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Reactive Interdiffusion of Components in a Non-Stoichiometric Two-Layer System of Polycrystalline Titanium and Cobalt Oxides

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Abstract

We demonstrated the possibility of using the mathematical form of Darken's theory, applied to the description of the Kirkendall effect in binary systems, to the description of reactive interdiffusion in non-stoichiometric polycrystalline film oxide systems with limited solubility. The aim of the study was the simulation of reactive interdiffusion under vacuum annealing of a thin film system consisting of two non-stoichiometric polycrystalline titanium and cobalt oxides. The non-stoichiometric nature of the system assumes the presence of mobile components, free interstitial cobalt and titanium cations in it. Phase formation occurs as a result of reactive interdiffusion and trapping of mobile components of the system on inter-grain traps. The proposed mechanism describes the formation of complex oxide phases distributed over the depth of the system.

A complex empirical research technique was used, involving Rutherford backscattering spectrometry, X-ray phase analysis and modelling methods. The values of the characteristic parameters of the process were determined by numerical analysis of the experimentally obtained distributions of the concentrations of the components within the developed model. During vacuum annealing of a thin film two-layer system of non-stoichiometric TiO_{2-x} - Co_{1-y}O oxides in temperature range $T = 773 - 1073$ K, the values of the individual diffusion coefficients of cobalt $D_{\text{Co}} = 5.1 \cdot 10^{-8} \cdot \exp(-1.0 \text{ eV}/(kT)) \text{ cm}^2/\text{s}$ and titanium $D_{\text{Ti}} = 1.38 \cdot 10^{-13} \cdot \exp(-0.31 \text{ eV}/(kT)) \text{ cm}^2/\text{s}$ were determined.

It was shown that for $T = 1073$ K, the phase formation of CoTiO_3 with a rhombohedral structure occurs. The extension of the phase formation region of complex cobalt and titanium oxides increases with an increase in the vacuum annealing temperature and at 1073 K it is comparable with the total thickness of the film system.

The model allows predicting the distribution of the concentrations of the components over the depth of multilayer non-stoichiometric systems in which reactive interdiffusion is possible.

Keywords: modelling, interdiffusion reaction, Kirkendall effect, interphases, polycrystalline films, complex oxides.

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1. Introduction

Theoretical concepts for the chemical reactions of the formation of phases of reaction products (intermetallic compounds, oxides) inside the diffusion zone separating the phases of the initial reactants are the most developed in solid state chemistry [1, 2]. In this case, a common feature of the mechanisms explaining the phase formation is the diffusion of atoms to the interphase boundary between two materials and the reactions occurring in the boundary layer.

For the polycrystalline state of materials and limited solubility of components, a mechanism of phase formation at grain boundaries throughout the entire thickness of the contacting materials is possible instead of layer-by-layer growth at the interface boundary. This approach allowed describing the interdiffusion and phase formation in polycrystalline metal-oxide thin film systems: Fe-TiO₂ and Co-TiO₂ [3–5]. In the study [6], it was extended for the thin film two-layer system of non-stoichiometric TiO_{2-x}-Co_{1-y}O oxides.

The mechanism of the phase formation distributed over the depth was implemented within the framework of numerical models of reactive interdiffusion [3–6], using the mathematical formalism of Darken's theory [7]. An advantage of the theory [7] is that the distribution of the concentrations of the components over the depth of a binary system are determined as a result of solving a boundary value problem for two differential diffusion equations. They contain one effective interdiffusion coefficient, which is a linear combination of the individual diffusion coefficients of the components.

The theory [7] was first proposed for the description of interdiffusion in a binary system with the unlimited solubility of components. In studies [8, 9], it was applied to the description of the formation and growth of boundary phases in the diffusion zone.

The initial assumption of the theory [7], and, consequently, the condition for the use of its mathematical formalism, was the position of the invariability of the molar volume of the system associated with a change in its composition as a result of chemical transformations.

In the study [10], the theory [7] was first developed for the bulk reactions of the formation of metal silicides during the interaction of a

film of silicide-forming metal Ni with SiC. The simulation results [10] differ significantly from the experimentally determined distribution of the components inside the extended reaction zone. In our opinion, this is due to not taking into account the change in the molar volume of the system in the process of silicide formation.

