

ELECTROLYTIC COMPOSITE NICKEL LAYERS WITH A NANO-SIZED Si_3N_4 DISPERSE PHASE

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Abstract. Composite layers with a nickel matrix and a nano-sized Si_3N_4 disperse phase were examined. The composite layers were produced by two deposition techniques, i. e., the chemical reduction and the electrochemical method. A disperse phase of the silicon nitride with grain dimensions of the order of 15 nm was used for depositing the nickel composite coatings. The paper discusses the results concerning the morphology and diffraction patterns of the silicon nitride powder and its contents in the material of the composite coatings. The chemical compositions, the surface topography and the structure of the nano-crystalline composite Ni/ Si_3N_4 and Ni-P/ Si_3N_4 coatings were studied in details. The microstructures of the coatings were examined in a transmission electron microscope (TEM) and a scanning electron microscope (SEM) equipped with EDS suitable for local chemical analyses. The ceramic phase was also examined by the XRD and TEM techniques. A comparative analysis of the results shows that the deposition techniques used for producing the composite coatings have an important influence on the contents and distributions of the nano-dispersed phase within the surface composite layers.

1. INTRODUCTION

Composite layers containing a metal matrix and a nano-sized disperse ceramic phase have been extensively studied in the recent years [1-3]. This results from the fact that by combining useful properties of the metals and non-metallic inclusions one can manufacture layers with specific, desirable properties that can perform various functions. Many possibilities in this area are offered by the composite layers with a nickel matrix, added with hard ceramic particles. Using nickel as the matrix and the Si_3N_4 powder as the disperse phase and applying adequate deposition techniques (of layers on a specific base), we can obtain significant by improve the useful properties, such as the hardness, wear resistance and corrosion resistance of hardware products [4,5]. By decreasing the particle size of the composite constituents one can obtain nano-composite layers with considerably better proper-

ties compared to those of its previous classic equivalent. Moreover, the composite layers whose one of the components has a grain size of the order of 1-100 nm form a new, very attractive group of modern materials [6-11]. The aim of the study was to produce composite nickel-based layers that contained the nano-sized Si_3N_4 disperse phase and to identify their structures. The composite layers were produced by two techniques; i.e., the chemical reduction and an electrochemical method. In both the methods the composite layers were produced by depositing simultaneously the metal and ceramic particles on a given substrate. It should be underlined that the processes producing of nanocomposite materials are complicated and quite difficult to realize in practice. Although numerous studies have been undertaken to construct models of composite layers, many elements of these models still require further precise explanations. This is so since many factors influ-

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ence the course of the process, such as e.g., the temperature of the process, the components and pH of the solution, the quantity, shape and size of the ceramic particles, and the chemical and physical interrelations between those factors. In the present study the composite layers were produced in bath solutions, which were mixtures of the ceramic disperse phases and a multi-component electrolyte. In this state, the particles of the ceramic phase, whose surface is strongly developed are dispersed uniformly in the electrolyte, and form with it a heterogeneous and thermodynamically instable two-phases system. Thus, to build the ceramic particles into the nickel matrix, it is necessary that the particles should be appropriately dispersed and that their suspension in the bath should be stable. It is extremely difficult problem when dealing with nano-sized disperse phases in realized processes [12-14]. This is because of the surface layers the bath solution should be mixed continuously. This mixing of the solution bath prevents the ceramic particles from sedimentation and ensures the homogeneity of the concentration of all the electrolyte components.

2. EXPERIMENTAL PROCEDURES

The Ni-P/Si₃N₄ composite layers were deposited by the technique of catalytic chemical reduction. This process consisted of simultaneous depositing of the Ni-P layer and the nano-sized Si₃N₄ disperse phase. The composite layers were produced in a multi-component bath that contained sodium dihydrogenhypophosphite(I), nickel chloride(II), the sodium citrate and powdered silicon nitride.

