INVESTIGATION OF THE MECHANICAL PROPERTIES OF ELECTROCHEMICALLY DEPOSITED Au-In ALLOY FILMS USING NANO-INDENTATION

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Thin Au-In alloy films containing different amounts of In were electrochemically deposited on a CuZn substrate with a 500-μm thickness. The thicknesses of the obtained films varied from 0.4 μm to 2.7 μm. The chemical and phase compositions, as well as the structures of the films, were investigated by XRF, XRD and SEM analysis. The mechanical properties of the films and substrates were investigated using nano-indentation experiments. As a result, load–displacement curves were obtained and two mechanical characteristics of the substrate and investigated films – indentation hardness and indentation modulus – were calculated using the Oliver & Pharr approximation method. The dependence of the indentation modulus and the indentation hardness on the depth of the indentation and the content of In, the structure and the phase compositions of the films were investigated and discussed as well.

Keywords: gold-indium alloy, electrochemical deposition, mechanical properties, nano-indentation

1 INTRODUCTION

The phase diagram of the gold–indium system shows the presence of several intermetallic compounds existing at a temperature lower than the melting point of Indium (~156 °C), including stable AuIn and AuIn2 phases with a cubic lattice, similar to the α-phase of gold. The indium phase starting from a 53 % mass fraction is tetragonal. The average microhardness obtained for the metallurgical alloy system Au–In is as follows: Au (99.999 %) = 0.660, α AuIn (8 % of amount fractions of In) = 1.700, η1-phase = 3.68, AuIn = 2.73, AuIn2 = 0.77 GPa and the alloy with 80 % of amount fractions of In = 2.07 GPa.2 The microhardness in the hardened condition of the compound Au3In2 (η2 phase) is 1.83 GPa, and increases in the uniformity of the phase deviations in the stoichiometric composition.3 In contrast to metallurgically obtained, the electrochemically deposited Au-In alloys are not well studied. At the same time, electrochemically deposited thin layers of Au–In alloys will find wide application (instead of pure gold coatings) in electrical engineering, micro-electronics, the manufacturing of various sensors, the jewelry industry, etc. The interest in studying the impact of the content of In in the Au–In alloy on a number of colors, decorative, optical, corrosion, mechanical and other properties, regardless of the method of their production, has also increased.4–6 The aim of the present work is to investigate the indentation hardness and the indentation modulus of electrochemically deposited thin layers of Au–In alloys as a function of the indentation depth and considering the effect on them of the nature of the substrate, the content of In, the structure and phase composition of the alloy films as well as the surface roughness of the films.

2 EXPERIMENTAL PART

The Au-In alloy films with thicknesses between 0.4 μm and 2.7 μm were deposited onto brass sheet substrates (2 cm × 1 cm × 0.03 cm) in a standard electrochemical glass cell equipped with two Pt anodes as the counter electrodes. The standard preliminary treatment of the brass cathode-substrates includes a procedure for electrochemical decreasing, followed by pickling in a 20 % water solution of sulphuric acid at room temperature. The investigated Au–In alloy films were electrodeposited...
in galvanostatic mode (in the range of cathodic current densities from 0.2 to 1.8 A dm$^{-2}$) of an acetate-citrate electrolyte (containing 1 g/L Au as a metal (KAu (CN)$_2$); 3 g/L In as a metal (InCl$_3$); 90 g/L CH$_3$COONa; 14 g/L citric acid). The electrolysis process was performed without any stirring of the electrolyte and at room temperature. The thickness, content of In and percentage composition (Au:In) of the thin alloy films were determined by X-ray fluorescence analysis (Fischerscope XDAL). The structure and morphology of the layer surface were investigated by scanning electron microscopy (SEM) using a JSM 6390 microscope. The phase composition was characterized by X-ray diffraction (XRD) using a PANalytical Empyrean Equipped with a multichannel detector (Pixel 3D) using Cu–K$_\alpha$ (45 kV-40 mA) radiation in the 20–115° 2θ range with a scan step of 0.01° per 20 s. The mechanical properties of the Au–In alloy films containing different amounts of In onto the CuZn substrate were investigated by means of nano-indentation experiments, using a Nano Indenter G200 (Keysight Technologies, USA), equipped with a Berkovich three-sided diamond pyramid with a centerline-to-face angle of 65.3° and a 20-nm radius at the tip of the indenter. We realized a series of 25 indentations on each sample probe. We used an indentation method that was proposed in $^7$. The indentation hardness and indentation modulus are determined using the stiffness calculated from the slope of the load–displacement curve during each unloading cycle. As a result load–displacement curves were obtained and two mechanical characteristics of the substrate and the investigated films – indentation hardness ($H_{IT}$) and indentation modulus ($E_{IT}$) – were calculated using the Oliver & Pharr approximation method.$^8$