In the case of Fe-TiO₂, Co-TiO₂ and TiO_{2-x}-Co_{1-y}O systems [3–6] the position on the invariability of the molar volume of the system is justified by the fact that the formation of substitutional solid solutions based on cobalt and titanium oxides occurs at the grain boundaries in the presence of sufficient free volume. It is also justified by the fact that only grain boundary metal atoms, constituting an insignificant fraction of the total oxygen-bound metal in the corresponding oxide, are involved in the solid-phase reaction.

The aim of this study was determination of the values of the parameters characterizing the process of reactive interdiffusion and phase formation in a thin film two-layer system of TiO_{2-x}-Co_{1-y}O oxides, based on the numerical analysis of the distribution of the concentrations of the metals within the model of reactive interdiffusion [6].

2. Experimental

A two-layer system of non-stoichiometric oxides was obtained by the method described in the study [6]. Magnetron-assisted sputtering of cobalt (UVN-75M unit) was carried out on single-crystalline silicon KEF 4.5 (100) wafers at the following modes: discharge voltage 420 V, current 0.5 A, rate 1.13 nm/s. The thickness of the Co films was set by the sputtering time and was ~ 100 nm. Subsequent thermal oxidation (in order to obtain cobalt oxide CoO films) was carried out in a quartz reactor of a resistive heating furnace in an oxygen flow with a flow rate of 30 l/h at $T = 673$ K for 30 min. Metallic titanium with the thickness of ~ 50 nm was deposited onto a layer of formed cobalt oxide by magnetron sputtering in the following modes: discharge voltage 380 V, current 0.3 A, rate 2.3 nm/s. Vacuum annealing was carried out at residual pressure of $R_{res} = 2.7 \cdot 10^{-3}$ Pa in the temperature range of 773–1073 K for 30 min. The distribution of the concentrations of the components over the depth of the system were determined by the Rutherford backscattering

spectrometry (RBS) method on proton and single-charged helium ion beams – 4 of electrostatic generator EG-5 in the Laboratory of Nuclear Physics of the Joint Institute for Nuclear Research.

The microstructure and thickness were determined by scanning electron microscopy (SEM) on cleavages of samples using a JSM-6510 LV scanning electron microscope with a resolution in a high vacuum of 4 nm. The phase composition of the two-layer film system was analysed by X-ray phase analysis (XRD) using a DRON 4-07 diffractometer in an automatic mode with an interval of 0.1° and a time of exposure at each point of 1 s (CoK_α -radiation, $\lambda = 1.79021 \text{ \AA}$). The obtained diffraction patterns were interpreted using the diffraction files of the JCPDS.

3. Simulation results

As a result of vacuum annealing, non-stoichiometric titanium and cobalt oxides were formed. In titanium oxide, the main defects are interstitial titanium ions, in CoO at low oxygen pressures, the dominant defect is cobalt ions in interstices [11].

In the model [6], it is assumed that, under non-stoichiometric conditions, in each of the oxides of the thin film two-layer $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ system, metal exists in two states. The first being partly in a stationary state bound to oxygen in the corresponding oxide state and the second being partly in a free state (in the form of interstitial Co^{2+} and Ti^{4+} metal cations) [11], capable of diffusion migration. With vacuum annealing of the system of $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ oxides, titanium and cobalt are formed at the grain boundaries of oxides as a result of interdiffusion of interstitial cations of one metal into a film of another metal oxide with irreversible capture on intergrain traps. Cation-capture reactions ((1) and (2) in [6]) provide the replacement of one cation by another, and the released cation passes into a free state and can participate in the interdiffusion process. The total concentration of each of the metals is the sum of the concentration of free interstitial cations, metal bound to the oxygen in the composition of traps at the grain boundaries of its oxide and the concentration of the oxygen-bound metal in the traps in the oxide phase of another metal.

