THE CHEMICAL TRANSFORMATIONS IN METAL FILMS UNDER INFLUENCE OF ELECTRON

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Introduction

It is known that changed of conditions of the films condensations (vacuum, rate of condensation, the substrate temperature), may be change of chemical composition of the thin films. Some chemical composition, which non- equilibrium in bulk samples, was to passing for polymorphic modifications (see, for example, [1]). They may be formed under influence of the size thermodynamic effects (the change of the phase equilibrium conditions). The further investigations show, what such non- equilibrium phases formed at the thermal annealing of the films samples in vacuum chamber or an electron beam directly in a microscope (the size of the one affected by an electron beam - 15 μm) in result of the interaction of the metal atoms with the atoms of residual gases. The experimental results of the investigations of the chemical transition in films with bcc (Cr,V, Mo), fcc (Ni, Co) and hcp (Co, Sc, Y) lattice have been presented in the work.

Experimental Detail

Films were condensed in a vacuum of 10^{-3} up to 10^{-4} Pa produced by a diffusion oil pump on the carbon substrates with films (the thin samples) or (001) NaCl (the relativity thick samples at the free type). Thickness of films and condensation rate were varied over a range as follows: d=30 up to 200 nm and ω=0.1 up to 1.0 nm/s accordingly. For diffraction and microscopic investigations were run using EMB-100A microscope, a plane spacing measurement accuracy was + 0.001- 0.002 nm.

Films placed on a microscopic grate have been annealed in a vacuum chambers at T=300 up to 700 K during 20 minutes and heating with an electron beam was 3 to 10 sec.

The temperature of the chemical transitions was defined at the thermocouple on one case and calibration dependence - on second case. For it's receive was provided special investigations in vacuum chamber with the "Orbitron" type pump (10^{-5} Pa). As the characteristic points using the temperature of the reduction of ScHx up Sc equal 420-470 K (at the T=420 K fcc-ScHx reflection (200) disappears and hcp-Sc reflection (002) appears on electron diffraction picture and completely finished at the T=470 K); the temperature of the phase transitions hcp-fcc in films Co (T=690 K); the temperature of the melting of Al films (T=830 K) and temperature reduction of CoO up Co (T=720-750 K).

Electrical resistance was measured on samples, which was annealing in vacuum chamber.

Experimental results

Films of metals with bcc lattice. The phase composition of the Cr films (substrate (001) NaCl) accorded bcc-phase Cr, CrO_x fcc-phase (x=1, the parameter of the lattice a=0,414 nm) or bcc-Cr+Cr_3O, where Cr_3O have of the lattice of type β-W with parameter a=0,458 nm. At the annealing in vacuum chamber or in column of electron microscope up 675 observed such chemical transition:

$$Cr,\ Cr+Cr_3O \rightarrow Cr_2O_3.$$

Oxide Cr_2O_3 (Fig.1,a) have lattice of type γ-Fe_2O_3 (a=0,835 nm) and transited in hcp- Cr_2O_3 + Cr_3O_4 + $CrO_{2.6}$. The results of investigation of the chemical transition in films V is like films Cr. At the annealing electron beam bcc-V, the amorphous or crystalline oxide Vo_x (Fig 1,b) (carbon

substrate) oxide V_2O_3 (Fig 1,c) with romboedricaly lattice is formed on scheme:

$$V, a\text{-}VO_x \text{ or } c\text{-}VO_x \rightarrow VO_x \rightarrow Vo_x + V_2O_3 \rightarrow V_2O_3.$$

The calculations of the diffraction pattern, which accorded the phases VO_x (x+1, a=0,405 nm) and V_2O_3 are given in the Table.