To deposit the composite Ni/Si₃N₄ layers by the electrochemical method a multi-component electro-

lyte (Watts bath) with an organic substance D1 and ceramic nano-disperse phase Si₃N₄ were used. During the deposition process the baths were mixed by a mechanical stirrer PX-OS 2000, manufactured by POLYMIX Company, which rotated with a speed of 1000 turns/min.

An amorphous powder of the silicon nitride was used to deposit the composite layers (Fig. 1). The average dimensions of the Si₃N₄ grains were of order of 15 nm (Fig. 2). The composite layers were produced in a bath that contained a nano-dispersive powder of silicon nitride in quantity of 20 g per 1 dm³ of the bath. The phase composition of the nitride silicon powder was determined with a Phillips PW 1830 X-ray diffractometer using a CuK_α copper lamp, at a wavelength of 0.15418 nm within the angle range from 20° to 90°. The structure of the Ni-P and Ni layers, which form the matrix of the composite, and the morphology of the ceramic phase were examined by transmission electron microscopy (TEM-JEM-1200EXII). The surface topography of the nickel and composite layers, and the diversification of their morphology were examined in a scanning electron microscope (SEM) of the HITACHI S-3500N type. The internal structure of the layers, their thickness and the concentration of the disperse ceramic phase within the volume of the composite were estimated by metallographic investigations on cross-sections of the layers, with the use of a scanning electron microscope (SEM). The chemical analysis of the

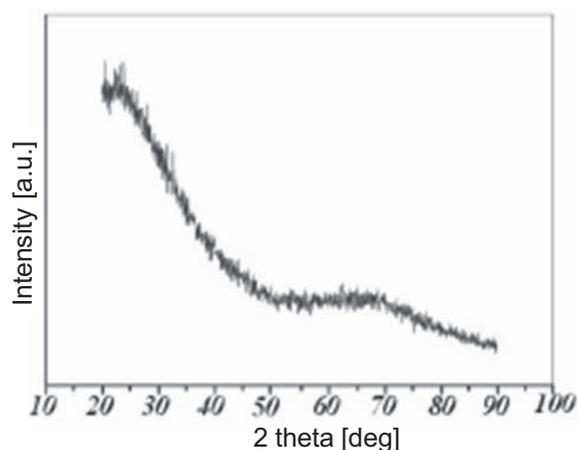


Fig. 1. Diffraction pattern of the Si₃N₄ powder.

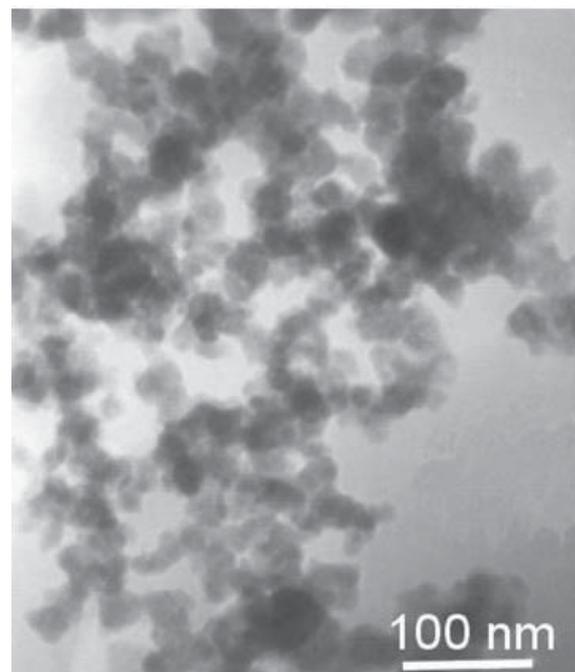


Fig. 2. TEM image of silicon nitride nanoparticles.

