Available online at www.worldscientificnews.com

World Scientific News

WSN 76 (2017) 12-18 EISSN 2392-2192

Manufacturing of thin nickel-rich alloy films on powder substrate using magnetron sputtering technique

Klaudia Bordolińska

Department of Chemistry, Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology, 19 Al. Armii Krajowej, 42-200 Czestochowa, Poland

E-mail address: kbordolinska@wip.pcz.pl

ABSTRACT

The magnetron sputtering technology has been applied to obtain five kinds of thin, nickel-rich layers on tungsten powder substrate. Circular plates (30 mm in diameter) of pure nickel (99.9%), inconel 600 (72% Ni, 17% Cr, 10% Fe), inconel 601 (63% Ni, 25% Cr, 7.6% Fe), inconel c-276 (51% Ni, 16.5% Cr, 17% Mo) and incoloy H / HT (35% Ni, 23% Cr, 39.5% Fe) were used as sputtering targets. The nickel-based layers have been deposited on pure tungsten powder (2 g; fraction 20-50 μm). After 2 hours of sputtering, the produced layers have been dissolved in 2M HCl solution. The obtained solutions were then analyzed on Ni^{2+}, Cr^{3+}, Fe^{2+} or Mo^{2+} ions. The analysis data allows for evaluation of the thickness of the obtained coatings.

***Keywords*:** magnetron sputtering, thin layers, ICP analysis, layer thickness

1. INTRODUCTION

Cathodic sputtering of target material in magnetron discharge plasma – allows manufacturing of tight and thin films or coatings on various substrates. The magnetron ionizes argon gas, then the ions are speed up towards the cathode where the target material is located. The released stream of target material atoms finally bombard the functional substrate [1]. Penning (1935) [2] was the first who applied magnetron sputtering for the film deposition. Magnetron sputtering has expanded rapidly over the last decade to the point where it has become established as the process of choice for the deposition of a wide variety of industrially important coatings [3,4]. In particular, magnetron sputtering now makes an important influence in application areas including low friction coatings, hard, wear-resistant coatings, decorative films, corrosion-resistant layers, and coatings having specific electrical or optical properties [5-8].

Magnetron sputtering method is of great importance not only for industrial applications but also for science and technology investigations. The experience in deposition of polycrystalline or amorphous metallic films, intermetallic compounds, alloys with given structure, protective and functional properties is still dynamically developed [9,10].

The use of the magnetron sputtering for the deposition on powder substrates meets some peculiarities and is fairly difficult task. To obtain uniform coatings stirring of powder (particles agitation) is required during the process of deposition. [11-14]

The present paper aims at manufacturing of thin nickel- and nickel-rich coatings on tungsten powder substrate using low temperature magnetron sputtering. The obtained deposits were subjected to acid dissolution and thoroughly analyzed with the use of ICP method. The intention of these initial tests was to define the sputtering process conditions that ensure obtaining of reproducible protective films on hydrogen storage material particles used in NiMH type batteries. According to previous studies of our team [15-18], thin layers obtained by magnetron sputtering on surface of active material ($LaNi_{4.5}Co_{0.5}$) are to prevent or slow down oxidation processes of alloy particles. The choice of nickel-rich alloys as target materials is justified by unique catalytic properties of nickel towards the H_2O/H_2 redox system.

2. EXPERIMENTAL

Table 1. Sputtering process conditions applied for coating of nickel-rich thin films on tungsten powder substrate

Deposition parameters	**Target materials**				
	pure nickel	inconel 600 (72% Ni, 17% Cr, 10% Fe)	inconel 601 (63% Ni, 25% Cr, 7.6% Fe)	incoloy H / HT (35% Ni, 23% Cr, 39.5% Fe)	inconel c-276 51% Ni, 16.5% Cr, 17% Mo)
Target-substrate distance	80 mm				
Target diameter	30 mm				
Sputtering time	120 min				

Base pressure of system	0.02 Pa
Sputtering pressure	6.5 Pa
Sputtering gas	Ar
Power on target	300 W
Substrate temperature	*ca* 50 °C
Sample stage rotation speed	26 rpm

A prototype high vacuum and low temperature sputtering device - DORA Power Pack, 570-640W [19] has been employed to manufacture thin nickel and nickel-rich coatings on spectral purity tungsten powder. As target materials the circular plates (ø ≈ 30 mm, $h \approx 4$ mm) of pure nickel (99.9%) and four nickel-based alloys: Inconel 600 (72% Ni, 17% Cr, 10% Fe), Inconel 601 (63% Ni, 25% Cr, 7.6% Fe), Inconel c-276 51% Ni, 16.5% Cr, 17% Mo) and Incoloy H / HT (35% Ni, 23% Cr, 39.5% Fe) have been applied. The mass of 2 g of tungsten powder (fraction of 20-50 μm) has been located in sputtering chamber at a distance of 80 mm from the surface of the cathode (target). The magnetron sputtering process was carried out in a vacuum chamber equipped with pumping system consisting of rotary- and diffusion pumps. The sputtering conditions were maintained, as shown in Table 1.

