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STUDY OF COPPER REMOVAL FROM LIQUID IRON

The technology of steel is projected to increase in the share-based processes for processing recyclable materials. On the one hand it creates the possibility of lowering the cost of producing steel, while the other is causing the pollution, which because of its physicochemical properties are difficult to remove. The group of this type of pollution is classified as copper. The lower reactivity to iron requiring the analysis of thermodynamic parameters of Fe-Cu system to identify how best to allocate them. The study was conducted for the basic kinetic analysis of Fe-Cu alloy containing 0,5 % wt. Cu and 1,5 % wt. Cu in the pressure range from 0,06 to 1 074 Pa and a temperature of 1 923 K The study was conducted in a vacuum induction furnace VIM-20-50 Seco Warwic.

Key words: copper, iron alloys, vacuum refining, induction furnace

Studija odstranjivanja bakra iz tekućeg željeza. Tehnologija čelika planira se tako da se poveća udio temeljenih na preradi reciklirajućih materijala. S jedne strane to stvara mogućnost smanjenja cijene proizvodnje čelika, dok s druge strane uzrokuje onečišćenje, uslijed fizikalnokemijskih svojstava, koje je teško ukloniti. U skupinu takve vrste onečišćenja ulazi i bakar. Niža reaktivnost sa željezom zahtijeva analizu termodinamičkih parametara sustava Fe-Cu da se odredi kako ih je najbolje predvidjeti. Studija je provedena za bazičnu kinetičku analizu slitine Fe-Cu koja sadrži 0,5 % Cu i 1,5 % Cu u intervalu tlakova od 0,06 do 1 074 Pa i temperaturi od 1 923 K. Studija je provedena u vakuumskoj indukcionoj peći VIM-20-50 Seco Warwic.

Ključne riječi: bakar, slitine željeza, vakuumska rafinacija, indukciona peć

INTRODUCTION

The global metallurgical industry is currently dominated by two technologies. One of them is based on the concept of obtaining pig iron in a blast furnace and its subsequent transformation into steel in oxygen-blown converters, whereas the second one consists in steel smelting based on secondary raw materials in electric arc furnaces (EAF). Within the recent years, the latter's share in the global production of steel varied from ca. 28 to 33 %, The forecasts imply that the proportions between the share of the EAF process and the conventional one (oxygen-blown converter) in the steel production will have been reversed by 2 050 a compared with the current status [1]. Thus the share of scrap used in the overall steel production is expected to increase from the present level of 45 % to 60 % at the expense of iron ores.

The steel scrap utilised under the technologies discussed is characterised by highly variable chemical composition. This results mainly from the fact that there are considerable changes taking place in the generic structure of the scrap processed in metallurgical aggregates. The share of the so-called home scrap in the charge material decreases with a simultaneous increase of the share of demolition (post-consumption) scrap. The noticeable decrease in the input of home scrap has

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necessitated in using increased amounts of demolition 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 said scrap ma 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 electrotechnical 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. An example of such a contaminant may be copper.

The high content of copper 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 to the fact that copper, similarly to tin, 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, copper exerts a negative influence on impact resistance and fatigue strength of steel. Indeed, it was the negative influence of copper on the properties of steel that has led

to the necessity of undertaking studies concerning the possible options of removing it from liquid steel alloys.

This paper constitutes a discussion on the analysis of the options of copper removal from iron by evaporation under the conditions of reduced pressure.

EXPERIMENTAL PART

The studies consisted in examining synthetic Fe-Cu alloys based on the ARMCO iron and grade M00B oxygen-free copper through melting in an induction furnace in the inert gas atmosphere.

All the experiments were performed using the VIM 20-50 one-chamber vacuum induction furnace manufactured by SECO-WARWICK. The equipment diagram has been provided in Figure 1.

At the beginning of the experiment, a sample of alloy of specific weight was placed in a magnesite or zirconium melting pot mounted inside the furnace coil. After the furnace was closed, a system of pumps was switched on to attain the pressure assumed for the aggregate.

At the beginning of the experiment, a sample of alloy of specific weight was placed in a magnesite or zirconium melting pot mounted inside the furnace coil. After the furnace was closed, a system of pumps was switched on to attain the pressure assumed for the aggregate. The pressure was obtained through a cooperation between a mechanical pump, a Roots pump and, when necessary, a diffusion pump. Another stage of the experiment was heating of the charge material up to the specific temperature.

After the metal had reached the temperature assumed, melting was conducted for 30 minutes. Samples of the metal were collected at specific and precise time intervals. The process temperature measurement was performed using a pyrometer and type PtRh-Pt thermocouples for the sake of the process control. After the test was completed, the liquid metal was poured into a graphite ingot mould. After the metal had solidified and the furnace cooled down, the chamber was opened. The copper content in the alloys tested was determined by atomic absorption spectrometry using an apparatus manufactured by Perkin Elmer.

The basic furnace parameters have been summarised in Table 1.