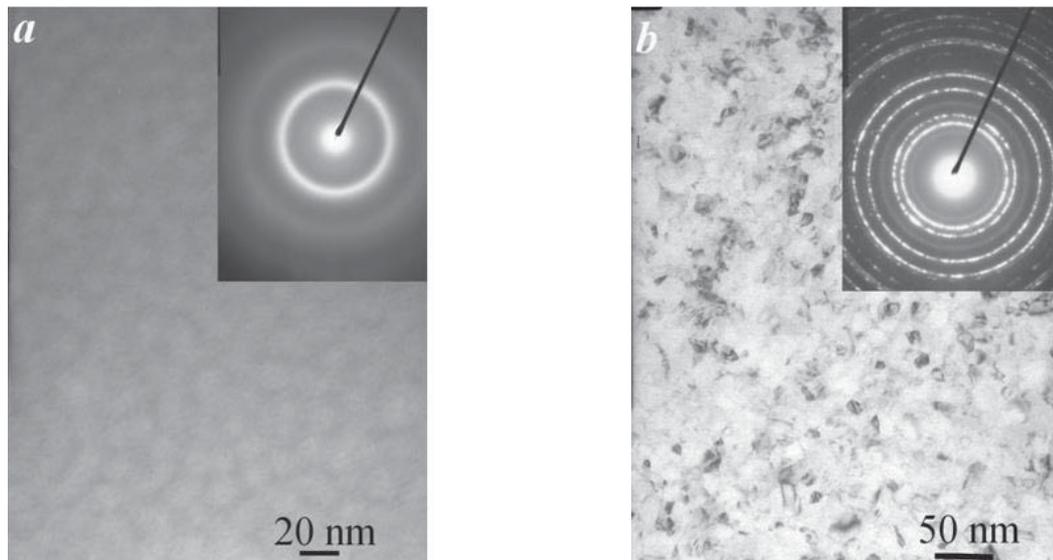


Fig. 3. Microstructure (TEM technique) of layers: a) Ni-P, b) Ni.

composite layer material was determined by the energydispersive spectroscopy method using a Noran Vantage attachment. The content of the nano-disperse ceramic phase Si_3N_4 in the material of the composite layers was determined by a computer method of image analysis.

3. RESULTS AND DISCUSSIONS

During the process of forming suitable properties of composite layers, the type and properties of the applied ceramic phase as well as of the matrix material, in which ceramic particles are included, must be carefully chosen. The matrix of the composite layers produced by the chemical method may constitute an amorphous solution of phosphorus in nickel (Fig. 3a). However, in the case of the layers produced by the electrochemical method, the matrix is formed by nano-crystalline nickel (Ni) (Fig. 3b) with the grain dimensions of the order of 30 nm. Both the Ni-P layers and the Ni layers had smooth, and glossy surfaces (Fig. 4), but, on the surface of the composite Ni-P/ Si_3N_4 and Ni/ Si_3N_4 layers, silicon nitride powder particles there were seen, which partially formed agglomerates. They were well pinned in the amorphous Ni-P matrix (Fig. 5a) and in the nano-crystalline matrix Ni (Fig. 5b). The presence of the ceramic phase has a very strong essential influence on the morphology and topography of the composite layer surface (Fig. 5). The distribution of the dispersed ceramic phase within the volume of the composite layers is shown in the photographs