The modelling method as a part of the complex empirical research methodology allows

determining the values of the characteristic parameters of the process by numerical analysis of the experimentally obtained distribution of concentrations of components within the model. The parameters of the model for reactive interdiffusion in a thin film system of $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ oxides [6], using the mathematical form of Darken's theory [7], include:

- individual titanium D_{Ti} and cobalt D_{Co} diffusion coefficients,
- the proportion of free metal in each phase of the system: titanium r_1 (in TiO_{2-x}) and cobalt r_2 (in Co_{1-y}O), which is a quantitative measure of the non-stoichiometry of the oxide phases of the system, as well as
- reaction rate constants ((1) and (2) in [6]) k_1 and k_2 capture of titanium and cobalt on grain boundary traps in the Co_{1-y}O and TiO_{2-x} phases, respectively.

The level of non-stoichiometry of oxides depends on the method of their preparation, temperature and composition of the annealing medium [11]. In the literature, there is a significant variation in the values of non-stoichiometry of TiO_2 and CoO oxides under conditions of low oxygen pressure and at high annealing temperatures from 0.001 to 0.5 at% [12].

For the studied oxides in the thin film state, there are no data on their non-stoichiometry; therefore, we will assume the same level of non-stoichiometry for both phases of the $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ system: for titanium and cobalt $r = r_1 = r_2 = 0.01$.

The example of calculation of the distributions of relative concentrations C of titanium ($I-5$) and cobalt ($I'-5'$) along the depth of the $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ system in the absence of chemical transformations, depending on its non-stoichiometry level r is shown in Fig. 1. As can be seen from Fig. 1, the intensity of mass transfer in the studied system depends significantly on the value r , determining the concentration level of mobile components. This dependence affects the values of the individual diffusion coefficients of titanium and cobalt, determined by numerical analysis of experimental distribution of concentrations within the model [6].

The values of the individual diffusion coefficients of titanium and cobalt in the $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ system were determined by numerical analysis of the experimental distribution of concentrations of the components within the model.

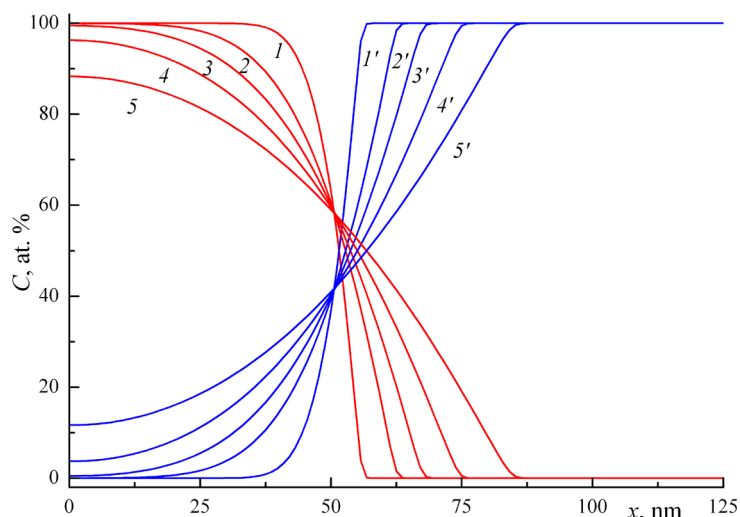


Fig. 1. Depth distribution of the relative concentrations of C of titanium ($1-5$) and cobalt ($1'-5'$) depending on the level of non-stoichiometry r of $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ systems. Calculation at $r=r_1=r_2, k_1=k_2=0, D_{\text{Co}}=1.0\cdot 10^{-15}\text{ cm}^2/\text{s}; D_{\text{Ti}}=1.0\cdot 10^{-15}\text{ cm}^2/\text{s}$ and with an annealing time of 30 min. Free metal fraction r : $1, 1' - 0.001$; $2, 2' - 0.005$; $3, 3' - 0.01$; $4, 4' - 0.02$; $5, 5' - 0.04$

