

## Electrophysical properties of double-layer nickel-base and vanadium-base films within the intermediate temperature range

A. Chornous, I. Protsenko\*, and I. Shpetnyi

Sumy State University, 2 Rimsky-Korsakov Str., Sumy 40007, Ukraine

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Phase composition of the double-layer Ni-base and V-base films obtained and annealed in vacuum of  $10^{-4}$ – $10^{-5}$  Pa within the temperature range of 700–900 K is studied by technique of electronography and transmission electron microscopy. Temperature dependence of resistance and temperature coefficient of resistance (TCR) was investigated. Comparison of TCR experimental data with the calculated data was made at  $T=300$  K on basis of semiclassical and macroscopic models and formula for TCR of alloys.

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### 1 Introduction

Study of physical properties, phase and element composition of film metal structures obtained by means of the layer by layer precipitation in vacuum, is of great interest from the point of view of creation of new materials for the electron micro-instrument-making industry [1, 2]. The double-layer films basically consisting of such transition d-metals as Ni, Co, Cr, V, Ti, Cu and others are also among such film structures. Earlier we have investigated the electrophysical properties of the film specimens basically consisting of Ni and Co, Co and Cr [3], Ni and Ti, Ti and Co [4], Cu and Cr [5]. Their thermal treatment was done at relatively low temperatures  $T_a < 0.3T_S$ , where  $T_S$  – is melting temperature for bulk specimens. Papers of the other authors were devoted to different aspects of this problem, for instance, to multilayer film systems basically consisting of Ti and Al [6], Cu and Cr [7], Cu and Nb [8] and the others. The characteristic peculiarity of the above-mentioned papers is rather narrow temperature interval (300–700 K) of investigation of electrophysical properties.

In this connection, the objective of this paper is to study regularities and peculiarities concerning electrophysical properties of Ni/V/S and V/Ni/S double-layer films (S- substrate) at higher temperature range of annealing  $T_a < 0.6T_S$ , i.e. within the intermediate temperature range.

According to data of the paper [9], the diagram of state for specimens basically consisting of Ni and V in bulk state is complex, as eutectic solutions, solid solutions and  $Ni_2V$ ,  $Ni_3V$ ,  $V_2Ni$  and  $V_3Ni$  intermediate phases arise there. When in film state, it is also necessary to suppose that the active phase formation will take place and will influence on electrical properties.

### 2 Technique of experiment

The Ni/V/S and V/Ni/S double-layer films were obtained by electron-beam evaporation at temperature 300 K in vacuum of  $\sim 10^{-4}$  –  $10^{-5}$  Pa created by ion pump NMDO-160. The investigation of phase composition and

\* Corresponding author: e-mail: protsenko@aph.sumdu.edu.ua



crystalline structure (with electron microscope EMMA-4) was conducted using free films obtained on the (001) NaCl crystals. To study an element composition by technique of secondary-ion mass spectrometry (apparatus MS-7201M), the substrates of pyroceramics were used. Thermal treatment of the specimens was made at temperature  $T_a \cong 700, 800$  or  $900$  K during 10-15 minutes. When investigating the electrophysical properties, the substrates of glass and polycore were used. The annealing of specimens was carried out by the following flowsheet: "heating - cooling" with rate of (2-3) K/min in the course of three cycles within the temperature range of 300–900 K. Thickness of the films was measured on the test plate by an interferometry method.

The investigation of phase composition and TCR measuring operation were carried out after cooling of specimens to the indoor temperature on the assumption that the phase composition stabilized on cooling and remained in conformity with the one at the temperature of annealing.

### 3 Phase composition

According to the investigation data obtained by electronography, single-layer Ni films have FCC structure within the whole temperature range with the lattice parameter close to the parameter of bulk Ni ( $a_0=0.3524$  nm [10]). The newly condensed and annealed within the temperature range of 300–700 K, single-layer V films with thickness  $d=20\div90$  nm have BCC structure with the lattice parameter  $a=(0.301\div0.302)\pm 0.001$  nm at  $a_0=0.3028$  nm [10]. The FCC traces  $VO_x$  ( $x\cong 1$ ) with the parameter  $a=(0.403\div0.416)\pm 0.001$  nm are fixed in the relatively thin V films annealed up to the temperature 800 K. When annealing temperatures are 900–1000 K, the phase  $VO_x$  partially transforms into  $V_2O_3$  phase.

