

INTERNAL-OXIDATION KINETICS OF Ag-Cd ALLOYS

KINETIKA NOTRANJE OKSIDACIJE ZLITIN Ag-Cd

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The oxidation kinetics of the Ag-Cd alloys with different Cd contents in mass fractions (9.5, 11, 12 and 16) % at (670, 750 and 795) °C during the production of Ag-CdO electrical-contact materials was investigated. It was found that the internal oxidation of the investigated Ag-Cd alloys generally follows the parabolic-rate law for all the applied oxidation times (5, 9.5, 20.5, 36 and 48) h. The parabolic-rate-law constant for the measured oxide-thickness gain was evaluated at every examined temperature and the Arrhenius-type equations were determined in order to describe the temperature dependence of the rate constants. Microstructures of the obtained Ag-CdO electrical-contact materials were investigated using a SEM-EDS analysis and the microstructure of a sample produced under the optimum process conditions is illustrated with the corresponding micrographs and chemical compositions.

Keywords: Ag-Cd oxidation kinetics, internal oxidation, electrical-contact materials, microstructure

Med proizvodnjo materialov Ag-CdO za električne kontakte je bila preiskovana kinetika oksidacije zlitin Ag-Cd z različno vsebnostjo masnih deležev Cd (9,5, 11, 12 in 16) % pri (670, 750 in 795) °C. Ugotovljeno je bilo, da se notranja oksidacija preiskovanih zlitin Ag-Cd ujema z zakonom parabolične odvisnosti hitrosti pri vseh časih oksidacije (5; 9,5; 20,5; 36 in 48) h. Konstanta parabolične odvisnosti hitrosti naraščanja debeline oksida je bila določena pri vsaki temperaturi preizkusa, prav tako je bila določena Arrheniusova vrsta enačbe za opis temperaturne odvisnosti konstant hitrosti. Mikrostruktura dobljenega materiala Ag-CdO za električne kontakte je bila preiskovana s SEM-EDS-analizami. Prikazana je bila mikrostruktura in narejena kemijska analiza vzorca, izdelanega v optimalnih razmerah.

Ključne besede: kinetika oksidacije Ag-Cd, notranja oksidacija, materiali za električne kontakte, mikrostruktura

1 INTRODUCTION

In the electrical industry most of the contact applications use the materials based on silver that include a combination of pure metals, alloys and metal powders. Silver is also used as a plated, brazed, or mechanically bonded overlay on copper and copper-based materials due to its high thermal and electrical conductivities.

When considering that electrical-contact materials are used in diverse service conditions and also that no metal has all the properties required to accomplish the objectives of different contact applications, in addition to the silver-type contacts, other types of contacts based on platinum-group metals, tungsten, molybdenum, copper, copper alloys and mercury can be found in the electrical industry.

The usefulness of an electrical-contact material also depends on a variety of electrical and mechanical properties, service life, load conditions and economical reasons.¹⁻⁵

The Ag-Cd groups of the contact alloys are widely used in tonnage quantities in the electrical and electronics industries because of their high electrical and thermal conductivities, high resistance to arcing, high welding-adhesion resistance, low-contact resistance, high hardness and strength. Cadmium improves the arc-quenching ability of silver and also increases its resistivity and mechanical strength.⁶⁻⁸

Silver cadmium oxide can be obtained using internal oxidation and powder metallurgy, and the manufacturing method has a significant influence on the properties and microstructure of this material.⁹

In the case of the internal-oxidation process, oxygen diffuses into an alloy and causes a sub-surface precipitation of the oxides of one or more alloying elements, which was the subject of the reviews by Birks et al.¹⁰

The process of internal oxidation occurs in the following manner: oxygen dissolves in the base metal and diffuses inward through the metal matrix containing previously precipitated oxide particles. The critical activity product for the nucleation of the precipitates is established at the reaction front (parallel to the specimen surface) with the inward-diffusing oxygen and the outward diffusion of the solute. When the rate-controlling step in the oxidation process is the diffusion of ions through a compact barrier layer of the oxide with the chemical potential gradient as the driving force, the parabolic-rate law is usually observed.¹¹ As the oxide grows thicker, the diffusion distance increases and the oxidation rate slows down.