To dissolve the obtained films the encapsulated tungsten powder samples were subjected to etching in 3 mL of 2M HCl solution. After filtration, the resulting solutions were analyzed quantitatively, using induced coupled plasma (ICP) method. The analysis allows to determine concentration of Ni^{2+}, Cr^{3+}, Fe^{2+} or Mo^{2+} ions, and hence - composition of the coatings.

3. RESULT AND DISCUSSION

From the analytical data the amounts of Ni, Cr, Fe and Mo present in the produced coatings for assumed sputtering time period have been calculated. The amounts of individual elements in the coatings formed using corresponding targets are presented in Fig. 1

The knowledge of mass of the powder taken for analysis (m_{powder} = 1g) and the mass of metallic constituents (m_{Ni}, m_{Cr}, m_{Fe} and m_{Mo}) in the final films makes it possible to evaluate the thickness of the sputtered layers. Assuming the particles are nearly spherical in shape and the distribution of target constituents (Ni, Cr, Fe or Mo) across the coating is homogeneus, the thickness of the obtained layer can be calculated from the following formula [11]:

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

where: d_W, d_{Ni}, d_{Cr}, d_{Fe} or d_{Mo} denote the density of individual elements (equal to 19.25, 8.91, 7.17, 7.87 or 10.28 g·cm^{-3}, respectively) and $\bar{r}$ is the average particle radius (in experimental conditions $\bar{r}$ = 0.0018 cm). The thickness of the protective layers, calculated from Eq.1, is presented for particular targets in Fig. 2.

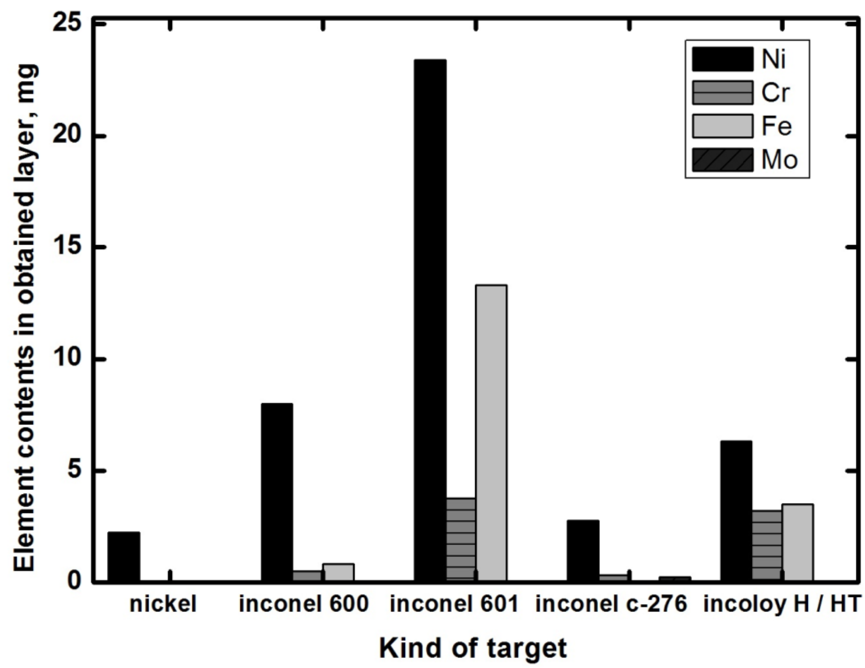

Figure 1. Amounts of Ni, Cr, Fe or Mo that enter the coating on tungsten powder substrate after 2h of sputtering of corresponding targets.

As it is seen in Fig 2, the thickness of sputtered layer is the largest (559 nm) for the target made of inconel 601 alloy. Pure nickel target is difficult to sputtering because it has ferromagnetic properties and this is why the layer obtained from nickel is the thinnest. Contrary to pure nickel, the nickel alloys containing Cr and Fe are easily sprayed. The layer obtained with the use of the incoloy H / HT target (35% Ni, 23% Cr, 39.5% Fe) has the composition (mass. %) very close to the target, namely proportions of the layer componets are as follows: [Ni]:[Cr]:[Fe] = 48 : 24 : 28.