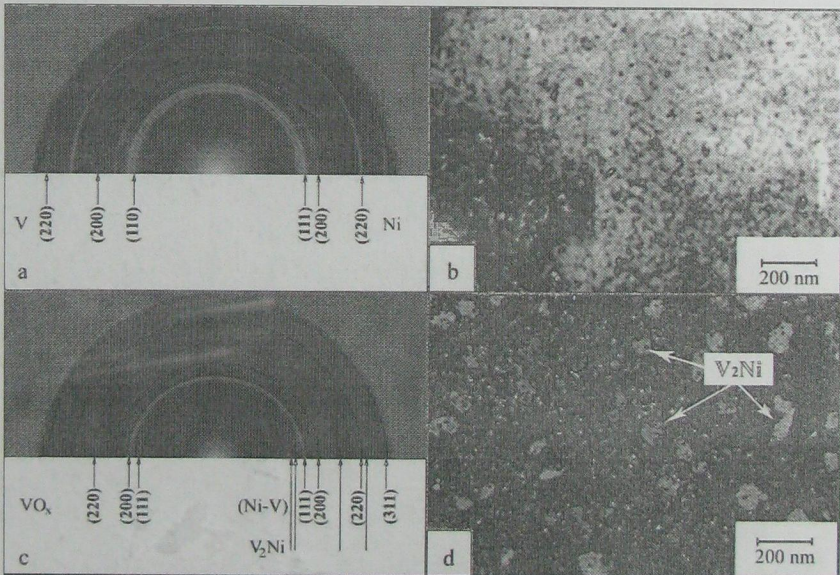


Fig. 1 Electron-diffraction pattern and crystalline structure of Ni(35)/V(45)/S films in non-annealed (a,b) and annealed up to  $T_a=800$  K (c,d) state, respectively.

The investigation of phase composition and crystalline structure of the double-layer films basically consisting of Ni and V with the thickness of individual layers of 20-70 nm revealed the following. The double-layer films in non-annealed state have FCC-Ni + BCC-V phase composition with the lattice parameters of Ni and V,



which are close to the parameter of single-layer films of these metals. Fig. 1 shows the typical diffraction and micro-structure for the Ni(35)/V(45)/S film taken as example (the thickness of individual layers in nm is given in brackets). The increase of Ni lattice parameter up to the value  $a=0.353\text{--}0.354$  nm and decrease of V lattice parameter to the value  $a=0.301$  nm is observed in the films annealed at temperature  $T_a \geq 700$  K. This phenomenon is connected with the formation of (Ni-V) FCC solid solution based on Ni crystal lattice and vacancies in V grains. Based on the dependence of the parameter (Ni-V) FCC solid solution upon the concentration of V [9], content of V makes up 5-9 atoms %. Since the lines in diffraction patterns of BCC-V in this case aren't recorded (except for the cases of large thickness of V layer), we come to conclusion concerning localization of its atoms on grain boundaries and on outside surface of (Ni-V) solid solution. The results of investigations of diffusion processes (Fig. 2) confirm this conclusion. To clear up this problem more correctly, we have studied temperature dependence of resistance and temperature coefficient of resistance (TCR) and have compared the experimentally obtained and calculated data within the frames of different models of TCR values at  $T=300$  K. When annealing up to temperatures 800-900 K, the phase composition undergoes changes connected with partial formation of metastable intermediate phase of  $V_2Ni$  and  $V_2O_3$  oxide. Generalized results of the diffraction and mass-spectrometric investigations are shown in Table 1 and in Fig. 3.

