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THE MASS TRANSFER ON THE SLAG – LIQUID METAL INTERPHASES

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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 Al_2O_3 - B_2O_3 - Na_2O or SiO_2 - B_2O_3 - Na_2O slag, effect of silica, aluminium and sodium precipitation may appear.

Key words: *copper, slag - liquid metal, metalic and nonmetalic inclusions*

Prijenos mase na međufaze troske - tekući metali. U radu su prikazani rezultati termodinamičke analize laboratorijskog ispitivanja obrazovanja međufaznog sloja troska - metal tijekom uvjeta reduciranja pri taljenju bakra. Značajna pojačanja redukcijskih procesa pokazuje da je moguće ne samo pročišćavanje metala. Izdvajanje nemetalnih uključaka iz bakra ili njegovih slitina vodi do obrazovanja mnogih drugi kemijskih spojeva i uključaka. Rezultati analize skeniranja površine troske - bakar pokazuje da se tijekom reduciranja troske Al_2O_3 - B_2O_3 - Na_2O ili SiO_2 - B_2O_3 - Na_2O može pojaviti efekt nastajanja precipitata silicijske kiseline, aluminija i natrija.

Ključne riječi: *bakar, troska - tekući metal, metalni i nemetalni uključci*

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 non-metallic inclusions being extracted is quickly established. The real metallurgical processes involve interaction of metal atmosphere, liquid slag and liquid metal as well as non-metallic inclusions [1 - 10]. It proves that there is a big discrepancy in the opinions on the structure and the

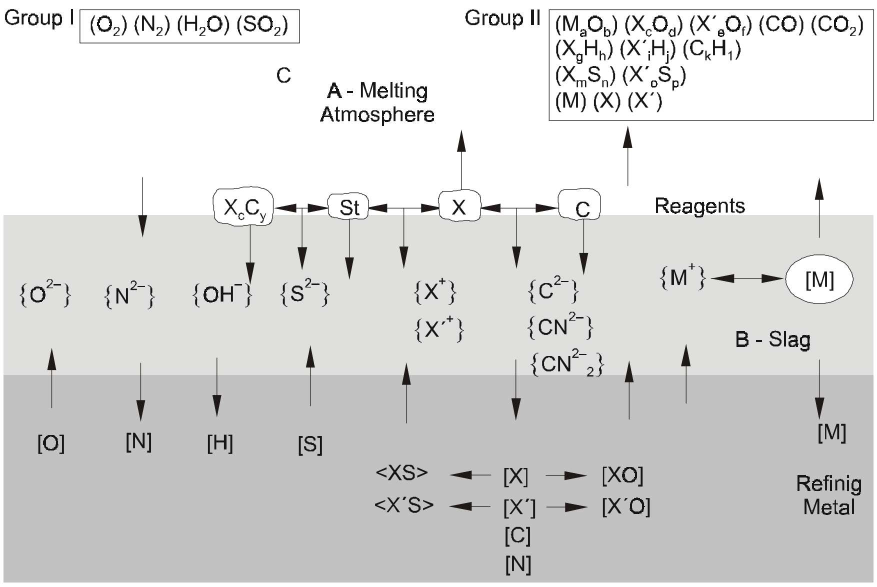

Figure 1. **A proposed scheme of refining process (real conditions under the cover) of a liquid metal with a carbide-cyanamid slag solution [10] where: A - the melting atmosphere, B - slag, C - gas, M - melting metal, X - reagent, St - reaction stimulator, {}- ions in the slag, [ ] - elements in the melting metal [8]**

Slika 1. **Prijedlog sheme pročišćavanja (stvarni uvjeti pod slojem) nekog tekućeg metala s otopinom trokse karbida-cijanomida [10] gdje je: A - atmosfera taljenja, B - troska, C - plin, M - metal koji se tali, X - reagens, St - stimulator reakcije, {}- ioni u troski, [ ] - elementi u metalu koji se tali [8]**

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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 - Al_2O_3 (reaction no. 3 - Table 1.), sodium oxides - Na_2O (reaction no. 9 - Table 1.) and shown that the similarly reaction CaC_2 with SiO_2, B_2O_3 and MnO is not possible (reaction 5 - 8).

