



# PHYSICO-CHEMICAL BEHAVIOR IN CO-SEGREGATION OF IMPURITIES AT THE SURFACE OF POLYCRYSTALLINE COPPER

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# Abstract

In this work, and in the temperature range of 300 to 875 K, The co-segregation of sulfur, carbon and phosphorus is treated at the surface of polycrystalline copper. We found that at high temperature, the sulfur surface concentration reaches 26%. Equilibrium and non equilibrium surface segregation energetic properties of sulfur were calculated after carrying out tests. Diffusion activation energy in the surface layer is  $E=136\pm15$  kJ/mol. within the inspected temperature range, we have settled the diffusion equation for sulfur in the surface sublayer of copper.

Keywords: co-segregation, diffusion, AES analysis, grain boundaries, sulfur, copper.

# 1. INTRODUCTION

It is well known that free surfaces and grain boundaries of materials are commonly the location of impurity segregation, regardless of their presence in small quantities in the bulk [1, 2]. The amount of these impurities at the surface might be multiples of the one in the bulk, and this particularity affects considerably the proprieties of the material [3]. Sulfur segregation principally changes the electronic emission propriety of the material, and also leads to the embrittlement of metals and their alloys. To estimate the surface composition, we often adopt the non destructive method of Auger electron spectroscopy (AES). From technologic and methodological point of view the study of the co-segregation of impurities at the surface of metals is a very important contemporary topic. In the case of copper surface cosegregation of species has been studied in many works [4-6], and it was shown that the surface equilibrium segregation at high temperature is defined by several parameters. Among these parameters we can mention the arrangement mode of the impurities and their concentration in the bulk, the sample structure, the crystallographic orientation of the grains etc...

When studying the segregation phenomenon we always focalize on the chemical composition and the structure of the surface as well as the kinetics of the process. A good knowledge of segregation kinetics leads to the determination of the main parameters of the ultrathin layer of the surface (some nanometers thickness) such as the diffusion coefficient of the segregated elements and the segregation activation energy [7].

the present work concerns the study by AES of the co-segregation of sulfur, carbon and phosphorus at the free surface of polycrystalline copper as well as the segregation kinetics of sulfur in the temperature range T= 300 to 875  $^{\circ}$ K.



## 2. EXPERIMENT

The studied material is composed of 99,7% of polycrystalline Cu, and other impurities including sulfur (~0,006%) and phosphorous (~0,004%). The samples were cut to a dimension of 8 mm x8 mm x2 mm by electroerosion. They have undergone a mechanical and electrochemical polishing, followed by an ultimate in-situ ionic abrasion by argon ions with an energy going from 500 to 1000 eV and a sample current density about 10-50  $\mu$ A/cm<sup>2</sup>. The AES analysis has been carried out in advanced ultrahigh vacuum (~10<sup>-8</sup> Pa) with a retarding grid analyser. The sulfur concentration at the surface is calculated on the base of Auger transition spectra of low energy: M<sub>2,3</sub>M<sub>4</sub>M<sub>4</sub> (60eV) Cu, LMM (120 eV) P, LMM (152 eV) S and KLL (272 eV) C, which correspond to an analysis depth of about 1 nm.

# 3. RESULTS AND DISCUSSION

The variation of the chemical composition of the surface with respect to the temperature  $X_S^{\sigma}(T)$  (S referring

to Sulfur and  $\sigma$  to the surface) with a step of 50° is calculated using the Auger spectra obtained upon analysis of the sample for different temperatures (figure 1). For each temperature, the duration maintaining time is such as we obtain a regular amplitude of the Auger spectrum so that a constant surface concentration is established. At that moment, we suppose that the surface layer is in equilibrium with the bulk phase. The results of the calculations of the chemical composition of the surface of polycrystalline copper are presented in figure 2.



**Fig. 1.** Auger spectra of copper surface in various conditions: **a** - immediately after introduction in the Auger spectrometer **b** - after argon ion-abrasion (energy argon ions of 1000 eV within 30 min.). **c**-heating at T = 575 K. **d** - heating at T = 875 K, primary electron beam energy Ep = 1800 eV, Ip = 20  $\mu$ A, voltage modulation Um = 3V.



Figure 1 shows that the gradual heating of copper surface leads to the segregation of S, C and P. The intensity of the Auger lines of sulfur and carbon starts to drop at the temperature range 425-475 °K (figure 2, curves 1 and 2). In contrast, the phosphorus one increases by T $\geq$ 570 °K (figure 2, curve 3). According to Auger spectra data, the surface concentration of sulfur at temperature 575 K is ~12%, and attains ~26% at 875 K. the surface composition of phosphorus in the temperature range 570 – 780 K is ~1 to 2%. Away from 780 K the phosphorus pick vanishes completely, which translates its replacement by sulfur atoms. The amount of carbon at copper surface rises slowly and stabilizes at ~10% going from 625 K. According to literature data [6], phosphorus being a less strong segregating than to S and C, it diffuses first to the surface, and when the temperature increases, we note the presence of the strongest segregating S and C, forming thus with copper a metallic compound Cu<sub>2</sub>S at the surface. In our case, such compound is not noticed despite a surface concentration of sulfur at high temperature close to the copper sulfide stoechiometry.