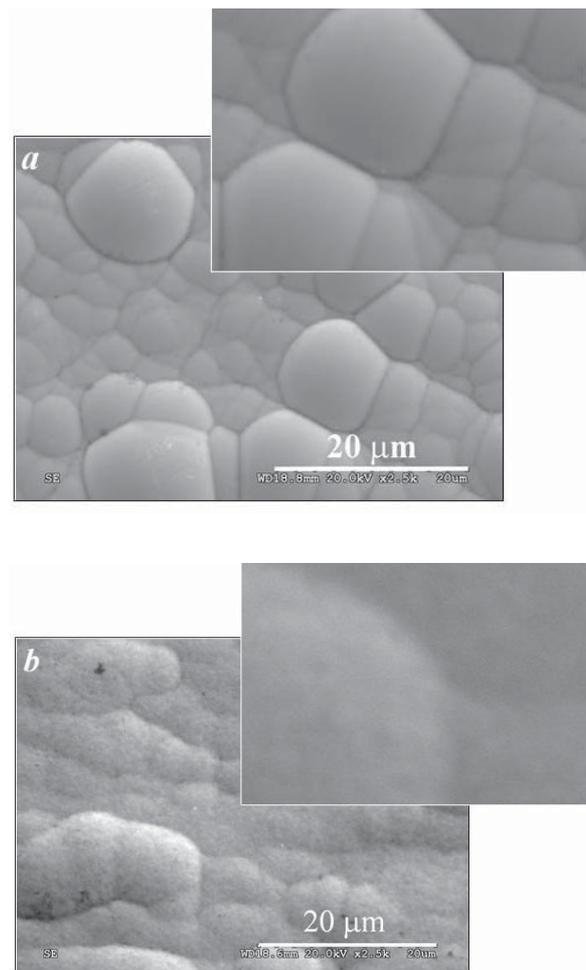


Fig. 4. Morphology (SEM technique) of layers: a) Ni-P, b) Ni.

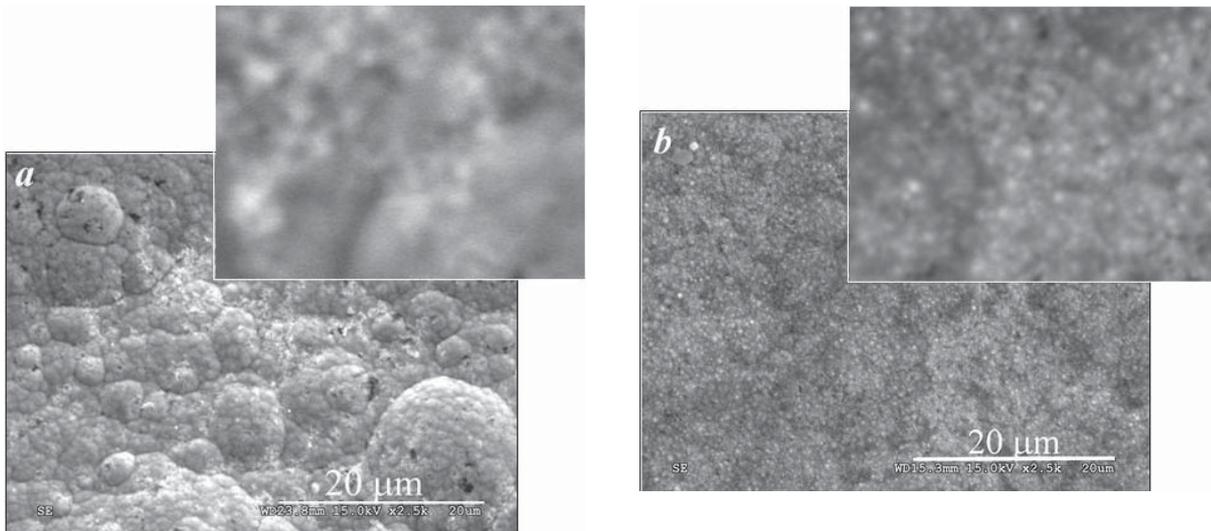


Fig. 5. Images of the nano-composite layers: a) Ni-P/Si₃N₄, b) Ni/Si₃N₄.

of their cross-sections (Fig. 6). The composite layers have a compact structure and a uniform thickness on the entire surface of the substrate. The particles of the Si₃N₄ powder formed small, evenly distributed agglomerates throughout the whole volume of the layers.

In the composite layers produced by the chemical method the dimension of agglomerates of ceramic phase are of order of 30-100 nm and in those produced by the electrochemical method they are of order of 20-50 nm.

