

## INTERNAL OXIDATION OF SILVER ALLOYS WITH TELLURIUM, SELENIUM AND SULPHUR

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Silver alloys with tellurium, selenium and sulphur fulfil the conditions for the internal oxidation. Microstructure of these alloys consists of matrix (dilute solid solution) and particles of intermetallic compounds. Internal oxidation of ternary alloys is very similar to that of the binary alloys, but there are also distinctions in thermodynamics properties of alloying elements.

At the direct oxidation of the particles of the intermetallic compound the phenomena of the selective oxidation was observed. Concentration of more reactive elements is increasing in the oxidized part of the particles of the intermetallic compound (Te in AgTeSe alloys). Therefore the precipitated oxides formed with diffusional internal oxidation are richer with less reactive alloying element (Se in AgTeSe alloy). In the precipitated oxide particles the concentration of selenium is more than twice higher than of tellurium.

**Key words:** internal oxidation, silver, alloy, compound, particle

**Unutarnja oksidacija legura srebra s telurom, selenom i sumporom.** Legure srebra s telurom, selenom i sumporom ispunjavaju uvjete za unutarnju oksidaciju. Mikrostruktura ovih legura sastoji se od osnove (razrijeđena kruta otopina) i čestica intermetalnih spojeva. Unutarnja oksidacija ternarnih legura veoma je slična onoj za binarne legure, ali postoje i razlike u termodinamičkim svojstvima legirajućih elemenata. Kod izravne oksidacije čestica intermetalnog spoja zapažena je pojava selektivne oksidacije. Koncentracija reaktivnijih elemenata raste u oksidiranom dijelu čestica intermetalnog spoja (Te u AgTeSe leguri). Prema tome precipitirani oksidi nastali difuzijskom unutarnjom oksidacijom su bogati s manje reaktivnim legirajućim elementom (Se u AgTeSe leguri). U percipitiranim oksidnim česticama koncentracija selena je dvostruko veća nego telura.

**Ključne riječi:** unutarnja oksidacija, srebro, legura, spoj, čestica

### INTRODUCTION

Silver alloys with tellurium, selenium or sulphur fulfil the conditions for the internal oxidation [1], but the ternary alloys with two of these elements realize the conditions of the so-called selective internal oxidation, although the internal oxidation is selective itself [2, 3]. Gibbs free energies (Figure 1.) of the discussed elements [4] are one of the selectivity indicators, though they could be double or triple oxides at the internal oxidation, respectively [5].

Low-alloyed binary and ternary silver alloys are two-phase with these elements. The microstructure of these alloys consists of the metal matrix, which is very diluted

solid solution of the silver and the intermetallic compounds [6]. They are compounds of silver with the alloying element in the binary alloys, and the solid solutions of the binary compounds [e.g.  $\text{Ag}_2(\text{Te, Se})$  and  $\text{Ag}_2(\text{Te, S})$ ] in the three-component alloys [7].

### EXPERIMENTAL WORK AND DISCUSSION

For the experiments the three-component silver alloys in combination with two alloying elements of Te-Se, Te-S and Se-S were made, thus the concentrations of the alloying elements were equal, but the common one was 1,3 mol % [8].

Internal oxidation of two or multi-phase silver alloys was taking place on two ways [9]:

- by the direct oxidation of the particles of the intermetallic compounds, and
- by the diffusional oxidation of the alloying elements of the solid solution.

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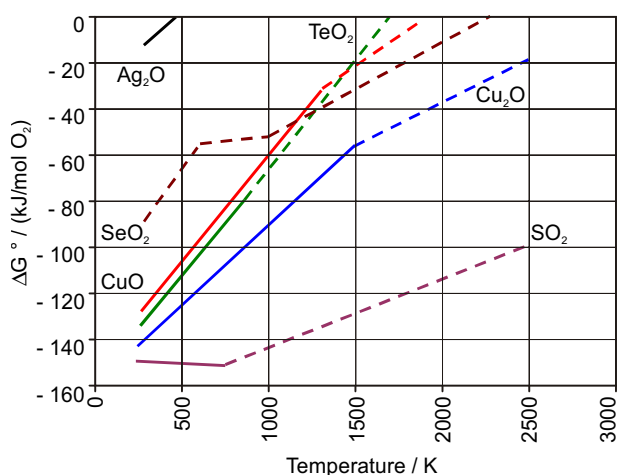


Figure 1. Gibbs free energies  
Slika 1. Gibbsove slobodne energije

The products of the direct oxidation are essentially larger than the oxides, which were precipitated from the solid solution.

The oxidation was taking place between 750 and 830 °C, where the molten products were also formed, which mainly affected on the progress of the oxidation [10]. Such cases are frequently characterized as the catastrophic oxidation [11].

