THE MASS TRANSFER ON THE SLAG – LIQUID METAL INTERPHASES

In the work the results of thermodynamic analysis and laboratory investigations of the formation of slag-metal interphases layer during reducing copper melting conditions have been shown. A considerable intensifying of the reduction processes proves that only refining of the metal is not possible. The extraction of non-metallic inclusions from copper or its alloys leads to formation of many another chemical compounds and inclusions. The results of the slag-copper surface scanning analysis shows, that during the reducing the Al₂O₃ - B₂O₃ - Na₂O or SiO₂ - B₂O₃ - Na₂O slag, effect of silica, aluminium and sodium precipitation may appear.

Key words: copper, slag - liquid metal, metallic and nonmetallic inclusions

INTRODUCTION

Slag extraction is commonly used in the casting processes of melting copper (Figure 1). According to W. Nernst principle of division in this type of configuration as in the metallurgical slag the process of refining the state of solution with the nonmetallic inclusions being extracted is quickly established. The real metallurgical processes involve interaction of metal atmosphere, liquid slag and liquid metal as well as nonmetallic inclusions [1 - 10]. It proves that there is a big discrepancy in the opinions on the structure and the

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**Figure 1.** A proposed scheme of refining process (real conditions under the cover) of a liquid metal with a carbide-cyanamide slag solution [10] where: A - the melting atmosphere, B - slag, C - gas, M - melting metal, X - reagent, St - reaction stimulator, \( \{\cdot\} \) - loss in the slag, \( \{\cdot\} \) - elements in the melting metal

**Slika 1.** Prijedlog sheme pročišćavanja (stvarni uvjeti pod poklopcem) nolok tegulj metala solucijom tropske karbida-cjamenida [10] gdje je: A - atmosfera taljenja, B - troska, C - plin, M - metal koji se talja, X - reagens, St - stimulator reakcije, \( \{\cdot\} \) - izgubi u troski, \( \{\cdot\} \) - elementi u metalu koji se tala

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basic features of slag (S) with the reagent (R) as well as the essence of their interaction with refined metal (M) and the atmosphere (A) of melting. Each of these phases has different properties, which change in contact with other phases. The analysis of metallurgical processes is usually limited to chemical composition of slag formed as a result of the reduction process. However, no more structure investigations have been attempted until now [4, 9].

In the presented work it has been decided to show the results of thermodynamic analysis and laboratory investigations of the inclusions formations and their chemical composition in the slag during reducing copper melting conditions.

**THERMODYNAMIC ANALYSIS**

The thermodynamic analysis (Table 1.) has confirmed the argument on low reducing effectiveness of the reaction of calcium carbide with aluminium oxides - \( \text{Al}_2\text{O}_3 \) (reaction no. 3 - Table 1.), sodium oxides - \( \text{Na}_2\text{O} \) (reaction no. 9 - Table 1.) and shown that the similarly reaction CaC\(_2\) with SiO\(_2\), B\(_2\)O\(_3\), and MnO is not possible (reaction 5 - 8).

A considerable intensifying of the reduction processes, which is reflected in the value of the reduction indicator, proves that only dissociation of carbides or reducing refining metal oxides is not possible.

The extraction of non-metallic inclusions from copper leads to formation of many other chemical compounds. For example the possibility of reduction CaC\(_2\) in to the slag based on the \( \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O} \) systems is shown Figure 2. The same problems is shown for the SiO\(_2\) - B\(_2\)O\(_3\) - \( \text{Na}_2\text{O} \) systems in the Figure 3.

Table 1. The thermodynamic analysis of the calcium carbide CaC\(_2\) with the slag component

<table>
<thead>
<tr>
<th>No</th>
<th>Equation of reaction</th>
<th>Gibbs free energy ( \Delta G^\circ ) / (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 3\text{CaC}_2 + 2\text{Al}_2\text{O}_3 \rightarrow \text{Al}_4\text{C}_3 + 3\text{CaO} + 3\text{CO} )</td>
<td>1200 / K + 550 / K 1500 / K + 190 / K</td>
</tr>
<tr>
<td>2</td>
<td>( \text{CaC}_2 + \text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + \text{CaO} + 2\text{CO} )</td>
<td>+ 490 / K + 200 / K</td>
</tr>
<tr>
<td>3</td>
<td>( 2\text{CaC}_2 + \text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + 2\text{CaO} + 3\text{CO} + \text{C} )</td>
<td>188 / K - 112 / K</td>
</tr>
<tr>
<td>4</td>
<td>( \text{CaC}_2 + \text{Al}_2\text{O}_3 + 8\text{C} \rightarrow \text{Al}_4\text{C}_3 + \text{CaO} + 5\text{CO} )</td>
<td>+ 675 / K + 1017 / K</td>
</tr>
<tr>
<td>5</td>
<td>( \text{CaC}_2 + 2\text{B}_2\text{O}_3 + 5\text{C} \rightarrow 2\text{B} + \text{C} + \text{CaO} + 6\text{CO} )</td>
<td>+ 419 / K + 604 / K</td>
</tr>
<tr>
<td>6</td>
<td>( \frac{1}{2}\text{CaC}_2 + \frac{3}{2}\text{SiO}_2 \rightarrow 2\text{Si} + \text{CaO} + \text{CO} + \text{C} )</td>
<td>+ 84 / K + 104 / K</td>
</tr>
<tr>
<td>7</td>
<td>( \frac{1}{2}\text{CaC}_2 + 7\text{MnO} + \frac{15}{2}\text{C} \rightarrow 2\text{MnC} + \frac{15}{2}\text{CO} )</td>
<td>+ 218 / K + 541 / K</td>
</tr>
<tr>
<td>8</td>
<td>( \text{CaC}_2 + \text{MnO} \rightarrow 3\text{Mn} + \text{CaO} + 2\text{CO} )</td>
<td>+ 106 / K + 154 / K</td>
</tr>
<tr>
<td>9</td>
<td>( \text{CaC}_2 + 2\text{Na} \rightarrow 4\text{Na} + \text{CaO} + \text{CO} + \text{C} )</td>
<td>- 171 / K - 46 / K</td>
</tr>
</tbody>
</table>