The results of the investigation of the oxidation-layer-thickness dependence on the temperature and time of the oxidation for the Ag-Cd alloys with different contents of Cd are presented in this paper. Previous investigations have shown that the oxidation process in this alloy has a parabolic behavior according to the

theoretical relation between the parabolic-rate constant of the metal oxidation and the self-diffusion coefficients in the oxide layer growing on the metal surface, given by Wagner.¹² But, Wagner's general equation in its original form could only be applied to the cases, in which the dependence of the self-diffusion coefficient on the equilibrium partial pressure of the oxidizer was known a priori.

Therefore, since the thickness of the oxide layer depends on the oxidation rate and the oxidation rate is directly correlated with the temperature, the oxidation time and the oxygen pressure, the Arrhenius equation, being widely used to describe the temperature dependence of the kinetic constants, was used for determining the activation energy for the oxidation processes in the studied Ag-Cd alloys.

2 EXPERIMENTAL PROCEDURE

Silver cadmium alloys with mass fractions (9.5, 11, 12 and 16) % of Cd were prepared using the Ag and Cd metals of 99.99 % purity. The alloys were first cast into ingots and then plastically deformed, at low temperatures, into the strips with a thickness of 2 mm. The prepared silver cadmium alloys were heated in an electro-resistive oven in air atmosphere under natural convection at the temperatures of 670 °C, 750 °C and 795 °C during (5; 9.5; 20.5; 36 and 48) h. The micro-structure observation and measurements of the thickness of the oxidized layer were done on the polished cross-sections of the investigated samples using a scanning electron microscope JEOL-JSM-6610LV with an energy dispersive spectrometer (EDS) and a metallographic microscope REICHART of the POLYVAR – MET type.

3 RESULTS AND DISCUSSION

3.1 Oxidation rate

The samples were measured before and after the internal oxidation. The graphic dependence of the relative change in the weight after (5, 9.5, 20.5, 36 and 48) h of the oxidation of the silver cadmium alloys with mass fractions (9.5, 11, 12 and 16) % of Cd is presented in **Figure 1a**. The inner oxidation of the Ag alloys with different Cd contents generally follows the parabolic-rate law for the examined time range up to 48 h at the temperature of 750 °C. In **Figure 1b** it can be seen that 60 % of Cd was oxidized after a 20.5 h oxidation of the silver cadmium alloy with 9 % Cd.

3.2 Oxidation kinetics

During the internal oxidation of the silver cadmium alloy, the cadmium species become depleted in the zones when the oxygen front moves into the silver cadmium alloy. As the oxidation front moves from the surface of

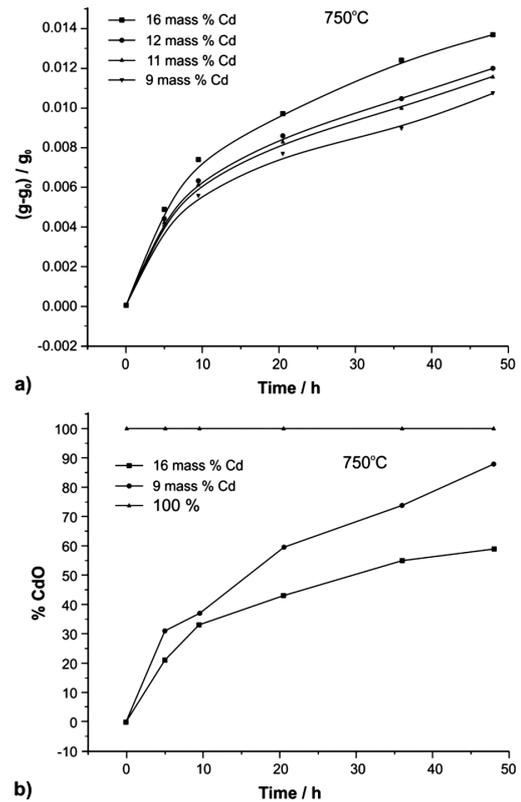


Figure 1: a) Dependence of the relative mass change during the oxidizing for the Ag-Cd alloys with different Cd contents at 750 °C; b) extent of the Cd oxidation for the Ag-Cd alloys with 9 % and 16 % Cd at 750 °C