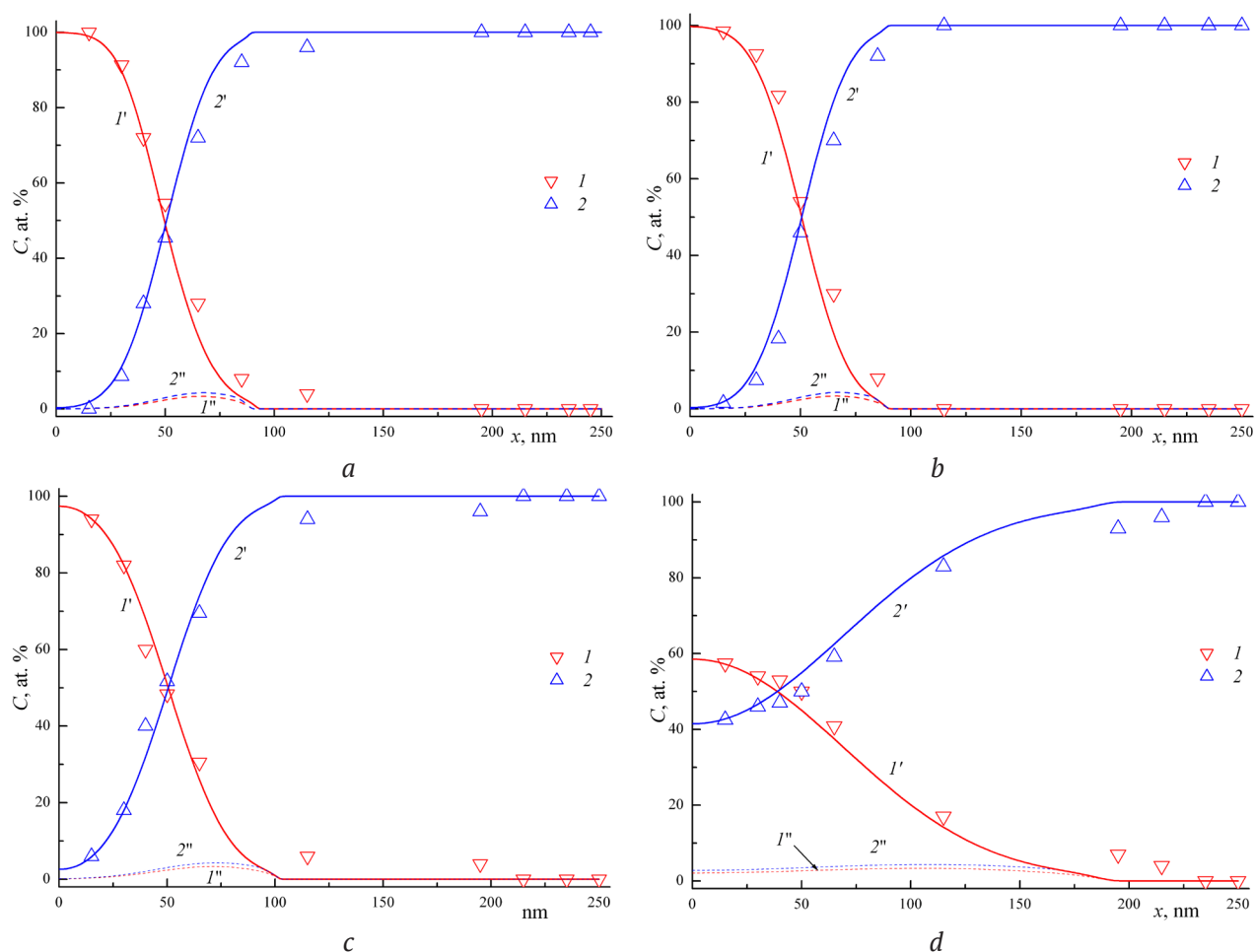


Fig. 2. Depth distributions of the relative total concentrations C (I, I') and oxygen-bound metals ($2, 2'$) in the $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ system: titanium trapped in the cobalt oxide Co_{1-y}O phase (I') and cobalt trapped in the titanium oxide TiO_{2-x} phase ($2'$). Annealing time was 30 min, temperature: 773 K (a); 873 K (b); 973 K (c); 1073 K (d). Points – experiment (RBS method), curves – calculation at D_{Co} and D_{Ti} values from Fig. 4 (points 1, 2)

The distribution of concentrations of titanium and cobalt over the depth of the $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ system obtained by the RBS method in comparison with the results of modelling of the total concentration of metals and its part captured by traps in the phases of titanium and cobalt oxides are shown in Fig. 2 a-d. The distributions of the latter characterize the region of phase formation of cobalt and titanium complex oxides. As can be seen from Fig. 2, the extension of this region increases with an increase in the vacuum annealing temperature and at 1073 K it becomes comparable with the total thickness of the film system (Fig. 2d). Thus, the process of phase formation does not occur at the interface, but has a character distributed over depth.

