Electrodeposition of high entropy alloy coating from water bath

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Abstract
High entropy alloys (HEAs) have been in focus of scientist for past few years owing to their predicted scratch, corrosion and temperature resistance and also to interesting magnetic properties. They are usually prepared by arc melting of at least 5 pure elements. This article deals with electrodeposition of such five-element alloy from water bath, which have not been yet reported. The HEA coating consisting of Fe, Co, Ni, Mn and Mo or Zn was successfully electrodeposited on steel, copper and other metallic substrates. Substrates were polished and treated by sonication in acetone prior to electrodeposition. Obtained thin layers were documented by optical microscopy and SEM techniques. Their exact composition was determined by EDS and XRF analysis. Scratch and accelerated corrosion tests were performed to assess their resistance properties. Electrochemical properties were determined by measurements of polarization curves.

Keywords: high entropy alloy; electrodeposition; SEM; polarization curves

Introduction
High entropy alloys (HEAs) are defined as alloys with solidified solution structure and consisting of at least five different elements in near equimolar ratio [1]. Possibility of formation and stabilization of such a complex solidified solution is granted by equation for Gibbs' energy (a), whose minimization leads to thermodynamic equilibria:

\[ G = H - TS \]  

(a)

where \( G \) [J] is Gibbs' energy, \( H \) [J] is enthalpy, \( T \) is thermodynamic temperature and \( S \) [J.K⁻¹] is entropy. High value of entropy has a major role in minimization of energy in those complicated disordered systems. Nowadays, the HEAs are widely studied. The research is focused mainly at alloy properties and their modification. Experiments regarding probability of a HEA formation based on different atomic radii and calculation of total entropy and stability field prediction in phase diagrams has been carried out [2, 3]. In the most promising qualities of the HEAs described until now belong their mechanical properties which can be sustained till 1500 °C. Yield value reaches to 3000 MPa and hardness by Vickers to 900 [4, 5, 6]. Fatigue stress is better handled than in cases of steel or titan alloys [7] as well as resistance to abrasive wear for steels with comparable hardness [8]. Corrosive protection surpasses that of steel 304 [9, 10]. HEAs are usually prepared from liquid phase – melted metals. [10, 11] Also the path from solid phase is accessible via mechanical alloying of pure powders or half-alloys and follow-up compaction. [12] Only few studies are available regarding HEA electrochemical deposition. [13, 14, 15] Electrochemical way of a HEA preparation should provide feasible technology for a HEA formation with high application potential and easily carried modification. Literature search of above mentioned articles has lead to a several possibilities of HEAs electrochemical deposition. Firstly, the coating was, as reported, plated from DMSO. The bath
contained Fe, Co, Ni, Mn and especially Bi, which is impossible to deposit from water bath. In case of water bath, Bi was exchanged for Zn or Mo.

**Methods**

Electrodeposition was carried out in DMSO solution that was vacuum distilled with BaO for water removal. LiClO₄ was used as an auxiliary electrolyte. Metals were used in form of chlorides or sulfates, only Bi as nitrate, dried in the oven and stored in vacuum desiccator. The water residue in the DMSO bath was determined by Karl-Fischer method. For water bath, the salts were used as received. As substrates copper, iron and aluminium sheets 2x5 cm were used. Substrates were polished by sandpaper and treated by sonication in acetone. Electrodeposition was performed with substrate as a cathode, Schöniger Pt electrode as anode and saturated Ag/AgCl auxiliary electrode, on VoltaLab PGZ controlled by VoltaMaster 4 (Radiometer Analytica SAS, France). The electrodeposition usually proceeded 30 minutes with current density 1.5 A/dm². In DMSO bath, the deposition was done in an inert nitrogen atmosphere (4.6 N). For water bath, standard laboratory conditions were used. After the deposition, the coated substrate was taken out of bath and washed with acetone or water and dried by stream of hot air. Coating composition was determined by energy dispersive X-ray spectroscopy (EDS) analysis during imaging by scanning electron microscope (SEM) VEGA3 (Tescan, Czech Republic). Composition data of samples not taken to SEM were acquired by handheld XRF Delta Professional spectrometer (BAS Rudice, Czech Republic). Thickness of deposited coatings was measured by Surffix Pro X (Phynix, Germany) gauge, by SEM and by Delta XRF. Potentiodynamic measurements were carried out in a conventional three-electrode arrangement. The samples were used as a working electrode, a Schöniger Pt mesh as a counter electrode and an Ag/AgCl electrode (E_{Ag/AgCl} (saturated KCl) = 199 mV vs. SHE at 25°C) served as a reference electrode. The electrodes were connected to VoltaLab PGZ 100 potentiostat controlled by VoltaMaster 4 program (Radiometer Analytical SAS, France). As electrolyte, 3.5% NaCl solution was used. Firstly, open-circuit potential (OCP) was stabilized for 600 s. Secondly, each sample was polarized between -250 and +250 mV with regard to the E_{corr} and scan rate was 1 and 0.5 mV/s. All measurements were carried out at room temperature.