Table 1 **Basic experimental parameters**

Temp. / K	Cu content in alloy / % wt.	Working pressure / Pa	Sample weight / g
1 923	0,509; 1,518	from 0,06 to 1,074	12 000

TEST RESULTS

The change of the copper concentration in the liquid iron during the melting process was correlated by the following logarithmic function:
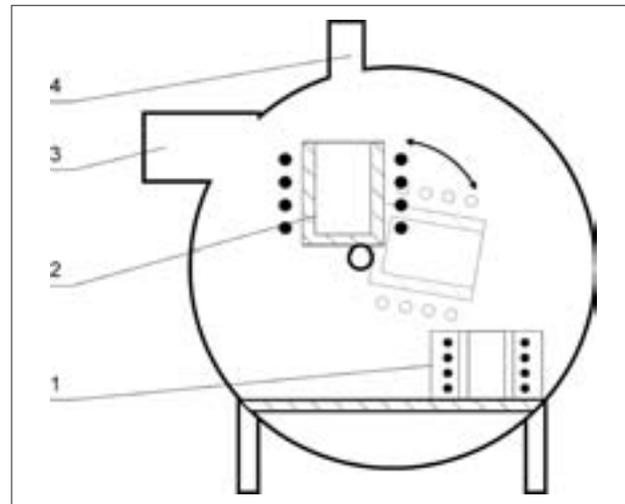

Figure 1 Diagram of the installation used in the Fe-Cu alloys vacuum refining test.
1 – ingot mould with a preheating unit,
2 – induction coil with a ceramic melting pot,
3 – outlet to the system of vacuum pumps,
4 – mounting of the temperature measuring system and the sampling mechanism.

$$-\log \frac{C_{Cu}^{t}}{C_{Cu}^{0}} = A \cdot t \qquad (1)$$

where:
C_{Cu}^{t} – copper concentration in the alloy after time
t / % wt.,
C_{Cu}^{0} – initial copper concentration / % wt.,
t – time / s,
A – equation constant.

In order to determine the value of the total mass transfer coefficient based on the experimental data obtained and entailing the process velocity, the following dependency was applied [2-7]:

$$2,303 \log \frac{C_{Cu}^{t}}{C_{Cu}^{0}} = -k \cdot \frac{F}{V}(t - t_{o}) \qquad (2)$$

where:
F – vaporisation areas (interfacial areas),
V – volume of liquid metal,
$(t-t_o)$ – process duration time.

For the sake of the calculations, the value of coefficient A from equation (1) was applied as describing the change of the copper concentration in the function of time.

The values calculated for the total experimental mass transfer coefficient based on equation (2) for the copper vaporisation from liquid metal have been summarised in Table 2.

ANALYSIS OF THE RESULTS

The research consisted in a kinetic analysis of the copper evaporation from iron entailing the impact of pressure on the said process. Under all the experiments conducted, the copper mass decrement was noticed on

Table 2 **Experimental mass transfer coefficients for the process of copper vacuum evaporation from Fe-Cu alloys**

Item	Cu content in alloy / % wt.	Temp. / K	Pressure / Pa	$k_{exp.} \cdot 10^{-5}$ / m·s^{-1}
1	1,518	1 923	1,074	0,42
2	1,518	1 923	1,074	0,41
3	1,518	1 923	212	0,69
4	1,518	1 923	212	0,65
5	1,518	1 923	101	1,00
6	1,518	1 923	101	0,97
7	1,518	1 923	56	1,46
8	1,518	1 923	56	1,53
9	1,518	1 923	49	1,79
10	1,518	1 923	49	1,68
11	1,518	1 923	40	2,19
12	1,518	1 923	40	2,31
13	1,518	1 923	5	4,12
14	1,518	1 923	5	4,19
15	1,518	1 923	0,5	4,90
16	1,518	1 923	0,5	4,70
17	1,518	1 923	0,06	4,43
18	1,518	1 923	0,06	4,81
19	0,509	1 923	1,013	0,17
20	0,509	1 923	1,013	0,36
21	0,509	1 923	526	0,61
22	0,509	1 923	526	0,59
23	0,509	1 923	425	0,58
24	0,509	1 923	425	0,57
25	0,509	1 923	202	0,79
26	0,509	1 923	202	0,74
27	0,509	1 923	101	0,89
28	0,509	1 923	101	0,86
29	0,509	1 923	101	0,83
30	0,509	1 923	101	0,84
31	0,509	1 923	5	2,85
32	0,509	1 923	5	3,08
33	0,509	1 923	1,2	3,77
34	0,509	1 923	1,2	3,75
35	0,509	1 923	0,13	4,51
36	0,509	1 923	0,13	4,38
37	0,509	1 923	0,06	4,78
38	0,509	1 923	0,06	4,95
39	0,509	1 923	0,06	4,58
40	0,509	1 923	0,06	4,74
41	0,509	1 923	0,06	4,58
42	0,509	1 923	0,06	4,65
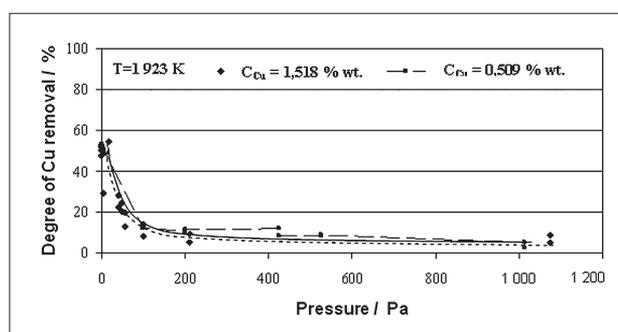
Figure 2 Change of copper mass decrement for the experiments conducted on various pressure levels