The evolution of the phase composition of the studied system during vacuum annealing, determined by the XRD method is shown in Fig. 3. After magnetron sputtering of titanium metal on the cobalt oxide layer (Fig. 3, curve 1), cobalt oxides phases were revealed in the film: cubic CoO modification with lattice parameters: $a = 4.240 \text{ \AA}$ (space group $Fm\bar{3}m$) [JCPDS Cardno. 01-075-0418] and Co_3O_4 with a face-centred cubic lattice of a spinel structure (space group $Fd\bar{3}m$) with lattice parameters: $a = 8.065 \text{ \AA}$. The diffraction pattern contains low-intensity reflections of titanium oxide TiO_2 in the tetragonal structure of rutile (space group $P4_2/mnm$), lattice parameters: $a = b = 4.5890 \text{ \AA}$, $c = 2.9540 \text{ \AA}$ [JCPDS Cardno. 01-073-1765]. The micrograph of the cleavage of the film system shows

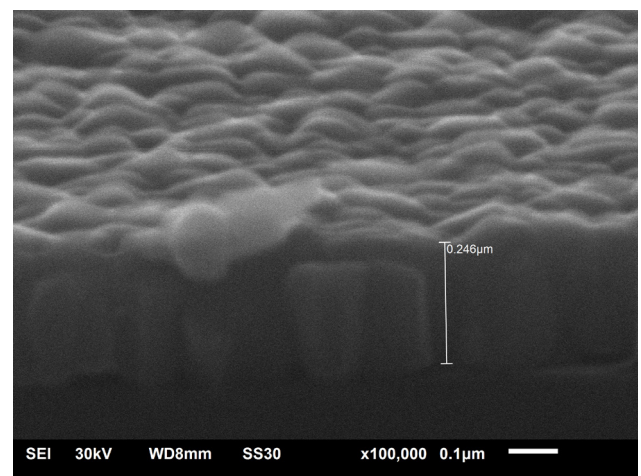
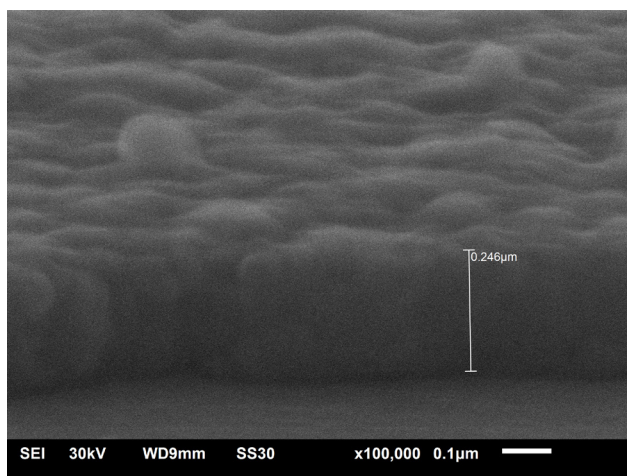
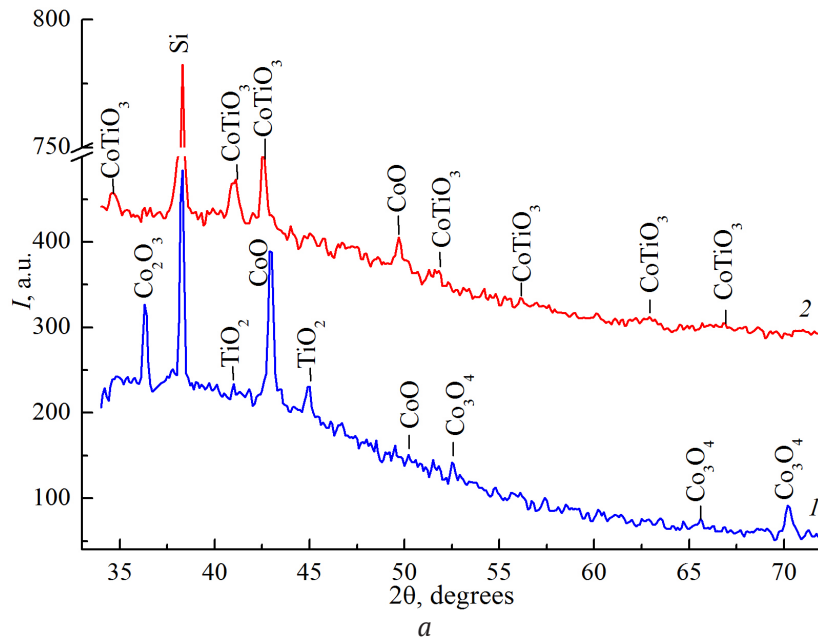


