Translated from *Uspekhi Khimii*, 48, 2034-2060 (1979) U.D.C. 541.128.1

Kinetics and Catalysis of the Oxidation of Titanium, Silicon, Germanium, and Gallium Arsenide

N.P.Peksheva and V.M.Strukov

A systematic account is given of the results of studies of the kinetics and catalysis of thermal gas-phase oxidation reactions of titanium, silicon, germanium, and GaAs. The influence of various factors (the nature of the reactant gas, the method of the preliminary treatment of the surface, and the nature of the substance oxidised) on the reaction kinetics has been estimated. The characteristics of the catalysis of heterogeneous oxidative processes are discussed and new ways of solving a number of practical problems are outlined.
The bibliography includes 133 references.

CONTENTS

I. Introduction 1092
II. Thermodynamics of the oxidation of titanium, silicon, germanium, and gallium arsenide 1092
III. Kinetics and mechanism of the oxidation of metals and semiconductors 1093
IV. Catalysis of the oxidation of titanium, silicon, germanium, and gallium arsenide 1099
V. Some practical applications 1104

I. INTRODUCTION

The development of microelectronics, radio engineering, and laser and space technology has necessitated intense research into the characteristics of the chemical interaction of metals, alloys, and semiconductors with other elements and also a more detailed investigation of the structure of solids and of solid-state reactions.

Reactions involving the thermal oxidation of titanium, silicon, germanium, and gallium arsenide are technological processes in the radio engineering and semi-conductor industry. In order to obtain oxide films with specified properties, it is important to investigate the thermodynamics, kinetics, and mechanisms of these reactions. In the development of modern electronic engineering it is urgently necessary to accelerate the growing of oxide layers. Heterogeneous catalysis plays an important role in the solution of such problems.

However, despite the abundance of experimental data[1-14], many problems of the kinetics and catalysis of heterogeneous Ti, Si, Ge, and GaAs oxidation reactions have been by no means adequately investigated. The use of catalysis in the technology for the preparation of oxide films is hindered by the fact that the mechanism and nature of the catalytic acceleration of the reaction have not been ultimately elucidated and the selection and preparation of the catalyst presents certain difficulties[15-18].

The present review surveys the results of studies on the kinetics and catalysis of the high-temperature gas-phase oxidation of titanium, silicon, germanium, and gallium arsenide and describes practical ways of employing heterogeneous catalysis in technology.

II. THERMODYNAMICS OF THE OXIDATION OF TITANIUM, SILICON, GERMANIUM, AND GALLIUM ARSENIDE

In the thermal oxidation of metals and semiconductors there is a decrease of the free energy ΔG°_{T}. Analysis of the thermodynamics of titanium oxidation reactions in various gaseous media (in air, water vapour, and carbon dioxide) in the temperature range 400-1000°C and of the interactions of silicon, germanium, and gallium arsenide with oxygen showed that the most probable products of the interaction are crystalline or vitreous TiO_2, SiO_2, GeO_2, and Ga_2O_3 films[1,2,6,9-11,19-27]. Reactions (1)-(7), occurring under these conditions, are virtually irreversible[29,30]:

$$Ti(solid) + O_2(gas) = TiO_2(solid), \quad (1)$$

$$Ti(solid) + 2H_2O(gas) = TiO_2(solid) + 2H_2(gas), \quad (2)$$

$$Ti(solid) + 2CO_2(gas) = TiO_2(solid) + 2CO(gas), \quad (3)$$

$$Si(solid) + O_2(gas) = SiO_2(solid), \quad (4)$$

$$Ge(solid) + O_2(gas) = GeO_2(solid), \quad (5)$$

$$2GaAs(solid) + \tfrac{3}{2}O_2(gas) = Ga_2O_3(solid) + As_2(gas), \quad (6)$$

$$2GaAs(solid) + \tfrac{3}{2}O_2(gas) = Ga_2O_3(solid) + \tfrac{1}{2}As_4(gas). \quad (7)$$

The results of the calculations of the principal thermodynamic characteristics of reactions (1)-(7) using literature data[28] are presented in Tables 1 and 2. Table 1 shows that a high negative standard Gibbs free energy and highly exothermic heats are characteristic of reactions (1)-(3), which indicates their virtual irreversibility[30].

The thermodynamic probability of the oxidation of silicon, germanium, and gallium arsenide via the reactions[11,31,32]

$$Si(solid) + \tfrac{1}{2}O_2(gas) = SiO(gas),$$
$$Ge(solid) + GeO_2(solid) = 2GeO(gas),$$
$$2GaAs(solid) + \tfrac{1}{2}O_2(gas) = Ga_2O(gas) + As_2(gas).$$

increases with increase of temperature to 1000-1300°C. The equilibrium GeO vapour pressure is significant (approximately 10^{-5} atm) already above 600°C. The partial pressures of SiO and Ga_2O are negligible even at approximately 1300°C and oxygen pressures up to 10^{-9} atm.[11]

The oxidation of gallium arsenide involves the formation of gaseous arsenic in the form of As_2 and As_4.[11,33-37] Under these conditions, the presence of As_4 molecules in

the gas phase is thermodynamically more probable (see Table 2).

Table 1. Temperature variation of ΔH°_T, ΔS°_T, ΔG°_T, and $\lg K_p$ for the thermal oxidation of titanium [reactions (1) to (3)].[130]

T, °C	ΔH°_T, kcal mole^{-1}	ΔS°_T, cal mole^{-1} K^{-1}	ΔG°_T, kcal mole^{-1}	$\lg K_p$
		Reaction (1)		
400	−224.988	−42.74	−196.224	63.73
500	−224.742	−42.40	−191.967	54.28
600	−224.511	−42.12	−187.741	47.01
700	−224.302	−41.89	−183.543	41.23
		Reaction (2)		
400	−107.762	−17.93	−95.695	31.08
500	−107.130	−17.05	−93.951	26.57
600	−106.535	−16.31	−92.296	23.11
700	−105.984	−15.72	−90.689	20.37
		Reaction (3)		
400	−90.159	−2.08	−88.760	28.82
500	−90.258	−2.21	−88.550	25.04
600	−90.440	−2.44	−88.310	22.11
700	−90.705	−2.73	−88.049	19.78

Table 2. Temperature dependence of $\lg K_p$ for the thermal oxidation of silicon, germanium, and gallium arsenide [reactions (1)–(7)].[133]

No. of reaction	$\lg K_p$			
	400°	500°	600°	700°
(4)	61.23	52.44	45.22	39.65
(5)	35.88	30.32	26.06	22.53
(6)	1.41	1.80	2.18	2.54
(7)	60.51	52.23	45.99	40.96

III. KINETICS AND MECHANISM OF THE OXIDATION OF METALS AND SEMICONDUCTORS

The rate of formation of thin films in the oxidation of metals and semiconductors are described by different equations depending on the temperature and the reaction time; it can obey the following laws[9,11,12,38–42]:

(1) A direct logarithmic relation:

$$y = k_1 \lg(B\tau + 1);$$

(2) An inverse logarithmic relation:

$$k_2/y = A + \lg \tau;$$

(3) A linear relation:

$$y = k_3\tau;$$

(4) A parabolic relation:

$$y^2 = k_4\tau;$$

(5) A cubic relation:

$$y^3 = k_5\tau,$$

where y is the thickness of the oxide film, τ the time, and A, B, and k_1–k_5 are constants. For thin films, logarithmic and cubic relations for their thickness as a function of time predominate, while for thick films the parabolic and linear relations predominate[43].

The study of the kinetics of the oxidation of titanium, silicon, germanium, and gallium arsenide led to the discovery of relations of three types[11,39]: linear, logarithmic, and parabolic (Fig. 1).

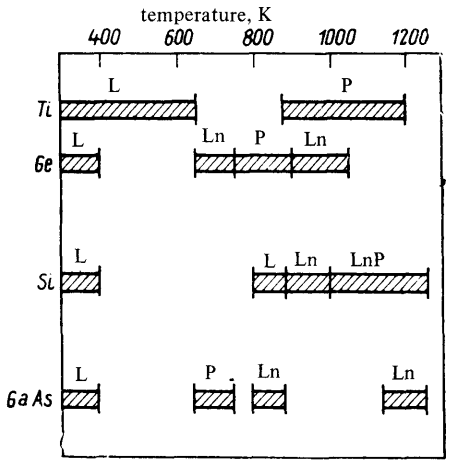


Figure 1. Dependence of the type of kinetic relation for the oxidation of titanium, silicon, germanium, and gallium arsenide on the process temperature: L = logarithmic relation; Ln = linear relation; P = parabolic relation; LnP = linear-parabolic relation.