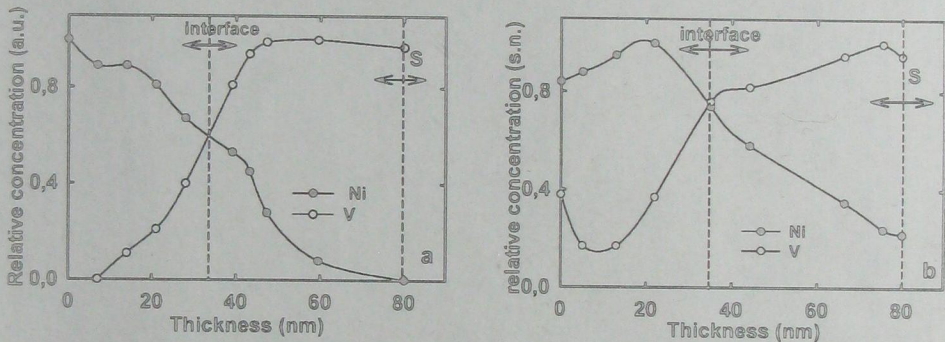


Fig. 2 Diffusion profile for Ni(35)/V(45)/S films in non-annealed (a) and annealed up to 700 K (b) state.

Table 1 Phase composition of the investigated specimens.

N	System ( $d_2/d_1$ , nm)	$T_a$ , K	$c_{Ni}/c_V$	Composition	Specimen character
1	Ni(20)/V(30)/S	300	0,82	Ni+V	Double-layer film (DLF)
		560		Ni+V	--
		610		Ni+V	--
		700		(Ni-V)+VO <sub>x</sub>	Single-layer film (SLF)
		830		--	--
2	Ni(35)/V(45)/S	300	0,96	Ni+V	DLF
		700		(Ni-V)+V+VO <sub>x</sub>	SLF
		800		(Ni-V)+VO <sub>x</sub> +V <sub>2</sub> O <sub>3</sub> +V <sub>2</sub> Ni	--
		900		--	--
		1000		(Ni-V)+V <sub>2</sub> O <sub>3</sub>	--
3	Ni(45)/V(50)/S	300	1,13	Ni+V	DLF
		700		(Ni-V)+V+VO <sub>x</sub>	SLF
		800		(Ni-V)+VO <sub>x</sub> +V <sub>2</sub> O <sub>3</sub> +V <sub>2</sub> Ni	--
4	Ni(40)/V(40)/S	300	1,27	Ni+V	DLF
		700		(Ni-V)+VO <sub>x</sub>	SLF



5	V(30)/Ni(18)/S	300		V+Ni	DLF
		610	0,78	V+Ni	-/-
		830		(Ni-V)+VO <sub>x</sub> +V <sub>2</sub> Ni	SLF
6	V(30)/Ni(22)/S	300		V+Ni	DLF
		610	0,92	V+Ni	-/-
		830		(Ni-V)+VO <sub>x</sub>	SLF
7	V(30)/Ni(40)/S	300		V+Ni	DLF
		610	1,70	V+Ni	-/-
		830		(Ni-V)+VO <sub>x</sub>	SLF
8	V(20)/Ni(50)/S	300		V+Ni	DLF
		700	3,17	V+Ni	-/-
		900		(Ni-V)+V <sub>2</sub> O <sub>3</sub>	SLF