Table 1. **The thermodynamic analysis of the calcium carbide CaC_2 with the slag component**
Tablica 1. **Termodinamička analiza kalcijum karbida CaC_2 s komponentama troske**

No	Equation of reaction	Gibbs free energy $\Delta G°_T$ / (KJ/mol) 1200 / K	1500 / K
1.	$3CaC_2+2Al_2O_3 \rightarrow Al_4C_3+3CaO+3CO$	+ 550	+ 190
2.	$CaC_2+Al_2O_3 \rightarrow 2Al+CaO+2CO$	+ 490	+ 200
3.	$2CaC_2+Al_2O_3 \rightarrow 2Al+2CaO+3CO+C$	– 188	– 112
4.	$CaC_2+Al_2O_3+8C \rightarrow Al_4C_3+CaO+5CO$	+ 675	+ 1017
5.	$CaC_2+2B_2O_3+5C \rightarrow B_4C+CaO+6CO$	+ 419	+ 604
6.	$CaC_2+SiO_2 \rightarrow Si+CaO+CO+C$	+ 84	+ 104
7.	$\frac{3}{2}CaC_2+7MnO_3+\frac{5}{2}C \rightarrow Mn_7C_3+\frac{3}{2}CaO+\frac{11}{2}CO$	+ 218	+ 541
8.	$CaC_2+MnO \rightarrow 3Mn+CaO+2CO$	+ 106	+ 154
9.	$CaC_2+2Na_2 \rightarrow 4Na+CaO+CO+C$	– 171	– 46

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 Al_2O_3 - B_2O_3 - Na_2O systems is shown Figure 2. The same problems is shown for the SiO_2 - B_2O_3 - Na_2O systems in the Figure 3.

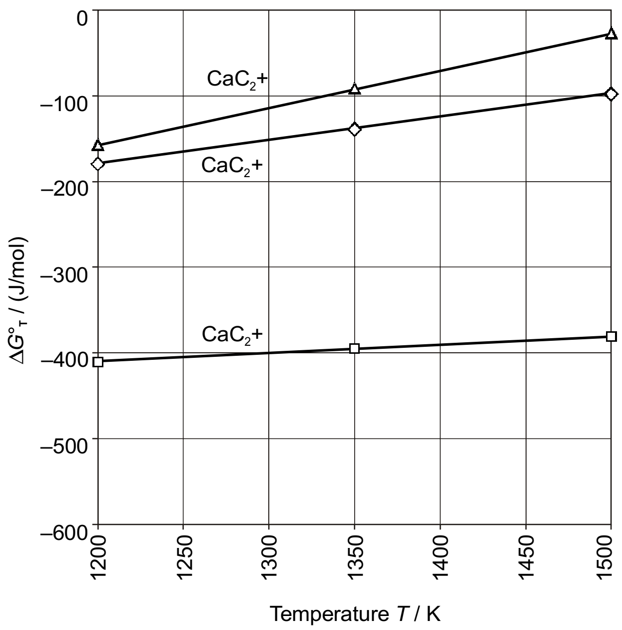

Figure 2. **The thermodynamical potential of reaction $\Delta G°_T$ of calcium carbide (CaC_2) with the oxides Al_2O_3, B_2O_3, Na_2O**
Slika 2. **Termodinamički potencijal reakcije $\Delta G°_T$ kalcijum karbida (CaC_2) s oksidima Al_2O_3, B_2O_3, Na_2O**

Authors 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.