Despite the satisfactory agreement between the experimental rates of oxidation, phase composition of the product, and other process parameters obtained by different workers, the treatment of the experimental results and of the oxidation mechanisms were different in different investigations[1,7,8,38,43–57]. Wagner[49,50] justifies a parabolic law governing the rate of growth. He postulates that, at comparatively high temperatures and for fairly high film thicknesses, the oxidation process takes place as a result of the diffusion of ions and electrons through the growing oxide; it is assumed that each volume element of the oxide is electrically neutral. The theory of Mott and Cabrera[51] explains the inverse logarithmic and parabolic variation of the rate of growth for comparatively thin films taking into account the influence of the electric field on the diffusion of ions in the oxide. However, Kubaschewski and Hopkins[43] believe that the films obtained in the oxidation of titanium at 300–500° C are somewhat thicker than should have been the case if their growth can be accounted for by the transport of material under the influence of the electric field. They begin with the hypothesis that microcavities are formed on the metal–oxide interface, i.e. they adopt the Evans theory[58], according to which the rate of formation of oxide films is determined by the transport of ions through a thin oxide film. The theory of Mott and Cabrera was subsequently developed by Hauffe and Ilschner[52], who explained the direct logarithmic relation for the rate of growth of the oxide film in the initial stages of the oxidation of metals and semiconductors.

A general model has been proposed for the mechanism of the growth of oxide films[53,54]. It is based on the treatment of processes involving the diffusion of ions and electrons through the oxide layer in which an electric field

created by these diffusing species operates. The difference between the proposed oxidation mechanism and those existing previously consists in the fact that, instead of one equation for the description of the diffusion of ions and electrons, two such equations are used in calculations of the rate of diffusion. This makes it possible (by combining the equations for total electric field) to simplify the description of the rate of growth of the oxide film thickness. However, the model suffers from the disadvantage that it does not take into account the transport process in the gas phase, the adsorption of oxidant on the surface of the oxide, and certain other factors[11].

The problem of the nature of diffusing species of oxidation remains controversial. Thus it has been shown[55] that an electric field at right angles to the outside film can accelerate or retard the oxidation of silicon, showing that the reaction takes place as a result of the transfer of ions through the oxide film. It has been established[56] that neutral oxygen atoms diffuse in addition to ions.

The rate of oxidation of gallium arsenide at comparatively low temperatures is controlled by diffusion through the oxide layer and at higher temperatures by the intrinsic chemical reaction between oxygen and gallium arsenide on the reaction interface[57]. This has been confirmed in studies[33,61] where the oxidation of GaAs was studied in oxygen at 600–900° C. It was established that the rate of oxidation below 600° C is insignificant, while on heating above 900° C the rate is so high that the oxidised specimen burns.

Thus the survey of literature data on the oxidation of titanium, silicon, germanium, and gallium arsenide shows that many problems of the kinetics and mechanisms for these chemical reactions are still unsolved. It is therefore of interest to investigate the influence of different factors on the oxidation kinetics: (a) the nature of the reactant gas; (b) the preliminary treatment of the metal surface; (c) the chemical composition of the alloy.

reflects mainly the growth of the oxide film, while the dissolution of oxygen continues at a rate determined by the oxygen concentration gradient and the diffusion coefficient of oxygen in the metal. The oxide lacks an appreciable protective capacity and has a porous structure, which facilitates the penetration of gaseous oxygen to the interface between the oxide and the metal. Region *C*, which characterises the oxidation of titanium at low temperatures, corresponds to a logarithmic law for the absorption of oxygen by titanium. Thus the difference between the types of kinetic curves is not associated solely with the temperature factor. The nature and mechanism of the oxidation and different stoichiometric compositions and crystal structures of the oxides formed on the metal surface play the main role.

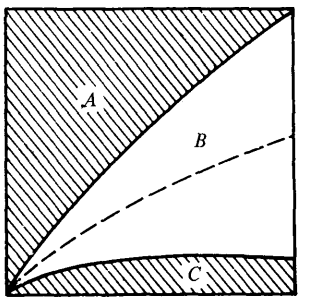


Figure 2. Titanium oxidation diagram: A) at high temperatures; B) at moderate temperatures; C) at low temperatures (*V* is the total amount of absorbed oxygen).

1. KINETICS AND MECHANISM OF THE OXIDATION OF TITANIUM IN AIR; IN WATER VAPOUR, AND IN CARBON DIOXIDE

The kinetics of the oxidation of titanium in various gaseous media have been little investigated at present as a function of temperature and the duration of heating of the metal. The oxidation of titanium is an extremely complex process, because, in contrast to other metals, the oxidation of titanium and its alloys leads to the formation of gas-saturated layers consisting of solid solutions of oxygen in α-titanium in addition to oxide films or scale.

Jenkins[62], who investigated the kinetics of the saturation of titanium with oxygen over a wide range of temperature, proposed a diagram illustrating the nature of the oxidation of titanium (Fig. 2). The diagram is divided into three main regions: *A*, *B*, and *C*. Region *A* characterises the oxidation at high temperatures in accordance with the parabolic law, which involves the simultaneous occurrence of two processes—the dissolution of oxygen and the formation of the oxide layer. The oxide grains are larger and better formed than at low temperature. Two-sided diffusion of oxygen and titanium through dense oxide layers takes place under these conditions. Region *B* corresponds to the oxidation of titanium at moderate temperatures where oxygen is absorbed via a parabolic law in the first stage and then, when the oxide thickness reaches a critical value, the latter is replaced by a linear law. The linear relation

The interaction of metals with gases is due to diffusion and can be represented by three main stages[59]: (1) the adsorption of the gas on the metal surface; (2) the initiation of a crystal of the new compounds; (3) crystal growth. At a certain stage of the adsorption process, where the gas does not dissolve in the metal, a second type of crystal lattice arises on the surface of the metal instead of the single type of lattice of the main metal as a result of the solid-phase reaction. The interface then consists of two coherently bound crystalline layers—the metal and the oxide. The formation of the lattice of the new compound on the surface of the metal obeys the principles of orientation and dimensional correspondence[60].

(a) Interference Films on Titanium

The oxidation of metals by atmospheric oxygen or other oxidants results in the formation on their surface of oxide films whose thickness may vary within very wide limits. It is usual to distinguish three types of films: thin (from several angstroms to 200–400 Å), medium (from 400 to 5000–10 000 Å), and thick (above 5000–10 000 Å)[40,63–66]. For a thickness exceeding 200–400 Å, the films begin to acquire a colour due to the interference of light (interference colours)[38,42,43,64]. The phenomenon of the interference colours of films on metals has been studied fairly widely, particularly for elements such as iron, nickel, copper, silicon, and germanium[67–74]. However, despite

the abundance of the literature on the oxidation of titanium, the formation and properties of interference films on this metal have not been widely described in the scientific literature and are considered in only one monograph[1] devoted to the oxidation of titanium and its alloys.

This presents[1] the colours of four orders of spectra but the question of the number of spectra remained open. In order to study this problem in greater detail, the colour spectra of oxide films on iodide titanium (~99.90% Ti), technically pure VT-1 titanium (≥99.5% Ti), and OT4-0 (≥96.5% Ti) and OT4-1 (≥95% Ti) alloys were investigated[130] between 500° and 800°C.[17,21,22,25,73,130] At 500°C the oxidation is comparatively slow; a long time is required even for the completion of the formation of films giving the first-order spectrum. At 700° and 800°C there is a rapid growth of oxide films and at higher temperatures continuous observation of the change of the colour of the film is difficult owing to the high rate of oxidation and heating of the metal to a red glow, which masks the colour. At these temperatures the colour of the film can be more conveniently determined by quenching the specimens. For example, blue films (in a first-order spectrum) on specimens of the OT4-0 alloy are formed at 500°, 600°, 700° and 800°C respectively after 6000, 342, 70 and 30 s.

