting additive for refining unalloyed zinc from iron, while aluminum and manganese – in case of zinc alloys.

REFERENCES