

Article

Combinatorial Design of an Electroplated Multi-Principal Element Alloy: A Case Study in the Co-Fe-Ni-Zn Alloy System

Péter Nagy ¹, László Péter ², Tamás Kolonits ³, Attila Nagy ² and Jenő Gubicza ^{1,*}

¹ Department of Materials Physics, ELTE Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary; nagyp@student.elte.hu

² HUN-REN Wigner Research Centre for Physics, P.O. Box 49, H-1525 Budapest, Hungary; peter.laszlo@wigner.hun-ren.hu (L.P.); nagy.attila@wigner.hun-ren.hu (A.N.)

³ Institute for Technical Physics and Materials Science, HUN-REN Centre for Energy Research, Konkoly-Thege Miklós. út 29-33, H-1121 Budapest, Hungary; kolonits.tamas@ek.hun-ren.hu

* Correspondence: jeno.gubicza@ttk.elte.hu; Tel.: +36-1-372-2876; Fax: +36-1-372-2811

Abstract: Multi-principal element alloys (MPEAs) are at the forefront of materials science due to their large variety of compositions, which can yield unexplored properties. Mapping the structure and properties of a compositional MPEA library in a reasonable time can be performed with the help of gradient samples. This type of specimens has already been produced in both bulk and layer forms. However, combinatorial MPEA coatings have not been synthesized by electroplating, although this method has a great potential to deposit a coating on components with complex shapes. In this study, a combinatorial Co-Fe-Ni-Zn coating with the thickness of 4 μm was synthesized by electrodeposition. The material exhibited a well-defined Zn gradient; therefore, the investigation of the effect of Zn concentration on the microstructure and mechanical properties was feasible without the production of an excessively large number of specimens. The Zn concentration was controlled laterally through mass transfer due to the unique geometry of the substrate, and it covered a concentration range of 18–44 at%. The chemical and phase compositions as well as the morphology of the as-processed samples were investigated in multiple locations using X-ray diffraction and scanning electron microscopy. The mechanical performance was characterized by nanoindentation. It was found that for any composition, the structure is face-centered cubic and the lattice constant scaled with the Zn concentration of the deposit. The hardness and the elastic modulus were consistent with values of about 4.5 and 130 GPa, respectively, in the Zn concentration range of 25–44 at%.

Keywords: multi-principal element alloy; gradient sample; electrodeposition; nanocrystalline microstructure; hardness



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1. Introduction

The investigation of multi-principal element alloys (MPEAs) has become one of the most rapidly progressing fields of materials science. MPEAs are constructed from three or more components with similar concentrations [1,2]. A subset of these materials is called high-entropy alloys (HEAs), which are built up of five or more components with a configuration entropy higher than $1.61R$, where R is the universal gas constant [3]. The disordered crystal structure of MPEAs can result in an enhanced strength, making these materials interesting from the point of view of structural applications [4,5]. In addition, MPEAs correspond to the unexplored middle parts of phase diagrams, motivating the extensive investigation into these materials in the recent decade [6–9].

MPEA and HEA materials have been produced in both bulk and thin layer forms [10–12]. MPEA thin layers were manufactured by diverse methods, such as direct current magnetron sputtering [13,14], thermal evaporation [15], cold spraying [16], radiofrequency sputtering [17], or multibeam sputtering [18]. The coatings of concave-shaped workpieces usually pose a significant challenge to many procedures that require a straight and open

pathway between the source and the target. Electrodeposition is a method that shows extraordinary potential for coating unconventionally shaped substrates, and this property offers yet unexplored opportunities in industrial applications. Electroplating is widely used in the industry for producing conventional metallic coatings [19]. However, there are only a few trials in the literature for the application of this technique in creating MPEA layers. For instance, a Co-Ni-W-Re-P amorphous layer was deposited with both direct current and pulse current electrodeposition methods, and it was shown that the coatings provide corrosion protection up to 73.8% efficiency [20]. Another study reported the impressive soft magnetic behavior of a pulse electrodeposited Co-Cu-Fe-Ni dual-phase thin film where the body-centered cubic (BCC) and face-centered cubic (FCC) phases coexist [21]. The mechanical properties of a Co-Fe-Ni-Zn MPEA film processed by pulse electroplating were also studied, and an outstanding hardness (9.2 GPa) was observed, which was explained by the nanocrystalline FCC microstructure, and the BCC and amorphous secondary phases [22].

The mechanical and functional properties of MPEAs can be tailored by changing their chemical composition [23]. The effect of stoichiometry on the microstructure and the properties motivates the processing of gradient MPEA samples. These are multi-component materials with a systematic and gradual composition change as a function of the location within the sample [24]. The advantage of combinatorial materials is that many different compositions coexist in a single sample, thereby reducing the time and effort required for mapping a full compositional library. Combinatorial samples in the form of thin films have been manufactured using plasma solid-state surface metallurgy [25], magnetron sputtering [26], plasma sputtering [27], and multibeam sputtering [28,29]. Combinatorial MPEA layers were successfully employed to investigate the composition-dependent microstructure and mechanical properties. For instance, it was found that in a Co-Cr-Fe-Ni combinatorial layer, the majority of the sample has a single-phase FCC structure while the highest hardness was obtained at the composition of 42% Co–45% Cr–5% Fe–8% Ni (at%), where the dominant phase was hexagonal close-packed (HCP) [28,29]. The magnetic behavior of the Al-Co-Cr-Fe-Mn system was studied as a function of the Al content [27]. In this MPEA system, the maximum magnetization was observed at an Al concentration of 8 at% [27]. Using a combinatorial sample, the phase composition in the Co-Cr-Fe-Mn-Ni library was also mapped [30]. Although, the combinatorial design concept was applied successfully for MPEA layers manufactured by different coating processing techniques, according to the knowledge of the authors electrodeposited combinatorial MPEA film has not been produced yet.

Earlier works dealing with the electrosynthesis of HEA- or MPEA-type layers have been reviewed systematically in our previous work (see [22], Introduction, Paragraphs 3 through 6) and in [31]. From the papers listed therein, less than a dozen works dealt with the electroplating of HEA/MPEA-type materials from conventional aqueous baths (excluding the works on composites) [20,21,32–41]. In all electrodeposition-related synthesis attempts, at most, a few selected compositions were achieved, occasionally with even dissimilar components. A single work set the target of synthesizing a compositional library with a quasi-continuous composition variation in micropillars [42]. However, in latter work, the sample geometry allowed a composition study only, and the deposit properties as a function of the constituent concentrations could not be revealed.

In this work, a combinatorial MPEA layer is processed by electrodeposition for the first time in a planar form, and the structure as well as the mechanical behavior are mapped as a function of the chemical composition. The Co-Fe-Ni-Zn MPEA system was selected for the present study in order to extend our former investigation performed on the composition 32% Co–27% Fe–21% Ni–20% Zn (at%) [22]. The chemical composition in the combinatorial coating was mapped by energy-dispersive X-ray spectroscopy (EDS). The phase composition and the microstructure were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The surface roughness was investigated by interferometry. The correlation between the microstructure and the mechanical performance characterized by nanoindentation was discussed.