A temperature of 600°C, at which there is a smooth transition from one colour to another, made it possible to observe and record the alternation of five interference colour spectra on iodide and technically pure titanium and the OT4-0 titanium alloy and four such spectra on the OT4-1 alloy. Comparison of the times required to complete the first-order spectrum at 600°C showed that the oxidation proceeds at the highest rate on the VT-1 alloy (80 s) and at the lowest rate on the OT4-1 alloy (460 s). With increase of the thickness of the coloured film, the oxidation process slows down (Table 3).

Table 3. The formation of interference films with a first-order spectrum on titanium and its alloys in oxidation in air at 600°C.[130]

Colour of film	Oxidation time of specimens, s		
	VT-1	iodide titanium	OT4-0
Pale yellow	8	18	30
Yellow	13	27	39
Brown	22	37	60
Violet	26	55	85
Dark blue	35	123	169
Blue	49	330	342
Pale blue	80	367	390

The mechanism of the formation of thin oxide films on metals, proposed by Mott and Cabrera, presupposes the generation of an electric field in such films[38,42,51,52,69,76-78] whose potential gradient reaches approximately 10^7 V cm^{-1}. Under the influence of such films, the metal cations acquire a high mobility and migrate at a high rate through the film towards its boundary with the gas, which leads to a fairly rapid growth of the film on the metal surface. With increase of film thickness, the potential gradient diminishes significantly and the oxidation slows down.

We shall apply this oxidation mechanism to metals which give rise to semiconducting *p*-type films with an excess of cationic vacancies[43]. The applicability of this theory to the explanation of the oxidation of titanium is apparently somewhat limited for the following reasons: (1) titanium gives rise to the oxide TiO_2, which is an *n*-type semiconductor (with a deficiency of anions)[43]; (2) titanium is characterised by unusually high solubility of oxygen, which penetrates into the bulk of the metal[5,6,19,43]; (3) a film, whose thickness amounts to hundredths of angstroms within the limits of the operation of the logarithmic law, grows on titanium[1,79].

In our view extensive study of the properties of interference films on titanium and its alloys can yield valuable information about the kinetics, catalysis, thermodynamics, and physicochemical properties of the oxide layers formed and about the mechanism of the interaction of metals with the medium.

(b) Oxidation in Air

Studies on the kinetics of the oxidation of titanium in air are particularly important. Their results are presented in numerous publications[1,8,39,44-48], where it is shown that appreciable differences in the nature of the oxidation of titanium in oxygen and in air are not observed during the initial period[1,8]. In the oxidation by air, the shape of the kinetic curves and the form of the kinetic relation are analogous to those obtained in the oxidation of titanium in pure oxygen (700–1000°C), but the degree of oxidation is lower than in oxygen[1,8]. The rutile lattice constants in the oxides obtained by oxidising titanium in air and in oxygen are the same at temperatures below 1100°C.[8]

Subsequently (at higher temperatures) titanium absorbs a much greater amount of gases in oxidation in air than in oxidation in oxygen. Above 1150°C the oxidation of titanium in air is faster than in oxygen[80]. The process is complicated by the fact that, in the high-temperature oxidation of titanium in air, the metal reacts not only with oxygen but also with nitrogen. It has been established[59,80] that nitrogen enters the crystal lattice of rutile in the course of the high-temperature oxidation with air, which leads to the formation of a perforated structure and an increase of the volume of the unit cell. The formation of rutile with a defective lattice facilitates the diffusion of titanium ions to the outer surface of the oxide layer and the diffusion of oxygen into the bulk of this layer, which promotes a more rapid oxidation. At the same time, there is no unanimous view in the literature concerning the rate of oxidation of titanium in oxygen and in air. Apart from the data quoted above, it has also been claimed[81,82] that the oxidation of titanium at 1200°C in pure oxygen is much faster than in air and that the rate of oxidation is virtually the same in the two cases at 1000°C.

Studies of the initial stages of the oxidation of titanium are particularly difficult in view of the difficulty of measuring the thickness of the oxide layer and the amount of substances which have reacted in the course of the high-temperature chemical interaction. The method of interference indicators has been used in studies of the kinetics of the initial stages of the oxidation of titanium[17]. The rate of oxidation was found by observing the interference of the light waves in oxide films of specified thickness, formed as a result of the heterogeneous chemical interaction of the metal with the oxidising medium. The main advantage of this method is that one has only to determine the colour of the oxide and not its thickness. The method of interference indicators permits comparative kinetic studies and enables one to determine the influence of the chemical composition of titanium alloys on the initial stages of their oxidation[22,29,75,83-85], the difference between the

rates of reaction in air[17,29,84,85], water vapour[24,29,84–86], and carbon dioxide[24,29,84,85,87], the influence of catalysts on the process kinetics[88–92], and the dependence of the kinetics of the initial stages of the oxidation of titanium on the method of polishing of the metal surface[23,93,94] and other factors.

Table 4. Chemical composition of titanium alloys[22].

Alloy	Concentrations of components, wt.%						
	Ti	Al	Mn	Fe	Si	C	others
VT-1	99.5	—	—	—	—	—	—
OT4-0	⩾96	0.2–1.4	0.2–1.3	⩽0.3	⩽0.15	⩽0.1	⩽0.8
OT4-1	⩾95	1.2–2.5	0.7–2.0	⩽0.3	⩽0.15	⩽0.1	⩽0.8

A comparative study of the kinetics of the growth of interference oxide layers in the thermal oxidation in air of specimens of technically pure titanium of type VT-1 and of OT4-0 and OT4-1 titanium alloys has been carried out[17,29,84,85] (Table 4). Metal specimens with dimensions 20 × 10 × 1 mm were subjected to isothermal oxidation at 500–650°C in a furnace with transparent quartz inspection windows for the visual observation of the changes in the colour of the film during the reaction.

Table 5. The colours of titanium oxide films as a function of the thickness of the oxide layer[1].

Colour of film	y, Å
Pale yellow	344
Yellow	349
Brown	447
Violet	492
Dark blue	515
Blue	536
Pale blue	542

Table 6. The activation energies (E, kcal mole^{-1}) for the oxidation of titanium alloys by air with formation of interference films having a first-order spectrum[22,23].

Alloy	Change in film colour		
	from yellow to brown	from brown to violet	from violet to dark blue
VT-1	15.700	23.000	28.800
OT4-0	24.400	26.800	29.000
OT4-1	26.200	27.000	39.200

The relations between the colour of the first-order spectrum and the thickness of the oxide film on titanium are presented in Table 5 for interference films. Experiments at different temperatures led to the determination of the time corresponding to the change in the colour of the oxide film within the limits of two chosen colours–from yellow to brown (Δy = 98 Å), from brown to violet (Δy = 45 Å), from violet to dark blue (Δy = 23 Å), and from dark blue to blue (Δy = 21 Å). The experimental results were expressed by plots of $\tau = \varphi(t^0)$ and $\lg \tau = \varphi(1/T)$. Fig. 3 illustrates the kinetics of the oxidation of titanium alloys by air accompanied by a change in the colour of the film from yellow to brown[84]. Table 6 presents the activation energies for the oxidation of titanium alloys in air found from plots of $\lg \tau = \varphi(1/T)$.

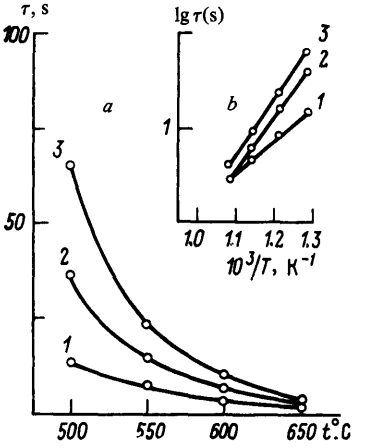


Figure 3. The film formation time τ in the yellow–brown colour range as a function of temperature t(°C) (*a*) and $1/T$ (*b*) in the oxidation of titanium alloys by air; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

(c) Oxidation in Water Vapour and Carbon Dioxide

In order to elucidate the influence of the nature of the oxidising medium on the rate of oxidation of titanium and its alloys, a study was made of the kinetics of the initial stages of the oxidation of the metal in water vapour and carbon dioxide under the conditions of the formation of an interference film with a first-order spectrum[24,29,84–87].

