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The kinetics of growth of high entropy alloy layers sputtered on Tungsten powder substrate

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ABSTRACT

Tungsten powder particles have been encapsulated with thin CrMnFeCoNi layers by magnetron sputtering method using high entropy alloy as a target. In the course of sputtering the powder surface has been periodically analyzed. The multimetallic coatings were being dissolved in 2 M HCl and the obtained solutions were analyzed by ICP method to determine Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions concentration. The aim of the analysis was comparison of atomic proportions of the elements in the target and in obtained layer and indirect determining of the layer thickness.

***Keywords*:** magnetron sputtering, high entropy alloy, nanolayers, ICP analysis

1. INTRODUCTION

Magnetron sputtering method belongs to PVD (Physical Vapor Deposition) methods, and is, in particular, applied for deposition of thin surface layers from gas phase on different substrates. This method consists in sputtering of target material with the use of inert gas ions. Magnetron sputtering belongs to advanced methods of surface modification of a variety of engineering materials. This technique allows to obtain a compact, homogenous metallic layers on special use substrates. Magnetron sputtering method has a lot of advantages such as high deposition rate, formation of durable, compact and dense coatings, low pollutants content, the ability of both mono- as well as multi-component layers manufacturing, low process temperature and precise control of process parameters [1-4]. The technological parameters of the sputtering process have a fundamental impact on the thickness, morphology and physicochemical properties of obtained layers. The most important parameters of the magnetron sputtering process are: substrate temperature, deposition time, inert gas pressure, sputtering power and, in case of powdered substrates, agitation of powder particles [1-4].

There exists a number of publications under the fabrication of both thin amorphous and crystalline layers to improve the performance of various substrates [5-8]. Due to unique properties, such as high mechanical strength and hardness, excellent abrasion resistance, high temperature stability including good oxidation and corrosion resistance, the high entropy alloys are becoming a promising material for use as thin coatings [9-12]. In World's literature there are only a few publications relating manufacturing and physicochemical properties of thin layers of high entropy alloys [13-16].

The purpose of present paper was to determine proportions of elements in the multi-component thin CrMnFeCoNi layers obtained on inert substrate by magnetron sputtering. The intended target material prepared for this study had equal molar content of all of the five elements. According to the chemical analysis, the final mass percentages of individual elements in the applied target were as follows: 18.54% Cr; 19.59% Mn; 19.92% Fe; 21.02% Co and 20.93% Ni.

2. EXPERIMENTAL

2. 1. Materials and methods

The CrMnFeCoNi thin coatings were deposited on the spectral purity Tungsten powder (powder fraction 20-50 μm) particles by magnetron sputtering using a 30 mm diameter high entropy alloy target, of CrMnFeCoNi formula, in DORA Power Back system [17]. The amount of 8.00 g of tungsten powder has been introduced into a 150 cm^3 drum-shaped container rotating with a rate of 26 rpm to agitate the powder during sputtering process. The process was carried out in a vacuum chamber equipped with a pump system consisting of a vacuum- and a rotary pumps. The substrate powder temperature was *ca* 50 °C. The sputtering process was carried out right through four time periods: 0.5; 1; 2 and 3 hours and each time amounts of 1 g of the powder (determined with an accuracy of 0.0001 g) have been taken for analysis. The vacuum in the reaction chamber was taken from Ar-gas and it was on the order of 0.1 – 1 Pa. The proportions of elements in obtained layers have been evaluated by the covered powder material dissolution in 2 M HCl and determining the Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions concentration in resulting solution, using the 4200MP-AES optical emission spectrometer (with induction induced plasma (Agilent, OES ICP).

2. 2. Result and discussion

The results of ICP analysis allowed to determine the amounts of the Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions in the solutions obtained by the powders acid etching. In Tab. 1. the element contents (per 1.00 g of the powder) in obtained layers corresponding to applied sputtering time periods are presented. The sputtering process was carried out in four steps (Note: for the last step (after 180 mins) only content of Cr and Fe has been determined in the etching solution).

Table 1. Element contents in the actual layer per 1.00 g of the powder

Sputtering time, mins	**Mass of elements, mg**				
	Mn	Cr	Fe	Ni	Co
30	0.0089	0.0067	0.0493	0.0392	0.0167
60	0.0258	0.0204	0.0647	0.0633	0.0373
120	0.2105	0.1048	0.2381	0.2331	0.2198
180	-	0.1906	0.4314	-	-

In the Fig. 1 the concentration of elements coming from MnCrFeCoNi thin layers *vs* sputtering time applied are presented. It can be seen that the proportions of individual elements determined for initial time periods (especially after 30 mins) are far different from these in the applied target. The closest proportions of the elements to these in the target (on the level of 20 mass %) occur after 120 minutes of sputtering process. The reason of the observed differences, particularly severe for the initial sputtering periods, can be ascribed to the differences in ionization energies of the individual elements [18]. Analogous behavior has been noted for two-component Fe-20% Cr target (on Cu substrate) in one of our earlier papers [18]: for earlier sputtering periods the Cr content in the layer was evidently lower (simultaneously, Fe - greater) than these after some final periods. Comparison of the concentration changes in the sputtered layer (Fig. 1) allows to believe that concentrations of the target components settle on a constant level after 60-120 mins of sputtering. After this period of time the concentrations of Mn, Ni and Co in the layer become close (± 3%) to these in the target (i.e. ≈ 20 mass%). The final concentration of Fe is a little greater (25 mass%) whereas that of Cr - a little lower (13 mass %) as compared to the corresponding presence in the target.

