

INTERNAL OXIDATION OF THE Cu-Se ALLOYS

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The purpose of our investigation was to perform the thermodynamic calculation of all possible reactions in the Cu-Se-O system and to explain the oxidation mechanism in various conditions. For such study, a model of copper with one single inclusion and alloy with 1.65 wt. % Se were made. Depending on time, the oxidation has been taking place at two different temperatures and two oxygen partial pressures. The oxidized samples have been investigated by DTA, optical and electron microscopy (SEM).

Key words: *oxidation, internal oxidation, thermodynamics, Cu-Se alloys*

Unutarnja oksidacija Cu-Se legura. Namjena istraživanja je izraditi termodinamički proračun svih mogućih reakcija u sustavu Cu-Se-O i obrazložiti mehanizme oksidacije u različitim uvjetima. Za takovo izučavanje izrađen je model bakra sa samo jednim uključkom i legura sa 1,65 mas. % Se. U ovisnosti od vremena, oksidacija se odvijala kod različitih temperatura i kod dviju različitih djelomičnih tlakova kisika. Oksidirani uzorci su bili ispitivani metodom DTA, optičkom i elektronskom mikroskopijom (SEM).

Ključne riječi: *oksidacija, unutarnja oksidacija, termodinamika, Cu-Se-legure*

INTRODUCTION

The influence of the different atmospheres on the reactions in which the chemical composition of materials is changing due to the oxidation is very significant. Selenium in the Cu-Se alloys is present in solid solution or in form of the (Cu₂Se) compound respectively, but however its solubility in the solid copper is negligible. The oxidation of these alloys proceeds if the oxygen partial pressure is high enough.

Beside the surface oxidation of the alloys, an internal oxidation is taking place too, which differs a great deal from that one in other two-phase alloys [1-6]. The oxidation of the surface commences to oxidize with formation of the continuous layer of copper oxide. By controlling of the oxygen partial pressure such surface oxidation can be prevented (for instance by heating of the sample in the powdery mixture of Cu₂O and Cu). The rate of the internal oxidation depends upon the oxygen diffusion in the metal and it obeys the parabolic law.

The purpose of our investigation was to accomplish the thermodynamic calculations of all possible reactions in the Cu-Se-O system and to establish the mechanism of

oxidation in various conditions. For the investigation of the oxidation process a cylindrical model of the Cu-S alloy with one single copper selenide inclusion and the alloy with 1.65 wt. % Se were prepared. The oxidized samples have been examined by DTA (differential thermal analysis), optical and electron microscopy.

THEORETICAL

Thermodynamics of the oxidation can be applied to establish the conditions of the surface or of the internal oxidation respectively. The oxidation of the metal or the alloy proceeds if the free energies of formations of oxides are negative and if the oxygen partial pressure is high enough, respectively. The oxidation process depends on many parameters: T , p_{O_2} , X_B , The internal oxidation consists of many sub processes, e.g.: oxygen adsorption and dissociation, solubility and diffusion of atomic oxygen and of alloying elements in the matrix metal, chemical reactions, precipitation, etc. If the oxygen partial pressure is so high that equilibrium between the dissolved oxygen and the atmospheric oxygen is not achieved, the surface oxidation of the basic metal can take place.

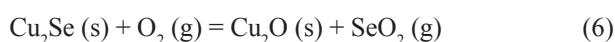
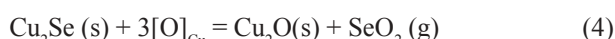
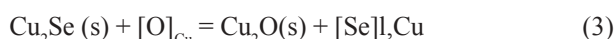
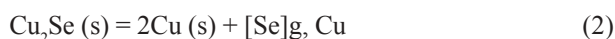
The thermodynamics of the internal oxidation in the discussed system is not known well. In references [7-11] the reactions, thermodynamic calculations and kinetic on

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the surface of solid copper or in the molten copper are presented respectively.

All the data needed for the calculations of the Gibbs free energies were obtained from the computer database of TAPP [12]. The calculation is given in the reference [13].