Slika 1: a) Odvisnost relativne spremembe mase med oksidacijo zlitin Ag-Cd z različno vsebnostjo Cd pri 750 °C, b) delež oksidacije Cd v Ag-Cd zlitinah z 9 % in 16 % Cd pri 750 °C

the strip toward the center, the concentration of the cadmium species becomes increasingly dilute as compared to the original composition. Hence, after the oxidation is completed, the cross-section will display a significant oxide-deficient or oxide-depleted zone in the center of the contact body. For some applications the presence of the depletion zone is detrimental, requiring its removal or displacement from the center. There are two common methods to achieve such a result. The first method takes account of the fact that an oxidation barrier, such as a ceramic glaze, is applied to one surface so that the oxidation can proceed only from one side. The second method is to laminate two silver cadmium sheets of the same size and to form a package by welding them along all four edges. After the oxidation, the sheets are separated. The oxide-deficient zone will appear on one side (the inner side of the package) of each sheet.^{5,12}

Figure 2 shows the dependence of the thickness of an oxidized layer for different Cd contents in the Ag-Cd alloys. After comparing the changes in the thickness of the oxidized layer with the temperature and time, it is obvious that the oxidation rate is the highest for the alloy with the smallest amount of Cd and the lowest for the alloy with largest amount of Cd.

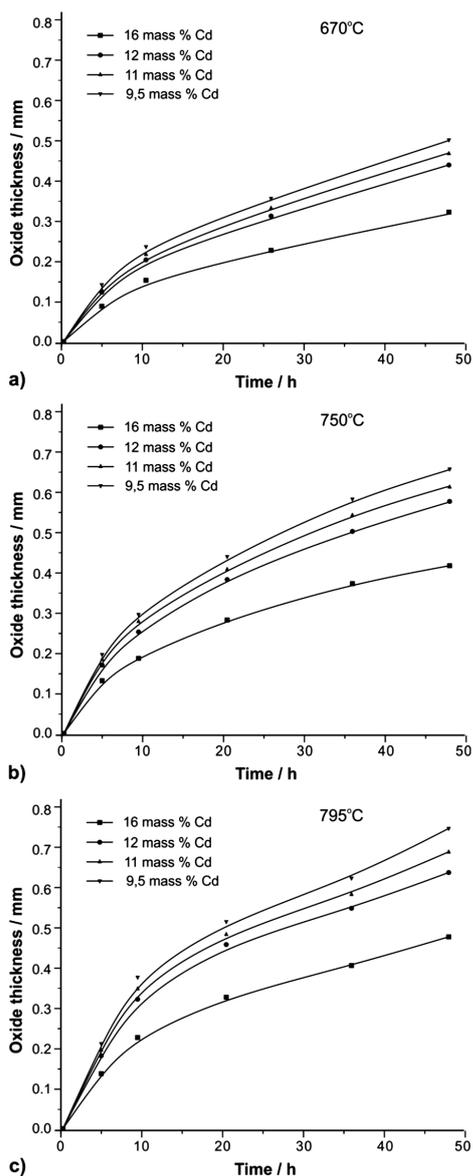


Figure 2: Dependence of the thickness of an oxidized layer for Ag-Cd alloys with different Cd contents; inner oxidation at: a) 670 °C, b) 750 °C and c) 795 °C

Slika 2: Odvisnost debeline oksidirane plasti pri zlitinah Ag-Cd z različno vsebnostjo Cd; notranja oksidacija pri: a) 670 °C, b) 750 °C in c) 795 °C

A mass content of 9–12 % of CdO in the Ag-CdO alloys successfully creates a decrease in the deformation and devastation of electrical contacts. With the concentrations of CdO above 12 %, an inner break is possible due to an intension caused by an increase in the grain diameter after the oxidation. The main difference is that the elevated temperatures promote ionic diffusion and, thus, the oxide formation can proceed to a much greater extent than at the low temperatures where only thin layers are formed.