№	VO_x (Experimental data)			V_2O_3 (Experimental and table data)				
	I, r.u.	d, nm	hkl	I, r.u.	d, nm	hkl	I, r.u. [2]	d, nm [2]
1.	m.	0.233	111	m.	0.366	102	m.	0.365
2.	V.S.	0.202	200	m.	0.270	014	S.	0.270
3.	S.	0.143	220	V.S.	0.247	110	m.	0.247
4.	l.	0.122	311	-	-	-	v.l.	0.232
5.	l.	0.117	222	l.	0.218	113	l.	0.218
6.	l.	0.101	400	m.	0.204	022	l.	0.203
7.	l.	0.083	420	-	-	-	m.	0.183
8.	m.	0.091	422	m.	0.173	116	V.S.	0.169
9.	-	-	-	l.	0.162	121	v.l.	0.161
10.	-	-	-	v.l.	0.152	212	v.l.	0.157

m.- medium, V.S.- very strong, S- strong, l.- low, v.l.- very low

The annealing of the amorphous or crystalline free films Mo by electrons stipulate for the recrystallization without chemical changes. In films on the carbon substrate observed such transition: a-Mo, c-Mo→fcc-MoC_x→hcp-Mo_2C (Fig. 1,d).

Films of metals with fcc lattice. At the annealing of the free films or films on the carbon substrate Ni and Co formation of the Ni_3N hcp-phase (T=520-

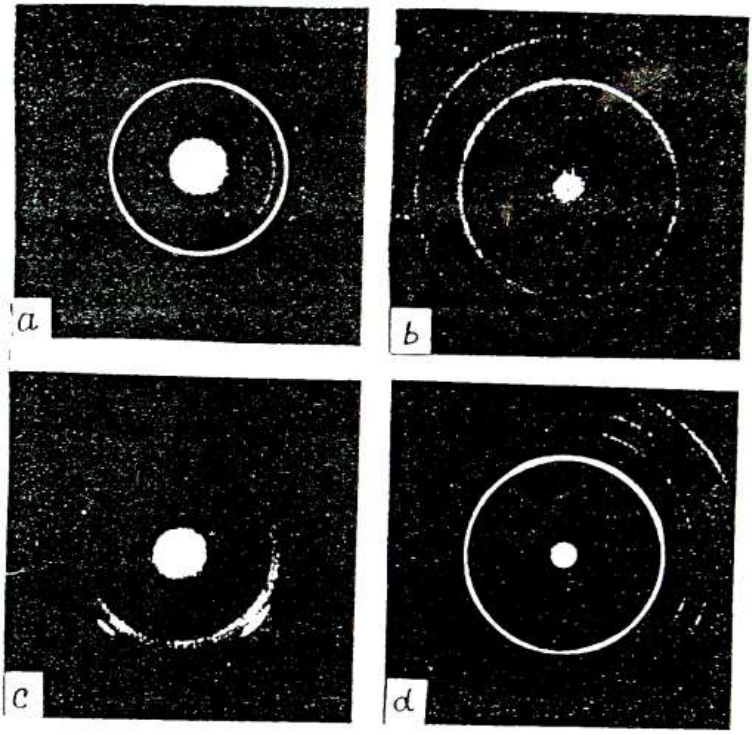

Fig 1 Electron diffraction patterns of Cr_2O_3 (a), VO_x(b), V_2O_3(c) and Mo_2C (d)

570 K); a=0,264 and c=0,433 nm) or fcc-phase CoO_x (x=1; T>640 K; a=0,426 nm). It is important to emphasize, that a formation Ni_3N take place [1] at the bonbandment fcc-Ni ions He^+, N^+ and Ar^+.

Let us note, that the free film hcp-Co begging oxidized later hcp→fcc transition at the T =690 K (Fig. 2,a). In the case of the carbon substrate the process of oxidation begin before phase transition (Fig. 2,b,c).

Films of metal with hcp lattice. The result of the experiment at the annealing of the Sc and Y films are equal. Under influence of the electron beam , two processes simultaneously carried are (us case for films Cr,V,Mo<Ni and Co): recrystallization on the field of the sharp gradient of the temperature