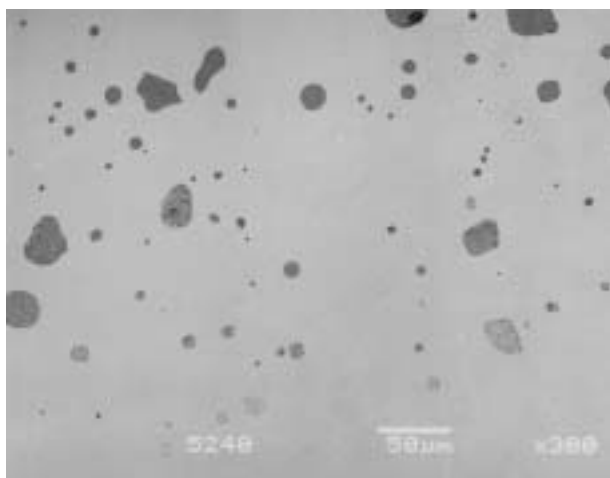


Figure 2. Widened front of the direct oxidized particles zone of the intermetallic compound in the AgTeSe alloy (830 °C, 4 h). SEM (PSE)

Slika 2. Prošireni front zone izravno oksidiranih čestica intermetalnog spoja u AgTeSe leguri (830 °C, 4 h), SEM (PSE)

In the AgTeSe alloy the direct oxidation starts with the preferential tellurium oxidation in the  $Ag_2(Te, Se)$  ternary intermetallic compound. The concentration of tellurium in the oxide is increasing, and likewise of the selenium in the non-oxidized part of the intermetal compound (between the solid silver selenide and telluride is the complete solubility respectively - isomorphous phase diagram).

In Figure 2. the part of alloy, in which the direct internal oxidation was taking place, is seen, where partly oxidized particles of the intermetallic compound are present. The chemical composition of the oxidized part (dark part) is: 59,36 wt. % Ag, 34,37 wt. % Te and 5,91 wt. % Se, but in the light non-oxidized part is: 62,53 wt. % Ag, 5,66 wt. % Te and 31,81 wt. % Se, and in the single-phase completely oxidized particle is: 63,48 wt. % Ag, 18,72 wt. % Te and 17,80 wt. % Se.

The fine oxidized precipitate formed by the diffusional internal oxidation has the following chemical composition of 70,66 wt. % Ag, 9,18 wt. % Te and 20,15 wt. % Se. For comparison the composition of one single particle of the intermetallic composition is as follows: 64,14 wt. % Ag, 16,78 wt. % Te and 19,08 wt. % Se.

In the AgTeS alloy (Figures 3., 4.) the sulphur is the most reactive element, therefore it starts to oxidize first. The remaining part of the particles of the intermetallic phase is rich on the tellurium, since the sulphur oxides form the new gas phase.

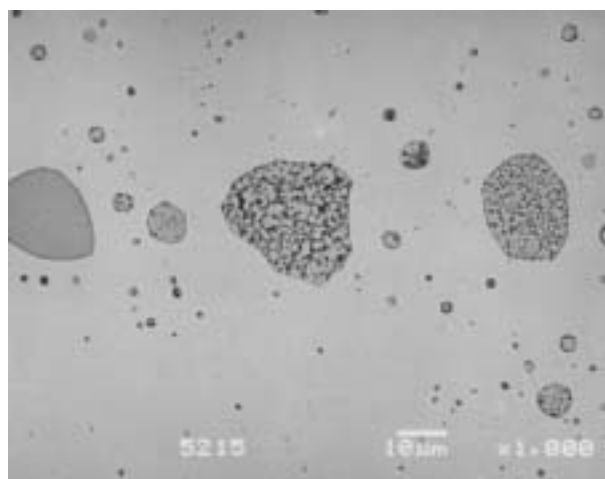


Figure 3. The group of the partially oxidized particles of the intermetallic compound of the AgTeS alloy in the zone of the internal oxidation (830 °C, 4 h). The average chemical composition of the particles is as follows: (left dark particle: 80,12 wt. % Ag, 19,88 wt. % Te) and (the particle in the middle - dark net: 74,81 wt. % Ag, 22,63 wt. % Te, 2,56 wt. % S); SEM (PSE)

Slika 3. Grupa djelomično oksidiranih čestica intermetalnog spoja AgTeS legure u zoni unutarnje oksidacije (830 °C, 4 h). Prosječni kemijski sastav čestica je slijedeći: (lijeva tamna čestica: 80,12 wt. % Ag, 19,88 wt. % Te, a tamne čestice u sredini: 74,81 wt. % Ag, 22,63 wt. % Te, 2,56 wt. % S), SEM (PSE)

After the completed direct oxidation of the particles of the  $Ag_2(Te, S)$  intermetallic phase the minimal sulphur concentration or zero one in the oxide was observed respectively. But in the metal matrix the fine gas pores were not observed, which should indicate the formation of the sulphur oxides after the diffusional mechanism.