2. Materials and Methods

Electrodeposition was carried out in an open beaker-type cell with a volume of 800 mL, thermostated at 55.0 ± 0.2 °C. The cathode was immersed into the electrolyte solution, and its active surface was horizontal, as shown in Figure 1. Figure 2 indicates the dimensions of the pentagon-shaped cathode, which was prepared from a brass plate. Before the electrolysis experiments, the cathode was mechanically polished to a mirror finish, first with gradually finer and finer emery papers and then with alumina suspensions with 15, 9, 3, and 1 μm particle sizes. The sides of the substrate were sealed with Scotch tape. The anode was a cylindrical nickel foil with a diameter almost as large as that of the beaker.

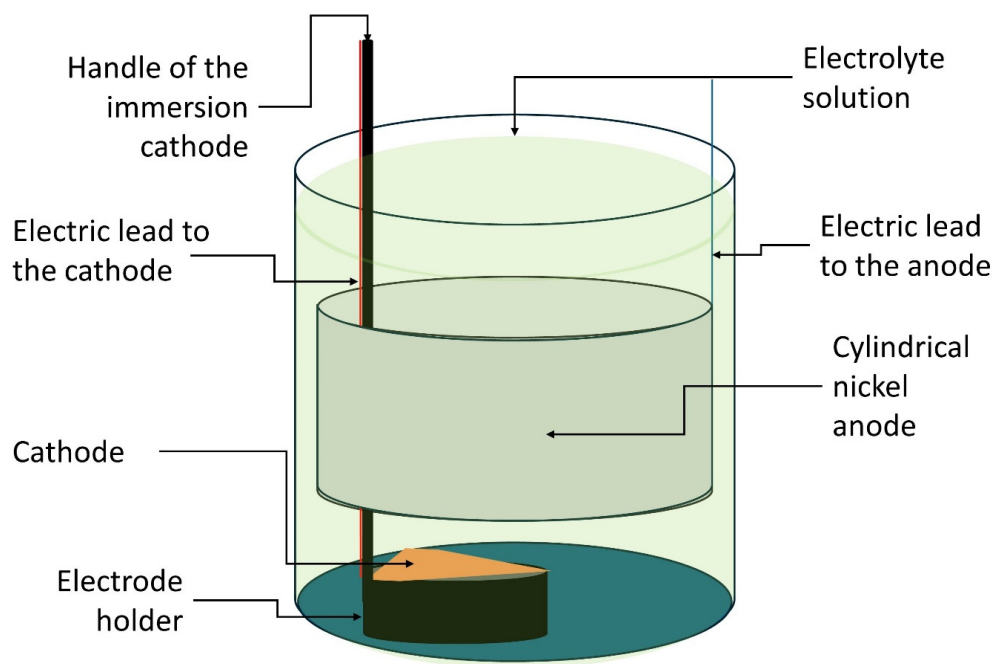


Figure 1. Schematic figure of the electrochemical cell.

The reason for the above-described electrode arrangement was the following. Asymmetric cathode–anode arrangements in any geometry tested led to a nearly even deposit composition. This is the consequence of the pulse plating method applied, which was used in order to obtain a deposit with good in-depth homogeneity [43–47]. However, pulse plating generally provides a more even coverage than d.c. plating, even in areas with uneven accessibility. Hence, this advantage of pulse plating had to be overcome in the present study addressing the preparation of gradient samples, which could be solved only by providing uneven mass transport conditions along the cathode surface. The circles in the left panel of Figure 2 indicate that the distance between the central line and the cathode edges is lower at the apex than at the bottom. Thus, the mass transport to the former point is faster, resulting in an increasing Zn^{2+} concentration in the electrolyte solution in the direction represented by the red arrow and a corresponding Zn concentration change in the deposit.

The starting electrolyte solution with the lowest Zn^{2+} concentration is shown in Table 1 (stock solution). For increasing the Zn^{2+} concentration, a semi-blank ZnSO_4 solution was added to the above-described bath, hence increasing the Zn ratio among the electroactive components. The largest Zn salt concentration was 0.0211 mol/L. All solutions were prepared using an ultrapure water obtained with ELGA Purelab Option R7 water purifier (ELGA LabWater/VWS Ltd., High Wycombe, UK). The pH of the starting solution was 3.2 ± 0.1 at room temperature, and it showed negligible variation upon the electroplating of several consecutive samples. Further details on the solution preparation are identical to those given in our previous work [22]. All electrical parameters of the pulse plating process were fixed (on-time current density: -33 mA cm^{-2} , on-time: 0.06 s, off-time: 0.7 s).

The power source was an Elektroflex EF453 potentiostat/galvanostat (Elektroflex, Szeged, Hungary) driven by a home-built program.

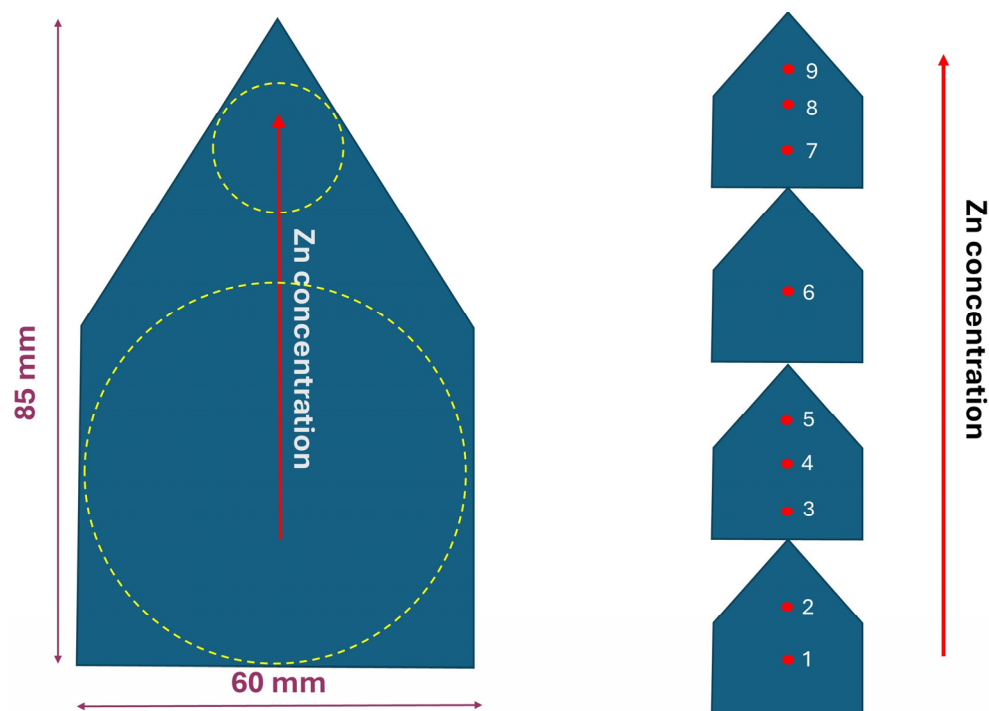


Figure 2. The schematic figure on the left side shows the specific shape of the substrate. In a single sample, the Zn concentration increases in the direction indicated by the red arrow. On the right side of the figure, it is shown that the targeted compositional range was achieved using a four-member sample series. The red spots in the schematics of the samples mark the position of the studied points and their reference numbers. The two circles in the left panel indicate that the distance between the central line and the cathode edges is lower at the apex than at the bottom. Therefore, the mass transport to the former point is faster, resulting in an increasing Zn^{2+} solution concentration in the direction represented by the red arrow, which yields a corresponding Zn concentration change in the deposit.