The kinetics of the oxidation of titanium in water vapour have been studied comparatively little. This problem has been described most completely in a monograph[1] and in a number of papers[95–97]. The studies showed that at a water vapour pressure of 1 atm and at 400–1200°C the oxide films grow faster than in air owing to the looser structure of the layer of scale. At 800–1000°C the thickness of the film increases in accordance with the same laws as in air[1].

The study[24,29,84–87] of the initial stages of the oxidation of titanium alloys in water vapour and carbon dioxide and comparison of the results with the oxidation kinetics in air showed that the nature of the oxidising medium has a significant influence on the rate of growth of the interference films. In the presence of water vapour the formation of a film having a standard colour is much faster on all three alloys in the range of experimental temperatures than in air and in carbon dioxide (Fig. 4).[24] For example, the change in the colour of the film from yellow to brown on specimens of the OT4-0 alloy at 550°C in water vapour,

air, and carbon dioxide takes place after 22, 230 and 287 s respectively. The apparent activation energies for the oxidation of titanium alloys in water vapour and carbon dioxide are presented in Table 7.

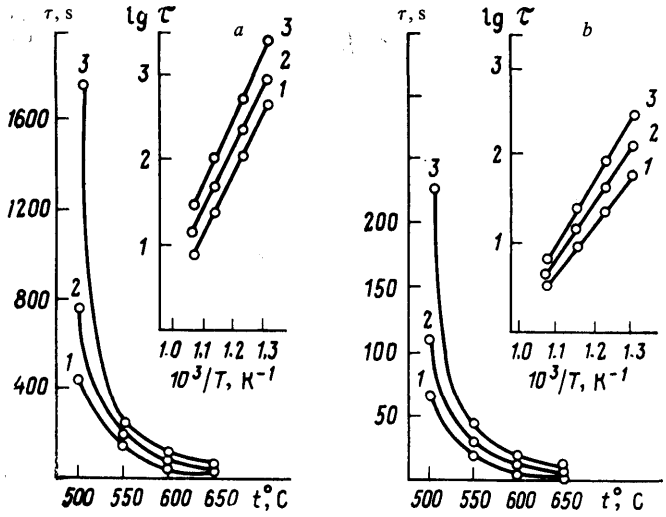


Figure 4. Dependence of the oxidation time τ of mechanically polished titanium alloy specimens on temperature in the formation of the film in the colour range from violet to dark blue: *a*) in carbon dioxide; *b*) in water vapour; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

Table 7. The activation energies (E, kcal mole^{-1}) for the oxidation of mechanically polished titanium alloy specimens in water vapour and carbon dioxide[24,29].

Alloy	Change in film colour			
	from yellow to brown	from brown to violet	from violet to dark blue	from dark blue to blue
	in water vapour			
VT-1	21.200	24.900	29.400	35.800
OT4-0	24.400	27.000	32.400	38.300
OT4-1	26.600	28.000	35.800	40.900
	in carbon dioxide			
VT-1	30.500	34.800	39.100	40.000
OT4-0	31.400	36.600	40.500	41.800
OT4-1	31.700	37.400	41.800	42.900

It follows from the analysis of the data presented in Tables 6 and 7 and in Figs. 3 and 4 that, in the formation of an oxide layer in air, water vapour, and carbon dioxide, technically pure VT-1 titanium is oxidised at the highest rate in all the intervals of the first-order colour spectrum investigated, while the lowest rate corresponds to the OT4-1 alloy with the highest aluminium content. According to some investigations[1,8,43], alloying with aluminium greatly increases the heat resistance of titanium alloys. The highest activation energies for the oxidation reaction correspond to specimens of the OT4-1 alloy under these conditions.

The retardation of the interaction of the metal with the medium as the thickness of the oxide layer (Figs. 5 and 6) increases and the increase of the activation energy for the process are characteristic of all three alloys. This can be explained by the fact that the oxide layer formed on the metal exhibits more effective protective properties and, by separating the reactants, strongly inhibits the chemical interaction and weakens the effect of the electric field arising on formation of interference oxide layers on metals[38,42,69].

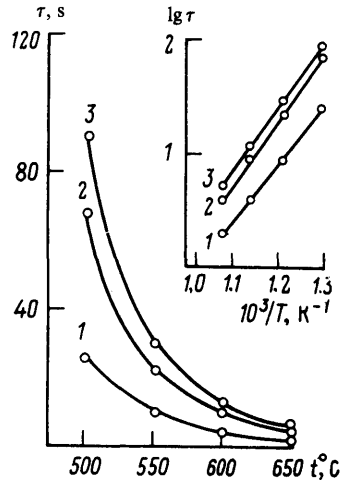


Figure 5. Dependence of the coloured film formation time in the oxidation of electrochemically polished titanium alloy specimens in water vapour on temperature in the colour range from yellow to brown; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

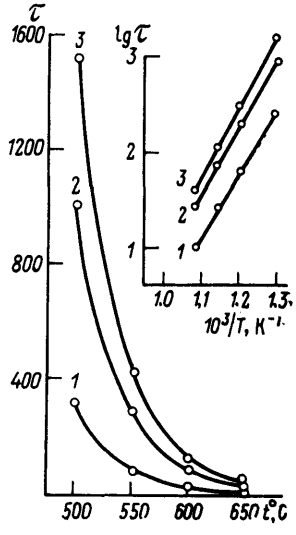


Figure 6. Dependence of the coloured film formation time in the oxidation of electrochemically polished titanium alloy specimens in carbon dioxide on temperature in the colour range from yellow to brown; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

An electron diffraction study of the phase composition of the interference films[98,99] formed in the thermal oxidation of titanium alloys in water vapour showed that the principal structural component of the films is rutile. The films obtained by oxidising the metal in CO_2 include three structural components: rutile, anatase, and titanium carbide[24,29].

The increase of the rate of oxidation of titanium in water vapour is due to the more porous structure of the oxide layer and the increase in the number of defects in the crystal lattice of rutile (an excess of titanium ions), which has been confirmed by electron microscope studies and is consistent with other data[95–97]. Under these conditions, there is a marked increase of the diffusional mobility of titanium ions. The diffusion coefficient of titanium ions in the oxide layer obtained in water vapour exceeds by 1–2 orders of magnitude that in the oxide obtained in air[1].

The decrease of the rates of the initial stages of the oxidation of the alloys during the formation of interference films with a first-order spectrum, in carbon dioxide is apparently associated with the formation of titanium carbide (a phase with a very great hardness and density in which the rate of diffusion of titanium ions is correspondingly reduced) in the surface layer of the metal. This is also indicated by the higher activation energy for the oxidation of titanium alloys in a stream of CO_2 compared with air and water vapour[24,29].

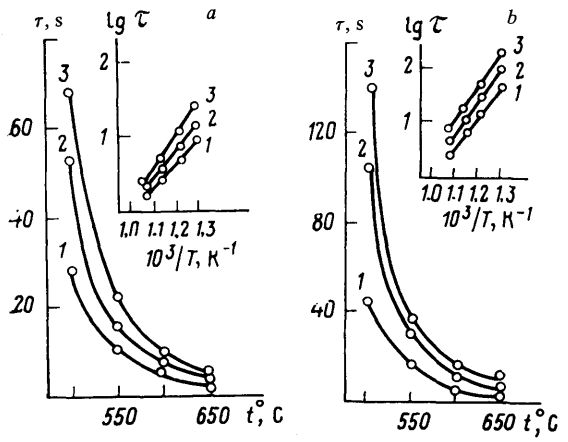


Figure 7. Dependence of the oxidation time for mechanically (*a*) and electrochemically (*b*) polished titanium alloy specimens on temperature (°C) in the formation of the film in water vapour in the colour range from brown to violet: *a*) water vapour; *b*) carbon dioxide; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

(d) The influence of the Method of Polishing the Surface on the Kinetics of the Oxidation of Titanium Alloys

The method of polishing the metal surface has an appreciable influence on its properties. For example, in electrochemical polishing the microgeometry and the physical and chemical properties of the surface are altered[100]. The method of preparation of the metal surface influences the kinetics of the initial stages of its oxidation[40]. However, the determination of the differences between the rates of oxidation of the surfaces of specimens of the metal having the same composition and structure but subjected to different types of treatment is experimentally difficult. The method of interference indication[17], which in the given instance is extremely sensitive and very promising, has been used to solve this problem.