The dependence of the scale thickness on the time can be used for determining the kinetic law for the oxidation rate. As the oxidized layer grows thicker, the

diffusion distance increases and the oxidation rate slows down. The rate (dx/dt) is inversely proportional to the oxide thickness (x) or:

$$\frac{dx}{dt} = \frac{k_p}{x} \quad (1)$$

Equation (1) can be rewritten as:

$$x dx = k_p dt \quad (2)$$

Upon an integration of equation (2):

$$\int_{x=0}^{x=x} x dx = \int_{t=0}^{t=t} k_p dt \quad (3)$$

On integration, the parabolic equation is obtained:

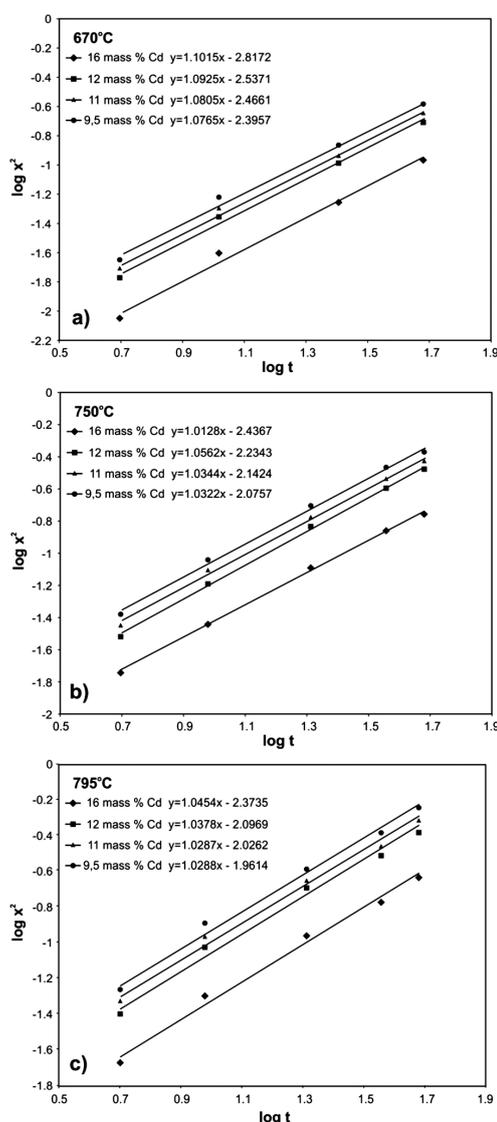


Figure 3: Logarithm of the oxide thickness versus the logarithm of the oxidation time for the Ag-Cd alloys with different Cd contents at: a) 670 °C, b) 750 °C and c) 795 °C

Slika 3: Logaritmem debeline oksida v primerjavi z logaritmom časa oksidacije za zlitine Ag-Cd z različno vsebnostjo Cd pri: a) 670 °C, b) 750 °C in c) 795 °C

$$x^2 = 2k_p t + c \quad (4)$$

and the parabolic-rate constant, k_p , can be determined from the experiment in the units of $\text{cm}^2 \text{s}^{-1}$ or a similar length squared per time units:^{12,13}

If one takes the logarithm of both sides of equation (4), the following is obtained:

$$\lg x^2 = \lg k_p + \lg t \quad (5)$$

A plot of $\lg x^2$ versus $\lg t$ can be done linearly and the parabolic-rate constants can be determined for the reaction carried out at several temperatures. The intercept of the line is $\lg k_p$.

The logarithm of the oxide thickness as a function of the logarithm of the oxidation time for the Ag-Cd alloys with different Cd contents at the investigated temperatures is presented in **Figure 3**, while the dependence of the parabolic-rate constant as a function of the inverse temperature oxidation of the Ag-Cd alloys with different Cd contents is shown in **Figure 4**.

