

ANALYSIS OF POSSIBILITIES FOR REMOVAL OF TIN FROM LIQUID IRON THROUGH EVAPORATION

J. Łabaj

Department of Metallurgy, Faculty Materials Engineering and Metallurgy, Silesian University of Technology Gliwice, ul. Krasińskiego 8, 40-019 Katowice, Poland

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Corresponding author: Jerzy Łabaj, Tel.: +486034371, Fax: +486034189, E-mail: jerzy.labaj@polsl.pl, Silesian University of Technology, ul. Krasińskiego 8, 40-019 Katowice, Poland

Abstract

The description of the metal evaporation process in the condition of an atmospheric pressure has got a special significance in the alloys smelting technologies as well as in the metallurgical waste materials treatment. The quantity of metals evaporated in the process depends on many factors from which the most important are: a kind of applied apparatus, conditions of the process, a metal bath composition and a kind of applied atmosphere. In order to state which factors have got the biggest influence on the evaporation rate it is necessary to carry out the experiments. The obtained results can be the base of a piece of information about the nature of phenomena occurring in an open system including condensate and gaseous phase. This work presents an analysis of the Fe-Sn system aimed to determine the impact of temperature (1873-2043K) and tin concentration (0.2-1.5 weight %) in liquid iron on a possibility of separation through vacuum refining. The Olette fugacity coefficient was determined for specifying the possibility of evaporating the constituent from liquid metal in the analyzed system. The calculation results were verified experimentally by vacuum induction melting of Fe-Sn alloy.

Keywords: iron, tin, iron alloys, evaporation

1 Introduction

The noticeable decrease in the input of home scrap has necessitated in using increased amounts of post-consumption scrap, which may constitute one of the possible sources of the steel impurities, in the metallurgical processes. The foregoing mainly results from the fact that the scrap contain steel components combined with other materials the occurrence of which in the metallic charge is considered detrimental. Such a group of contaminants includes non-ferrous metals (copper, tin, lead, zinc, bismuth, etc.) originating from metallic coatings, varnish or components of electro-technical devices. When one deals with contaminants easily removed in the metallurgical process, the increase of their content in the charge material does not pose a serious problem. It is otherwise when the charge material contains increased contents of non-ferrous metals the removal of which in the steel smelting process is particularly difficult. As examples of such contaminants, one can mention copper and tin. Unfortunately, in the cases of both these metals, a considerable increase of their content in steel scrap has been observed within the recent years. The high content of tin in scrap is to a considerable extent reflected by this metal's content in, for instance, steels manufactured by application of the EAF technology. Due the fact that, tin similarly to copper, forms low-melting eutectic compounds with iron, that

are released during the solidification at the grain boundary, it is possible that, on high content of the problematic metal, the hot steel becomes brittle. Furthermore, tin exerts a negative influence on impact resistance and fatigue strength of steel. Indeed, it was the negative influence of tin on the properties of steel that has led to the necessity of undertaking investigations concerning the possible options of removing it from liquid steel alloys [1,2].

The phenomenon of evaporation of volatile constituents of metal bath plays an important role in many technological processes of extractive metallurgy including vacuum steel treatment operations, melting of steel and special alloys in vacuum induction furnaces, non-ferrous metal rectification processes or scrap metal processing [3-13].

On one hand the vacuum technologies help obtain high purity metals widely used in many industries, but on the other hand they help remove impurities that cannot be removed using other methods.

2 Calculation procedure

2.1 Equilibrium gas phase composition above the liquid Fe-Sn solution

In order to calculate partial pressures of vapours of gas phase constituents, the following chemical reactions were taken into account:



The basic compounds that were used for calculations were dependences describing changes in enthalpy of free evaporation processes [14]. Dependences (3,4) were used for calculations of equilibrium pressure of gas phase monomers, however the equilibrium pressures over p_i^o pure bath were calculated using data concerning the standard enthalpy of free evaporation of individual constituents.

$$p_i = p_i^o \cdot a_i = p_i^o \cdot \gamma_i \cdot X_i = \left[\exp\left(-\frac{\Delta_p G_i^o(T)}{RT}\right) \right] \cdot \gamma_i \cdot X_i \quad (3)$$

and

$$K_j = \exp\left(-\frac{\Delta_p G_j^o(T)}{RT}\right) \quad (4)$$

where: p_i and p_i^o - [Pa] pressures of i-of the constituent over the solution and over the pure bath, respectively

γ_i - activity of "i" constituent in the alloy coefficient,

X_i - mole fraction of "i" constituent in the alloy,

R - [J·mol⁻¹·K⁻¹] gas constant, ,

T - [K] absolute temperature,

K_j - equilibrium constant of j-of this reaction proceeding with the participation of gas phase constituents,

$\Delta_p G_j^o(T)$ - [J·mol⁻¹] standard free enthalpy of evaporation processes and chemical reactions proceeding with the participation of gaseous phase,.