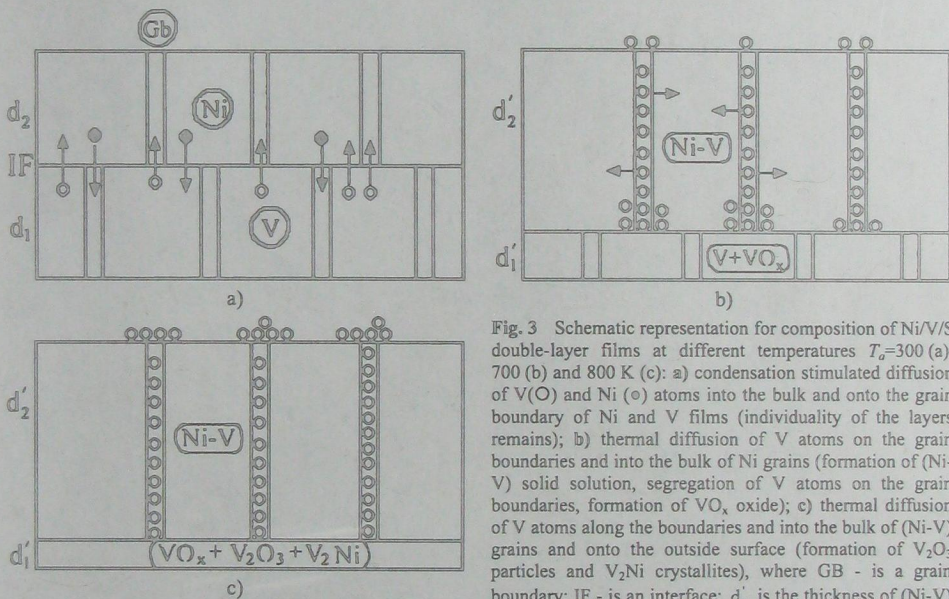


Fig. 3 Schematic representation for composition of Ni/V/S double-layer films at different temperatures  $T_0=300$  (a), 700 (b) and 800 K (c): a) condensation stimulated diffusion of V(O) and Ni (o) atoms into the bulk and onto the grain boundary of Ni and V films (individuality of the layers remains); b) thermal diffusion of V atoms on the grain boundaries and into the bulk of Ni grains (formation of (Ni-V) solid solution, segregation of V atoms on the grain boundaries, formation of VO<sub>x</sub> oxide); c) thermal diffusion of V atoms along the boundaries and into the bulk of (Ni-V) grains and onto the outside surface (formation of V<sub>2</sub>O<sub>3</sub> particles and V<sub>2</sub>Ni crystallites), where GB - is a grain boundary; IF - is an interface;  $d_2'$  is the thickness of (Ni-V) solid solution layer;  $d_1'$  is the thickness of heterogeneous layer.

#### 4 Influence of temperature on electrophysical properties

Typical dependences of resistance of double-layer films for three thermo-stabilizing cycles within the temperature range of 300–700 K and 300–900 K are shown in Fig.4. Let's analyze the resistance behavior during the first cycle «heating-cooling».

Within the temperature range from 300 to  $\theta_1=370$ –380 K we observe that the resistance increases as the temperature increases. At  $T=\theta_1$ , which coincides with the Debye temperature for vanadium ( $\theta_{Dv}=380$  K [10]), the inflection on the curve of the  $R(T)$  dependence with the subsequent decrease of the resistance or with slower tendency to the increase takes place. The next peculiarity reveals in the form of the minimum at temperature  $\theta_2=608$  K. Let's note that the minimum at temperature  $\theta_2$  is also typical for the  $R(T)$  dependences



in single-layer Ni films. Within the temperature range  $\theta_1 - \theta_2$ , the course of the resistance/temperature change depends on a condensation rate of the films. Thus, the rate being rather high, the films are more defective and their resistance when annealing decreases that is connected with crystalline structure imperfection healing. Deceleration of precipitation to  $\omega=0.2$  nm/s gives us opportunity to obtain specimens with lower concentration of defects and will influence on the character of the  $R(T)$  dependence.

When analyzing the reverse course of the  $R(T)$  dependence during the first cycle of thermal stabilization, let's note the following. The cooling curve comes higher than the heating curve and then, depending on an extent of the diffusion course and the phase formation processes at high temperatures, the curves may intersect (Fig. 4 a, b) within the temperature range of 450–590 K or not intersect (Fig. 4 c). When heating and cooling during next cycles, the resistance increases as the temperature increases. It is necessary to note that for the second and the third cycles of thermal treatment, the heating curves are in general lower than the cooling curves. The  $R(T)$  dependences for these cycles superpose. Hence, we can say that the processes of thermal stabilization and mass transfer (interdiffusion, formation of solid solutions and formation of other phases) are completed in the investigated film specimens, though one can't observe the clearly expressed peculiarities during the transition from Ni + V phase composition to (Ni-V) solid solution on the  $R(T)$  dependences.

