

## THE MECHANISM OF LIQUID COPPER DEOXIDATION DURING ARGON BLOWING

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Using the method of argon (with specified oxygen content) blowing, the possibility of copper deoxidation has been considered on the basis of specific thermodynamic data. Despite the oxygen exceeding its equilibrium content in argon, a significant copper deoxidation during blowing has been experimentally observed. The explanation of this phenomenon can be the reaction of oxygen with the crucible material. In the present study, graphite and Al<sub>2</sub>O<sub>3</sub> crucibles were used. The stirring effect of gaseous bubbles promotes passing the substrates to and removing the products from the reaction zone.

*Key words:* metallurgy, liquid copper, deoxidation, argon

**Mehanizam dezoksidacije tekućeg bakra propuhivanjem argonom.** Koristeći postupak propuhivanja argonom (s određenim sadržajem kisika) razmatrana je mogućnost dezoksidacije bakra na temelju posebnih termodinamičkih podataka. Neovisno, što kisik prelazi ravnotežnu koncentraciju u argonu, praktički je utvrđena znakovita dezoksidacija bakra propuhivanjem argonom. Objašnjenje ove pojave može biti reakcijom kisika s materijalom lonca. U ovom radu rabljeni su lonci od grafita i Al<sub>2</sub>O<sub>3</sub>. Utjecaj miješanja plinskih mjehura podupire prolaz substrata i također odstranjivanje produkata iz zone reakcije.

*Gljučne riječi:* metalurgija, tekući bakar, dezoksidacija, argon

### INTRODUCTION

Dissolution of gases in liquid metals is a negative aspect of metallurgical processes. For example, oxygen or hydrogen, when dissolved in liquid metal, causes creation of bubbles in solidifying ingots and, as a consequence, leads to formation of defects during the process of rolling. A series of deoxidation techniques are employed, one of which is the method of metal blowing with inert gas, most frequently argon [1, 2].

A relationship of gas solubilities in liquid metals ( $c_A$ ) and their partial pressures above metal ( $p_A$ ) is described by Sievert's law:

$$c_A = k_s \sqrt{p_A} \quad (1)$$

Gases or diatomic pairs, such as H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> or S<sub>2</sub>, typically dissociate when dissolved in metal. In the case of oxygen, for example, the following reaction occurs:



The equilibrium constant in this reaction is the value of  $k_s$  from Sievert's equation. The direction of the reaction course is determined here by the change of its free enthalpy  $\Delta G$ .  $\Delta G$  values in processes of oxygen dissolution in various metals, depending on temperature, are

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listed in Table 1. Table 1 also contains the values of equilibrium constant  $k_s$  for respective temperatures, equilibrium pressures corresponding to these temperatures and respective values of oxygen content in liquid metal.

Table 1 **The changes of free enthalpy of the oxygen dissolution processes in chosen liquid metals, equilibrium constants and equilibrium pressures for given oxygen concentration in metals [3, 4].**

Metal	$\Delta G$ / J/mol	Equilibr. constant	T / K	Equilibr. Pressure / Pa	Oxygen content / % wgt
Ag	-17054 +27,7T	0,32	1173	$9,93 \times 10^3$	0,1
Co	-97912 +10,4T	156	1873	$4,15 \times 10^{-4}$	0,01
Cu	-86361 +7,17T	6,21	1473	$2,63 \times 10^{-1}$	0,01
Fe	-116760 +2,88T	2690	1873	$1,42 \times 10^{-6}$	0,01
Ni	-96744 +16,39T	70	1873	$2,03 \times 10^{-3}$	0,01
Pb	-106043 +31,4T	$8 \times 10^9$	673	$1,6 \times 10^{-17}$	0,1
Sn	-192070 +50T	$8 \times 10^8$	673	$1,5 \times 10^{-17}$	0,01

Gas contained above the metal dissolves in it accordingly to Sievert's law. The rate of this process in mild, non-stirred bath depends on the diffusion rate of the gas from the metal surface into the bath. The diffusion process lasts as long as the equilibrium of oxygen in the metal layer and inside the bath has been reached. If the gas pressure above the metal is less than it is defined by the equilibrium condition determined by the solubility law, the gas will diffuse from the metal to the atmosphere above the metal surface. In Table 1, it is shown that oxygen can be very easily removed from silver [5].

