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Influence of copper content in steel on the rate of copper removal by evaporation

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ABSTRACT

Purpose: The paper provides an analysis of the results of studies upon the rate of copper evaporation from liquid Fe-Cu alloys. Based on the results obtained for the change in the copper concentration in liquid bath, the value of the overall copper mass transfer coefficient was estimated. Due to the fact that the alloy composition may affect all the constituent stages of the evaporation process, the analysis undertaken concerned both the mass penetration process occurring in the liquid phase and the evaporation reaction taking place on the interface.

Design/methodology/approach: The studies of the copper evaporation from liquid steel were conducted using an induction furnace. Based on the results obtained for the change in the copper concentration in liquid bath, the value of the overall copper mass transfer coefficient was estimated. The studies were conducted under the pressures of 0.06 Pa and 101 Pa at the temperature of 1998 K. The copper content in the alloys examined varied from 0.198 to 1.518% by weight.

Findings: The overall mass transfer coefficients established based on the study results assumed values within the range from $4.2 \ 10^{-5}$ to $4.8 \ 10^{-5} \ ms^{-1}$ for the tests conducted under the pressure of 0.06 Pa and from $8.3 \ 10^{-6}$ to $1.0 \ 10^{-5} \ ms^{-1}$. for those conducted under the pressure of 101 Pa.

Practical implications: The main point of the EAF process is a transfer of the scrap components to the steel being melted. Some metals introduced into the bath together with the scrap may exert a negative impact on its properties. An example of such a contaminant may be copper. This metal is characterised by limited solubility in iron and it is released on grain boundaries at temperatures of hot processing.

Originality/value: The studies conducted proved that, for the pressure of 0.06 Pa, the overall mass transfer coefficient value on the copper content in the alloy increased from 0.198 to 1.518 % by weight grows by ca. 15 %. This growth is caused by numerous factors including the increase in the value of the copper activity coefficient in liquid iron.

Keywords: Scrap; Copper; Steel; Evaporation; Vacuum refining; Mass transfer

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PROPERTIES

1. Introduction

Within the last decade, production of crude steel increased all around the world from 850 million Mg in 2000 to 1.41 billion Mg in 2010. For the sake of comparison, in the same period, our domestic entities manufactured 10.5 and 8 million Mg correspondingly which means that within the timeframe analysed, the Polish metallurgy reduced its output by more than 20% whereas the global output was increased by 70 %. Having investigated the leading crude steel production technologies, one may claim that for many years now, the predominant processes are BOF and EAF, however, the second technology's share varied in the period in question between 28 and 33 %. The only change implied by a forecast for the year 2050 (Fig. 1) is that the global output share of processes conducted in electric arc furnaces is assumed to rise compared to the technologies based on basic oxygen converters. The foregoing has been illustrated with the data provided in Fig. 2. A similar trend can be observed for domestic steelworks which has been illustrated with the data in Table 1.



Fig. 1. Forecasted share of the individual technologies in crude steel production in the year 2050 [1-3]

Table 1.

|--|

| Domestic crude steel | Years | | | | | |
|---|-------|------|------|------|------|------|
| production, million Mg | 2005 | 2006 | 2007 | 2008 | 2009 | 2010 |
| Total | 8.4 | 10.0 | 10.6 | 9.7 | 7.1 | 8.0 |
| EAF process | 3.0 | 4.2 | 4.4 | 4.5 | 3.9 | 4.0 |
| EAF production share in total crude steel output in Poland, % | 35.7 | 42.0 | 41.5 | 46.4 | 54.9 | 50.0 |

The main iron bearing raw material used in the steel production based on the EAF process is steel scrap. Other charge components include fluxing agents, carburising agents, deoxidising agents, slag frothing agents as well as alloy additives. Purity of the steel obtained in the process in question mainly depends on the quality of the scrap used as well as its chemical composition. Nowadays, for the sake of crude steel production processes conducted in the country, more than 5 million Mg of scrap is used, with more than 4 million Mg for the EAF process.

The electric steel melting process is based on processing of steel scrap which may be divided into three main groups, namely home process scrap, post-production scrap and demolition scrap. From the technological point of view, the most advantageous solution is to use as much home process scrap as possible in the steelmaking as it ensures that high-purity steel is obtained. Unfortunately, for several years now, both in the country and abroad, one may observe a considerable drop in the quantity of this kind of scrap in the market. It is also the reason for a significant decrease in the share of home scrap in the total amount of scrap being processed by steelworks. This trend has been depicted with regard to domestic steelworks in Fig. 2.



Fig. 2. Share of home scrap in the total amount of scrap processed by domestic steelworks

The main point of the EAF process is a transfer of the scrap components to the steel being melted. Hence the hazard of contaminating the product is considerably high. Some metals introduced into the bath together with the scrap may exert a negative impact on its properties.