In Fig. 3 the percentages of Ni, Cr, Fe and Mo in the resulting coatings are presented. It is worth noting that presence of nickel in the resulting coatings is predominant, in all of cases clearly greater than that in the target material. Having in mind well documented catalytic properties of nickel, this observation is of great practical importance.

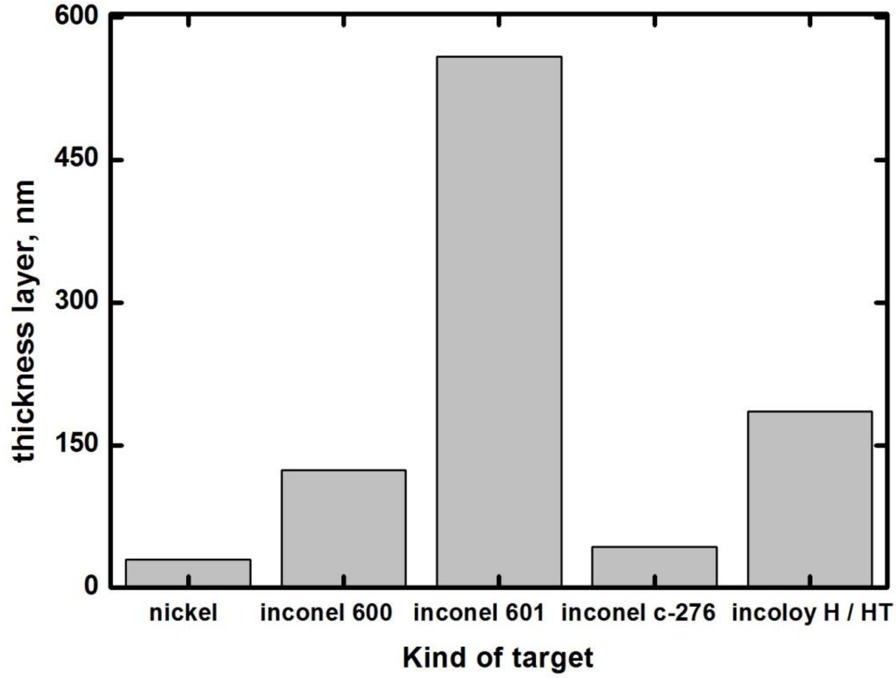

Figure 2. Calculated thickness of obtained thin layers -depending on-kind of the target.

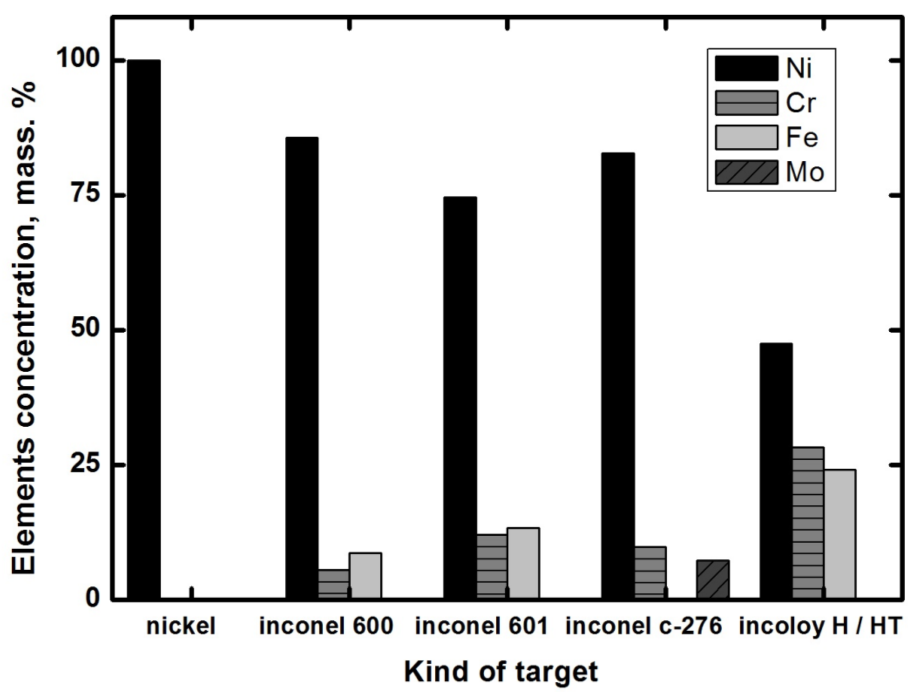

Figure 3. Elements concentrations of obtained thin layer depending on the kind of target.