The thermodynamic data on oxygen solubility in copper (Table 1) show that oxygen equilibrium pressure above copper containing 0,01% of dissolved oxygen equals  $2,63 \times 10^{-1}$  Pa. It means that if vacuum better than  $2,63 \times 10^{-1}$  Pa is applied at 1473 K, the concentration of oxygen remaining in liquid copper after deoxidation can be less than 0,01%. It also defines the condition of the purity of inert gas which can be a recipient of dissolved gas. To be the carrier gas for 0,01% oxygen dissolved in liquid copper, inert gas should theoretically contain less than  $2,63 \times 10^{-4}$  % of oxygen. It is determined by the condition of oxygen diffusion into a bubble of argon. Assuming the process of carrying of dissolved oxygen into argon is stationary, it can be described by a simplified diffusion equation:

$$\frac{dm}{dt} = A_p k_d (c_m - c_g) \quad (3)$$

where:

$\frac{dm}{dt}$  – amount of dissolved gas passing into an inert gas bubble within a time unit,

$A_p$  – liquid-gas (bubble) interface,

$k_d$  – diffusion coefficient,

$c_m$  – oxygen concentration in metal,

$c_g$  – oxygen concentration in a gas bubble.

If Sievert's law is applied, the value of gas concentration in a bubble in equation (3) should be substituted by  $k_s \sqrt{p_{O_2}}$ . When equilibrium pressure in a gas bubble is reached,  $c_m$  will reach the value of  $k_s \sqrt{p_{O_2}}$  and diffusion ends. Inert gas should not contain an amount of oxygen greater than equilibrium pressure, because it would mean diffusion of this gas into the metal. The deoxidation kinetics is complicated by the fact that the process of liquid metal deoxidation using the method of blowing with argon is not stationary as well as the presence of surface active elements.

On the basis of the thermodynamic data, the possibility of liquid copper deoxidation through blowing it with argon containing a given amount of oxygen was considered as well as experiments with the use of graphite crucibles and  $Al_2O_3$  crucibles were conducted.

## STUDY

In the study, electrolytic copper containing 0,018 – 0,022 % argon was used. For blowing, argon containing 0,03 % oxygen (on the average) was applied, which theoretically was too much contamination for reducing the content of oxygen dissolved in copper to the value of 0,01 %. The equilibrium pressure of oxygen above copper containing 0,018 % of this gas equals  $9,49 \times 10^{-1}$  Pa, which corresponds to the  $8,4 \times 10^{-4}$  % of oxygen content in argon. Despite this, a significant decrease in the content of oxygen in copper was observed when blowing copper with argon at 1500 K, both in graphite and  $Al_2O_3$  crucibles.

In the case of graphite crucibles, the deoxidation mechanisms may consist in binding of oxygen dissolved in liquid copper to the crucible carbon in the following reaction:



This reaction is facilitated by small partial pressure of carbon monoxide. The free enthalpy value of the mentioned  $\Delta G_1$  reaction can be determined when the free enthalpies for the reactions of oxygen dissolution in copper and combustion of solid graphite giving the carbon monoxide product are known. If the enthalpy change  $\Delta G_2$  corresponds to the reaction  $[O]_{Cu} = 0,5O_{2g}$  and  $\Delta G_3$  corresponds to the reaction  $C_{st} + 0,5O_{2g} = CO_g$ , the free enthalpy for the reaction (4) is as follows:

$$\Delta G_1 = \Delta G_2 + \Delta G_3 \quad (5)$$

If  $\Delta G_2 = +86361 - 7,17T$  [6] and  $\Delta G_3 = -111340 - 87,36T$  [7], the equation (5) allows to obtain the standard free enthalpy of the binding reaction of oxygen dissolved in copper to the carbon  $\Delta G_1$ , expressed in J/mol:

$$\Delta G_1 = -25000 - 94,53T \quad (6)$$

Summing up, copper deoxidation with the use of graphite is determined by carbon monoxide pressure  $p_{CO}$  in the reaction zone. The equilibrium constant for the reaction (4) is described as follows:

$$k = -\frac{p_{CO}}{a_O} \quad (7)$$

where:

$a_O$  – oxygen activity in copper.