This indicates that the thermal diffusion process is rate controlling, with oxygen or cations or both diffusing through a compact layer. The rate of diffusion through an oxide film depends on a number of factors, such as the temperature, oxygen partial pressure and structure of the oxide.¹²⁻¹⁴

At the temperatures higher than the melting point of a metal, the lattice diffusion dominates through the crystalline oxide formed on the metal and, at the lower temperatures, the diffusion via the oxide-grain boundaries is predominant. In this case, the rate of oxidation of a metal or alloy depends on the oxide-grain size, which is often dictated by the substrate-grain orientation, surface pretreatment, etc.⁹ A deviation from the parabolic-oxidation behavior is often observed and can be a result of the oxide-grain-size change with time and at a particular temperature. In this case, the number of oxide-grain-boundary 'easy diffusion paths' decreases

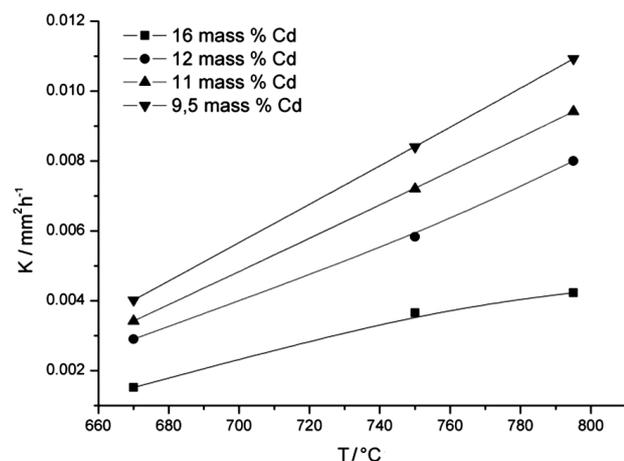


Figure 4: Dependence of parabolic-rate constants versus temperature oxidation of the Ag-Cd alloys with different Cd contents

Slika 4: Odvisnost konstant paraboličnih hitrosti od temperature oksidacije zlitin Ag-Cd z različno vsebnostjo Cd

with time, causing an apparent decrease in the oxidation rate. When the rate-controlling step in the oxidation process is a diffusion of ions through a compact barrier layer of oxide with the chemical potential gradient as the driving force, the parabolic-rate law is usually observed¹⁵ and then the change in the oxidation rate with the temperature will follow the Arrhenius equation:^{11,16-18}

$$k_p = A e^{-\frac{E_a}{RT}} \quad (6)$$

where k is the rate constant, A is the frequency factor (or pre-exponential factor), R is the molar gas constant, E_a is the activation energy, and T is the temperature (K). If we take the natural logarithm of both sides and the rearrangement, this equation can be put in the linear form:

$$\ln k_p = \ln A - \frac{E_a}{RT} \quad (7)$$

so that the constants can be calculated using a linear regression. This type of linearization, which allows fitting a straight line into the transformed experimental data, has been used for nearly a century.¹⁹⁻²³ Most of the constants reported in the literature were obtained using this method. And therefore, a plot of $\ln k_p$ versus $1/T$ can be made, or a linear regression performed, after the rate constants have been determined for a reaction carried out at several temperatures. The Arrhenius plot is shown in **Figure 5**. For a particular reaction, the following rate constants were obtained when the reaction was studied at a series of temperatures.

Using the data presented in **Figure 4** and the Arrhenius plot of the parabolic-rate constants for the oxidation of the Ag-Cd alloy, shown in **Figure 5**, the activation energy was calculated as $36 \pm 2 \text{ kJ/mol}$ and shown in **Table 1**.