The study of the surface morphology was carried out by SEM using a MIRA3 scanning electron microscope (Tescan, Brno, Czech Republic). Secondary electron images were recorded with acceleration voltages varying in the range of 5–20 kV. The same SEM instrument was used for the investigation of the chemical composition on the surface of the as-processed samples. The EDS measurements were performed with the help of an EDAX Element analyser system (EDAX Inc., Mahwah, NJ, USA) on spots with about 0.1 mm^2 surface areas. The acceleration voltage was 20 kV.

A Zygo New View 7100 white light interferometric surface analyser (Zygo Co., Middlefield, CT, USA) was used to measure the surface properties of the electrodeposited Co-Fe-Ni-Zn gradient MPEA coatings. The results for the coatings were compared with that of the uncoated substrate. A $10\times$ magnification objective with a built-in Mirau interferometer was used for the measurements (Zygo Co., Middlefield, CT, USA). The resulting topological images have a vertical resolution of 0.1 nm and a lateral resolution of $1.5 \text{ }\mu\text{m}$. The size of the investigated area was $0.94 \text{ mm} \times 0.70 \text{ mm}$. The top corner points of the substrates (see Figure 2) were used as reference points for each sample, and the topography was measured together with the surface roughness properties at given distances from this point (32, 38, 44, 50, 56, 62, and 66 mm) along the vertical axis of symmetry. The locations of the surface topography measurement points were thoroughly correlated to those of the structural and mechanical studies. From the measured 3D surface profile, the surface

roughness (i.e., the average absolute deviation from the mean plane) and occasionally the line roughness (i.e., the average absolute deviation from the mean line) were determined.

Table 1. Concentrations of the compounds used for the preparation of each solution. The precursor compounds of the resulting deposit are listed in the order of their concentration and in the reverse order of their deposition preference.

Name of the Chemical [Formula of the Compound Used for the Bath Preparation]	Concentration of the Component (mmol/L)	
	Starting Solution	Semi-Blank ZnSO ₄ Solution
Nickel chloride [NiCl ₂ ·6H ₂ O]	164	0
Iron(II) ammonium sulfate [(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O]	134	0
Cobalt chloride [CoCl ₂ ·6H ₂ O]	56.4	0
Zinc sulfate [ZnSO ₄ ·6H ₂ O]	13.4	360
Potassium chloride KCl	164	0
Boric acid [H ₃ BO ₃]	250	250
Saccharin [C ₇ H ₅ NO ₃ S]	27.3	0
Ascorbic acid [C ₆ H ₈ O ₆]	5.7	0
Sodium dodecylsulfate [CH ₃ (CH ₂) ₁₁ OSO ₃ Na]	1.4	0

Cross-sectional SEM/EDS measurements were performed using a Scios 2 DualBeam microscope (manufacturer: Thermo Fisher Scientific, Waltham, MA, USA). During the measurements, a trench with a depth of a few tens of micrometers was made in the sample by a high-energy focused ion beam (FIB) of Ga⁺ ions. Then, the surface of the cross-section was polished with low-energy Ga⁺ ions, and EDS measurements were carried out with an X-MAX^N 20 detector (manufacturer: Oxford Instruments, Abingdon, UK). During these EDS measurements, the sample was tilted, and an electron beam with an energy of 30 keV and a high current of 3.2 nA was used.

The phase composition was studied by XRD using a Smartlab X-ray diffractometer (manufacturer: Rigaku, Tokyo, Japan). The instrument was used in Bragg–Brentano configuration with CuKα radiation (wavelength: $\lambda = 0.15418$ nm). The diffraction patterns were recorded between the scattering angles of 40 and 100° with a step size of 0.02°.

The mechanical properties of the samples were characterized via nanoindentation, using a HIT300 indenter instrument (manufacturer: Anton Paar TriTec SA, Neuchatel, Switzerland). The penetration depth of the Vickers indenter head was recorded during loading and unloading at a constant loading rate of 1.66 mN/s. Both loading and unloading took 30 s. The maximum load was kept as 50 mN for 10 s before unloading. For each of the nine measurement points shown in Figure 2, eleven indentation measurements were performed in a circular area with a radius of ~0.5 mm. The distance between the neighboring measurement points shown in Figure 2 was at least 9 mm; therefore, the indentations made in close vicinity of these points were suitable for the characterization of its composition-dependent mechanical behavior. The hardness and the elastic modulus were determined with the Oliver–Pharr method using an assumed value of 0.3 for the Poisson’s ratio of the samples [48]. The hardness and elastic moduli presented in this

study were determined by averaging the eleven values obtained in the vicinity of each measurement point.

3. Results

The red spots on the right side of Figure 2 show the points where detailed analyses were performed. Table 2 lists the chemical compositions in these locations as measured on the surface of the samples by EDS. It can be seen that in the selected points, the concentration of Zn varied between 17.7 and 44.1 at%, with a step size of about 2–4 at%, as shown in Table 2. Simultaneously, the Co concentration decreased with increasing Zn content, as shown in Figure 3. On the other hand, the variation in Fe and Ni concentrations versus the position reference number showed a far from monotonous trend (see Table 2). However, the average of the Fe and Ni concentrations decreased monotonously as a function of the Zn content, as revealed in Figure 3. Both Co concentration and the average of the Fe and Ni concentrations varied approximately linearly within a Zn content range of 17.7–44.1 at%. The main conclusion of the composition analysis is that the addition of the precursor compound of the element with the highest deposition preference (in this case, Zn) mainly depresses the deposition of the next element in the preference row (Co). As clearly shown in Figure 3, the decrease in the Co mole fraction alone is as large as that of the other elements together (Fe and Ni) with increasing Zn concentration in the Co-Fe-Ni-Zn MPEA deposit.

Table 2. The chemical compositions (in at%) obtained by EDS for the locations marked as red spots in Figure 2.