The constant determined in the (6) equals  $k = 7 \times 10^5$  at 1473 K, which means that liquid copper deoxidation occurs. Blowing copper with inert gas only enhances this reaction through stirring and restoring the reaction zone located on the crucible sides.

In the case of graphite crucibles, it was observed that after blowing copper with argon, the oxygen content in copper was approximately 0,004 %. The oxygen content in copper was measured with the Leco apparatus.

During the process of copper blowing in  $Al_2O_3$  crucibles, it was observed that after blowing the oxygen content in metal was 0,005 %. While the mechanism of liquid copper deoxidation through blowing it with argon is

obvious in a graphite crucible, the oxygen decrease in copper while blowing it in an  $\text{Al}_2\text{O}_3$  crucible is more complicated. Oxygen is a surface active element not only at the liquid copper-gas interface [8], but also at the interface of liquid metal-refractory material [9]. The maximum surface oxygen excess at the liquid copper-gas interface equals  $21 \times 10^{14}$  mol/cm<sup>2</sup>, and it equals  $34 \times 10^{14}$  mol/cm<sup>2</sup> at the liquid copper-solid aluminium oxide interface. A high oxygen activity at the interface of liquid copper-solid aluminium oxide indicates that a chemical reaction occurs. On this surface, a significantly greater amount of excessive oxygen is seen and, regarding the structure of copper surface layer [6], it should be assumed that there are advantageous conditions for the formation of compounds such as  $\text{CuO} \cdot \text{Al}_2\text{O}_3$  or  $\text{Cu}_2\text{O} \cdot \text{Al}_2\text{O}_3$ . This hypothesis was confirmed by X-ray radiography analysis of the surface of the crucible in which copper was molten, as the presence of  $\text{CuO} \cdot \text{Al}_2\text{O}_3$  spinels was observed.

## DISCUSSION

The study of copper deoxidation through copper blowing with argon containing oxygen above the equilibrium value for oxygen dissolution in liquid copper showed that it also caused metal deoxidation despite the excessive amount of oxygen in argon. However, the mechanism of this process is different from vacuum deoxidation or deoxidation with gas containing oxygen of the content far less than the equilibrium value for a given temperature. Nevertheless, the results obtained during deoxidation in the graphite crucibles (oxygen decrease from 0,02 % to 0,004 %) and  $\text{Al}_2\text{O}_3$  crucibles (oxygen decrease to 0,005 %) proved a good efficiency of this process in both types of crucibles.

The process is based on the reaction of oxygen dissolved in copper with the crucible material. The reaction is facilitated by the stirring effect of the gas introduced into the crucible. Intensive stirring enhances passing substrates to and removing products from the reaction zone. When metal blowing with argon containing oxygen above the equilibrium concentration is applied, the

adsorption of excessive oxygen at the metal-gas (bubble) interface should be taken into account. In this process, a specific layer of oxygen and metal ions is formed [9]. Contact of the bubble with the crucible surface causes the bubble's surface oxygen binding and leads to the decrease in oxygen content in the bubble. As a consequence, oxygen adsorption from the metal occurs, which means the decrease in oxygen content in the liquid metal volume.

## SUMMARY

Copper deoxidation through blowing copper with argon containing more oxygen than its equilibrium value is caused by the reaction of oxygen with the crucible material. For graphite crucibles, the reaction product is carbon monoxide, and for  $\text{Al}_2\text{O}_3$  crucibles, the products are spinels, such as  $\text{CuO} \cdot \text{Al}_2\text{O}_3$  or  $\text{Cu}_2\text{O} \cdot \text{Al}_2\text{O}_3$ . A similar mechanism is observed during the reactions with refractory lining and covering slag materials which cause deoxidation during blowing other metals (mainly all types of steel) with argon in ladles.

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**Note:** The responsible translator for English language is G. Siwiec.