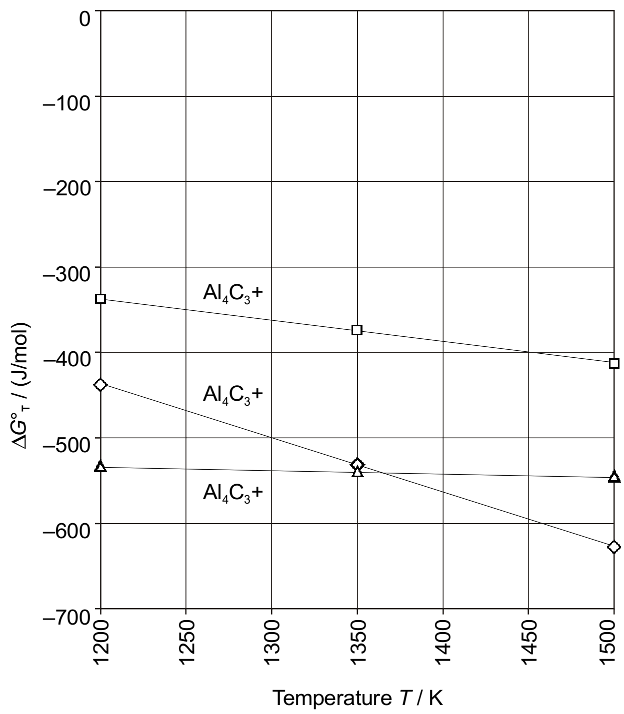

Figure 3. **The thermodynamical potential of reaction $\Delta G°_T$ of aluminium carbide (Al_4C_3) with the oxides SiO_2, B_2O_3, Na_2O**
Slika 3. **Termodinamički potencijal reakcije $\Delta G°_T$ aluminijum karbida (Al_4O_3) s oksidima SiO_2, B_2O_3, Na_2O**

EXPERIMENTAL PROCEDURE AND RESULTS

The slag of composition (specified: Al_2O_3 - 35 %, SiO_2 - 35 %, CaO - 5 %, Na_2O - 15 %, MgO - 8 %, CaF_2 - 2 %) with additions of 40 % calcium carbide (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 grinded. 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.

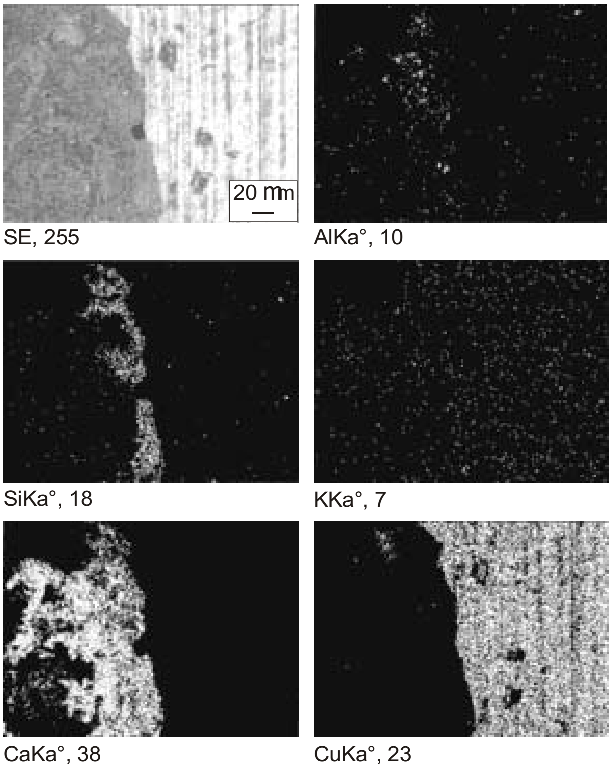

Figure 4. **Scanning electron micrograph of the slag-copper interfaces surface**
Slika 4. **SEM na razdjelnoj površini između troske i bakra**

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 of 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

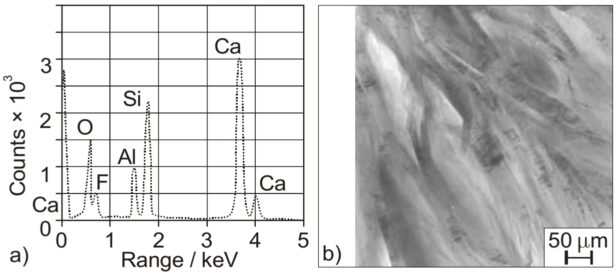

Figure 5. **a) X-ray spectrum from the matrix, b) Transmission electron micrograph showing the matrix of the investigated slag**
Slika 5. **a) EDX iz matrice, b) TEM koji pokazuje matricu ispitivane troske**

carbon signal confirmed that the 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 alu-