At the present, investigations are continued to find the process parameters that prevent the agglomeration of the nano-sized ceramic phase. The degree of the dispersion of the ceramic Si₃N₄ phase in the layers produced by the electrochemical method is greater (Fig. 6b) than that in the layers produced by the chemical method (Fig. 6a). The results of linear analyses of the distribution of the individual elements, present in the composite layers are shown in Fig. 7. This analysis shows that the distribution of the elements is relatively uniform within the entire material of the Ni-P/Si₃N₄ as well as of Ni/Si₃N₄ layers. Table 1 shows the results of the chemical analysis of the elements building layers that are referred to the layer cross-section areas shown in Fig. 6. The element contents are expressed in atomic and weight percent. Irrespective the deposition technique applied the contents of the nano-disperse ceramic phase particles are similar in the Ni-P/Si₃N₄ layers as well as in the Ni/Si₃N₄ layers. The content of the ceramic Si₃N₄ phase in the composite layers produced by the chemical

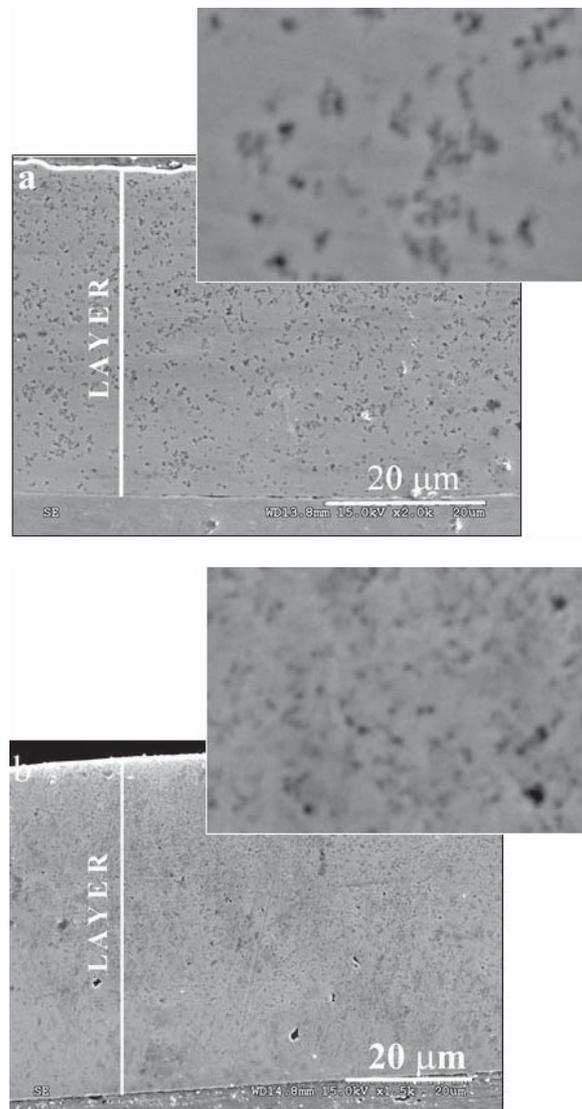


Fig. 6. Images of the material composition in the cross section of layers: a) Ni-P/Si₃N₄, b) Ni/Si₃N₄.

Table 1. Contents of the elements in the composite $\text{Ni-P/Si}_3\text{N}_4$ and $\text{Ni/Si}_3\text{N}_4$ materials.

Elements	Layer			
	$\text{Ni-P/Si}_3\text{N}_4$		$\text{Ni/Si}_3\text{N}_4$	
	Atom [%]	Wt [%]	Atom [%]	Wt [%]
Ni	72.47	87.44	86.10	95.92
P	11.87	7.56	-	-
Si	1.98	1.14	1.96	1.04
N	2.6	0.75	1.3	0.34
Other(C, O)	11.08	3.11	10.64	2.7

method is of the order of 7.4% vol. and those produced by the electrochemical method it is equal to 8% vol.