**Results and discussion**

**Plating from DMSO solution**

Plating was done from solution of chloride salts in dry DMSO, as Bi salts create a hydroxide precipitate upon contact with water. Coatings were spread as homogenous black layer on exposed part of cathode (Figure 1). The coatings were poorly compact therefore they needed to be analyzed as scratched-off powder. The poor compactness is partially caused by character of the coating – it consists of microparticles, especially their size and shape compared to each other. These parameters are affected by composition of such a layer. In pursue of better adhesion to substrates several types of etching and activation were tested - acidic and basic solution indulging, grinding, ultrasound and organic solvent washing. The best adhesion was achieved by

![Figure 1: HEA coating BiFeCoNiMn deposited from DMSO on iron sheet.](image-url)
dipping the substrate in 5% nitric acid for 1 minute after grinding and washing the final deposited coating by careful splash of acetone. Slow drying by stream of hot air lead to a quite thick porous layer of HEA. Chemical composition of prepared coatings is in Table 1. Expected percentage ratio in the coating was 20 %. The equimolar composition ratio was not met, especially in case of Bi with only 2 % abundance, although the attempts to increase its concentration in plating bath were tested as well as variation of potential during experiment. Obtained coatings had a needle or lamellar structure with typical shape size of 30 μm (Figure 2). White objects at the picture match to the crystalized particles of bath salts that emerged after insufficient wash of the coating. Sufficient wash of the coating would cause falling off the layer from substrate and consequently loss of product. In the light of above mentioned results, further experiments in DMSO were concluded as unnecessary and the research focused on water bath path.

Table 1: The HEA coatings composition and mass.

<table>
<thead>
<tr>
<th>deposited from</th>
<th>sample</th>
<th>method</th>
<th>Fe % (mol)</th>
<th>Co % (mol)</th>
<th>Mn % (mol)</th>
<th>Ni % (mol)</th>
<th>Mo % (mol)</th>
<th>Zn % (mol)</th>
<th>Bi % (mol)</th>
<th>m (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>Fe °1</td>
<td>EDS</td>
<td>26.0</td>
<td>29.1</td>
<td>13.5</td>
<td>29.3</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
<td>8.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>Cu 61</td>
<td>EDS</td>
<td>8.09</td>
<td>32.4</td>
<td>2.51</td>
<td>34.0</td>
<td>22.9</td>
<td>-</td>
<td>-</td>
<td>6.2</td>
</tr>
<tr>
<td>H₂O</td>
<td>Cu 68</td>
<td>EDS</td>
<td>14.4</td>
<td>29.6</td>
<td>0.70</td>
<td>15.7</td>
<td>-</td>
<td>39.3</td>
<td>-</td>
<td>2.6</td>
</tr>
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</table>

Plating from water bath

The metal chlorides or sulfates were used with boric acid and sodium citrate as support compounds in excess for creating baths. Bi was exchanged for Mo or Zn. The coatings were homogenous and well spread on substrate exposed area. The coating compactness is well visible at images Figure 3 and 4, where trace of Line test during SEM imaging can also be seen. As some of the coatings had the adhesion problem (Figure 5), similar procedure with dipping, grinding and organic solvent washing was followed to increase adhesive effects. This time, the grinding provided enough activity for a good electrochemical deposition (Figure 6). Washing and drying did not cause any coating fall-off and no special care had to be taken for those layers. For
the layer dissolution for liquid sample analysis, the strong concentrated mineral acids needed to be used (HCl, H₂SO₄, HNO₃). Chemical composition of the HEA coatings are listed in Table 1. All prepared samples were in concordance with the definition of HEA in the meaning of composition of five different elements, only the equimolar ration is still under development. More experiments with variation of bath salts concentration and current density will be done to achieve this ideal state. Unlike the porous coatings from DMSO – soft on touch and easily scratched off, water based HEAs had a compact structure with usually matted metallic surface. In case of Mo coatings, the surface looked shiny (Figure 3).

Table 2: Polarization curves parameters

<table>
<thead>
<tr>
<th></th>
<th>( E_{\text{corr}} ) (mV/Ag/AgCl)</th>
<th>( f_{\text{corr}} ) (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_51 bare</td>
<td>-222,8</td>
<td>0,0259</td>
</tr>
<tr>
<td>Cu_78 1 mV/s</td>
<td>-619,6</td>
<td>0,0135</td>
</tr>
<tr>
<td>Cu_78 0.5 mV/s</td>
<td>-537,6</td>
<td>0,0127</td>
</tr>
</tbody>
</table>

Figure 5: SEM image of HEA coating with cracks.

The coating thickness, which was unmeasurable for coatings from DMSO (porosity lead to probe digging in different depth giving unreasonable or too scattered results), slightly varied around 2 μm for HEAs deposited from water bath and exhibited no detectable step transition. From the mass deposited during all experiments we can tell, that the deposition under the same conditions proceeds better on Fe and Cu than on Al sheets, also the deposition without grinding does not proceed at all in case of Al unlike on Fe or Cu where, probably, no oxide layer is created in normal aerated laboratory conditions. Results from fitting polarization curves (Figure 6, Table 2) prove that the coatings are better resistant to corrosion, especially compared to substrate material.
Conclusion
In form of coating several types of materials composing of Fe, Co, Ni, Mn and Zn or Mo were successfully electrodeposited. The DMSO bath showed no positive results as the coating exhibited very low adhesion and compactness. The experiments showed that the HEAs are well deposited on Cu and Fe substrates from water bath. SEM images confirmed compactness of obtained coatings. Analysis of polarization curves produced corrosion parameters proving higher corrosion resistance than bare substrates. Also the coating protects the substrate from scratch and other mechanical damage. From the results we can state, that the applied coatings have great potential to become easily modified protective material.

Acknowledgment
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References
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