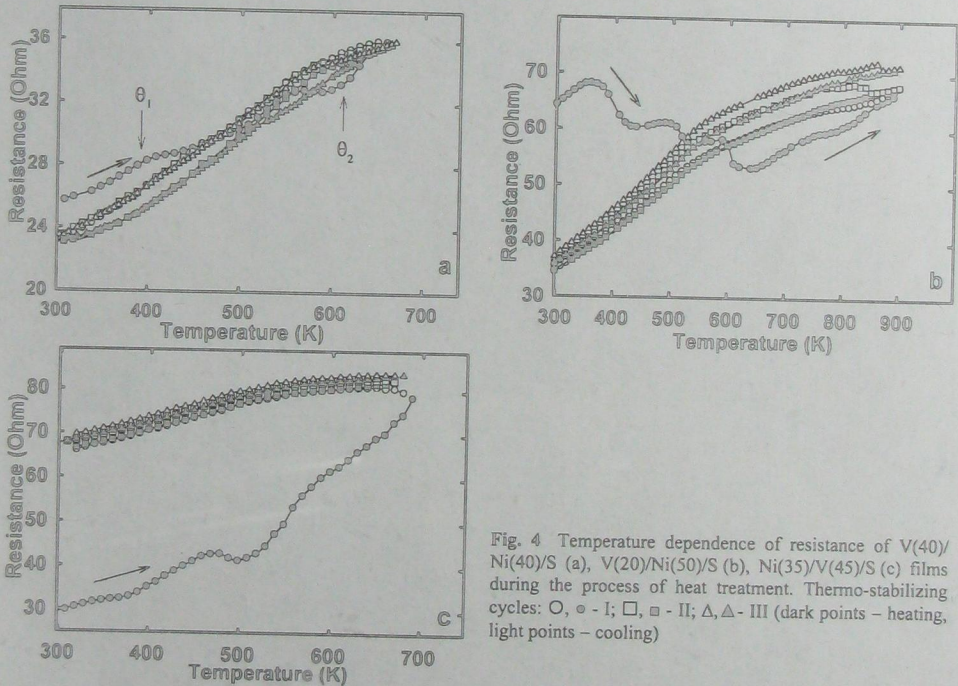


Fig. 4 Temperature dependence of resistance of V(40)/Ni(40)/S (a), V(20)/Ni(50)/S (b), Ni(35)/V(45)/S (c) films during the process of heat treatment. Thermo-stabilizing cycles:  $\circ, \ominus$  - I;  $\square, \square$  - II;  $\Delta, \Delta$  - III (dark points - heating, light points - cooling)

Let's analyze the character of temperature dependence of resistivity ( $\rho$ ) and temperature coefficient of resistance (TCR) for the films undergone the thermal treatment. For the single-layer Ni films according to data from literature sources (refer, for instance, to [11]), which are also confirmed in the other data of investigations, the peculiarities reveals for the  $\rho(T)$  and TCR ( $\beta$ ) on  $T$  dependences at Debye and Curie temperature ( $\theta_{0D}=465$  K,  $\theta_{0C}=631$  K [10]). The  $\rho(T)$  dependence up to Curie temperature is non-linear one and rectifies in  $\rho \sim T^2$  coordinates and at the same time it does not practically differ from the analogous one for the bulk specimens [12]. Such character of the  $\rho(T)$  dependence and the peculiarity at Curie temperature relate to



electron-magnon interaction. Values of Debye and Curie temperatures for the film specimens depend on the thickness [11]. So, Debye temperature ( $\theta_D$ ) drops to 395 K at  $d=30$  nm, and Curie temperature ( $\theta_C$ ) drops to 570 K. The investigations of the double-layer films where one of the layers is Ni (refer, for instance, to [4]) show that there is the clearly expressed peculiarity at Curie temperature in graphs.

Temperature dependence of resistivity for the films with  $d=51.1$  and  $211.5$  nm is represented in paper [13]. The peculiarity in the area of Debye temperature ( $\theta_{DB}=380$  K [10]) is fixed on it. The slightly shown changes on the curve of the  $\rho(T)$  dependence and correspondingly the peculiarity on the  $\beta(T)$  at Debye temperature are observed according to the data of our investigations (Fig. 5 a).

When analyzing data given in Figure 5 b, c, it is necessary to note the following. The displays of the peculiarities on  $\rho(T)$  and  $\beta(T)$  at  $\theta_D$  and  $\theta_C$  depend on both the ratio of concentration of individual metals and the processes relate to the mass transfer in volume of a film specimen. Change of temperature  $\theta_C$  and  $\theta_D$  values with respect to bulk specimens is connected not only with dimensional effects as in single-layer specimens, but also with concentration effects. As a result of display of the last ones, the transition area within the environment of characteristic temperatures is more washed out, because the value of these temperatures for each grain depends on penetration of atoms of different sort into it.