The most probable reactions in system Cu-Se-O are:



EXPERIMENTAL

In Figure 1. the scheme of the sample for the investigation of the Cu-Se alloy oxidation with one single inclusion of copper selenide in the copper tube is presented. Copper tube was made of the phosphorus-deoxidized cop-

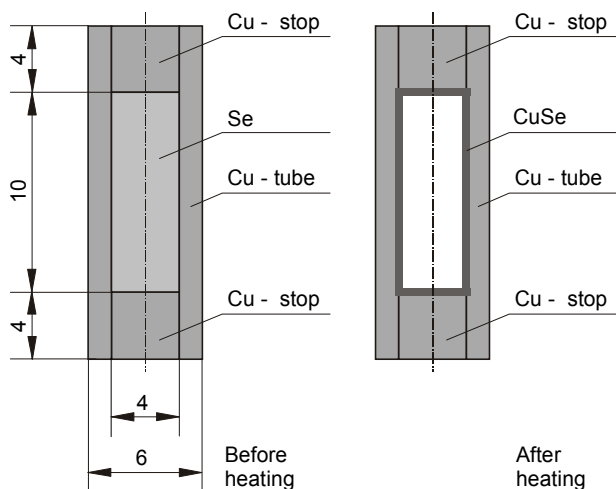


Figure 1. The scheme of the model for examination of the oxidation of the Cu - Se alloy
Slika 1. Shema modela za određivanje oksidacije Cu-Se legura

per and thus a small concentration of phosphorus remained in copper. It was filled up with selenium and closed with the copper plug. During the heating of the sample, selenium reacted with the copper into the Cu_2Se phase, which represented the upper mentioned inclusion.

The oxidation process of such samples has been performed in a vertical tube resistance furnace. In our investigation atmospheres with two different oxygen partial pressures ($p_{\text{O}_2} = 1$, and the atmosphere where the oxygen par-

tial pressure was equal to that in Cu_2O , $p_{\text{O}_2} = p_{\text{O}_2}$ in Cu_2O), and two different experimental temperatures of 800 °C and 1000 °C were applied. Depending on experimental conditions, the exposure to oxidation lasted up to 48 hours.

In case of $p_{\text{O}_2} = 1$, the sample has been placed on a ceramic holder with a K- type thermocouple. The gas has been supplied through the bottom of the vertical tube furnace and the gaseous oxidation products have been removed through the top of it. The samples in the furnace have been heated with the same heating rate in an inert atmosphere of argon (99.999 %) until the oxidation temperature was reached. Then oxygen was introduced into the furnace and the sample was kept at this temperature for the predetermined period. Cooling of the sample was taking place again in the inert argon atmosphere.

In case of $p_{\text{O}_2} = p_{\text{O}_2}$ in Cu_2O , the sample has been placed into the ceramic crucible together with the Cu_2O powder. Argon has been inserted through the bottom of the vertical tube furnace and the gaseous oxidation products have been removed through the top of it as in the previous case.

After the oxidation, the mass of the entire sample and the thickness of the peeled oxide layer have been measured. The formation of copper selenide was checked by DTA. The oxidized samples were examined by optical microscopy and SEM. The samples were marked by the type of alloy, the temperature and duration of experiment, and the applied atmosphere, i.e. Cu - Se alloy was oxidized on 800 °C for 36 hours in the oxygen atmosphere where $p_{\text{O}_2} = 1$.

RESULTS AND DISCUSSION

The variations of the thickness of the oxide layers and the mass changes of the non-oxidized and oxidized samples are presented in Figure 2. The thickness change of the oxide layer is related to the mass change of the sample. It is evi-

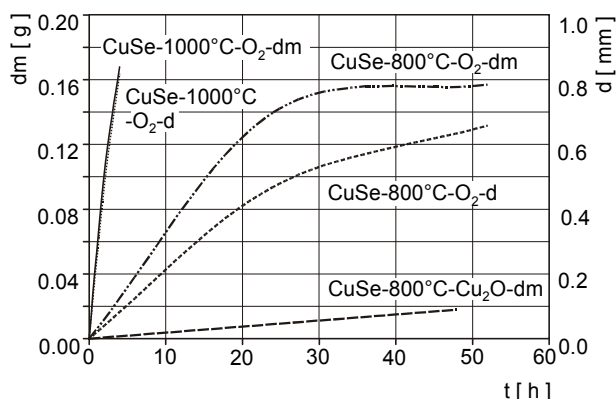


Figure 2. Thickness (d) of the oxide layer and mass changes (dm) during the oxidation process
Slika 2. Debljina oksidne kore (d) i promjena mase (dm) kod procesa oksidacije

dent from Figure 2. that the mass change of the oxidized samples is small in the case of $p_{O_2} = p_{O_2}$ in Cu_2O .

