Electrodeposition and characterization of homogeneous and graded composition Co–Fe–Ni–Zn multi-principal element alloy films

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One of the most dynamically developing fields of materials science focuses on studying equiatomic or near-equiatomic materials with three or more elements. In these materials, neither of the components can be classified as either solvent or solute. This material family is frequently called as multi-principal element alloys (MPEAs) or compositionally complex alloys (CCAs). These material classes also include high-entropy alloys (HEAs) in which the number of principal elements is five or higher with near-even atomic concentrations.
MPEAs can be manufactured with a wide range of traditional metallurgical techniques (such as mechanical alloying, arc-melting, quenching, physical vapour deposition, laser ablation, *etc.*), but the number of electrochemical processing attempts is very limited. MPEA electrodeposition works apply various approaches: (i) dilute solution of the precursor materials in a non-aqueous solvent; (ii) classical electrodeposition from aqueous baths; and (iii) electroreduction of metal oxide pellets. Due to the small number of paper published so far, only a few selected compositions were studied.
In this study, a Co–Fe–Ni–Zn MPEA was processed by pulse electroplating for the first time [1]. The reason of choosing pulsed electrodeposition as preparation techniques was multifold, such as to achieve an even in-depth composition, to obtain nanocrystalline layers and to curtail the surface roughening commonly observed in electroplating. The bath used was based on metal chloride precursor compounds and traditional additives. Electrodeposition was performed at 55 °C for obtaining a relatively homogeneous material on a tantalum substrate (deposits prepared at ambient temperature were prone to both a phase separation and a development of local morphological diversities).
In a custom-made symmetrical electrochemical cell, a compositionally very homogeneous deposit could be obtained with a nominal component ratio of 32 at.% Co, 27 at.% Fe, 21 at.% Ni and 20 at.% Zn. The optimization of the bath composition was a time-consuming procedure due to the large variation in the relative deposition preference of the alloy components (mostly because of the anomalous nature of the codeposition process).
The film has a main fcc phase with the lattice constant of about 0.3620 nm. The average grain size was as small as ~12 nm. The size distribution was wide spanning from 5 to 27 nm. The microstructure also contains a bcc minority phase and ~2 nm thick amorphous boundaries separating polycrystalline columns. This amorphous phase is enriched in Ni and depleted of Fe. XRD suggests that the bcc minority phase has a smaller crystallite size compared to the main fcc structure.
The average hardness and elastic modulus determined by nanoindentation were 9.2 and 197 GPa, respectively. This hardness is much higher than the values reported formerly on fcc MPEAs processed by other methods (3.6 to 6.9 GPa) which can be explained by the very small grain size and the existence of the bcc and amorphous minority phases.
An asymmetric electrodeposition cell configuration was developed for preparing alloys of gradient composition (sample library approach, [2]). It was found that the element with the smallest precursor compound concentration, Zn, was gradually replaced with the next element in the preference row, Co. Therefore, the Zn concentration range of 14-44 at.% could be scanned. Since this study could be performed with a different type of substrate (brass), the texture of the main fcc phase changed to 211, and the amorphous regions were also missing, hence leading to somewhat smaller hardness values than the homogenous sample plated onto Ta foil. The lattice constant scaled with the Zn concentration of the deposit, and the hardness optimum was found at 36 at.% Zn.

Acknowledgement: Partial financing under grant no. VEKOP-2.3.3-15-2016-00002 and VEKOP-2.3.2-16-2016-00011 from the European Structural and Investment Funds is acknowledged. UNKP-23-3-II-ELTE-123 scholarship grant obtained by P. Nagy covered a partial cost of the present research.

References

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