Formation of solid solutions based on Ni lattice may be one of the reasons of the fact that the peculiarity at  $\theta_C$  becomes less pronounced and disappears gradually (Fig. 5 c). Angle of inclination changes on the curve of the  $\rho(T)$  dependence at temperature 730–740 K that may be connected with the beginning of intermetallic phase formation.

## 5 Comparison with theory and prognosis of electrophysical properties of double-layer films

The dependence of TCR of double-layer films on the thickness of individual layers is satisfactorily described by the semi-classical (Dimmich [14]) or semi-phenomenological (Protsenko et al. [3]) models. For the latest case the working relation has the following form:

$$\beta = \beta_1 + \beta_2 - \frac{d_1\beta_2\rho_2 + d_2\beta_1\rho_1}{d_1\rho_2 + d_2\rho_1}, \quad (1)$$

where  $\rho_i$  is the resistivity of  $i$ -layer.

The analysis, which we have carried out, reveals that both models describe the electrophysical properties of double-layer films quite effectively. Thus according to [3,4,8], disagreement between the experimentally obtained data ( $\beta$ ) and calculated on the basis Dimmich model data ( $\beta_{cal}$ ) makes up no more than 70%, if identity of individual layers remains in film systems (i.e. there is no diffusion processes or low diffusion processes take place). Relation (1) has rather better compliance with the experimentally obtained results. According to the data represented in Table 1, the identity of individual layers practically remains up to  $T_a \leq 700$  K that is also confirmed by the comparison of  $\beta$  and  $\beta_{cal}$  values (for instance, experimentally obtained value of  $\beta=2.93 \cdot 10^{-3} \text{K}^{-1}$  for the system V(30)/Ni(70)/S after annealing up to 700 K complies with  $\beta_{cal}=3.92 \cdot 10^{-3} \text{K}^{-1}$  value (calculated on the basis Dimmich model) and  $\beta_{cal}=3.61 \cdot 10^{-3} \text{K}^{-1}$  value (calculated by the relation (1)) rather well). At the same time, identity of individual layers disappears at  $T_a > 700$  K and the film system constitutes a single-layer film, the input component of which represents (Ni-V) solid solution (influence of  $\text{VO}_x$ ,  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{Ni}$  specks for film conductivity is insignificant). Due to this, it is necessary to compare  $\beta$  value with  $\beta_{cal}$  value calculated on the basis of the relation for alloy, which for this case can be written in the following form:

$$\beta = \frac{\beta_1}{1 + \frac{c_2\rho_2}{c_1\rho_1}} + \frac{\beta_2}{1 + \frac{c_1\rho_1}{c_2\rho_2}}, \quad (2)$$



where  $\beta_i, \rho_i$  – TCR and resistivity of single-layer films;  $c_1 = \frac{D_1 d_1 \mu_1^{-1}}{D_1 d_1 \mu_1^{-1} + D_2 d_2 \mu_2^{-1}}$ ;  $c_2 = \frac{D_2 d_2 \mu_2^{-1}}{D_1 d_1 \mu_1^{-1} + D_2 d_2 \mu_2^{-1}}$  – concentration of atoms of the 1 and 2 layers; ( $D_i, \mu_i$  – density and molar mass).