In Figure 3. the DTA curves of the model of the Cu-Se (S, Te) samples are shown. The course of the inclusion formation inside of the copper tube has been observed. At the temperature interval between 250 and 500 °C the reaction of the copper selenide formation was taking place. At 800 °C to 1000 °C the inclusion of the copper selenide had been format already inside of the copper tube.

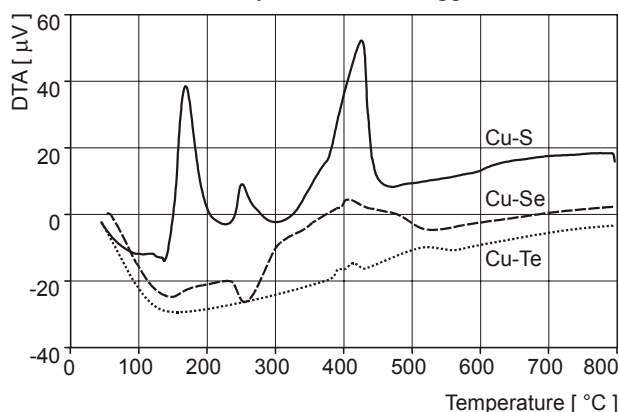


Figure 3. DTA curves of the Cu-Se (S, Te) alloys
Slika 3. DTA krivulje Cu-Se (S, Te) legura

The dependence of the oxidation time of the samples on the thinning of the copper tubes in at various atmospheres is shown in Figure 4. The same shape of the tube as for the non-oxidized sample (a) was observed on the $CuSe-800^{\circ}C-48h-Cu_2O$ sample (d), which was oxidized in the atmosphere, where the surface oxidation was not taking place.

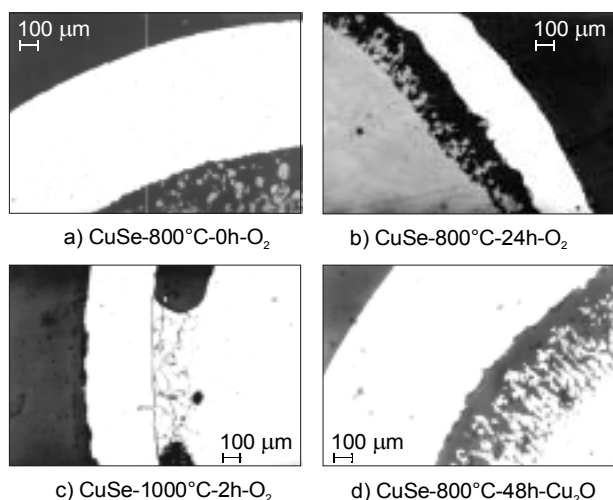


Figure 4. Structure of copper tubes at the model investigation (optical microscope)
Slika 4. Struktura bakarne cijevi pri modelnom istraživanju (optički mikroskop)

The microstructure of the oxidized $CuSe-1000^{\circ}C-2h-O_2$ sample is presented in Figure 5. The microstructures of the oxidized inclusions at 1000 °C show the evidence of

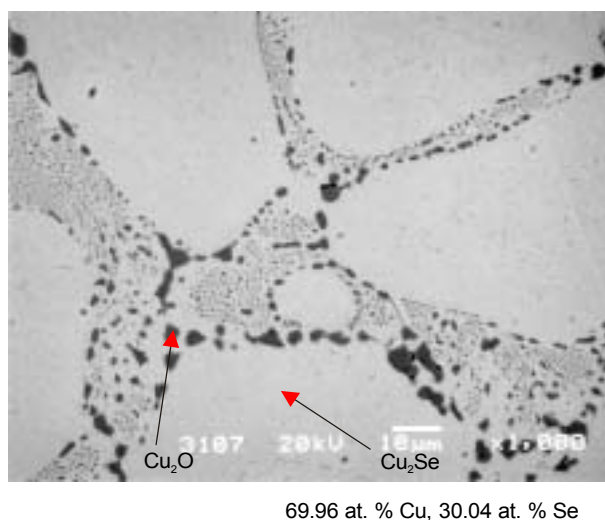


Figure 5. Eutectic of Cu_2O-Cu_2Se between the selenide inclusion and copper in the sample of $CuSe-1000^{\circ}C-2h-O_2$ (SEM)

Slika 5. Eutektik Cu_2O-Cu_2Se između selenidnog uključka i bakra u uzorku $CuSe-1000^{\circ}C-2h-O_2$ (SEM)

the oxidation of the $CuSe$ inclusion. The eutectic between copper oxide and selenium oxide with the rest of selenide inclusion is also observed.