As it has been mentioned earlier, the main prospective purpose of present, preliminary tests was to distinguish sputtering parameters to obtain reproducible protective films on active particles of hydrogen storage materials applied in NiMH type batteries. To avoid possible analytical errors resulting from substrate dissolution (hydrogen absorbing materials, e.g. of $LaNi_5$ type, contain large amounts of nickel) the tests described in present paper were carried out on tungsten powder, which is comparatively resistant to HCl solution. It seems the kind of metal substrate has secondary influence on composition of sputtered layers. However, this supposition should be confirmed by independent methods (e.g. XPS analysis of surface layers). Such kind of tests are in progress now and will be a subject of our forthcoming papers.

3. CONCLUDING REMARKS

The nickel-rich, thin surface layers can successfully be manufactured on powdered tungsten substrate using magnetron sputtering method. Owing to ferromagnetic properties of pure nickel, the use of pure nickel targets cannot be recommended for effective sputtering. It results from the research performed that application of targets made of inconel type alloys is very much efficient and ensures high concentrations of Ni in final coatings. Among five kinds of nickel-based materials the best results have been achieved using inconel 601 alloy (63% Ni, 25% Cr, 7.6% Fe). The thickness of the obtained coating for this alloy appeared to have been definitely the greatest and the amount of nickel in the final layer using this alloy was as large as 75 mass percent.

Acknowledgement

The author express their gratitude to professor Jerzy Gęga for his help in ICP examinations.

References

[1] O. K. Alexeeva, V. N. Fateev, *International Journal of Hydrogen Energy*, 41 (5) (2016) 3373-3386

[2] F. M. Penning, Coating by cathode disintegration, Patent 2 146 025 AH01J41/06, H01J41/20, H01J41/00, C23C14/35, USA (1939)

[3] L. Xie, P. Brault, J.M. Bauchire, A.L. Thomann, L. Bedra, *Journal of Physics D: Applied Physics*, 47 (22) (2014) 224004

[4] K. Sarakinos, J. Alami, S. Konstantinidis, *Surface and Coatings Technology*, 204 (11) (2010) 1661-1684

[5] C.A. Davis, *Thin Solid Films*, 226 (1) (1993) 30-34

[6] U. Helmersson, M. Lattemann, J. Bohlmark, A. P. Ehiasarian, J. T. Gudmundsson, *Thin Solid Films*, 513 (1-2) (2006) 1-24

[7] Y. Pauleau, *Vacuum*, 61 (2-4) (2001) 175-181

[8] J. T. Gudmundsson, J. Alami, U. Helmersson, *Surface and Coatings Technology*, 161 (2-4) (2002) 249-256

[9] O. K. Alexeeva, D. M. Amirkhanov, A. A. Kotenko, M. M. Chelyak, *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, *Springer* (2007) 95-103

[10] O. K. Alexeeva, B. L. Shapir, V.N. Sumarokov, E. A. Vinogradova, *International Journal of Hydrogen Energy*, 24 (2-3) (1999) 235-239

[11] Stefaniak, K. Bordolińska, *Ochrona przed Korozją*, 58 (7) (2015) 261-263

[12] K. Bordolińska, A. Stefaniak, P. Pawlik, *Hutnik*, 82 (10) (2015) 666-669

[13] Z. Yu, Z. G. Shen, *Indian Journal of Physics*, 89 (2015) 489-494

[14] X. Yu, Z. Shen, Z. Xu, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 265 (2) (2007) 637-640

[15] Stefaniak, K. Bordolińska, M. Sozańska, *Ochrona przed Korozją*, 59 (9) (2016) 330-333

[16] K. Bordolińska, H. Bala, *Ochrona przed Korozją*, 60 (4) (2017) 102-104

[17] K. Bordolińska, A. Stefaniak, H. Bala, *Ochrona przed Korozją*, 59 (2) (2016) 43-45

[18] Stefaniak, K. Bordolińska, H. Bala, *Ochrona przed Korozją,* 59 (4) (2016) 91-93

[19] J. Dora, Zasilacz rezonansowy, Patent PL nr 313150, Urząd Patentowy RP (1996), Poland.

(Received 18 May 2017; accepted 06 June 2017)