Positions	Co (%)	Fe (%)	Ni (%)	Zn (%)
1	30.7	27.4	23.6	17.7
2	28.5	27.7	22.7	20.5
3	27.7	21.5	25.6	24.6
4	25.9	23.2	22.1	28.3
5	22.7	24.4	20	32.8
6	22.8	15.3	25.8	35.8
7	20.5	10.1	29	39.5
8	20.9	11.9	24.8	42.3
9	19.1	16.9	19.9	44.1

The above trend can be expected from the mutual deposition preference of the components, which is traditionally named anomalous codeposition. The reason for such a behavior is that intermediates form from various Me^{2+} ions in different ratios than their bulk concentration ratios in the bath. One type of model treats these intermediates as solute $\text{Me}(\text{OH})^+$ species [49–51], while another approach is to calculate the ratio of relative surface coverages by various partly discharged $\text{Me}(\text{OH})$ intermediates [52–54]. The ratio of the intermediates regulates the kinetics of the deposition process, and the deposit composition depends on the mutual exclusion of the intermediates of each metal. This is why the component concentrations have to be selected in reverse order of deposition preference (see also Table 1). Although, the models of anomalous codeposition are typically elaborated and controlled experimentally for binary (or, exceptionally, tertiary [54]) alloy deposits, the predictions of both above-mentioned basic assumptions are the same for more complex deposit formulations, too.

Figure 4 shows cross-sectional SEM-EDS and BSE images at location No. 6. This figure reveals that the film thickness was about 4 μm . Figure 4 also shows a Pt layer on the surface with a thickness of about 1.3 μm , which was deposited on the surface of the film before cutting the lamella by a FIB for the cross-sectional study. Based on the calculation of the mass deposited during electroplating, no considerable differences in film thickness

are expected with the varying composition. As Figure 4 shows, no in-depth composition variation in the deposit was found.

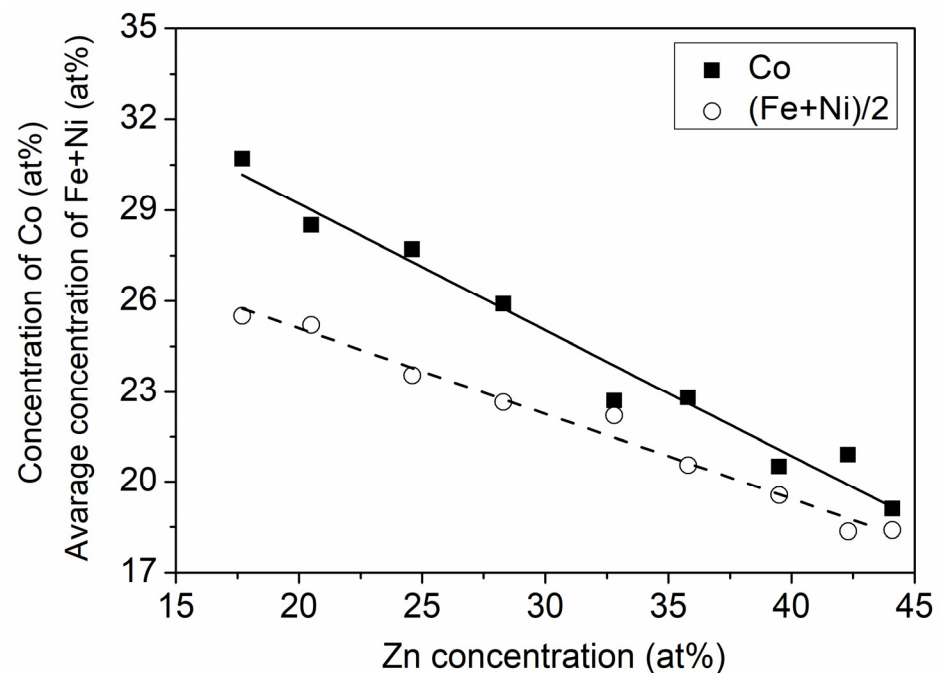


Figure 3. The concentration of Co and the average of the Fe and Ni contents as a function of Zn concentration, as obtained for the studied combinatorial Co-Fe-Ni-Zn MPEA sample. The straight lines are only a guide for the eyes. The R^2 values of the fitted lines are 0.97 and 0.98 for the concentrations of $(Fe + Ni)/2$ and Co, respectively.

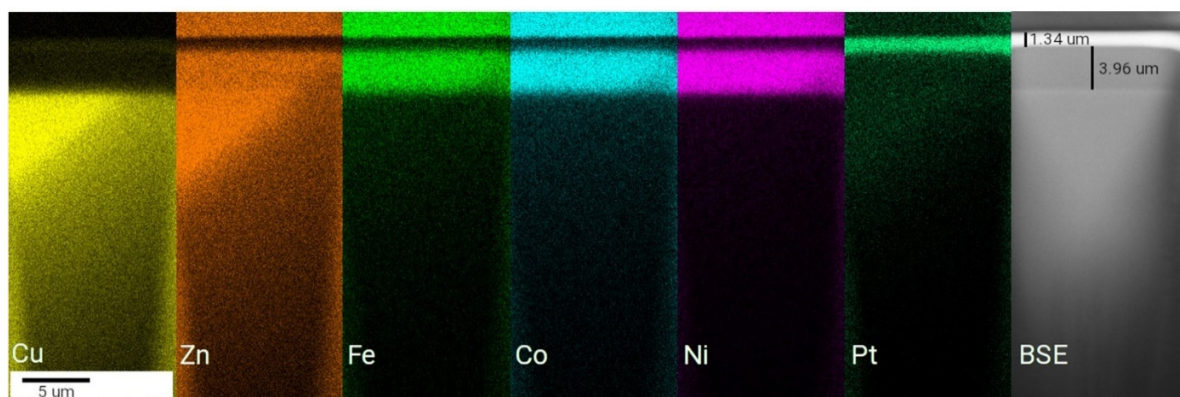


Figure 4. SEM-EDS images of the cross-section of the coating. The cross-section was prepared at location No. 6 (see Figure 2). The thickness of the layer is 3.96 μm , as indicated in the BSE image. The brass substrate is at the bottom of the images, where both Zn and Cu were found but all other deposit elements were missing.

In Figure 5, the surface of the polished substrate and a selected spot of the deposit on the same substrate (around position No. 6) are compared. It can be seen that the surface of the deposit is similarly as smooth as the polished substrate and the deviation from the mean surface does not exceed 100 nm. Spikes in the quantitative profile are common in surface interferometry and can be attributed to surface contamination.