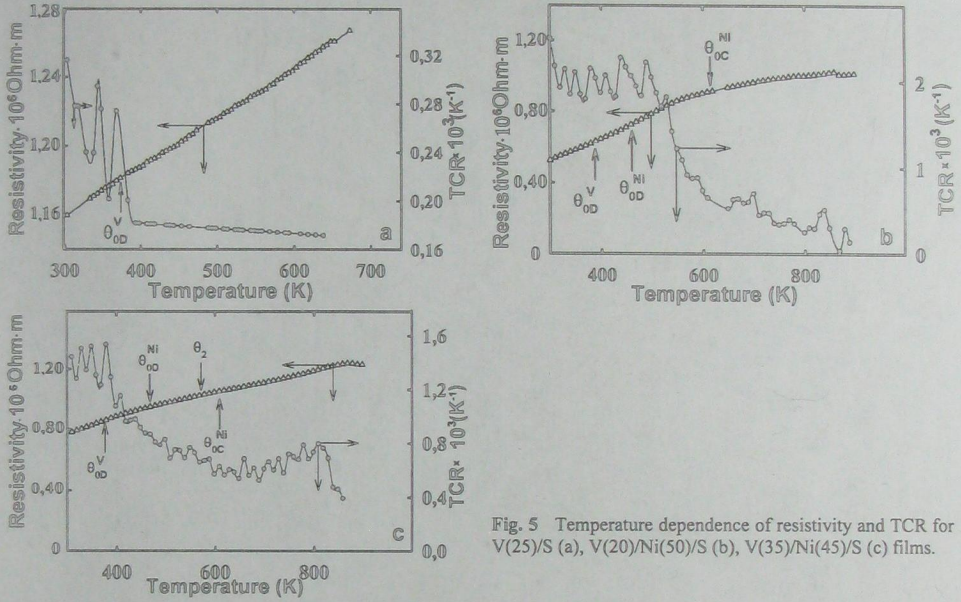


Fig. 5 Temperature dependence of resistivity and TCR for V(25)/S (a), V(20)/Ni(50)/S (b), V(35)/Ni(45)/S (c) films.

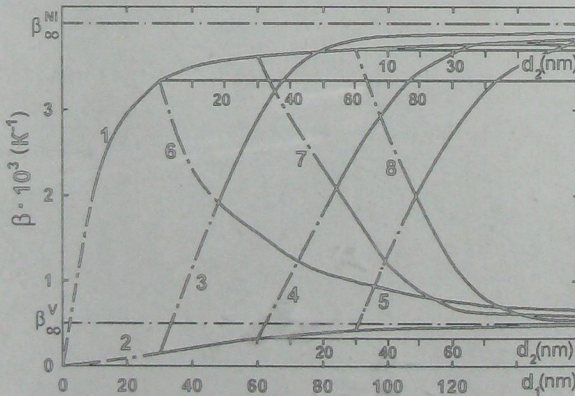


Fig. 6 Dependence of TCR on thickness for double-layer Ni/V/S and V/Ni/S films: 1, 2 – experimental  $\beta(d_2)$  dependencies for Ni and V films; 3-5; 6-8 – calculated  $\beta(d_2)$  graphic charts for Ni/V/S and V/Ni/S films.

Calculated on the basis of the relation (2)  $\beta$  values complies satisfactorily with experimentally obtained values for the film systems, in which (Ni-V) solid solution has formed, and ratio of  $(c_{Ni}/c_V) \approx 1$  (for instance, in case for the system Ni(35)/V(45)/S at  $T_a = 700K$   $\beta = 6.2 \cdot 10^{-4} K^{-1}$ , and  $\beta_{cal} = 3.8 \cdot 10^{-4} K^{-1}$ ).



Consequently, assessment of  $\beta$  value within the frames of Dimmich model or by the relations (1) and (2) confirms indirectly our conclusions concerning phase composition, the conclusions we have come to on the basis of diffraction investigations.

Since the relation (1) is easier and at the same time complies rather better with the experimental results  $\left(\frac{\beta_{cal} - \beta}{\beta} \leq 20 - 70\%\right)$  in comparison with Dimmich model, it gives opportunity to predict the electrophysical properties of double-layer films within the wide range of thicknesses in the form of two-dimensional diagrams. The example of such calculation on the basis of the relation (1) for double-layer films at defined specified values of  $d_1$  is shown in Fig. 6. All  $\beta(d_2)$  graphic charts originate in the points, which belong to  $\beta(d_1)$  dependences for reference layer and approximate asymptotically from below (Ni/V/S films) or from above (V/Ni/S films) to  $\beta_{x2}$  value. Let us note that the trend only to TCR increase up to asymptotic  $\beta_x$  ( $\beta_x$  - TCR, where  $d \rightarrow \infty$ ) value takes place in single-layer films.