In Figure 6., the back scattered electron (BSE) micrograph of the partial oxidized $CuSe-1000^{\circ}C-2h-O_2$ sample is shown. The formation of the copper selenide inclusions

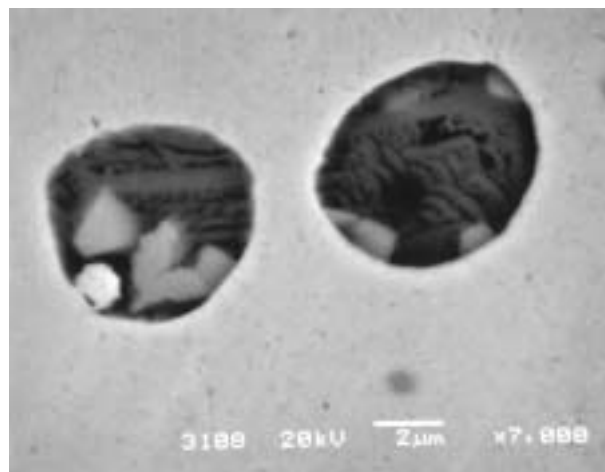


Figure 6. Partly oxidized inclusion in the sample of $CuSe-1000^{\circ}C-2h-O_2$ (SEM)

Slika 6. Djelomično oksidiran uključak u uzorku $CuSe-1000^{\circ}C-2h-O_2$ (SEM)

in the copper metal matrix was caused by the diffusion of selenium. Selenium precipitated into the copper defects and it reacted with copper into sulphide. EDS analysis shows that such inclusion is composed by Cu, Se, O.

In Figure 7. the microstructures of non-oxidized and oxidized alloys of Cu-Se with 1.65 mas% Se are presented. On the sample, which was oxidized at 800 °C the multiphase

structure of the inclusion was observed, that confirms it was partly oxidized. At 1000 °C partly oxidized inclusions are seen on the edge and in the middle of the sample. Inclusions on the edge are more oxidized than those in the middle.

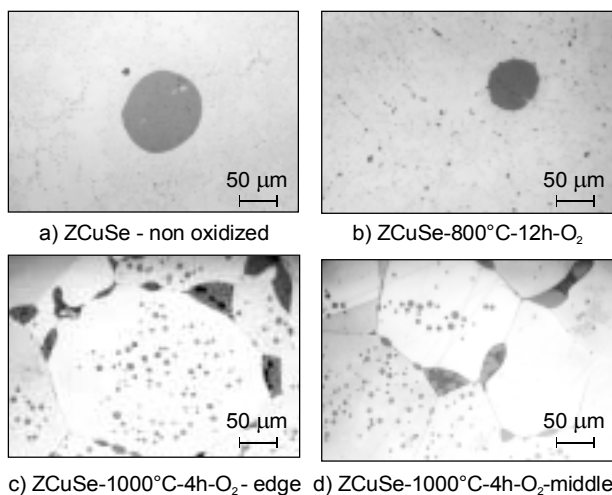


Figure 7. Microstructure of the inclusions in the sample of Cu-Se at different temperatures of oxidation (optical microscope)
 Slika 7. Mikrostruktura uključka u uzorku ZCu-Se na različitim temperaturama oksidacije (optički mikroskop)

The distribution of the elements was observed on the inclusion of the ZCuSe-1000 °C-4h-O₂ sample (Figure 8.),