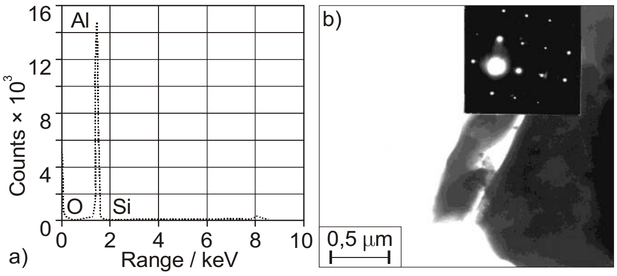

Figure 6. **The transmission electron microanalysis a) and micrograph b) of the precipitates consist of aluminium**
Slika 6. **a) TEM, b) mikrograf precipitata koji sadrži aluminij**

minium or blocky precipitates of around 8 μm of aluminium with oxygen (Figure 7.). The microanalysis of these sug-

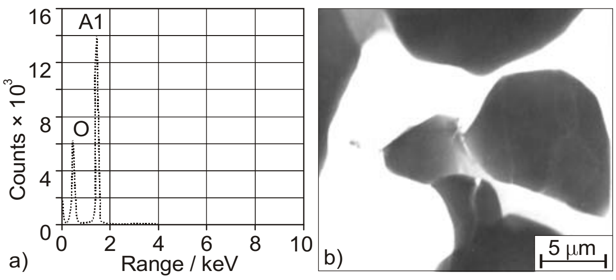

Figure 7. **a) X-ray spectrum, b) Transmission electron micrograph of Al.-O**
Slika 7. **a) EDX, b)TEM Al.-O**

gests their identification as Al_2O_3. Figure 8.a shows a bright field micrograph of regular precipitate of size about 0,5 μm. The selected area diffraction pattern (SADP) from the area visible in Figure 8.a, suggests good agreement with [010] zone axis orientation of Al_4O_4C phase. The qualitative microanalysis of the phase is presented in Figure 8.a.

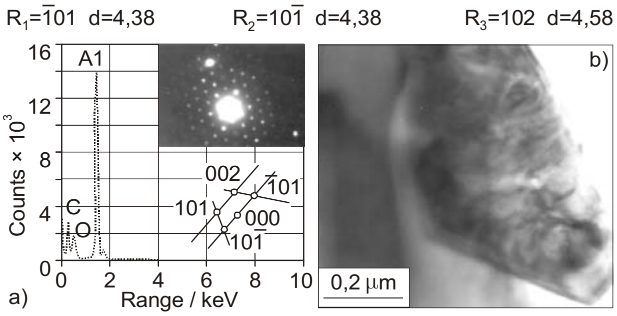

Figure 8. **a) X-ray spectrum and diffraction from precipitate, b) Transmission electron micrograph of Al_4O_4C precipitate and SADP showing [020] zone axis orientation of Al_4O_4C in the inset**

Slika 8. **a) EDX i difrakcija iz precipitata, b)TEM precipitata Al_4O_4C i SADP pokazuje [020] zonu orijentacije osi u Al_4O_4C u umetku**

There is possible reaction within the analysed carbide slag that occurs between aluminium and silicon with its

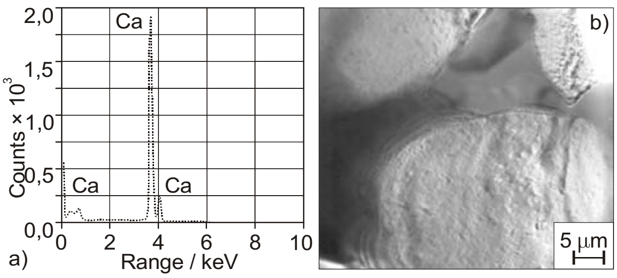

Figure 9. **a) X-ray spectrum, b) Transmission electron micrograph of noncrystalline Ca**

Slika 9. **a) EDX, b) TEM nekristaličnog Ca**

product (Figure 9., 10., 11.) or suggested nanocrystalline precipitate of calcium or silicium.