Fig. 3. Diffraction patterns (a) and micrographs of the $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ film cleavage after magnetron sputtering (b) and vacuum annealing at $T = 1073 \text{ K}$ (c)

two layers: the lower cobalt oxide layer with a thickness of ~ 200 nm and the upper titanium oxide layer with a thickness of ~ 40 nm (Fig. 3 a). After vacuum annealing at $T = 1073$ K (Fig. 3, curve 2) as a result of the interaction of CoO and TiO_2 the complex oxide CoTiO_3 is formed rhombohedral modification (space group $R\bar{3}$ (148), with lattice parameters: $a = b = 5.044$ Å, $c = 13.961$ Å [JCPDS Cardno. 00-001-1040]). A homogeneous film with a thickness of ~ 246 nm, which remained unchanged during annealing, can be seen on a micrograph of the cleavage of the film in Fig. 3 b.

The temperature dependence of the individual diffusion coefficients of cobalt and titanium is shown in Fig. 4 (points 1 and 2 for cobalt and titanium, respectively). In the temperature range of 773–1073 K, they vary within $D_{\text{Co}} = 1.75 \cdot 10^{-14} \div 1.04 \cdot 10^{-12} \text{ cm}^2/\text{s}$, $D_{\text{Ti}} = 1.25 \cdot 10^{-15} \div 4.5 \cdot 10^{-15} \text{ cm}^2/\text{s}$. At these values of the parameters, a good correspondence was obtained between the experimental distributions (points) to the calculated ones for the total titanium (curves 1) and cobalt (curves 2') concentrations (Fig. 2 a-d) with unchanged values of $k_1 = 1.10 \cdot 10^{-21} \text{ cm}^3/\text{s}$, $k_2 = 1.10 \cdot 10^{-25} \text{ cm}^3/\text{s}$, $r_1 = r_2 = 0.01$.

The approximation of the temperature dependences in Fig. 3 by the Arrhenius equation provides the individual diffusion coefficient of cobalt in the $\text{TiO}_{2-x}\text{-Co}_{1-y}\text{O}$ film system:

$$D_{\text{Co}} = 5.1 \cdot 10^{-8} \text{Exp}(-1.0 \text{ eV}/(kT)) \text{ cm}^2/\text{s} \quad (1)$$

and titanium

$$D_{\text{Ti}} = 1.38 \cdot 10^{-13} \text{Exp}(-0.31 \text{ eV}/(kT)) \text{ cm}^2/\text{s} \quad (2)$$

As can be seen from Fig. 4, values of D_{Co} and D_{Ti} are close to the values of the individual diffusion coefficients of titanium and cobalt in the Co– TiO_2 metal-oxide system obtained by numerically analysing the distributions of the concentrations (the secondary-ion mass spectrometry method) using the deep reactive interdiffusion model, implementing the same approach [4]. The higher values of the individual diffusion coefficient determined for cobalt in comparison with the results of the study [4] are explained by different methods for determining the distribution of the concentrations, formation methods, and the difference in the level of non-stoichiometry of the studied Co– TiO_2 and $\text{TiO}_{2-x}\text{-Co}_{1-y}\text{O}$ systems.