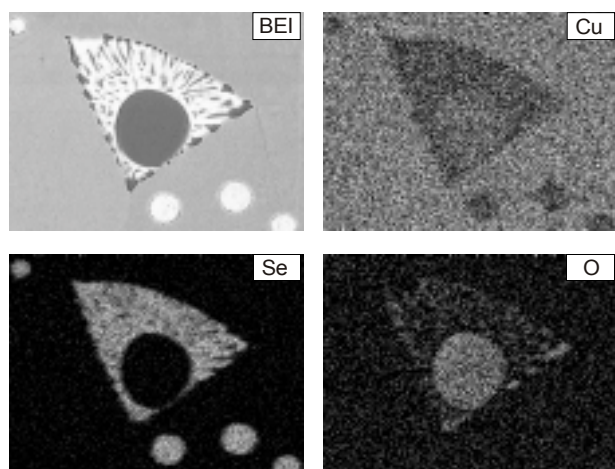


Figure 8. The distribution of the elements in the partly oxidized inclusions on the sample of ZCuSe-1000°C-4h-O₂, rob (SEM)
 Slika 8. Raspodjela elemenata u djelomično oksidiranom uključku u uzorku ZCuSe-1000°C-4h-O₂, rob (SEM)

which is located close to the sample edge, and on the BSE micrograph in the middle of the same sample (Figure 9.). It shows that the bright spots represent the copper selenide and the dark ones the copper oxide. The eutectic phase between the copper selenide and the copper oxide, which is molten at the oxidation temperature, appears in the inclusion. It is observed also, that the small inclusions, which

are located in the copper grains, are less oxidized. The inclusion in the middle of the sample is less oxidized and

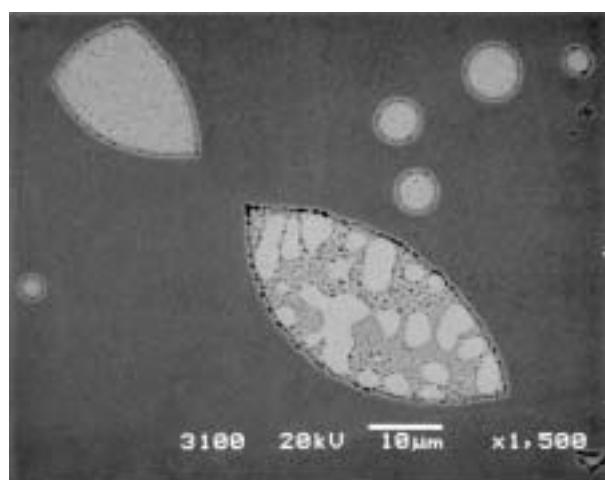
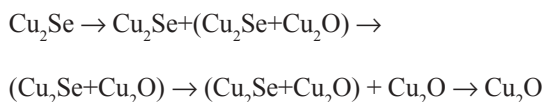


Figure 9. Partly oxidized inclusion in the sample of ZCuSe-1000°C-4h-O₂, middle
 Slika 9. Djelomično oksidiran uključak u uzorku ZCuSe-1000°C-4h-O₂, sredina

is composed by the copper selenide (bright spots) and the eutectic phase between the copper selenide and oxide (two-phase region) respectively.

From the performed investigations the mechanism of the internal oxidation of the Cu-Se alloys can be described in the similar way as it was done for the oxidation of the Cu-Te alloys [14]. The course of the oxidation of the selenide inclusion is:



where the (Cu₂Se+Cu₂O) phase is the eutectic.

Formed selenium diffused on the surface of the copper matrix and then it oxidized with the atmospheric oxygen. Such course of the internal oxidation of the Cu-Se alloys was confirmed by the thermodynamic calculations and by the oxidation experiments of the model and of the real alloy respectively.

CONCLUSIONS

The surface and the internal oxidation respectively are often present in the Cu - Se system if the oxygen partial pressure is sufficiently high. The reactions between all known components have been considered by thermodynamic calculations of the Cu-Se-O system. Such calculations enable us to establish which compounds are stable and which reactions proceed in this temperature range. On the surface of the Cu-Se alloy the reactions between copper oxides and

the selenides are possible, where the copper oxide and SeO_2 are formed. Thermodynamically the most probable are the decomposition of copper selenides and oxidation of copper into Cu_2O inside of the alloy respectively.

In oxidation of the Cu-Se alloy model with one single inclusion the diffusion of selenium through the copper has been observed which caused the formation of copper selenide inclusions in the copper matrix. Partial oxidation of the inclusion inside of the copper tube and also in the copper matrix has been observed. In our investigation it was established, that on the inclusion site the internal oxidation of the selenide was taking place by the formation of the copper oxide, and the selenium was diffusing towards the surface of copper, where it oxidized.

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