The thermodynamical potential of reaction \( \Delta G^\circ \) of calcium carbide (\( \text{CaC}_2 \)) with the oxides \( \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O} \) was also showed that the products of carbides dissociation in the slag, during extraction processes, were possible as well as analysis by means of electron microscopy.
EXPERIMENTAL PROCEDURE AND RESULTS

The slag of composition (specified: \( \text{Al}_2\text{O}_3 \), 35 %, \( \text{SiO}_2 \), 35 %, \( \text{CaO} \), 5 %, \( \text{Na}_2\text{O} \), 15 %, \( \text{MgO} \), 8 %, \( \text{CaF}_2 \), 2 %) with additions of 40 % calcium carbide (\( \text{CaC}_2 \)), was melted in reduction atmosphere at 1350 K for 20 min. It was cast to the metal mould of 300 K in order to “freeze” the slag structure. The cast material was crushed and ground. The obtained powder was glued with resins and formed in 3 mm discs. Next, the discs were dimpled and ion milled with Gatan Duo Mill 600 down to thin foils. TEM observation were performed in Philips CM20 TWIN (at 200 kV). The chemical microanalysis was performed using Link eXL 1 EDS attachment. The chemical composition of the slag is shown in the results of the surface slag-copper investigations show a scanning electron micrograph in Figure 4.

![Figure 4](image)

**Figure 4.** Scanning electron micrograph of the slag-copper interfaces surface

The results of the slag-copper surface scanning analysis (Figure 4.) show, that during the application of these slag in the reducing conduction, effect of silica, aluminium and calcium precipitation may appear. Figure 5.a shows a transmission electron micrograph taken of the slag matrix. The X-ray spectra acquired from this matrix (Figure 5.b) shows the presence of Ca, Si, Al, F, Na and O which is in good agreement with its initial chemical composition. The presence of Ca and simultaneously the lack of significant carbon signal confirmed that the \( \text{CaC}_2 \) reacted with other slag components as in the real processes of metallurgical slag refining from copper alloys. The microanalysis of the precipitates in Figure 6. shows that slag consists of aluminium or blocky precipitates of around 8 \( \mu \text{m} \) of aluminium with oxygen (Figure 7.). The microanalysis of these sug-
There is possible reaction within the analysed carbide slag that occurs between aluminium and silicon with its product (Figure 9., 10., 11.) or suggested nanocrystalline precipitate of calcium or siliconium.

The slag observation shows not only metallic aluminium, calcium or non-crystalline silica precipitate but also complex compounds formation with Al, Si, Ca and F (Figure 12.), graphite precipitates and certainly oxides of Al, Si and Ca.

**SUMMARY AND CONCLUSION**

The thermodynamic analysis and laboratory investigations have confirmed that the aluminium silicate slag in reduction conduction is of special interest. The reaction product of aluminium oxide, and carbon is presented in Figure 7. - 10. The reaction mentioned above, seems to be dominant during metallurgical slag ravelling in the reduction conduction. Basic reaction describing the carbide dissociation mechanism is:

\[
\{ X_{m} C_{n} \rightarrow \{ XX^{m} \} + \{ C^{n} \} \quad (1)
\]

To stand of carbon as of ion \{ C^{+} \} is impossible acceptable, because element this having construction 1s^{2} s^{2}p^{2} can create following ions:

\[
\{ C^{-} \} \rightarrow \{ C^{2-} \} + 3e \quad (2)
\]

or \{ C^{+} \} + 5e \quad (3)

or \{ C^{2-} \} + 2e \cdot C^{+} + 1e \quad (4)

or \{ C^{+} \} - 3e \quad (5)

Described with equalizations [5] ionic reactions explain specificity of influence of carbon in carbide slags. Show, that his melting and strong influence reducing results from occurrences in slag mostly of ions \{ C^{2+} \} or \{ C^{+} \}. Released in this manner in slag, electrons are main
link in mechanism exchanges of ions on border of distribution of phases S-M. According to [11] the Al₂O₃ contains at least 7 to 15 % of Al₂C₃ (6).

$$\text{Ca}_2\text{C}_2 + \text{Al}_2\text{O}_3 = \text{Al}_2\text{OC} + \text{CaO} + \text{CO}$$

or

$$\text{Ca}_2\text{C}_2 + 2\text{Al}_2\text{O}_3 = \text{Al}_2\text{O}_4\text{C} + \text{Ca} + \text{CO}_2$$

(6)

Presented investigations explain the existence of noncrystalline of silicon or even its complex with calcium and aluminium. The same problem is with metallic calcium. The results of the local chemical analysis have shown, that besides carbide-oxides Al₂O₄C or aluminium carbide, on the surface of slag-copper the metallic inclusions are observed. Therefore the author thinks that the existence of aluminium, calcium or silicon in the surface slag’s-metal it is necessary to mean as passing, local state in the complexity reaction in the slag.

To described observation is extremely importance, because to explain the possibility the currency reaction of reduction non- and metallic copper inclusions with metallic aluminium, calcium or silicon.

REFERENCES