In order to investigate the influence of the method of treatment of the surfaces of titanium alloys on the kinetics of their oxidation in different gaseous media, specimens of technically pure VT-1 titanium and OT4-0 and OT4-1 titanium alloys were subjected to two types of polishing: mechanical polishing to give a roughness of class 10–12 and electrochemical polishing in an electrolyte solution: the composition of the electrolyte and the process conditions have been described[101–103]. It has been shown that in the gaseous media investigated the initial stages of the oxidation of titanium specimens subjected to electrochemical polishing in the course of the formation of colour films with a first-order spectrum are much slower compared with specimens subjected to mechanical polishing (Fig. 7).[94] For example, the change in the colour of the film from violet to dark blue on mechanically polished specimens of the OT4-1 alloy at 550°C in water vapour, air, and carbon dioxide takes place after 45, 116, and 210 s, while on electrochemically polished specimens the corresponding times are 80, 660, and 756 s respectively.

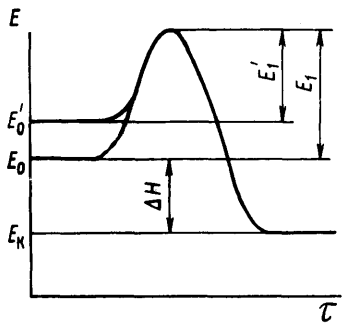


Figure 8. Variation of the energy levels of the surface atoms in the polishing process; E is the activation energy, τ is the time, E_0 and E_0' are the initial energy of the atoms in the surface layer for the electrochemically and mechanically polished specimens respectively, E_1 and E_1' are the activation energies for their oxidation, ΔH is the heat of the chemical reaction, and E_e is the energy of the reaction products.

The appreciable difference between the rates of the initial stages of the oxidation reaction can be explained by the fact that the energy levels of the atoms in the surface layer are higher for a mechanically polished (cold-worked) surface than for an electrochemically polished surface (Fig. 8).[94] The cold-worked layer, usually concentrated in the surface region, is removed by electrochemical polishing[104,105]. Furthermore, after electrochemical polishing one observes an increased resistance to gaseous corrosion due to the presence of a continuous thin and stable

oxide film on the surface of the metal[104,106–108]. On the other hand, in the case of mechanical polishing the scratches and foreign inclusions on the surface prevent the creation of such a continuous oxide layer and oxidation proceeds at a higher rate. With increase of the thickness of the coloured films, the rates of oxidation of both mechanically and electrochemically polished specimens of titanium alloys decrease in air, water vapour, and carbon dioxide.

Table 8 presents as an example the activation energies for oxidation in water vapour for specimens subjected to electrochemical polishing. Comparison of the data in Tables 6–8 shows that the activation energies for the oxidation of electrochemically polished titanium alloy specimens are appreciably higher than for mechanically polished specimens.

Table 8. The activation energies (E, kcal mole^{-1}) for the oxidation of electrochemically polished titanium alloy specimens by water vapour[84,94].

Alloy	Change in film colour			
	from yellow to brown	from brown to violet	from violet to dark blue	from dark blue to blue
VT-1	23.900	25.600	32.200	38.500
OT4-0	26.800	28.800	34.200	40.200
OT4-1	27.500	29.700	36.400	41.700

Regardless of the method of preliminary treatment of the surface, among the three alloys investigated technically pure VT-1 titanium and the OT4-1 alloys are oxidised at the highest and lowest rates respectively. Correspondingly, higher activation energies are characteristic of OT4-1 alloy specimens than of the VT-1 titanium.

Thus the method of interference indicators made it possible to observe the influence of the method of polishing the surface on the kinetics of the oxidation of titanium alloys of different composition in different gaseous media.

2. KINETICS OF THE OXIDATION OF GERMANIUM AND GALLIUM ARSENIDE

The kinetics of the thermal oxidation of germanium in air have been investigated[90,91,109,110] in the temperature 575–625° C in the region of the colour change at the GeO_2 film from colourless to green; with increase of the thickness of GeO_2 layers, an appreciable increase of the activation energy for the process is observed—from 47 to 128 kcal mole^{-1}.

Mathematical treatment of the results of the experiment on the oxidation of GaAs plates of AGET brand with atmospheric oxygen yielded[133] the following relations between the oxidation time τ and the temperature T in the range 600–675° C in different oxide colour ranges:

from colourless to brown:

$$\tau \simeq 52.48 \cdot 10^{-7} \exp(9950/T);$$

from brown to violet:

$$\tau \simeq 32.62 \cdot 10^{-17} \exp(33080/T);$$

from violet to dark blue:

$$\tau \simeq 12.59 \cdot 10^{-21} \exp(42300/T);$$

from dark blue to blue:

$$\tau \simeq 31.62 \cdot 10^{-24} \exp(47900/T).$$

It was shown that the activation energy for the formation of the β-Ga_2O_3 oxide film on the gallium arsenide specimens increases with increasing thickness of the oxide, within the limits of the first interference colour spectrum, from 19.81 to 95.32 kcal mole^{-1}.[133] This finding has been explained in a number of studies[11,42,77,78].

IV. CATALYSIS OF THE OXIDATION OF TITANIUM, SILICON, GERMANIUM, AND GALLIUM ARSENIDE

It is known that, in selecting catalysts for a given reaction, it is necessary to choose the latter from substances which are known as catalysts of analogous reactions and which form with initial reactants and the reduction products compounds which can be readily decomposed[111–115]. For titanium, silicon, germanium, and gallium arsenide heterogeneous oxidation processes, the optimum catalysts employed were therefore platinum, palladium, and silver, which are traditional catalysts of a large class of oxidation reactions[116].

1. METHODS OF PREPARATION OF THE CATALYSTS

The platinum, palladium, and silver catalysts have been obtained by electrolysing 3% aqueous solutions of chloroplatinic acid, palladium chloride, and potassium silver cyanide respectively. The carriers were platinum, silver, and nichrome. In addition, the platinum catalyst has been obtained by the thermal decomposition of $H_2[PtCl_6]$. For this purpose, a 50% aqueous solution of $H_2[PtCl_6]$ was deposited on the surface of a silicon plate and the latter was heated in air for 5 min at 700–1000° C. This resulted in the appearance of dispersed platinum on the silicon, which served as a carrier.

The use of electrolysis and of the thermal decomposition of chemical compounds for the preparation of disposed metals made it possible to obtain by a relatively simple technology catalysts with a comparatively high activity. Direct deposition of platinum and palladium blacks and of dispersed silver on a nichrome carrier or on the surface of the specimen being oxidised, for example, silicon, makes it possible to reduce the consumption of platinum, palladium, and silver under these conditions.

The degree of dispersion of the catalysts was determined by X-ray diffraction[98]. The average size of the crystals was 15, 230, and 2650 Å for palladium, platinum, and silver respectively, which corresponds approximately to the following specific surfaces ($m^2\ g^{-1}$): 370 for Pd, 12 for Pt, and 2.2 for Ag.[26,89,90].

2. THE ACCELERATING CATALYTIC EFFECT OF CATALYSTS ON THE OXIDATION OF TITANIUM, SILICON, GERMANIUM, AND GALLIUM ARSENIDE

(a) Catalysis of the Oxidation of Titanium

There is virtually no information in the literature about the kinetics of the growth of interference oxide layers on titanium in the presence of catalysts. We investigated

the catalytic oxidation of titanium by air in the presence of dispersed platinum, palladium, and silver in the temperature range 400–550°C.[88–92] The interference colours of the films were used as the indicator. Specimens of the OT4-0 titanium alloy (Ti ≥ 96.5%), subjected to mechanical polishing to a roughness class of 10–12, were used in the experiments. A study was made of the kinetics of the film growth within the limits of the formation of the yellow–brown–violet–dark blue–blue first-order spectrum with the catalyst arranged parallel to the surface of the specimen being oxidised and in contact with it[99]. On formation of interference rutile films (TiO_2), the local catalytic action of platinum, palladium, and silver was observed for the first time. It was found that in the presence of these metals the rate of growth of the oxide layer in the region of direct contact between the catalyst and the specimen is much higher compared with the rest of the surface. Thus at 400°C the formation of a blue film in the absence of a catalyst takes place over a period of 130 h and 45 min, while in the presence of platinum the reaction takes 4 min and 12 s, i.e. the oxidation of titanium is accelerated by a factor of 1868. The degree of acceleration of the oxidation process depends on the nature of the catalyst employed, the temperature of the reaction zone, and the thickness of the film formed (Tables 9 and 10). Table 10 presents a quantitative estimate of the parameter of the local-catalytic acceleration (K) of the titanium oxidation reactions in the presence of the platinum and silver catalysts, K being defined as the ratio of the times required for the formation of the TiO_2 interference film with a standard colour in the absence and in the presence of a catalyst.