Table 1 presents values of free enthalpy for the Fe-Sn system were obtained from the thermodynamic data base of HSC Chemistry 6 [15].

Table 1 Free enthalpy [kJ/mol] of reactions proceeding in the Fe-Sn system within the range of temperatures 1873-2048 K [15]

Reactions proceeding in the Fe-Sn system	Free enthalpy [kJ/mol]							
	Temperature [K]							
	1873	1898	1923	1948	1973	1998	2023	2048
$\text{Sn}_{(l)}=\text{Sn}_{(e)}$	103.256	100.674	98.092	95.510	92.928	90.346	87.764	85.182
$\text{Fe}_{(l)}=\text{Fe}_{(e)}$	190.254	183.915	177.610	171.338	165.097	158.886	152.706	146.554

The value of iron activity equal to one was adopted for calculations. For calculating the coefficient of tin activity in the liquid alloy the following dependency was used [16]:

$$\ln \gamma_{\text{Sn}} = \ln(\gamma_{\text{Sn}}^{\infty}) + \varepsilon_{\text{Sn}}^{\text{Sn}} \cdot X_{\text{Sn}} \quad (5)$$

where:

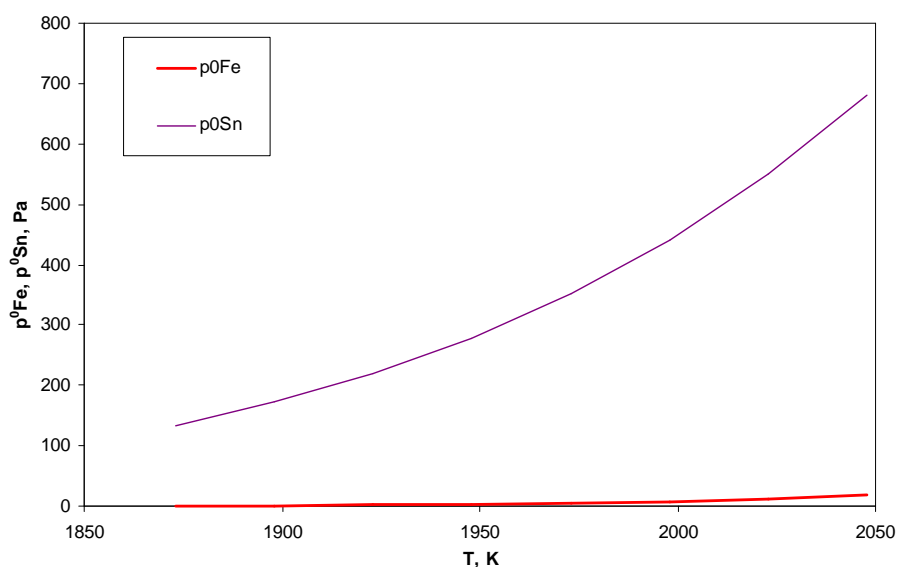
$$\ln(\gamma_{\text{Sn}}^{\infty}) = 2597.325 / T - 0.438811 \quad (6)$$

It was also adopted that:

$$\varepsilon_{\text{Sn}}^{\text{Sn}} = -0.29 \quad (7)$$

where: $\varepsilon_{\text{Sn}}^{\text{Sn}}$ - interaction parameter.

Fig. 1 presents equilibrium vapour pressures for pure constituents of iron and tin. **Fig. 2** presents changes in tin vapour pressures depending on the temperature and its content in liquid iron as obtained from the calculations. The analysis of equilibrium composition of the gas phase over Fe-Sn liquid solutions has shown that the value of equilibrium pressure for tin does not exceed the value of iron vapour pressures within the entire range of concentrations and temperatures applied.