The thickness of produced layers (h) can be approximately estimated on the basis of initial substrate powder mass (m_{powder}) and amounts of metallic components in the layer, assuming uniform distribution of the elements across the layer and nearly spherical shape of the particles (with average radius of $\bar{r}$), similarly as it has been shown in [18]:

$$h = \frac{1}{3m_{\mathrm{powder}}} d_W \cdot \bar{r} \cdot \left(\frac{m_{\mathrm{Fe}}}{d_{\mathrm{Fe}}} + \frac{m_{\mathrm{Cr}}}{d_{\mathrm{Cr}}} + \frac{m_{Mn}}{d_{Mn}} + \frac{m_{Ni}}{d_{Ni}} + \frac{m_{Co}}{d_{Co}} \right) \qquad (1)$$

where: d_W is the density of Tungsten, and d_{Fe}, d_{Cr}, d_{Mn}, d_{Ni} and d_{Co} denote the densities of individual elements. Note: for sputtering time equal to 180 mins, the concentrations of Mn, Co and Ni have been assumed to be the same as these settled after 120 mins.

In Fig. 2 the layer thickness calculated from Eq. (1) is presented as a function of sputtering time. It results from Fig. 1, that after first initial 60 minutes, the layer thickness starts to linearly increase with further sputtering time with a practically constant rate of *ca* 10 nm per hour.

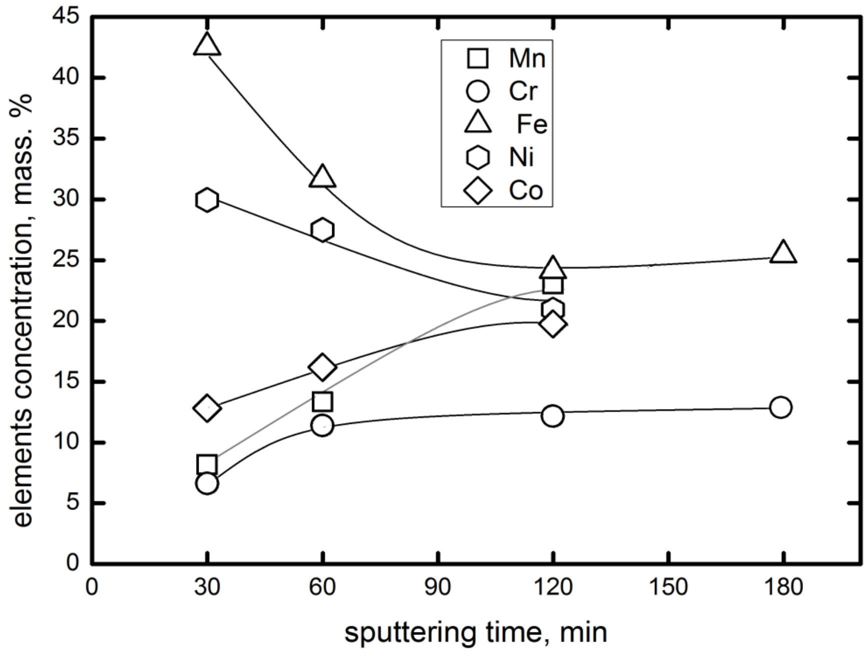

Figure 1. Concentration of individual elements in the sputtered MnCrFeCoNi thin layer as a function of sputtering time

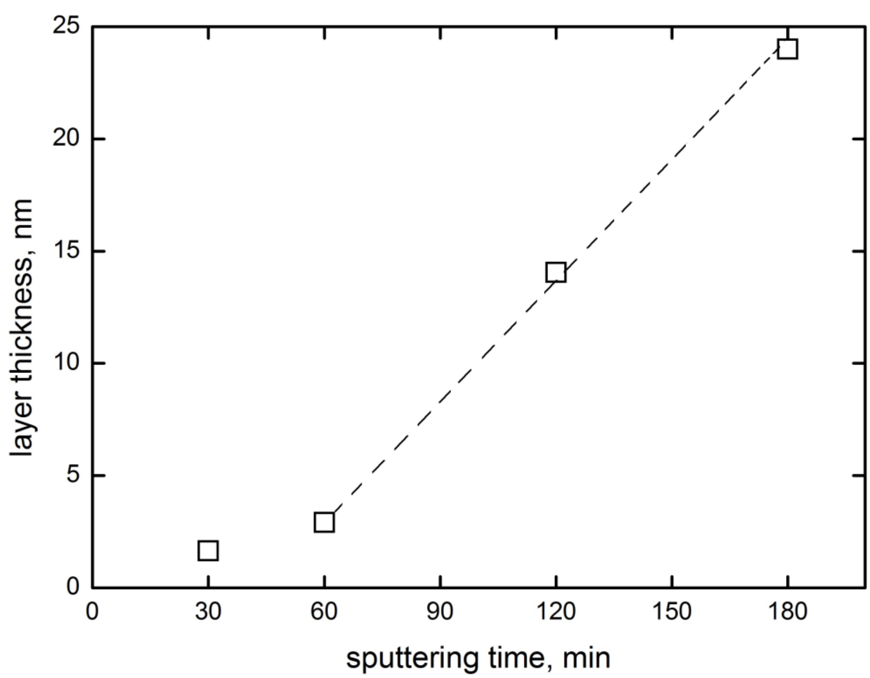

Figure 2. Calculated (from Eq.1.) thickness of obtained MnCrFeCoNi thin layers *versus* sputtering time

3. CONCLUDING REMARKS

The thin, (≈ 25 nm) multicomponent MnCrFeCoNi layers can be successfully deposited on Tungsten powder substrate using magnetron sputtering method. During initial period of sputtering the proportions of individual elements significantly differ from these in the applied target. After longer times (> 60 mins) the metal concentrations in the layer show a tendency to settle on a constant level, close to that in the target. Simultaneously, after the first 60 mins, further increase of layer thickness becomes directly proportional to the sputtering time.

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