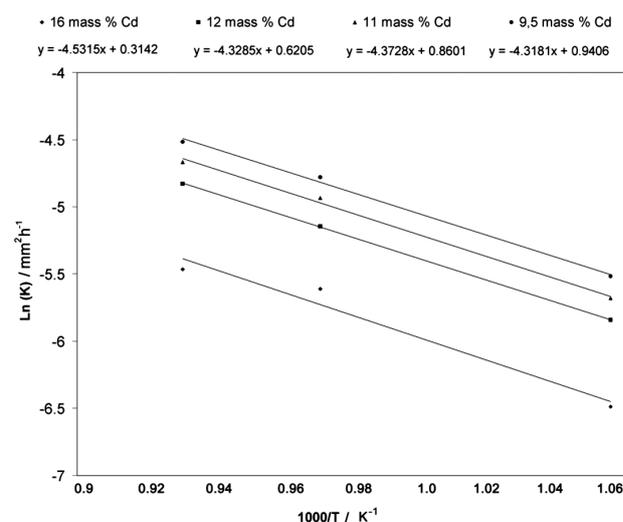


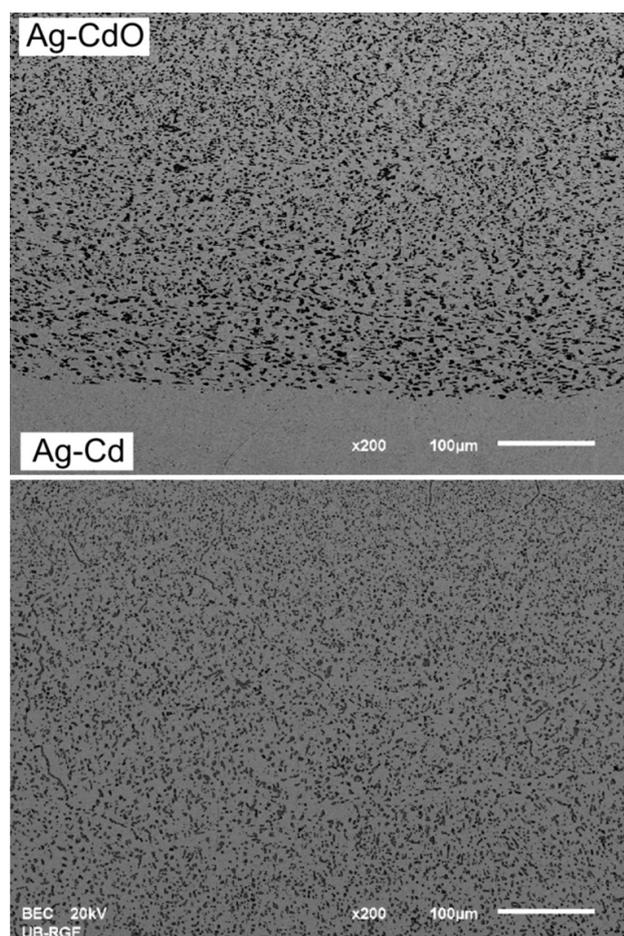
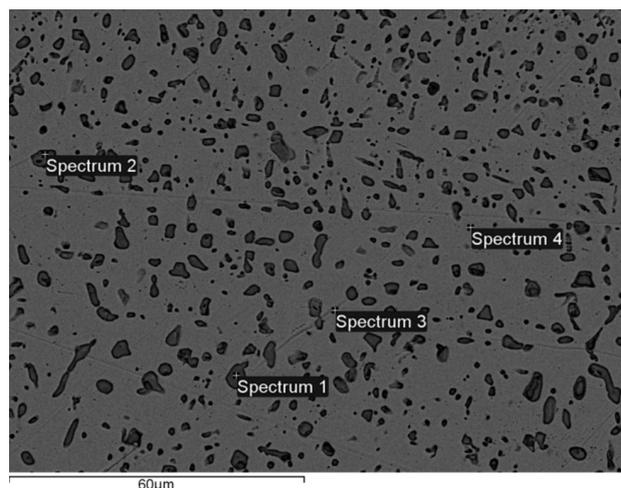
Figure 5: Logarithm of the parabolic-rate constants versus the inverse temperature for the oxidation of the Ag-Cd alloys

Slika 5: Logaritem konstant paraboličnih hitrosti v primerjavi z inverzno vrednostjo temperature pri oksidaciji zlitin Ag-Cd

Table 1: Parabolic-rate constants and activation energy of the oxidation of the Ag-Cd alloys with different Cd contents**Tabela 1:** Konstante parabolične hitrosti in aktivacijska energija zlitin Ag-Cd z različno vsebnostjo Cd

Material composition in mass fractions	K/(mm ² h)			Activation energy of oxidation kJ/mol
	670 °C	750 °C	795 °C	
16 % Cd	$1.52 \cdot 10^{-3}$	$3.66 \cdot 10^{-3}$	$4.23 \cdot 10^{-3}$	38
12 % Cd	$2.90 \cdot 10^{-3}$	$5.83 \cdot 10^{-3}$	$8.00 \cdot 10^{-3}$	36
11 % Cd	$3.41 \cdot 10^{-3}$	$7.20 \cdot 10^{-3}$	$9.41 \cdot 10^{-3}$	38
9.5 % Cd	$4.02 \cdot 10^{-3}$	$8.40 \cdot 10^{-3}$	$10.92 \cdot 10^{-3}$	36

Considering that the anti-welding behavior and wear resistance of the electrical-contact materials can be improved with a uniform dispersion of the metal oxide particles in a soft silver matrix, the ultimate goal of the investigations is an optimization of the internal-oxidation process parameters that promote the formation of the optimum microstructure, i.e., obtaining of a good and homogeneous oxide dispersion within the silver matrix.