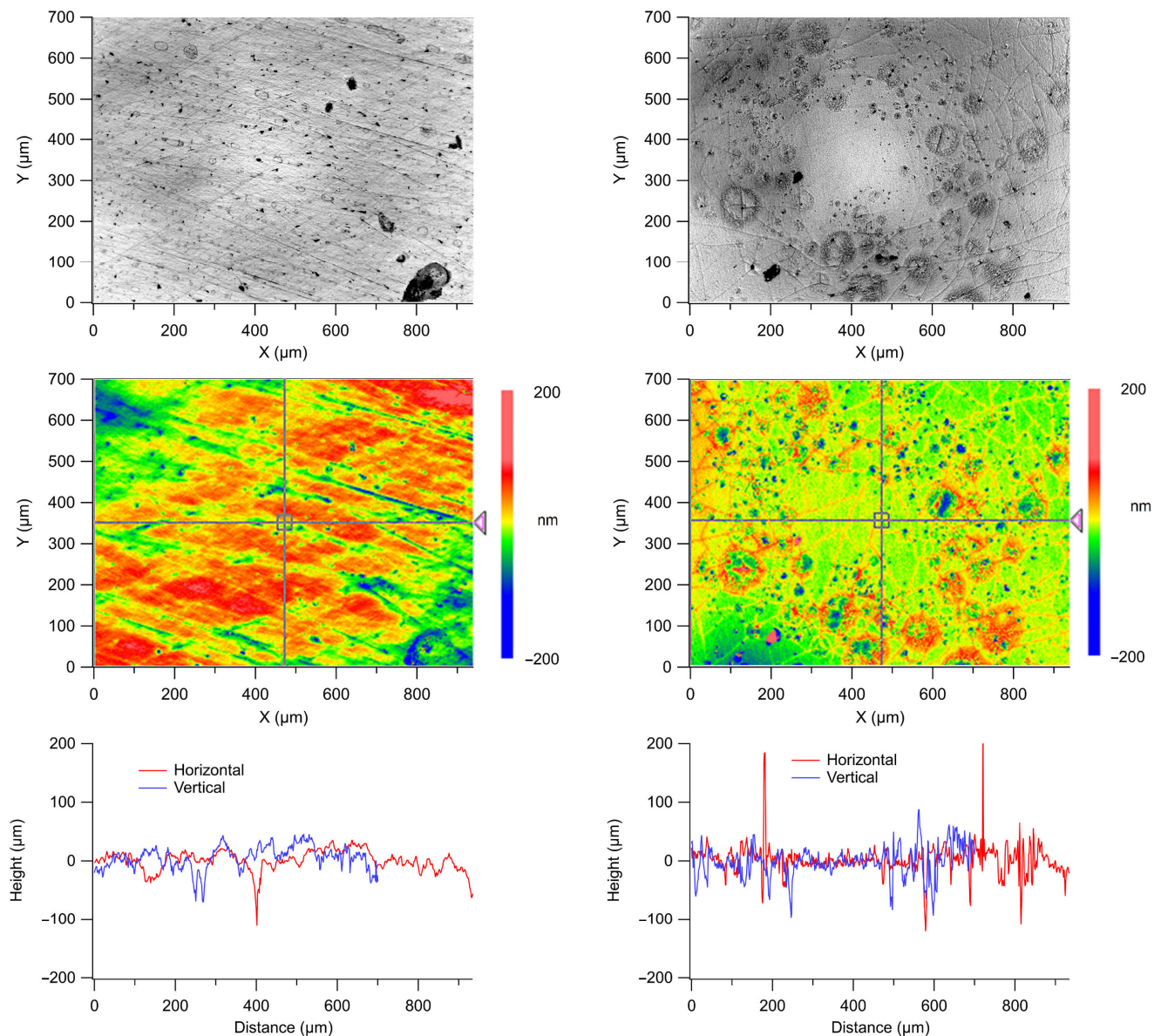


Figure 5. Top row—optical microscopic images of the surface; middle row—measured surface topology; bottom row—characteristic cross-sectional line-cut profiles. The left panel refers to the substrate, while the right panel shows a selected area of the deposit around position No. 6.

Figure 6 shows surface roughness maps obtained by interferometry at positions 3, 6, and 8 in order to reveal the effect of Zn content on layer morphology. The studied area was $600 \times 600 \mu\text{m}^2$. The zero level in the maps was adjusted under the condition that the average height must be zero. Then, the average of the absolute values of the heights was used for the characterization of roughness. For location Nos. 3, 6, and 8, the roughness values were 13, 50, and 26 nm, which suggests an essentially smooth coating surface, irrespective of the composition. An additional study of the surface morphology was performed by SEM and the trend found with increasing Zn content is illustrated in Figure 7, where areas with dimensions of $4 \times 4 \mu\text{m}^2$ are shown at locations 3, 6, and 8. It is revealed that at this scale, the surface roughness increased with increasing Zn concentration.

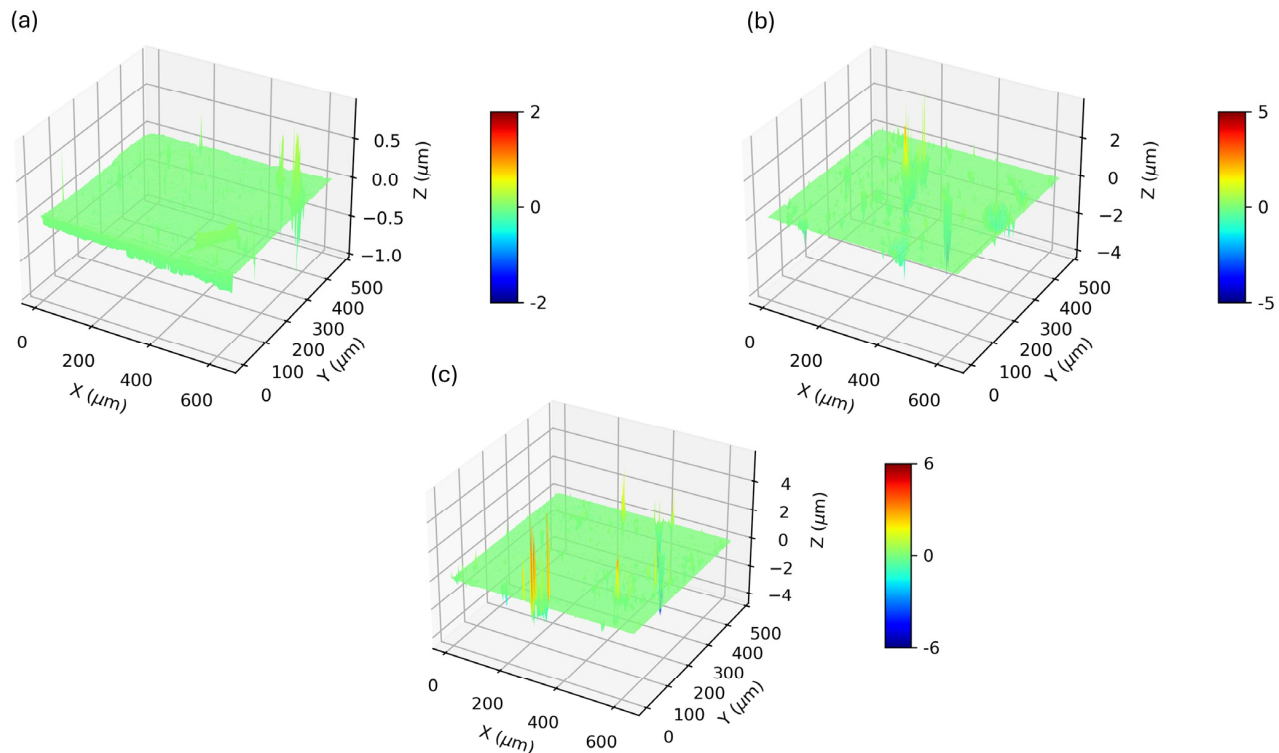


Figure 6. Surface roughness maps obtained by interferometry in positions (a) 3, (b) 6, and (c) 8 (the position reference numbers are defined in Figure 2, and the corresponding local compositions are listed in Table 2). The color code indicates the height in direction Z in micrometer units.