Fig.2. Surface concentration in polycrystalline copper for different heating temperatures: 1 - S, 2 - C, 3 - P

We have followed the MacLean model [9] to study the segregation kinetics for sulfur. Auger spectra of Cu and S are registered in time lapses during the isotherm maintaining process at a given temperature. From to the obtained results, we have plotted the variation of sulfur surface concentration with respect to the heating

 $C_{s} = \frac{X(t) - X(0)}{X(\infty) - X(0)}$  time  $X_{S}^{\sigma}(T)$ , as well as the variation of the sulfur surface relative concentration with respect to the square root of t [10]: (1)

where X(0) s the mole fraction of the component in the interphase at the starting time, X(t) and  $X(\infty)$  are respectively the mole fractions at instant t and at equilibrium state. The sulfur concentration profiles obtained by the isotherm heating of copper with respect to the maintaining time are presented in figure 3.





Fig.3. Surface sulphur concentration with time at different heating temperatures

Curves in figure 3 can be divided into two zones, each one corresponding to a defined process. The first zone is characterized by a rapid raise of the surface concentration of sulfur when temperature increases as well as by a saturation value of the concentration. In this zone the concentration varies proportionally to  $\sqrt{t}$ . The second zone traduces more complex processes at the surface of the metal (related to the possibly formation of sulfides), that are followed by a slow increase in the impurity concentration and end up when the concentration stabilizes at  $X_S^{\sigma}(T)$ . With the increase of the temperature, the shift from the first zone to the second one becomes much noticeable.

Surface segregation kinetics permits to calculate the diffusion coefficient of the impurity during the process of segregation as well as its activation energy. For small time lapses of the process [10]:

$$C_{S} = \frac{\left[X(t) - X(0)\right]}{\left[X(\infty) - X(0)\right]} = k\sqrt{t}$$
(2),

where  $k = \frac{2b^2}{\beta a^3} \sqrt{\frac{D}{\pi}}$  is the coefficient of the proportionality ( $\beta$  the saturation coefficient in the interface, a

and b are the dimensions of the solute bulk atoms). The values of the coefficient k for each heating temperature can be obtained by plotting the variation of the sulfur concentration with respect to  $\sqrt{t}$ . Thus, the diffusion coefficient is calculated using the following equation:

$$D = \frac{\pi a^6 \beta^2 k^2}{4b^4} \tag{3}$$

The first zone of the four curves in figure 3 can be presented otherwise. By dividing each concentration in this zone by the highest saturation concentration (which corresponds to the saturation at 875 K), we plot the variation of these normalized concentrations with respect to  $\sqrt{t}$  (figure 4).





Fig.4. Variation of the normalized surface concentrations of sulfur Cs with respect to the square root of time

The segregation activation energy *E* can be estimated using Arrhenius law:

$$D = D_0 \, \exp\!\left(-\frac{E}{RT}\right) \tag{4}$$

We plot the curves of the variation of the diffusion coefficient *D* with respect to 1/T in logarithmic scale for the different considered heating temperatures (figure 5). The obtained value of the activation energy for sulfur diffusion during its segregation at the polycrystalline copper surface is  $E=136\pm15$  kJ/mol. The value of the diffusion coefficient  $D_0$  is 3,4 10<sup>-3</sup> cm<sup>2</sup>/s. Thus, in the temperature range 675-875 K, we can express the diffusion equation as follows:





A comparative analysis of the obtained results is difficult due to the lack in works for sulfur diffusion kinetics in copper, in addition to the non reliability of the values of the diffusion coefficient found in literature. For



solids, such data are valid, in the best cases, at one order of magnitude [11]. This diffusion coefficient in monocrystals is generally much less (by some orders of magnitude) than in polycrystals. Moreover, bulk diffusion near to the surface layer depends on the microstructure of this layer. Thus, in CFC structures the calculated value of the (110) grain energy is higher than the (111) grain one, which leads to values very different of the energies of bulk gap formation [12]. This energetic approach permits to estimate the bulk concentration of gap equilibrium, and consequently, the bulk diffusion coefficient. The results in [13] show close values of sulfur diffusion coefficient and the diffusion of copper itself, which gives evidence of gap diffusion mechanism of sulfur. According to data in [14] the activation energy of the bulk autodiffusion in monocrystalline copper is  $E_s$ =189 kJ/mol. For the surface case and according to the crystalline orientation, this activation energy varies from 100 to 164 kJ/ mol.

By the method of isotopic tracers, and for T $\geq$ 1100 K, a temperature dependence of the sulfur diffusion coefficient in monocrystalline copper has been established In the works of Ladet [15], with an activation energy E<sub>S</sub>=1,8 eV/atom. It has been shown that for lowest temperatures, the influence of dislocations on the sulphur diffusion is much conspicuous than in the case of autodiffusion. This difference corresponds to the effect of sulfur segregation to the dislocations. A much closer value of the diffusion activation in monocrystalline copper has been obtained in [16]: E<sub>S</sub>=165 kJ/mol. According to authors in [16], sulphur forms with copper a solid solution and diffuses through the gaps.

### CONCLUSION

By comparing the results of our work obtained for the copper surface of nanometric thickness (figure 3) with the data mentioned in literature for the sulfur bulk diffusion in copper we have noted that at high temperature, the value of diffusion coefficient calculated according [16] has a magnitude higher than our value. At low temperatures, the two values converge. The small value of the activation energy obtained in our work compared to that in [16] can be related to the effect of the surface.

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