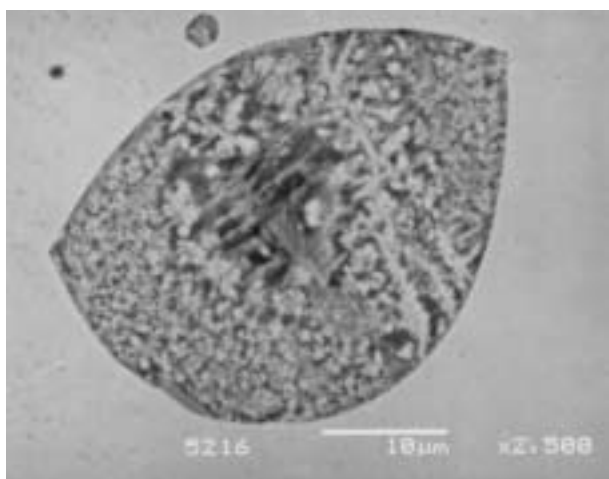


Figure 4. **Partially oxidized particle of the intermetallic compound in the middle of the sample of the AgTeS alloy (830 °C, 24 h); SEM (PSE)**

Slika 4. **Djelomično oksidirana čestica intermetalnog spoja u sredini uzorka AgTeS legure u zoni unutarnje oksidacije (830 °C, 4 h); SEM (PSE)**

Likewise in the AgSeS alloy (Figure 5.) the sulphur is most reactive element. Sulphur oxidized the first and so the gaseous oxides were formed, which were created in the contact with the intermetallic phase particles. In the AgTeS al-

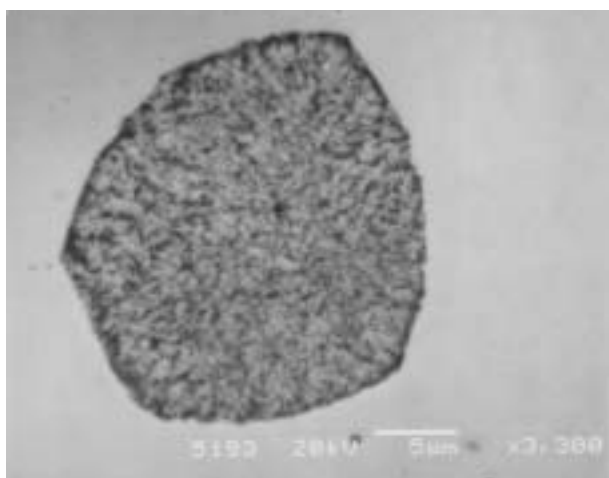


Figure 5. **Partially oxidized particle of the intermetallic compound in the AgSeS alloy (830 °C, 2 h); SEM (PSE)**

Slika 5. **Djelomično oksidirana čestica intermetalnog spoja u AgSeS leguri (830 °C, 2 h); SEM (PSE)**

loy the sulphur is the most reactive element, therefore it starts to oxidize first. The remaining part of the particles of the intermetallic phase is rich on the selenium, thus sulphur concentration is low or even zero at the last stage respectively. The fine gaseous precipitates formed by the direct oxidation were also not observed at that alloy.

The same mechanism of the oxidation is taking place for the alloys with sulphur, but it differs for the AgTeSe alloys. At the direct oxidation of the AgTeSe alloys the tellurium oxidizes first and the non-oxidized part of the particles of the intermetallic compound becomes richer on the selenium, therefore the concentration and the activity of the selenium in the solid solution are increasing. Therefore one part of the selenium is dissolved in the silver phase, but on the contrary the activity of tellurium in the oxide is decreasing and part of it diffuses into the oxidized particle of the intermetallic phase. Thus the solid solution becomes richer on the selenium and poorer on the tellurium. Therefore the oxides formed by the direct oxidation are richer on tellurium, and those formed by the diffusional oxidation are richer on the selenium.

## CONCLUSIONS

At both alloys the sulphur is the most reactive element, which oxidizes first at the direct oxidation. It creates the independent gaseous phase of its oxides and thus it is extracting from the particles of the intermetallic compound, which becomes richer either on the tellurium or on the selenium. Therefore the oxides formed by the direct oxidation are  $\text{Ag}_2\text{SeO}_3$  or  $\text{Ag}_2\text{TeO}_3$  and the gaseous pores of the sulphur oxides at the final stage of the oxidation. The diffusional formed oxides are not gaseous at the direct oxidation probably due to the sulphur oxidation from the solid solution on the large gaseous pores.

That explanation is supported by the relatively high diffusional rate of the sulphur in the silver phase and by the high energy, which is needed for the creation of the gaseous pores in the solid metal matrix.

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