Table 9. Time required for the formation of interference rutile films in the catalyst–specimen contact zone[89,90].

Colour of film	Catalyst	Time, min			
		400° C	450° C	500° C	550° C
Brown	None	780	47	7.17	4.2
	Dispersed Ag	5.00	2.5	1.75	1.20
	Pt black	2.25	1.5	1.00	0.83
Violet	None	2970	270	26.42	10.75
	Dispersed Ag	6.5	3.00	2.17	1.33
	Pt black	3.15	1.85	1.30	1.00
Dark blue	None	5520	1140	85	19.66
	Dispersed Ag	8.1	4.6	3.17	1.83
	Pt Black	3.75	2.1	1.42	1.20
Blue	None	7845	2520	270	66
	Dispersed Ag	10.2	6.75	4.08	2.55
	Pt Black	4.2	2.4	1.6	1.35

The data presented in Tables 9 and 10 show that, with increase of the thickness of the TiO_2 oxide layer, the efficiency of the catalyst increases. Thus at 400°C platinum black accelerates the formation of the brown rutile film by a factor of 346, the violet film by a factor of 943, the dark blue film by a factor of 1470, and the blue film by a factor of 1868. With increase of temperature, the activity of the catalyst falls. For example, dispersed silver accelerates the formation of the violet rutile film by a factor of 457 at 400°C, 90 at 450°C, 12 at 500°C, and 8 at 550°C.

A difference between the catalytic activities of platinum, palladium, and silver was observed by the method of interference indication. The initial stages in the oxidation of the test alloys in the presence of platinum black take place at a higher rate than in the presence of dispersed silver. Thus the formation of a blue film on specimens of type OT4-0 at 400°C in the presence of platinum and silver catalysts takes place after 220 and 610 s respectively.

Table 10. The local catalytic acceleration (the values of K) for the oxidation of the OT4-0 titanium alloy in the presence of platinum and silver[89].

Colour of film	Pt				Ag			
	400° C	450° C	500° C	550° C	400° C	450° C	500° C	550° C
Brown	346.6	31.3	7.1	5.0	158	18.8	4.0	3,5
Violet	942.8	145.9	20.3	10.7	456.9	90.0	12.1	8.0
Dark blue	1472	542.8	59.8	16.3	681.5	247.9	26.8	10.7
Blue	1867.8	1050	168.7	48.8	771.2	373.0	66.0	25.8

(b) Catalysis of the Oxidation of Silicon

Polished plates of type KEF, oriented in the (111) plane, which catalysed oxidation by atmospheric oxygen in the range 450–1350°C, were used in the experiments on the catalytic oxidation of silicon[117,118,129]. The platinum, palladium, and silver catalysts, deposited on carriers in the form of a needle, were mounted with the aid of a special device over the silicon plate undergoing oxidation at right angles to its surface[117,118].

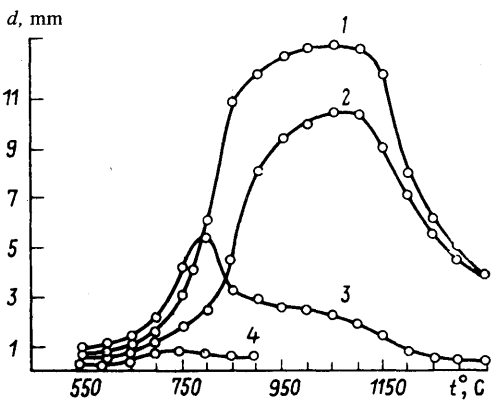


Figure 9. Dependence of the diameter d of the interference zone in the oxidation of silicon on temperature for platinum black (curves *1* and *2*), palladium black (curve *3*), and dispersed silver (curve *4*); wire carrier: *1*) and *3*) platinum; *2*) nickel–chromium; *4*) silver; oxidation time 5 min.

The observation of a sharp increase in the rate of oxidation of silicon in the presence of platinum, palladium, and silver must be regarded as the principal result of these experiments[92,109,117,118]. For example, at 700°C the rate of growth of the blue SiO_2 film with a thickness of 1500 Å increases by a factor of 10^4 in the presence of the platinum

catalyst. Comparison of the silicon oxidation times in the presence and absence of platinum black showed[92] that K increases with decrease of temperature and with increase of the thickness of the oxide layer obtained.

The diameter of the interference zone in the catalytic oxidation of silicon depends on the type of the catalyst, temperature, and oxidation time. Thus in the course of 5 min the diameter of the interference zone reaches its maximum value at 1000–1100°C for platinum black, at 800°C for palladium black, and at approximately 750°C for dispersed silver (Fig. 9).[117,133] Platinum and silver are characterised by the greatest and smallest zone diameters respectively.

A marked weakening of the catalytic activity of the metals takes place at the temperature of the most effective sintering and recrystallisation, which is usually two-thirds of the melting point. Indeed, Fig. 9 shows that a sharp decrease in the diameter of the interference zone begins at 1100–1150°C for platinum and palladium black. The diameter of the interference zone also depends on the type of carrier employed. Thus the use of platinum as the carrier for platinum black results in a zone with a larger diameter than in the case of nichrome (Fig. 9).

Comparison of the times required for the formation of a silicon dioxide layer 15400 Å thick at 700°C in the presence of platinum and palladium blacks and dispersed silver shows that the activities of these catalysts increase in the sequence Ag < Pd < Pt.

The influence of geometrical factors, particularly of the length and thickness of the layer of catalytically active substance deposited on the carrier as well as its distance from the surface of the specimen, has been studied[119]. The experiments were performed with two arrangements of the catalyst (Fig. 10): (a) platinum (or palladium) black was at a distance s from the end of the needle; (b) platinum (or palladium) black covered the wire carrier over a length l from the point of its contact with the specimen.

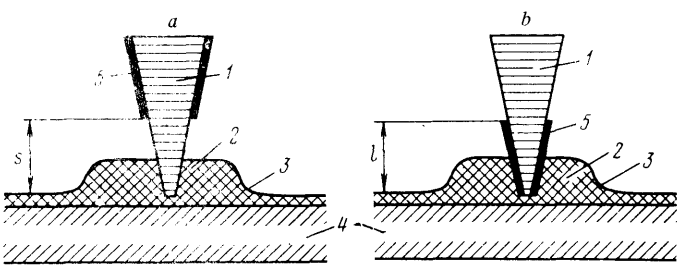


Figure 10. Schematic illustration (*a*) and (*b*) of the positioning of the catalyst relative to the silicon specimen: *1*) platinum or nichrome needle; *2*) SiO_2 film; *3*) interference colour rings; *4*) silicon plate; *5*) platinum or palladium black.

It was found that an increase of s reduces the catalytic effect. The catalytic effects of platinum black deposited on platinum and nichrome carriers differ significantly. The thickness of the SiO_2 film grown over a period of 5 min is independent of the extent l of the blackened section of the platinum wire.

Thus, with the aid of platinum, palladium, and silver catalysts, it is possible to achieve the local growth of oxide layers on silicon at temperatures of approximately 500–600°C at which the process virtually does not occur in the absence of the catalyst. The rate of the process depends significantly on temperature, the type of catalyst employed, and the distance of the active substance on the carrier from the silicon specimen.

The kinetics of the catalytic oxidation of silicon were determined by the mathematical treatment of the curves for the increase in the thickness in the SiO_2 film[129] obtained using platinum or silver foil, in contact with the surface of the specimen undergoing oxidation, as catalyst carriers. It was established that an increase of the film thickness with time is linear in the presence of platinum black and parabolic in the presence of palladium black and dispersed silver (Table 11). The activation energy for the oxidation process depends on the type of the catalyst. The oxidation of silicon in the presence of platinum black proceeds with a lower activation energy than in the presence of palladium black and dispersed silver; the activation energies at 500–700°C are 9.16, 9.75, and 12.76 kcal mole^{-1} respectively.