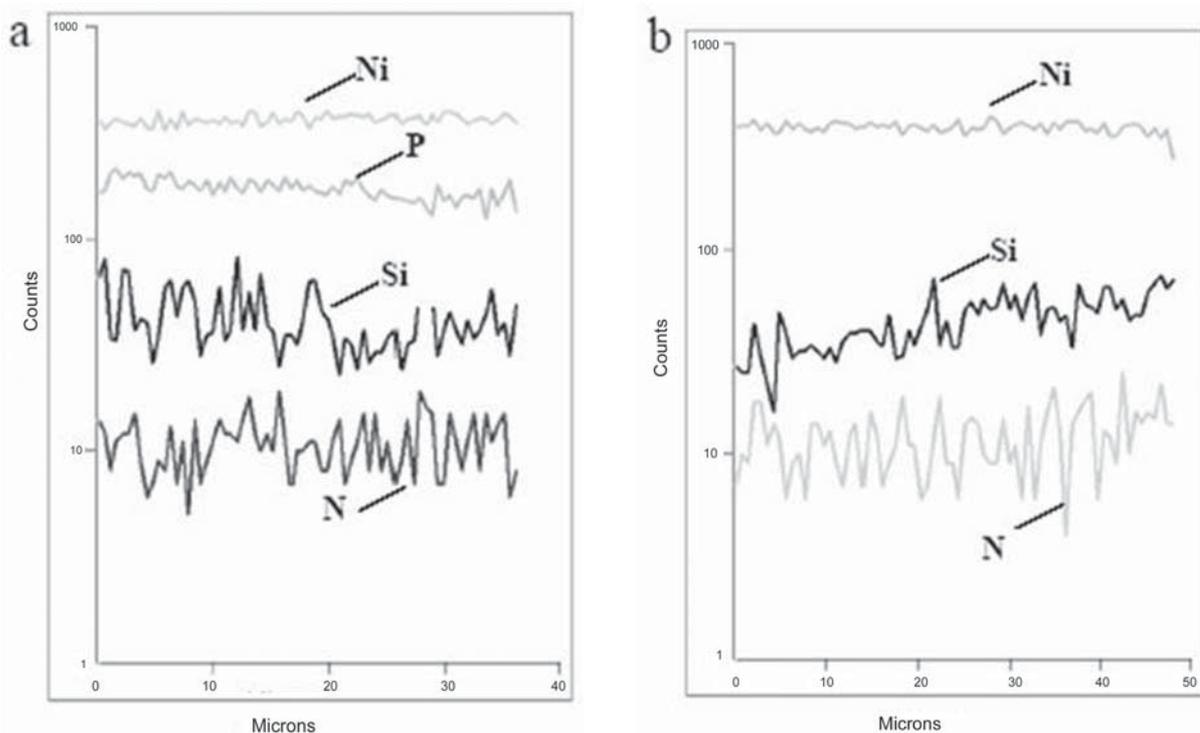
4. CONCLUSIONS

The results obtained show that:

- The composite layers produced by the chemical method ($\text{Ni-P/Si}_3\text{N}_4$) as well as by the electrochemical method ($\text{Ni/Si}_3\text{N}_4$) have compact structures and uniform thickness within their whole volume.
- The matrix of the composite layers produced by the chemical method is an amorphous solution

of phosphorus in nickel (Ni-P), whereas the matrix of the layers produced by the electrochemical method is composed of nano-crystalline nickel (Ni) alone.

- The distribution of the ceramic Si_3N_4 phase within the volume of the composite material is uniform in both types of layers.
- The content of the ceramic Si_3N_4 phase in the composite layers produced by the chemical method is of order of 7.4% vol. and in those produced by the electrochemical method it is equal to 8% vol.

**Fig. 7.** EDS analysis of the composite materials: a) $\text{Ni-P/Si}_3\text{N}_4$, b) $\text{Ni/Si}_3\text{N}_4$.

Further investigations aimed at determining the optimal parameters of the process are planned to be carried out in the near future.

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