**Fig.1** Change in equilibrium pressure of iron and tin for pure constituents

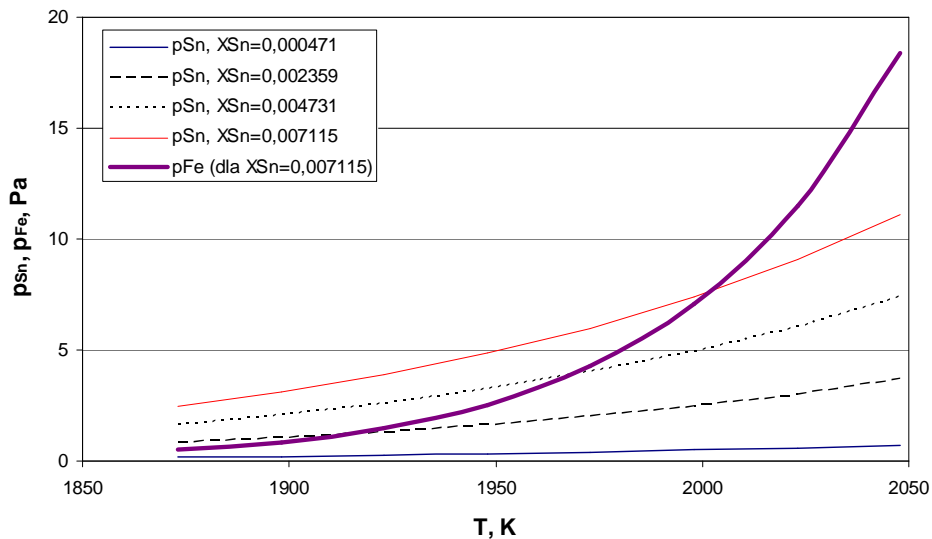


Fig.2 Change in equilibrium pressure of tin depending on its content in liquid iron

2.2 Fugacity coefficient

According to Olette [17] the quantity that describes the possibility of evaporating a constituent from a liquid metal alloy under reduced pressure is the so-called fugacity coefficient, or evaporation coefficient. For a binary alloy, in the case when we deal with metal vapours in an atomic form, the fugacity coefficient is determined by the following dependency:

$$\Phi_i = \left(\gamma_i \cdot \frac{p_i^0}{p_A^0} \right) \cdot \left(\frac{M_A}{M_i} \right)^{0.5} \quad (8)$$

where: Φ_i – fugacity coefficient,
 M_A – molar mass of the main constituent of the alloy,
 M_i – molar mass of the evaporating constituent.

According to Olette the evaporation of a constituent in a metal form is possible when the following condition is fulfilled:

$$\Phi_{i(ij)} > 1 \quad (9)$$

The change in the fugacity coefficient of tin vapours within the range of temperatures 1873÷2048 K is presented in **Fig. 3**.

The data presented in **Figure 3** show that Olette's condition is met for liquid Fe-Sn alloys within the analyzed range of temperatures, which indicates that it is possible to remove tin through evaporation in the melting process under reduced pressure.

3 Experimental verification

The tests were synthetic Fe-Sn alloys made from ARMCO iron and tin by melting in an induction furnace under an inert atmosphere. All the experiments were carried out in an

induction vacuum furnace VIM 20-50 made by SECO-WARWICK This unit is equipped with the latest technology used in industrial vacuum. These include heel inductor electric drive, control panel for controlling and monitoring the process parameters, mold resistance heater introduction of alloying system and mechanism of sampling.

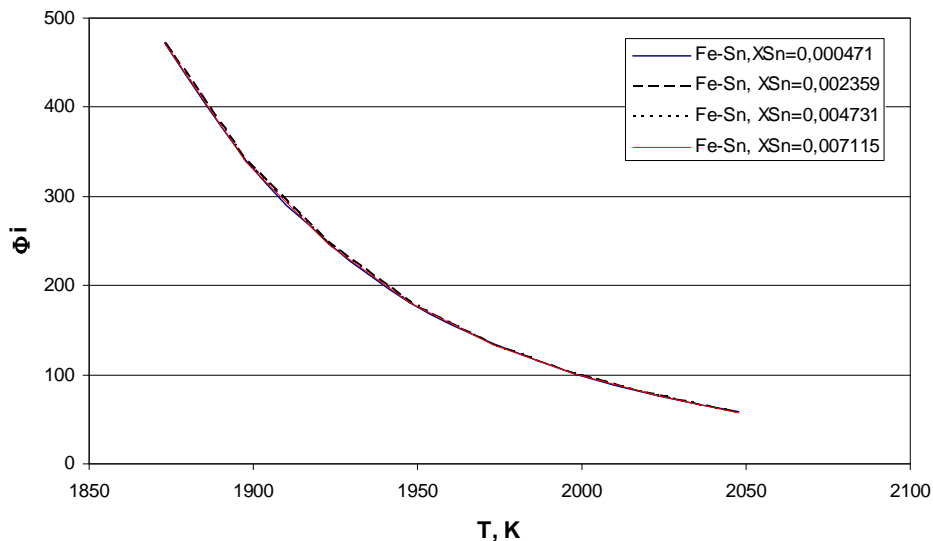


Fig.3 Change of the fugacity coefficient for tin vapours depending on its content in liquid iron and on temperature