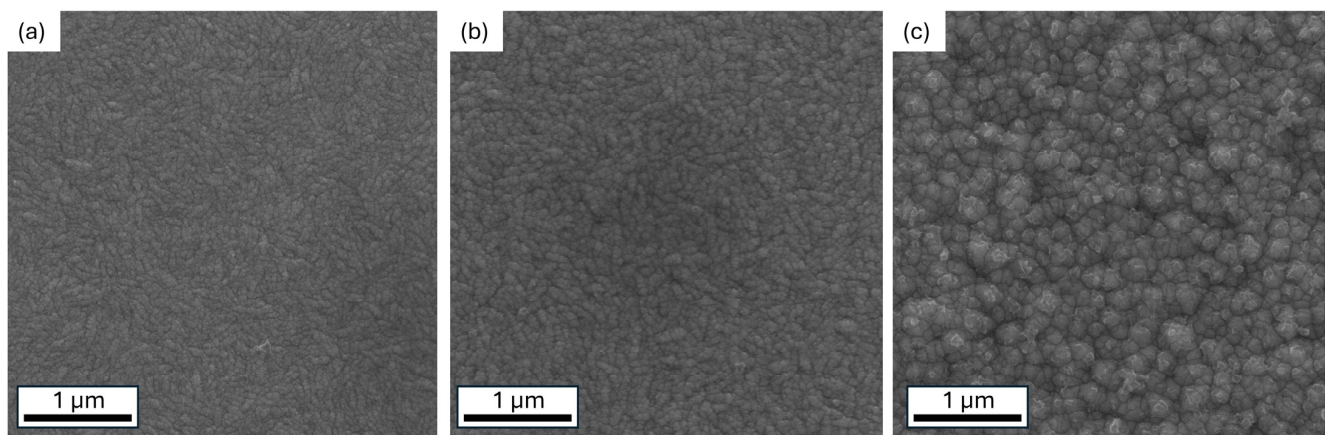


Figure 7. SEM images showing the morphology of the layer in positions (a) 3, (b) 6, and (c) 8 (the position reference numbers are defined in Figure 2, and the corresponding local compositions are listed in Table 2).

XRD revealed that the structure of the film is FCC, irrespective of the chemical composition. As an example, Figure 8a shows an XRD pattern taken at the near-equimolar position of the combinatorial layer (position No. 4). The peaks of both the FCC layer and the FCC brass substrate appeared in the diffractogram. The large intensity of peak 220 of the FCC film suggests a crystallographic texture in which planes {220} are lying preferably parallel to the coating surface. Since the other reflections are weak, only peak 220 was used for the evaluation of the lattice constant and the crystallite size of the FCC layer versus the chemical composition. Figure 8b shows that reflection 220 was shifted to lower scattering angles with increasing position number of the studied locations. The lattice constant (denoted as a) determined from the position of peak 220 is plotted as a function

of the Zn concentration in Figure 9. This plot suggests that the lattice parameter increases approximately linearly with increasing Zn content. It is noted that an additional small peak can be observed at a diffraction angle of about 79.5° . This peak appears only on the diffractograms taken at locations with a relatively high concentration of Fe (above 21 at%, i.e., for points with Nos. 1–5). Thus, it is suggested that this small peak may be related to an iron-based secondary phase. However, because of the low intensity of the peak and the absence of other corresponding peaks, it could not be identified. Most probably, this phase has no significant contribution to the behavior of the layer due its very low fraction (1–2%, as estimated from the XRD peak intensities).

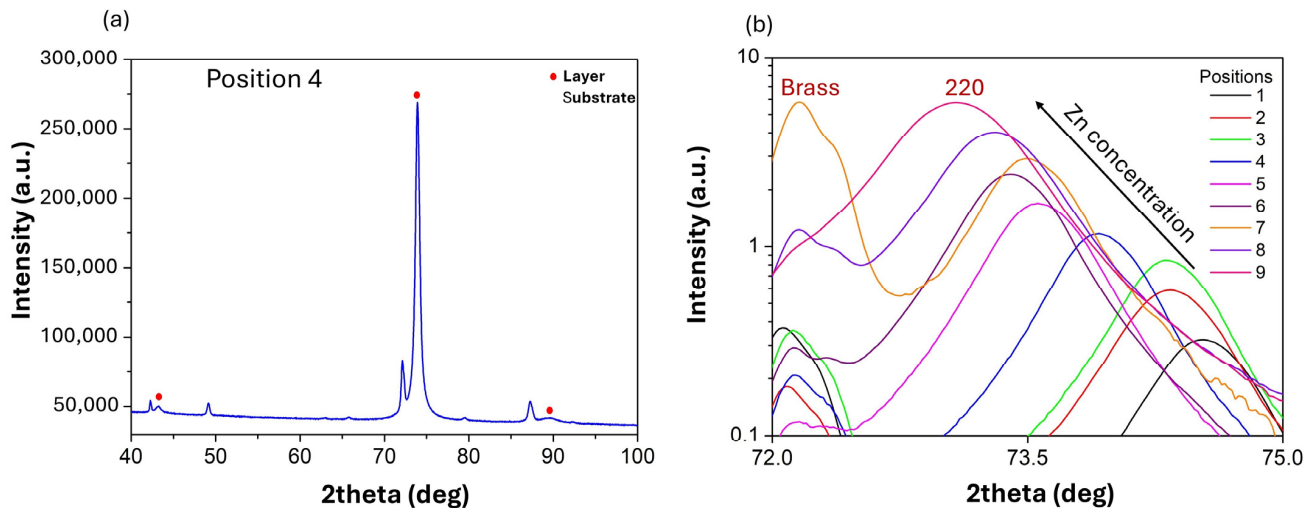


Figure 8. (a) XRD pattern taken at the position exhibiting near-equimolar composition in the combinatorial layer (position No. 4). (b) Magnified parts of the XRD patterns obtained at the different positions in the film, showing the shift in peak 220 of the FCC phase due to the different chemical compositions. The intensity at the different patterns in (b) was divided using different factors for a better visualization of the peak shift.