Table 11. Variation of the SiO_2 film thickness (y, Å) with time (τ, min) in the oxidation of silicon in air in the presence of catalysts[129].

Temperature, °C	Pt black	Dispersed silver	Pd black
500	$y = 1042\ \tau$	$y^2 = 33.16 \cdot 10^4\ \tau$	$y^2 = 80.66 \cdot 10^4\ \tau$
600	$y = 2329\ \tau + 3 \cdot 10^3$	$y^2 = 83.26 \cdot 10^4\ \tau$	$y^2 = 189.33 \cdot 10^4\ \tau$
700	$y = 3550\ \tau + 5.2 \cdot 10^3$	$y^2 = 121.93 \cdot 10^4\ \tau$	$y^2 = 444.66 \cdot 10^4\ \tau$

The equations for the rate constants for the catalytic oxidation of silicon, determined from the experimental data, are presented in Table 12, For the platinum catalyst, they are evidently different in the temperature ranges 500–700°C and 800–900°C.

Table 12. Dependence of the equations of the rate constants for the growth of the silicon oxide film on the type of catalyst employed and temperature[133].

Catalyst	500–700° C	800–900° C	Dimensions of rate constant
Pt black	$k = 4.08 \cdot 10^5 \exp(-4.62/T)$	$k = 1.86 \cdot 10^6 \exp(-5.01/T)$	A min^{-1}
Pd black	$k = 3.39 \cdot 10^9 \exp(-6.44/T)$	—	A^2 min^{-1}
Dispersed Ag	$k = 1.95 \cdot 10^8 \exp(-4.93/T)$	—	A^2 min^{-1}

The time (τ, s) corresponding to the appearance of SiO_2 films whose thickness corresponds to complete second-order (3500 Å) and eighth-order (15400 Å) colour spectra in the presence of platinum black varies with temperature in the following manner[129]:

For 3500 Å: $\tau \simeq 8.79 \times 10^{-2} \exp(5730/T)$, $E \simeq 11350$ cal mole^{-1};
For 15400 Å: $\tau \simeq 8.67 \times 10^{-4} \exp(11950/T)$, $E \simeq 27700$ cal mole^{-1}.

With increase of the oxide film thickness, the activation energy E for the oxidation of silicon increases.

Table 13 lists the times corresponding to the formation of SiO_2 films of different thickness in the isothermal oxidation of silicon in air in the presence (τ_2) and absence (τ_1) of $H_2[PtCl_6]$ at 700–1000°C and the increments in the rate of oxidation ($K = \tau_1/\tau_2$).[133] Evidently an increase of temperature lowers the efficiency of the catalyst.

Table 13.

Temperature, °C	SiO_2 film thickness, A	τ_1, min	τ_2, min	K
700	750	10 000	5	2000
800	1250	2 500	5	500
900	1500	700	5	140
1000	1750	300	5	60

(c) Catalysis of the Oxidation of Germanium

On direct contact with the specimen undergoing oxidation, platinum or palladium black leads to a local acceleration of the oxidation of germanium of type GES [32,90,91,109] at temperatures above 350°C (Table 14).

Table 14. Time required for the formation of the interference films in the catalyst–germanium specimen contact zone[90].

Colour of GeO_2 film (order of spectrum)	Catalyst	Time, min			
		350° C	400° C	450° C	500° C
Dark blue (I)	Pt black	5.0	3.25	1.0	0.75
" "	Pd black	10.1	5.4	1.5	1.1
Blue (I)	Pt black	6.0	4.0	1.25	1.0
" "	Pd black	15.3	7.1	1.8	1.25
Yellow (II)	Pt black	7.5	5.0	1.5	1.2
" "	Pd black	>30	8.7	2.2	1.4
Red(II)	Pt black	9.0	5.5	2.0	1.5
" "	Pd black	—	10.2	3.1	1.7
Green (II)	Pt black	10.0	6.25	2.5	1.8
" "	Pd black	—	13.5	4.25	2.1
Green (III)	Pt black	>30	7.5	3.0	2.1
" "	Pd black	—	17.1	5.1	2.8

It was found (Table 17) that, in the formation of interference oxide layers on germanium platinum is more active than palladium. The use of platinum and palladium catalysts makes it possible to oxidise germanium at an appreciable rate at approximately 400°C, i.e. 200° below the temperature in the absence of catalysts.

(d) Catalysis of the Oxidation of Gallium Arsenide

On heating in air, gallium arsenide begins to be oxidised at an appreciable rate above 600°C.[36,37] However, the use of the thermal oxidation method is significantly restricted by the fact that, on heating above 600°C, gallium arsenide crystals decompose appreciably to liquid gallium and gaseous arsenic in accordance with the equation

$$4GaAs(solid) = 4Ga(liq.) + As_4(gas).$$

A decrease of temperature and an increase of the rate of oxidation of GaAs are therefore of great practical interest.

In the presence of a platinum catalyst in contact with the specimen surface being oxidised the rate of oxidation of GaAs increases appreciably. Table 15 shows that the increase of the rate is greater the greater the thickness of the oxide layer.

Table 15. Dependence of the GaAs oxidation time in the absence (τ_1) and presence (τ_2) of platinum black and of the increment in the rate of oxidation $K = \tau_1/\tau_2$ on the thickness of the Ga_2O_3 oxide film[133].

Colour of β-Ga_2O_3 film (order of spectrum)	τ_1, min	τ_2, min	K
Brown (I)	1050	0.33	3150
Violet (I)	1350	0.41	3220
Dark blue (I)	1800	0.75	3600

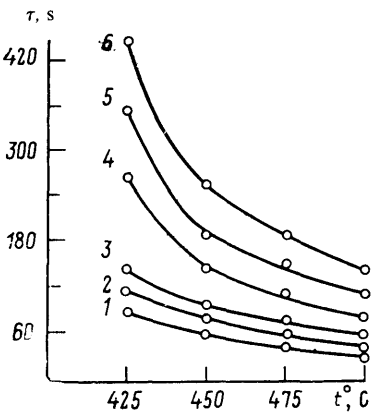


Figure 11. Temperature variation of the oxidation time τ of gallium arsenide in the presence of the platinum catalyst in contact with the specimen under-going oxidation before the appearance of brown (curve *1*), violet (curve *2*), dark blue (curve *3*), blue (curve *4*), yellow (curve *5*), and orange (curve *6*) oxide films.

The employment of platinum black reduces the GaAs oxidation temperature and makes it possible to obtain on the latter oxide films at a technologically acceptable rate at temperatures in the range 425–500°C (Fig. 11). The activation energy for the catalytic oxidation of GaAs varies in the range 9.4–21.1 kcal mole^{-1}.

3. THE INFLUENCE OF CATALYSTS ON THE OXIDATION OF TITANIUM, SILICON, AND GERMANIUM AT A DISTANCE

The catalytic oxidation of titanium, silicon, and germanium has been carried out[26,27,32,88–92,109,110,117–119] both with direct contact between them and dispersed metals and with the specimens undergoing oxidation placed at a certain distance from the catalyst. It was observed[27,89,90] that platinum and palladium coated with the corresponding blacks exert a catalytic influence on the rate of oxidation of titanium, silicon, and germanium placed at some distance from the catalyst (Tables 16–18). This effect begins to be observed at approximately 400°C. Table 17 shows that the growth of the SiO_2 film is observed in the course of approximately 4 min from the start of the oxidation; the subsequent reaction entails hardly any change in the thickness of the oxide film. An increase of the oxidation temperature (above 1000°C for platinum and above 800°C for palladium) lowers the catalytic influence of the dispersed metals (Fig. 12). The activity of the catalyst decreases with increasing distance between the dispersed metal and the specimen being oxidised. The catalytic activity of platinum black is higher than that of palladium black (Tables 16–18).