3.1 Methodology

A sample experiment of a certain weight of the alloy was placed in a magnesia crucible, which is mounted inside the coil of the furnace. Next the furnace was closed, a system of pumps was switched on to attain the pressure assumed for the aggregate. The pressure was set through a cooperation between a mechanical pump, a Roots pump and, when necessary, a diffusion pump. The next stage of the experiment was to heat the charge to a certain temperature. After reaching the desired temperature by metal melting was carried out by the time 30 minutes. Temperature measurement process takes place by means of pyrometer and PtRh-Pt thermocouple. The liquid metal after the melting of the graphite mold cast. The tin content in the investigated alloys were determined by atomic absorption spectrometry using a Perkin Elmer apparatus. All experiments were carried out at a temperature of 1898-1948 K in the pressure range from 0.05 Pa to 24 Pa.

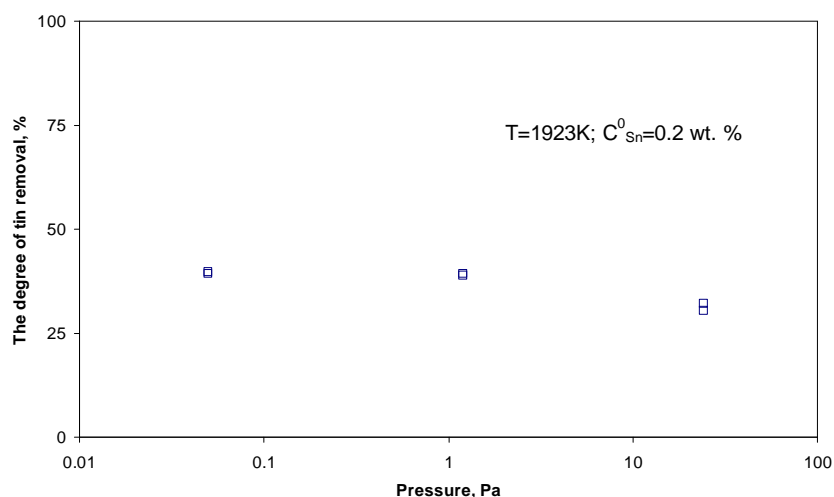
3.2 Results of the experimental verification

In literature, a description of the removal of tin from liquid iron alloys by vacuum refining is presented by Savova and colleagues [3] and Zaitsev [4]. The present study include a higher content of tin in iron.

The results remove the tin from Fe-Sn alloy by the evaporation under reduced pressure shown in **Table 2**. It includes the value of the initial and final concentration of tin in the alloy and the degree of tin removal in the process. In **Figs. 4** shows the results of experimental studies on the effect of the pressure dependence of the degree of tin removal from analyzed alloys.

Table 2 The results of changes in concentration of tin in liquid iron in the process of vacuum melting

Number of experiments	Sample weight, g	Process temperature, K	Working pressure, Pa	The initial content of tin in the alloy, wt. %	The final content of tin in the alloy, wt. %	The degree of tin removal, %
1	12000	1898	2.00	0.2	0.1249	37.55
2	12000	1898	2.00	0.2	0.1238	38.10
3	12000	1923	0.05	0.2	0.1205	39.75
4	12000	1923	0.05	0.2	0.1214	39.30
5	12000	1923	1.20	0.2	0.1217	39.15
6	12000	1923	1.20	0.2	0.1225	38.75
7	12000	1923	24.30	0.2	0.1394	30.30
8	12000	1923	24.30	0.2	0.1359	32.05
9	12000	1948	2.00	0.2	0.1199	40.05
10	12000	1948	2.00	0.2	0.1196	40.20

**Fig.4** Change of tin weight loss for the experiments conducted on various pressure levels

4 Conclusions

On the basis of the analysis of the equilibrium composition of a gas phase over liquid Fe-Sn solutions one may conclude that:

1. The determined values of Olette fugacity coefficient indicate a possibility of removing tin through evaporation.
2. An increase of the tin content in a liquid alloy results in an increase of tin vapour pressures, however such increase is lower within the entire range of the analysis compared to iron vapours. It means that the removal of tin from liquid iron can be done only to a small extent through evaporation of tin monomer.
3. The results of tin removal of 30 - 40%, depending on the process temperature and pressure, confirm the possibility of removing this element in the vacuum refining process

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