3 RESULTS AND DISCUSSION

Table 1 shows the results of the XRF analyses on the chemical composition, thickness ($\delta$) and the micro roughness ($R_a$ and $R_z$) of the tested alloy samples and the brass substrate on which they were deposited. From the results it can be seen that the interval of changes in content 49–63 % for the mass fractions of indium in the resulting thin alloy layers and changes of their micro roughness. Information about the surface morphology and the structure of the electrodeposited pure Au and In coatings of the working electrolyte for the preparation of the alloy coatings of which in the first case the presence of In ions is excluded, and in the second case, the presence of Au ions is excluded, give the microphotographs presented in Figure 1a and 1f. While the Au coating is dense and uniform, formed by spherical crystallites having a size ~ 0.5–1.2 μm (Figure 1a), the coatings of In have an uneven thickness – over the fine crystal thin indium layer which covers the entire surface.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Content in mass fractions, (w/%)</th>
<th>$\delta$, μm</th>
<th>$R_a$, μm</th>
<th>$R_z$, μm</th>
<th>J, A dm$^{-2}$ deposition time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Brass substrate (pickled)</td>
<td>Cu – 65.80; Zn – 34.20</td>
<td>300</td>
<td>1.61</td>
<td>9.13</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Au/Brass</td>
<td>Au – 100</td>
<td>0.64</td>
<td>1.13</td>
<td>4.77</td>
<td>1.0; 20</td>
</tr>
<tr>
<td>3.</td>
<td>AuIn/Brass</td>
<td>Au – 50.6; In – 49.4</td>
<td>0.56</td>
<td>1.14</td>
<td>4.90</td>
<td>1.8; 7</td>
</tr>
<tr>
<td>4.</td>
<td>AuIn/Brass</td>
<td>Au – 45.8; In – 54.2</td>
<td>0.75</td>
<td>1.40</td>
<td>5.37</td>
<td>1.2; 15</td>
</tr>
<tr>
<td>5.</td>
<td>AuIn/Brass</td>
<td>Au – 44.1; In – 56.0</td>
<td>1.42</td>
<td>1.15</td>
<td>5.00</td>
<td>0.6; 20</td>
</tr>
<tr>
<td>6.</td>
<td>AuIn/Brass</td>
<td>Au – 37.0; In – 63.0</td>
<td>2.76</td>
<td>1.50</td>
<td>8.93</td>
<td>0.2; 30</td>
</tr>
<tr>
<td>7.</td>
<td>In/Brass</td>
<td>In – 100</td>
<td>0.49</td>
<td>1.18</td>
<td>3.83</td>
<td>1.0; 20</td>
</tr>
</tbody>
</table>

Figure 1: SEM microphotographs of deposited a) Au 100 %; f) In 100 % and Au–In alloy layers in which the content of indium (in mass fractions, (w/%) is: b) 49.4 % In, c) 54.2 % In, d) 56.0 % In and e) 63 % In (samples No. 2, 3, 4, 5, 6 described in Table 1)

Table 1: Chemical composition, thickness, $R_a$ and $R_z$ of the investigated Au–In alloy layers and the substrate on which they are deposited

Tablea 1: Kemijska sestava, debelina, $R_a$ in $R_z$ preiskovanih AuIn plasti in podlage, na katero so bile nanešene
of the brass substrate, they grew, not fully coalesced, spheroidal agglomerates with size ~ 1–10 μm (Figure 1f). The influence of changes in the content of indium on the surface morphology and structure of the Au–In alloy layers is presented in Figures 1b to 1e. From the microphotographs it is clear that at the lowest content of indium (49.4 %) (Figure 1b) the film has a morphology and structure that is different from that of the pure gold film. The alloy coating is formed by homogeneously distributed agglomerates of a size of the base several times larger than that of the spherical grains constituting the gold coating. Moreover, there was no phase heterogeneity in the regime of back scattering electrons. The reasons for this conclusion give the images on the left-hand side of the SPI electron microscopic image (Figure 1b), obtained in the regime of back scattering electrons (BEI), while the right-hand part of the photograph shows an image that was obtained in the regime of a secondary-electron image (SEI). With the same purpose (the recording of possible phase heterogeneity) are the SPI electron microscopic images for a higher content of In (Figures 1c to 1e). Increasing the content of indium in the alloy layer to ~ 54 % (Figure 1c), leads to a levelling of the morphology, respectively, to a finer structure compared with those at a content of ~ 49 % (Figure 1b), in which an even greater degree was observed in the next amount (~ 56 %) of indium (Figure 1d). Obviously, the observed differences in morphology are not related to the phase, but are related to the topographic heterogeneity. When the content of co-deposited In, however, reached 63 %, the morphology and the structure drastically change; they are characterized by large aggregates (3–15 μm), composed of crystallites with dimensions of 0.5–1 μm. Moreover, the BEI image (left-hand side) of the electron microscopic micrograph, at this content (Figure 1e)
parameters regarding the % of mass fractions of In (6.502). Only in the alloy composition containing over 63 of both the phase AuIn2 and the tetragonal phase of In

- The indentation hardness increases too, and after 6.502% content of In, the indentation hardness increased too and after this (from 54.2 to 63 % content of In) it starts to decrease. It is obvious from Figure 6 that with an increase in the In content up to 56.0 % and 63 % the indentation modulus of the investigated Au–In films decreases. This could be explained by the influence of the simultaneously existing two phases on the surface electrode: In and AuIn2. The effect of the non-regularity is very strong due to the different type of crystal lattice – tetragonal in case of the In phase and cubic in the case of the AuIn2 phase. Most probably, the inhomogeneity of these two phases, as well as their roughness limit the accuracy, due to the randomly of both phases during the performed measurements.

4 CONCLUSIONS

In the present work the mechanical properties of electrochemically deposited thin layers of Au–In alloys as a function of the indentation depth and considering the effect on them of the nature of the substrate, the content of In, the structure and the phase composition of the alloy films as well as the surface roughness of the films were investigated. The results showed that with an increasing content of In from 0 % to 49.4 %, the indentation hardness increased too and after this (from 54.2 % to 63 % content of In) it starts to decrease. Moreover, with an increase in the In content up to 56.0 % and 63 % the indentation modulus of the investigated Au-In films decreases. This could be explained by the influence of the simultaneously existing two phases on the surface electrode: In and AuIn2. The effect of the non-regularity is very strong due to the different types of crystal lattice: tetragonal in the case of the In phase and cubic in the case of the AuIn2 phase.

Acknowledgments

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5 REFERENCES

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Figure 6: Dependence of the indentation modulus on the content of In
Slika 6: Odvisnost modula vtiskovanja od vsebnosti In