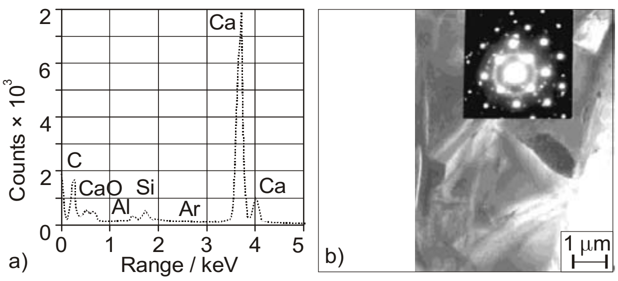

Figure 10. **X-ray spectrum (a) and micrograph (b) of the nanocrystalline precipitate of calcium**

Slika 10. **a) EDX, b) mikrograf nekristaličnog precipitata kalcija**

The slag observation shows not only metallic aluminium, calcium or nono-crystlline 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.

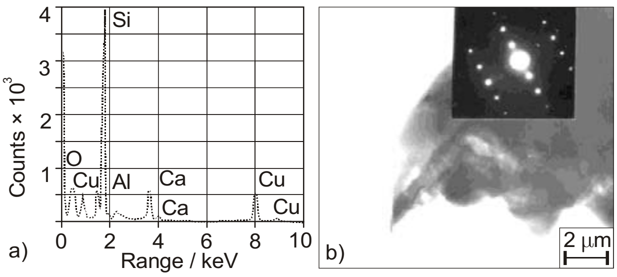

Figure 11. **X-ray spectrum (a) and micrograph (b) of the nanocrystalline precipitate of solecism**

Slika 11. **a) EDX, b) mikrograf nekristaličnog precipitata silicija**

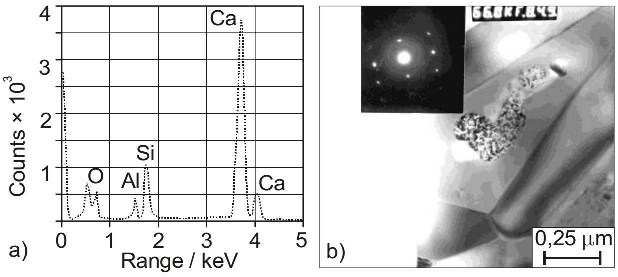

Figure 12. **X-ray spectrum and micrograph of the complex compounds formation**

Slika 12. **a) EDX, b) mikrograf stvaranja složenih spojeva**

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 ravening in the reduction conduction. Basic reaction describing the carbide dissociation mechanism is:

$$\{ X_m C_n \} \rightarrow \{X^{m+}\} + \{ C^{n-}\} \quad (1)$$

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

$$\{C^-\}\{C^{2+}\} + 3e \quad (2)$$

$$\text{or}\ \{C^{4+}\} + 5e \quad (3)$$

$$\text{or}\ \{C^+\} + 2e\ \langle C \rangle + 1e \quad (4)$$

$$\text{or}\ \{C^{4-}\} - 3e \quad (5)$$

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 $\{ C^{4+} \}$. 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 Al_4O_4C contains at least 7 to 15 % of Al_4C_3 (6).

$$CaC_2+Al_2O_3 = Al_2OC+CaO+CO$$
$$\text{or } CaC_2+2Al_2O_3 = Al_4O_4C +Ca +CO_2 \qquad (6)$$

Presented investigations explain the existence of noncrystlline 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 Al_4O_4C 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 metalic copper inclusions with metallic aluminium, calcium or silicon.

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