4. Conclusions

We showed the possibility of using the mathematical form of Darken's theory [7] for the description of reactive interdiffusion in non-stoichiometric polycrystalline film oxide systems with limited solubility.

The reactive interdiffusion model [6] provides a good description of the experimental distribution of the concentrations of titanium and

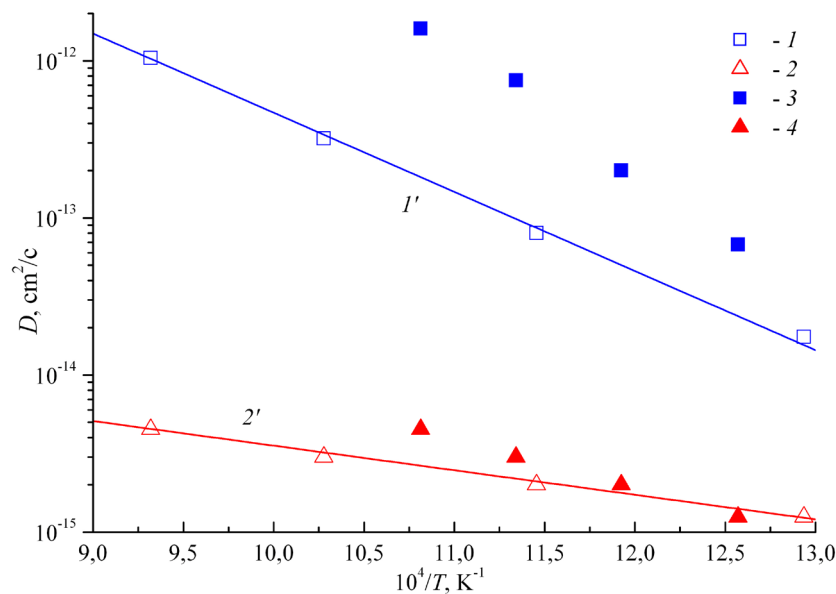


Fig. 4. Temperature dependence of individual diffusion coefficients of metals in $\text{TiO}_{2-x}\text{-Co}_{1-y}\text{O}$ and Co– TiO_2 film systems. The points are the results of numerical analysis for cobalt (1, 3) and titanium (2, 4); curves 1', 2' – approximation by the Arrhenius equation for cobalt (1) and titanium (2), (3, 4) – results of the study [4]

cobalt over the depth of a two-layer film system of non-stoichiometric $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ oxides during vacuum annealing in the temperature range of 773–1073 K.

The values of individual diffusion coefficients (temperature dependences (1) and (2)), characterizing the process of reactive interdiffusion and phase formation in a thin-film two-layer system of $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ oxides have been determined.

The extension of the region of phase formation of complex cobalt and titanium oxides increases with an increase in the vacuum annealing temperature and at 1073 K it becomes comparable to the total thickness of the film system.

Individual diffusion coefficients of cobalt and titanium in the $\text{TiO}_{2-x}-\text{Co}_{1-y}\text{O}$ system determined by numerical analysis and the level of non-stoichiometry are in good agreement with the literature data [13–15]. In the study [16], for the annealing of nanocrystalline TiO_2 films in an Ar atmosphere, the grain boundary diffusion coefficient was $1.04 \cdot 10^{-15} \text{ cm}^2/\text{s}$ at $T = 673 \text{ K}$. The scatter in the values of the grain boundary diffusion coefficient is assumed to be associated with structural changes at the grain boundaries and the formation of an amorphous grain boundary phase [17, 18]. Grain boundary complexes were observed in the WO_3 and TiO_2 system, doped with CuO [19, 20]. These grain boundary phases are not numerous, have a nanometer width, and therefore are not visible in microscopes with a low resolution. As a result, the determined coefficients of grain boundary diffusion at different temperatures did not correspond to the values determined for single crystals.

The model allows predicting the distribution of concentrations of components over the depth of multilayer non-stoichiometric systems, in which reactive interdiffusion is possible.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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