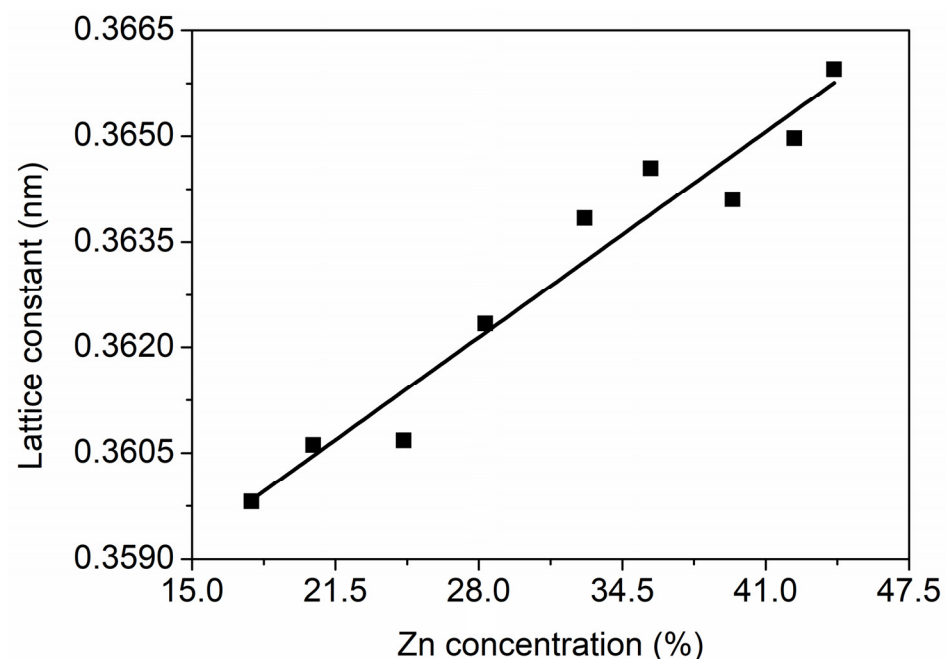


Figure 9. The lattice parameter as a function of the Zn concentration determined in locations 1 to 9 (the position reference numbers are defined in Figure 2). The straight line is only a guide for the eyes. The R^2 value of the fitted line is 0.94.

An apparent crystallite size was determined from the breadth of reflection 220 using the following formula (Scherrer equation): $\lambda / (\cos\theta(\Delta 2\theta))$, where θ is the Bragg angle and $\Delta 2\theta$ is the peak breadth in radians. This calculation gave 18 ± 2 nm for the crystallite size, irrespective of the chemical composition. It should be noted, however, that this value of the crystallite size is an underestimation of the real size of crystals in the coating since the diffraction peaks were broadened not only due to the smallness of the crystallites but also owing to lattice defects such as dislocations and twin/stacking faults [55]. Moreover, since the chemical composition continuously varied in the combinatorial sample, in the volume illuminated by X-rays, the lattice spacing value may have a distribution that can also yield an XRD peak broadening [56]. Furthermore, the X-ray diffractometer gives an additional contribution to the width of the peak, which is called instrumental broadening. The different contributions of profile broadening were added, resulting in the measured peak width [55]. As a result of these additional contributions, the peak broadening caused by the crystallite size solely should be lower than the measured $\Delta 2\theta$, i.e., the size of the crystals is certainly higher than 18 nm, calculated from the measured peak breadth using the Scherrer formula presented above. Nevertheless, the orders of magnitude of a real crystallite size must be some tens of nanometers, i.e., the coating is nanostructured, irrespective of the chemical composition.

Figure 10 shows the hardness and the elastic modulus values versus the Zn concentration for the nine studied locations. Below the Zn concentration of 25%, the hardness and the elastic modulus were 3.0 ± 0.6 and 110 ± 10 GPa, respectively. Between Zn contents of 25 and 44%, the hardness was higher and consistent with a value of 4.5 ± 0.5 GPa, while the elastic modulus was also slightly elevated (130 ± 10 GPa) compared to the values obtained below the Zn concentration of 25%. Nevertheless, the Zn content has only a moderate effect on the mechanical performance.

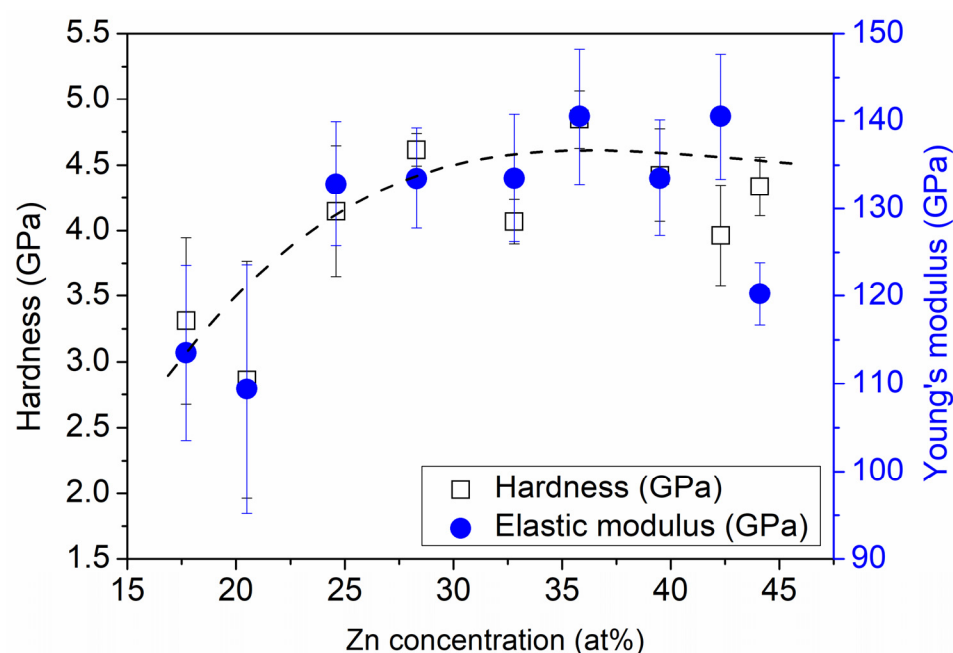


Figure 10. The hardness and the elastic modulus as a function of the Zn concentration. The curve shows the trend suggested by the data and is only a guide for the eyes.