### Conclusion

The results of investigations represented in this paper allows us to come to the conclusion concerning the fact that individuality of layers remains to a great extent in the double-layer films annealed up to  $T_a < 700\text{K}$ , though interdiffusion of elements takes place even during the process of condensation. Increase of Ni lattice parameter that we observe at  $T_a \geq 700\text{K}$  can be explained by the formation of (Ni-V) solid solution.

Since concentration of V atoms is limited, the considerable proportions of them in the film specimen is in the form of segregation on the grain boundaries, or on outside surface of Ni film at higher  $T_a$  values, and here V BCC phase is not revealed by diffraction method. Atoms of this type should influence on  $\rho$  or  $\beta$  value, since their presence on the grain boundaries results in change of grain boundary transmission coefficient electron. Compliance of the experimental and calculated data can be explained by this phenomenon. Moreover, it may be assumed that inclusions of oxides or  $V_2Ni$  do not exert any distinct influence on electrophysical properties.

Furthermore, we would like to attract your attention to the fact that, when analyzing the temperature dependence of resistance of the film or bulk specimens, either deviation of the dependence from linearity or observation of minimum during the first or the second thermo-stabilizing annealing of films takes place. The results of investigations given in papers [15, 16] evidence that the pointed out minima also take place just in bulk specimens (for instance, in nichrome [15] or in alloys of Fe-Al-C [16]). Just as in the film specimens, onset of minima on the curve of the  $\rho(T)$  dependence for bulk specimens relates either to phase transitions or to decay of alloys. One of the aspects of the investigations of temperature dependence of  $R$  and  $\beta$  on  $T$  will be connected with synthesis across the whole thickness of sample of one or another transition phase to study its electrophysical properties.

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### References

- [1] S. I. Kasatkin, L. I. Kosse, and V. V. Malcev et al., *Mikroelektronika* 25, 65 (1996) (Russ).
- [2] G. I. Frolov, *Zhurnal tehnichekskoi fiziki* 71, 50 (2001) (Russ).
- [3] I. Yu. Protsenko, L. V. Odnodvoretz, and A. M. Chornous, *Met. Phys. Adv. Tech.* 18, 47 (1999).
- [4] I. Yu. Protsenko, A. M. Chornous, and O. V. Schovkopljias, *Voprosi atomnoj nauki i tehniki* 2-3, 102 (1998) (Russ).
- [5] L. V. Odnodvoretz, S. I. Protsenko, and A. I. Saltykova, *Metallofizika i noveishie tehnologii* 21, 71 (1999) (Russ).
- [6] R. Schäd, P. Belien, and G. Varbanek et al., *J. Mag. and Mag. Mat.* 182, 65 (1998).
- [7] H. Nakai, K. Fudaba, and K. Shinzawa et al., *Thin Solid Films* 317, 202 (1998).
- [8] M. Fenn, A. K. Petford-Long, and P. E. Donovan, *J. Mag. and Mag. Mat.* 198-199, 231 (1999).
- [9] *Diagramy sostojanija dvukhslojnykh metallicheskih sistem*. Vol. 2 / Edited by Ljakischev N. P. Moscow: Mashinostroenie, (1996) 1024 (Russ).



- [10] Fiziko-khimicheskie svoystva elementov: Reference-book / Edited by Samsonov G. V. Kyiv: Naukova dumka (1965) 807 (Russ).
- [11] V. B. Loboda, I. Yu. Protsenko, and M. D. Smolin et al., *Ukrainskij fizicheskij zhurnal* 30, 435 (1985) (Russ).
- [12] E. A. Belskaja and V. E. Peletskiy, *Teplofizika vysokikh temperatur* 19, 525 (1981) (Russ).
- [13] A. Borodziuk-Kulpa, B. Stolecki, and C. Wesolowska, *J. Mater. Scien.* 16, 1661 (1981).
- [14] R. Dimmich, *Thin Solid Films* 158, 13 (1988).
- [15] V. N. Gondalov, A. S. Nagin, and P. V. Novichkov et al. , *Electronnoe stroenie i fiziko-khimicheskie svoystva splavov*. Kyiv: Naukova dumka, 78 (1965) (Russ).
- [16] V. A. Andryuschenko, L. V. Bekenev, and I. E. Gnatjuk, *Metallofizika i noveishie technologii* 22, 10 (2000) (Russ).