Let us consider an example of copper. This metal is characterised by limited solubility in iron and it is released on grain boundaries at temperatures of hot processing. This causes a hazard of incipient melting and steel cracking [4]. Bearing in mind that copper is often introduced into steel along with demolition scrap, one may be certain to claim that a change in the generic structure of the scrap remelted in electric furnaces may cause that reduced quality steel is obtained. Furthermore, removing copper from a liquid steel bath is a very complex and technologically advanced process. The permissible content of copper in steel scrap is currently 0.3 % by weight.

One of the options of copper removal from the liquid steel is its evaporation under the conditions of reduced pressure. This paper provides a discussion on the results of studies of the impact exerted by copper content in bath on the rate of its removal in the steel remelting process conducted in an induction furnace.

2. Research methodology

The study in question concerned synthetic Fe-Cu alloys. They were made of the Armco iron and deoxidised copper of grade M00B. The copper content in the alloys examined varied from 0.198 to 1.518 % by weight.

All tests were conducted using the VIM 20-50 vacuum furnace manufactured by SECO–WARWICK. The device featured stateof-the-art technological solutions applied in industrial vacuum devices. They included an inductor tilt electric drive, a resistance heater for the ingot mould, an alloy additives feeding system and a sampling mechanism. The studies to determine the impact of the alloy composition on the copper evaporation rate were conducted at the temperature of 1923 K for the measuring system pressure of 0.06 and 101 Pa respectively. The copper content in the alloy examined was altered within the range from 0.198 to 1.518% by weight.

3. Test results

The preliminary thermodynamic analysis conducted implied that the alloys examined satisfied Olette's condition determining the option of copper evaporation from the alloys in question [5]. In order to determine the value of the overall copper mass transfer coefficient, the following dependence was applied:

$$2.303 \log \frac{C_{Cu}^{t}}{C_{Cu}^{o}} = -k_{Cu} \cdot \frac{F}{V}(t-t_{o})$$
(1)

where:

F – evaporation areas (interfacial areas), m^2 ,

 $V - liquid metal volume, m^3$,

(t-t_o) – process duration time, s,

 C_{Cu}^{t} , C_{u}^{0} , C_{u}^{0} – respectively, ultimate and initial copper concentration in iron,

k – overall mass transfer coefficient, m s⁻¹.

The copper mass transfer coefficient values established from dependence (1) based on experimental data have been collated in Table 2.

4. Analysis of the study results

From a kinetic point of view, the process of copper evaporation from liquid iron can be divided into three main stages:

- copper transfer from the body of the liquid phase to the interface,
- copper evaporation from the liquid metal surface,
- transfer of the copper vapours from the interface to the core of the gaseous phase.

The alloy composition may influence all the constituent stages of the evaporation process. In the case of the mass transfer in the liquid phase, this impact may be evidenced in both the diffusion coefficient and the near surface velocity of induction stirred metal [6, 7].

| Tal | ble | 2. |
|-----|-----|----|
| 1 a | one | 4. |

| EXDEFINIENTAL CODDEL MASS MANSIEL COETHCIENT VAL | Ext | perimental | copper mass | transfer | coefficient | values |
|--|-----|------------|-------------|----------|-------------|--------|
|--|-----|------------|-------------|----------|-------------|--------|

| Experimental copper ma | ass transfer co | Jernelent value | 5 |
|------------------------|-----------------|-----------------|---------------------|
| Cu content in alloy, | Temp., | Pressure, | k _{exp.} , |
| % by weight | K | Ра | m s ⁻¹ |
| 1.518 | 1.923 | 101 | 1.00E-05 |
| 1.518 | 1.923 | 101 | 9.69E-06 |
| 1.518 | 1.923 | 0.06 | 4.43E-05 |
| 1.518 | 1.923 | 0.06 | 4.81E-05 |
| 1.056 | 1.923 | 0.06 | 4.61E-05 |
| 1.056 | 1.923 | 0.06 | 4.67E-05 |
| 0.509 | 1.923 | 101 | 8.95E-06 |
| 0.509 | 1.923 | 101 | 8.63E-06 |
| 0.509 | 1.923 | 101 | 8.39E-06 |
| 0.509 | 1.923 | 101 | 8.41E-06 |
| 0.509 | 1.923 | 0.06 | 4.78E-05 |
| 0.509 | 1.923 | 0.06 | 4.95E-05 |
| 0.509 | 1.923 | 0.06 | 4.58E-05 |
| 0.509 | 1.923 | 0.06 | 4.74E-05 |
| 0.509 | 1.923 | 0.06 | 4.58E-05 |
| 0.509 | 1.923 | 0.06 | 4.65E-05 |
| 0.198 | 1.923 | 0.06 | 4.43E-05 |
| 0.198 | 1.923 | 0.06 | 4.29E-05 |
| | | | |

In the study in question, in order to determine D_{Cu-Fe} , the Darken equation for binary solutions was applied [8].

$$D_{AB} = (X_B \cdot D_A + X_A \cdot D_B) \times \left(1 + \frac{d \ln \gamma_A}{d \ln X_A}\right)$$
(2)

where:

Table 2

 D_A , D_B – self-diffusion coefficient for component A and B respectively, m^2s^{-1} ,

 X_A , X_B – content of component A and B in the solution respectively, mole fraction,

 γ_A – activity coefficient for solution component A.