the level of 5 to 56 %. The foregoing data have been illustrated in Figure 2.

Based on the examinations conducted, values of the total experimental mass transfer coefficient (k_{Cu}) have been determined. They amounted from $0,17 \cdot 10^{-5}$ to $4,8 \cdot 10^{-5}$ (Table 2). The results obtained conform well with the values provided in various publications (Table 3) as reported by other authors.

The largest impact of pressure on the process being examined was observed in the pressure range from 10 to 100 Pa. An identical impact was also noticed in other processes including evaporation of manganese from liquid iron [4], lead from copper [5] and zinc from the Zn-Ag-Pb alloy [8]. Therefore, one could assume that for the said range of pressure values, the process in question is determined by the mass transfer in the liquid and gaseous phase.

The studies conducted have implied a considerable impact of pressure on the process rate. For the pressure below 10 Pa, there was practically no pressure impact on the process rate observed (Figure 3). This means that for such pressure values, the process analysed is not determined by the mass transfer in the gaseous phase [9-11].

CONCLUSIONS

The analysis of the results obtained in the experiments of vacuum refining of Fe-Cu alloys in an induction furnace conducted under the study discussed have led to the following conclusions:

Table 3 **Experimental mass transfer coefficients determined for the process of copper evaporation from iron alloys**

Item	Temp. range / K	Pressure range / Pa	Experimental mass transfer coefficient / ms^{-1}·10^{-5}	Refer. item
1	1 873	no data	2 – 2,3	[9]
2	1 683 - 1 873	1-100	1,95-6,38	[10]
3	1 923 - 1 973	133-101,325	0,1-4	[11]
4	1 898 -1 998	0,06 -1,074	0,17-4,8	author's studies
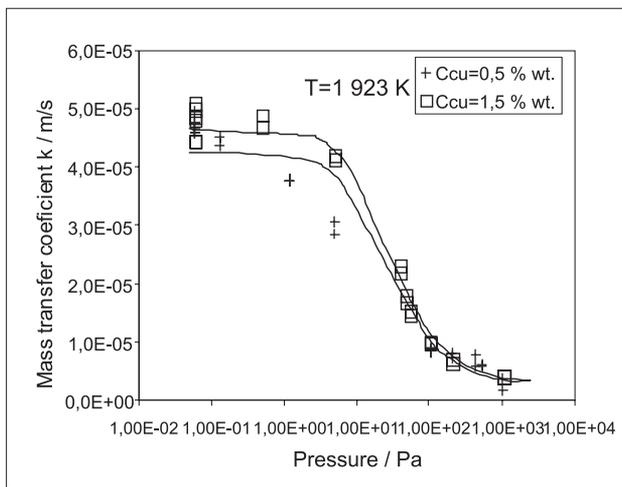
Figure 3 Pressure impact on the mass transfer coeffi-
cient for the process of copper evaporation
from liquid iron

1. Within the whole range tested, in terms of pres-
   sure, temperature and chemical composition, the
   change in the copper concentration in iron during
   melting in a vacuum induction furnace can be de-
   scribed by means of an equation of the 1st order
   chemical reaction;

2. Within the range of pressure values from 10 to
   100 Pa, a strong dependence between the mass
   transfer coefficient and pressure is observed in
   the system which may indicate that, within the
   said range of pressures, a change in the process
   control takes place and the mass transfer
   resistances in the gaseous phase overlap with the
   resistances occurring in the liquid phase; On the
   pressure values below 10 Pa, the kinetic parame-
   ters are stabilised, therefore one deals with a pro-
   cess determined by the mass transfer in the liquid
   phase as well as with the phenomena taking place
   in the interfacial area. However, within the range
   of pressure values above 100 Pa, one can assume
   that the process takes place in the diffusion re-
   gion and it is controlled by the mass transfer
   resistances in the gaseous phase;

3. The results obtained enable determination of an
   optimum set of technological parameters of the
   vacuum refining process for iron containing cop-
   per. The process in question should be conducted
   under the pressure of ca. 10 Pa, since further pres-
   sure reduction in the system does not influence
   the process rate and may cause a considerable in-
   crease of its costs.

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Note: Nowak P. is responsible for English language, Katowice, Poland.