4. Discussion

XRD revealed that in the studied composition range, the MPEA layer has a single-phase FCC structure. This observation is in accordance with the prediction made on the basis of the valence electron concentration (VEC) [57]. VEC is obtained as the average of the VEC values of the constituents weighted by their atomic fractions [58]. It was suggested that if a cubic structure forms in an MPEA, the FCC phase is stable if the VEC value is higher

than 8 while the structure is BCC when the VEC is lower than about 7 [58]. If the VEC value is between 7 and 8, the two phases coexist. For the presently studied Co-Fe-Ni-Zn MPEA, the VEC values of the pure constituents are the following: 9, 8, 10, and 12 for Co, Fe, Ni, and Zn, respectively. Thus, using the concentrations listed in Table 2, the average VEC values were calculated for the nine positions studied in this work and plotted as a function of the Zn content in Figure 11. It can be seen that the VEC values varied between 9.4 and 10.4, predicting a single-phase FCC structure in accordance with the experimental results. Moreover, the average VEC increased more or less linearly with increasing Zn content.

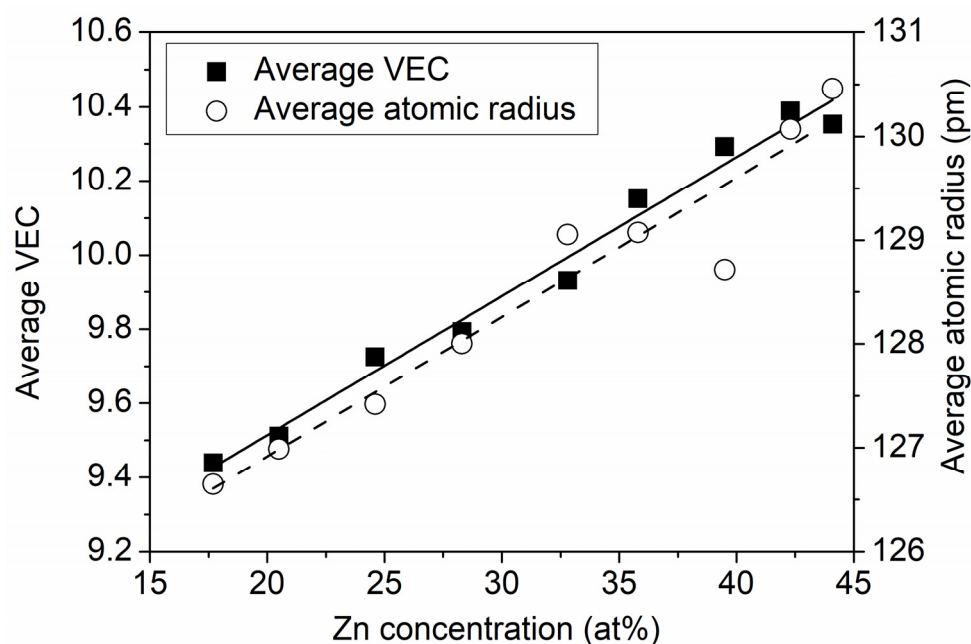


Figure 11. The average VEC and the average atomic radius as a function of Zn concentration. The straight lines are only a guide for the eyes.

Figure 9 shows that the lattice constant of the FCC phase in the combinatorial coating increased with increasing Zn concentration. This effect can be attributed to the very large size of Zn atoms among the constituent elements. Indeed, in an FCC structure, the atomic radii of Co, Fe, Ni, and Zn are 125, 126, 125, and 137 pm, respectively [59]. In this list, the metallic atomic radii were used since the constituent elements form metallic alloys in the studied material. This type of atomic radius is defined as half the distance between the centers of the adjacent atoms in a single-component solid body. The average atomic radii for the different chemical compositions were determined from the element concentrations listed in Table 2 and the radii of the constituents. Then, the obtained average atomic radius versus the Zn concentration was plotted, shown in Figure 11. An approximate linear relationship can be observed between the two quantities. Therefore, the increase in the lattice constant with increasing Zn content can be explained by the change in the average atomic size in the close-packed FCC structure.

The hardness and the elastic modulus values practically did not change when the Zn concentration varied between 25 and 44 at%. Most probably, the unchanged phase composition and texture as well as the consistent crystallite size contributed to this effect. On the other hand, the elastic constants and the threshold stress of plasticity inside the crystals are expected to be influenced by the chemistry of the material. Nevertheless, this effect seems to be marginal in the studied compositional range. On the other hand, the hardness and the Young's modulus observed formerly for an electrodeposited MPEA film with the composition of 32% Co–27% Fe–21% Ni–20% Zn (at%) were much higher (9.2 and 197 GPa, respectively [22]) than the values determined for a similar composition in the presently studied layer (position No. 1 or 2, see Table 2). Indeed, for location No. 1 or 2, the

hardness and the elastic modulus were about 3 and 110 GPa, respectively. For the hardness, the deviation was larger than that for the Young's modulus. This difference between the mechanical performance of the present and the previously investigated coatings can be attributed to the secondary phases observed in the former material. Indeed, in the previously studied layer, additional BCC and amorphous minor phases coexisted with the main FCC matrix, which can increase the hardness considerably and also alter the elastic modulus significantly. The difference in the microstructures of the two films was caused by the difference in the processing conditions. For instance, the formerly used Ta foil substrate was replaced by brass in the present study, and this resulted in very different crystallographic textures in the two films. It should be noted, however, that the dominant orientation of the deposit differed from that of the brass substrate.

5. Conclusions

A combinatorial MPEA layer was successfully processed by electrodeposition for the first time. The experiments were conducted in the Co-Fe-Ni-Zn compositional library, and the following conclusions were drawn from the results:

1. In the as-deposited sample with a thickness of about 4 μm , the Zn content varied between 18 and 44 at%, mainly at the expense of Co, but the average concentrations of Fe and Ni also decreased when the Zn content increased. In the whole studied compositional range, the structure was a single-phase FCC, in accordance with the prediction of the empirical VEC rule. The lattice constant of the FCC phase increased with increasing Zn content, which was successfully explained by the variation in the average atomic radius in the close-packed FCC structure. The layer had a 220 crystallographic texture and a nanocrystalline microstructure with a crystallite size of about 18 nm, irrespective of the chemical composition.
2. The hardness and the elastic modulus of the combinatorial coating were about 4.5 and 130 GPa, respectively, for the Zn concentrations between 25 and 44 at%. For lower Zn contents, both mechanical parameters had smaller values (3 and 110 GPa for the hardness and the Young's modulus, respectively). These values were much lower than those obtained for a formerly studied electrodeposited Co-Fe-Ni-Zn layer with similar composition, which can be attributed to the secondary BCC and amorphous phases in the previously investigated coating. This difference in the phase composition was caused by the partly dissimilar processing conditions.
3. The relatively small variation in the mechanical properties as a function of the deposit composition as well as the small surface roughness of the deposits support electroplating as a prospective technology for the successful preparation of MPEA coatings with good mechanical performance. Should a minor variation in deposit composition arise from either the uneven current distribution or the uneven precursor supply, the resulting composition variation would not deteriorate the desired high coating hardness. This aspect of the electrodeposition process may play a crucial role in potential industrial applications, especially in cases where even current density (and concomitantly, even deposit composition) cannot be achieved due to the complex shape of the workpieces.

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