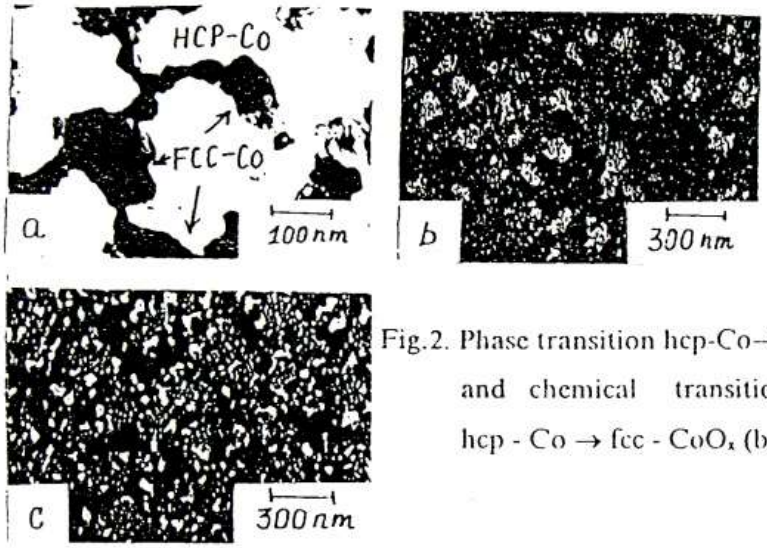

Fig.2. Phase transition hcp-Co→fcc- Co (a) and chemical transition hcp - Co → fcc - CoO_x (b,c)

and strains and chemical transformation. At the annealing of the films type hcp-Sc or Y or fcc-ScH_x (x=2, a=0,478 nm) or Yh_x (x=2, a=0,529 nm) phase Sc_2O_3 (a=0,989 nm) and Y_2O_3 (a=1,0697 nm) with bcc lattice type Mn_2O_3 are formed (Fig. 3).

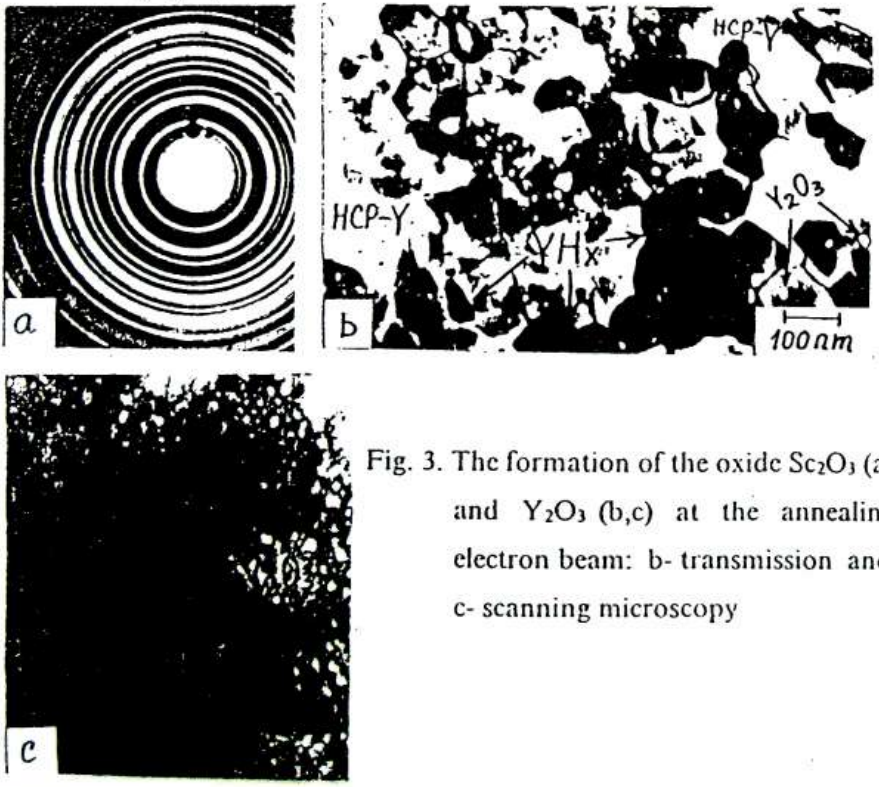

Fig. 3. The formation of the oxide Sc_2O_3 (a) and Y_2O_3 (b,c) at the annealing electron beam: b- transmission and c- scanning microscopy

The temperature of the transition to phase Sc_2O_3 and Y_2O_3 equal 1020 and 770 K accordingly. A comparison conditions of the form of the phase Me_2O_3 (Me-Cr,V,Y and Sc) indicated, that a form Sc_2O_3 take place on the base metastable bcc- phase of Sc.

Measurement of the electrical resistance

The conductivity of the ScH_x, Yh_x x is metallic; the conductivity of the CrO_x , CoO_x and Vo_x is semiconductor; the phase Me_2O_3 appeared classic dielecturs.

References

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