**Figure 6:** SEM micrograph of an Ag-CdO composite obtained with the internal oxidation of the Ag-11 % Cd alloy (Ag-CdO11); a) pure Ag-Cd and an oxide layer of Ag-CdO; b) oxide layer of Ag-CdO**Slika 6:** SEM-posnetek kompozita Ag-CdO, dobljenega z notranjo oksidacijo zlitine Ag-11 % Cd (Ag-CdO11); a) čisti Ag-Cd in oksidna plast Ag-CdO; b) oksidna plast Ag-CdO**Figure 7:** SEM micrograph of a cross-section of the Ag-11 mass % Cd alloy (Ag-CdO11) with the annotated points of the EDS analysis**Slika 7:** SEM-posnetek preseka zlitine Ag-11 % Cd (Ag-CdO11) z označenimi točkami, kjer je bila izvršena EDS-analiza

As an illustration of the optimum microstructure of the Ag-CdO electrical-contact materials obtained in the process investigating the internal oxidation, a characteristic SEM micrograph of the Ag-CdO composite obtained with the internal oxidation of the Ag-11 % Cd alloy (Ag-CdO11) is given in **Figure 6**.

The results of a further microstructural analysis using EDS are presented in **Table 2** and the selected points used for the analysis are marked in **Figure 7**.

Table 2: Results of the EDS analysis of the Ag-11 % Cd alloy (Ag-CdO11) for the electrical-contact material**Tabela 2:** Rezultati EDS-analize zlitine Ag-11 % Cd (Ag-CdO11) za električne kontakte

Spectrum	w(Ag)/%	w(Cd)/ %	w(O)/ %
1	0	83.55	16.45
2	4.99	78.76	16.25
3	97.92	2.08	0
4	97.91	2.09	0

Figures 6 and 7 display a microstructure of the material upon the completion of the oxidation process, which consists of the CdO particles embedded in a silver matrix. It should be noted that in order to provide a good bond between the contact material and the contact holder by soldering, about 25 % of the total thickness of the electrical-contact material must not be oxidized, as illustrated in **Figure 6**. The presented EDS results (**Table 2**) corroborate the observed microstructure and illustrate the Ag and CdO-rich regions.

4 CONCLUSION

The present study on the oxidation behavior of the Ag-Cd alloys with different contents of Cd, carried out in the air environment at the temperatures of 670 °C, 750 °C and 795 °C during (5, 9.5, 20.5, 36 and 48) h using a

microstructure observation and measurements of the thickness of the oxidized layer revealed the following:

The thickness of the oxidized layer during the heating depends on the following process conditions: the temperature and duration of oxidation, the amount of cadmium in the Ag-Cd alloys and the oxygen pressure on the surface of the alloy.

The oxidation kinetics of the alloys follows the parabolic-rate law suggesting a diffusion-controlled growth of the oxide film.

The activation energy, E_a , and the pre-exponential factor were determined using the Arrhenius equation, fitting $\ln k_p$ vs $1/T$ at the temperatures of 670 °C, 750 °C and 795 °C. The activation-energy value of 36 ± 2 kJ/mol indicates a mixed effect of diffusion and temperature on the kinetics of the mentioned process of the internal oxidation of Ag-Cd alloys. This is in accordance with the observation given in⁵ that the temperature has the highest influence on the process of an inner oxidation⁵ because, at higher temperatures, the inner oxidation is faster according to Wagner's expression of the parabolic-rate constant for an internal oxidation where the solute element is part of the denominator.¹²

The aim of this study is to gain a better basic understanding of the controlling processes in the coarsening of the cadmium oxide phase in the internally oxidized silver cadmium alloys.

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