Values of the self-diffusion coefficient for liquid copper and iron within the range of temperatures analysed were determined based on the following dependences [9, 10]:

$$\begin{array}{ll} D_{Cu} = 14.6 \cdot 10^{-8} \cdot exp(-9700/RT) & (3) \\ D_{Fe} = 3.66 \cdot 10^{-9} \cdot exp(-2860/RT) & (4) \end{array}$$

Table 3 contains the diffusion coefficient values obtained for copper diffusion in liquid iron for the alloys studied.

| able 5. | | | | | | | | |
|-----------|-------------|-----|--------|----|-----|-----|------|--|
| Diffusion | coefficient | for | copper | in | liq | uid | iron | |

| Temp. | $D_{\text{Fe-Cu}}, m^2 s^{-1}$ | | | | | |
|-------|--------------------------------|-------------------------|-------------------------|-------------------------|--|--|
| K | 1.5 % wt. Cu | 1 % wt. Cu | 0.5 %wt. Cu | 0.2 % wt. Cu | | |
| 1898 | 7.8132·10 ⁻⁹ | 7.8407·10 ⁻⁹ | 7.8682·10 ⁻⁹ | 7.8902·10 ⁻⁹ | | |
| 1923 | 7.8756·10 ⁻⁹ | 7.9034·10 ⁻⁹ | 7.9312·10 ⁻⁹ | 7.9535·10 ⁻⁹ | | |
| 1948 | 7.9369·10 ⁻⁹ | 7.9650·10 ⁻⁹ | 7.9931·10 ⁻⁹ | 8.0156·10 ⁻⁹ | | |
| 1973 | 7.9971·10 ⁻⁹ | 8.0255·10 ⁻⁹ | 8.0539·10 ⁻⁹ | 8.0767·10 ⁻⁹ | | |
| 1998 | 8.0562·10 ⁻⁹ | 8.0849·10 ⁻⁹ | 8.1136·10 ⁻⁹ | 8.1366·10 ⁻⁹ | | |

When the process is indeed determined by this constituent stage, the process rate should depend on the alloy composition. This effect was observed for the experiments conducted for under the pressure of 0.06 Pa where the copper evaporation rate increased along with its content in iron. The foregoing has been illustrated with the data provided in Fig. 3.



Fig. 3. Influence of the copper content in alloy on the rate of copper evaporation

The maximum evaporating copper flux from the liquid iron surface to the gaseous phase is determined by the Langmuir-Knudsen equation. It assumes the following form:

$$N_{Cu}^{e} = \frac{\alpha \cdot p_{Cu}^{o} \cdot \gamma_{Cu} \cdot M_{Fe} \cdot C_{Cu}}{\rho_{Fe} \sqrt{2\pi RTM_{Cu}}}$$
(5)

where:

a – evaporation coefficient,

p⁰_{Cu} – equilibrium pressure over pure copper, Pa,

 g_{Cu} – Cu activity coefficient,

 M_{Fe} – Fe molar mass, g/mol,

 C_{Cu} – evaporating component concentration,

 r_{Fe} – iron density, g/m³,

 $M_{Cu}-Cu$ molar mass, g/mol.





Equation (5) implies that the copper flux depends to a considerable extent on the product of the vapour pressure over pure component and the activity coefficient for the copper present in the solution. Figure 4 depicts the sample changes in the copper activity in the alloys analysed in the function of temperature, whereas Fig. 5 depicts the change in the product of the activity coefficient and the value of vapour pressure over pure copper [11]. The activity coefficient values for the copper present in alloys of 1.5 % by weight of Cu are ca. 5 % lower than those of the alloys containing 0.2 % of Copper by weight. The results obtained confirm the clear dependence between the copper content and the evaporation rate.



Fig. 5. Change of the activity coefficient product for copper in liquid iron and pressure of vapours over the pure component for the alloys containing up to 1.5 % by weight of Cu

5. Conclusions

The study results obtained evidencing the impact of the alloy composition on the copper evaporation rate at the temperature of 1923 K and the measuring system pressure of 0.06 and 101 Pa imply that the process rate increases as the copper content in the alloy grows. For the pressure of 0.06 Pa, the increase in the mass transfer coefficient for the alloys examined equals ca. 15%. It was also confirmed by the activity coefficient values obtained for the copper present in the alloys studied, being ca. 5% lower than in the alloys of lower copper content.

Bearing in mind the practical aspect of the steel vacuum refining process for the copper removal, when the content of this element in the charge materials is low, one should expect its duration time to be extended which may affect the process economy.

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