Table 16. Time required for the formation of rutile interference films with the catalyst acting at a distance (500°C).[89]

Distance from catalyst to specimen, mm	Catalyst	Time, min			
		brown film	violet film	dark blue film	blue film
0.1	Pt black	1.5	2.0	3.0	4.1
0.1	Pd black	1.5	2.3	3.7	4.8
0.5	Pt black	5.0	5.8	6.5	7.5
0.5	Pd black	5.0	6.9	8.0	10.0

Table 17. Dependence of the SiO_2 film thickness on the growth time at 650°C.[27]

Catalyst	Distance, mm	Film thickness, Å					
		1 min	2 min	3 min	4 min	5 min	6 min
Pt black	0.1	2000	2500	3900	5400	5400	5400
Pt black	0.4	1500	2000	3000	4260	4260	4260
Pt black	0.8	1000	1250	1500	2000	2000	2000
Pd black	0.1	1750	2000	2500	3500	3500	3500
Pd black	0.4	1250	1500	1750	2500	2500	2500

4. EXOELECTRON EMISSION FROM THE SURFACES OF DISPERSED PLATINUM, PALLADIUM, AND SILVER

The application of the method of exoelectron emission[120–123] makes it possible to obtain information about the energetic inhomogeneity, the density of defects, and the number of active centres on the surfaces of the catalysts investigated.

Exoelectron emission from the surfaces of compact platinum and platinum and palladium blacks was studied in a vacuum of approximately 10^{-5} mmHg on a specially designed apparatus[124] permitting the heating of the test catalyst to 400°C. An appreciable increase of the intensity of exoemission from the surfaces of the dispersed metals relative to the background level was observed on platinum black from 300°C, on palladium black from 350°, and on compact platinum from 370°C (Fig. 13). The most intense exoemission was observed for platinum black and the least intense for compact platinum. Evidently the energy of the liberation of the electron from the surface of platinum black is lower than from the surface of palladium black and compact platinum; in terms of increasing numbers of active centres, the catalysts can be arranged in the sequence compact platinum < Pd black < Pt black.

Table 18. Dependence of the time required for the formation of GeO_2 interference films and of the increment in the rate of oxidation of germanium (K) on the type of catalyst (450°C).[90,133]

Catalyst	Distance from catalyst to specimen, mm	Colour of GeO_2 film (order of spectrum)					
		dark blue (I)	blue (I)	yellow (II)	red (II)	green (II)	green (III)
		Time, min					
Pt black	0.1	1.0	1.5	2.0	2.5	3.0	4.0
Pt black	0.5	3.2	4.3	5.15	5.5	6.0	7.0
Pd black	0.1	3.0	4.5	5.0	6.0	7.0	9.0
Pd black	0.5	3.5	5.0	6.0	7.0	9.0	15
		K					
Pt black	0.1	1924	2198	2514	2841	3306	3620
Pt black	0.5	642	760	1005	1282	1651	2058
Pd black	0.1	602	731	977	1184	1416	1600
Pd black	0.5	550	658	838	889	1100	—

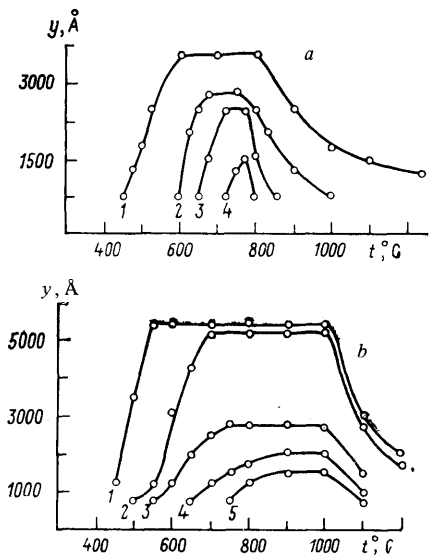


Figure 12. Temperature dependence of the SiO_2 film thickness in the oxidation of silicon in the course of 5 min in the presence of palladium (*a*) and platinum (*b*) catalysts: distance of the catalyst from the specimen surface (mm): *1*) 0.1; *2*) 0.4; *3*) 0.8; *4*) 1.0; *5*) 1.2.

5. GENERAL CHARACTERISTICS AND MECHANISMS OF THE REACTIONS INVOLVING THE CATALYTIC OXIDATION OF THE METALS AND SEMICONDUCTORS INVESTIGATED

Analysis of the experimental data for the catalytic acceleration of the oxidation of titanium, silicon, germanium, and GaAs by platinum, palladium, and silver[26,27,32,88-92,109,110,117-119,129] reveals the following features.

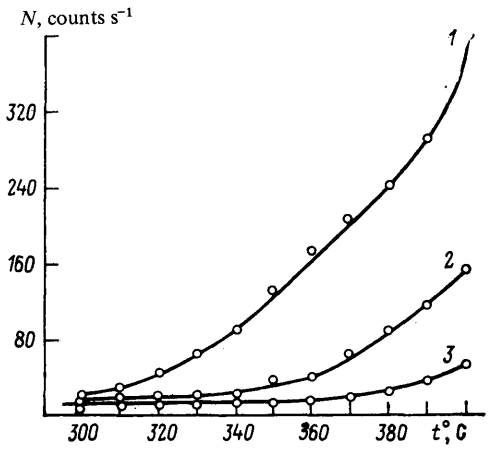


Figure 13. Temperature dependence of the intensity of exoelectron emission (N) from the surfaces of dispersed platinum (curve *1*) and palladium (curve *2*) and compact platinum (curve *3*).

Platinum, palladium, and silver catalysts accelerate the oxidation of the above metals and semiconductors above 350°C, the rate of reaction increasing by a factor of 100 to 1000. The catalyst accelerates the oxidation reactions both on contact and at a distance. The catalytic effect is more pronounced on direct contact between the catalysts and the specimens being oxidised. The catalysts accelerate the oxidation process in a zone directly adjoining them. The greatest catalytic activity among the dispersed metals employed is shown by platinum black and the smallest by dispersed silver.

In the presence of catalysts the Ti, Si, Ge, and GaAs oxidation temperature is reduced by hundreds of degrees and the rate of oxidation remains acceptable in practice. The efficiency of the catalysts increases with increasing thickness of the oxide layer formed (TiO_2, SiO_2, GeO_2 and Ga_2O_3).

Sintering of platinum and palladium blacks and of dispersed silver reduces the activity appreciably at temperatures amounting to two-thirds of the melting point of the catalyst. The difference between the laws governing the oxidation process in the presence of platinum, palladium, and silver catalysts (linear for platinum and parabolic for palladium and silver) is due to the unequal rates of their sintering, reducing the catalytic influence of the activated metals on the oxidation process.

The observed features can be accounted for in terms of modern ideas concerning the oxidation of metals and semiconductors[1,9,11,12,14,38-43,46,49-54,58,59,64,65,125] and heterogeneous catalysts[16,18,111-116,126-128].

The TiO_2, SiO_2, GeO_2, and Ga_2O_3 oxide films formed in the interaction of titanium, silicon, germanium, and gallium arsenide with oxygen cause a separation of the initial reactants in space. The subsequent reaction is limited by the migration of titanium, silicon, germanium, gallium, and oxygen ions through the growing oxide film. The diffusion process occurs in consequence of the generation of concentration gradients and of an electric field in the growing oxide layer[49-54]. The overall charge transfer current density j_i is then defined by the expression[14]

$$j_i = -c_i v_i (\Delta\mu_i + z_i e E) \ ,$$

where c_i is the concentration of species, v_i the mobility of the charges, $\Delta\mu_i$ the change in the chemical potential, z_i the valence of ions of type i, e the electronic charge, and E the electric potential gradient.

The large surface of the catalysts is capable of retaining considerable amounts of chemically adsorbed oxygen, the redistribution of which increases the oxygen concentration gradient in the oxide films and the electric field strength with increase of film thickness on metals and semiconductors. This increases the charge transfer current density and the rates of chemical interaction. In addition, the increase of the electric field strength lowers the activation energy for the oxidation process (for example, from 30-43 kcal mole^{-1} [9,11,12,14] to 9-13 kcal mole^{-1} [109,110,129,131] for silicon). As a result, the significant increase of the ionic diffusion flux density and the decrease of activation energy lead to an increase of the rate of oxidation in the presence of catalysts by factors of hundreds and thousands.

According to the existing electronic theories of heterogeneous catalysis[111,114,128], the gas, for example, oxygen, is activated by its chemisorption on the active centres of the catalyst surface and the activation is accompanied by the transfer of electrons from the catalyst to the adsorbed atoms. The amount of adsorbed oxygen is greater the greater the number of active centres from which electrons pass to oxygen comparatively readily. The results obtained by the method of exoelectron emission suggest that the number of these active centres is greater on platinum black than on palladium black. This apparently explains the higher catalytic activity of platinum black despite its smaller degree of dispersion.

The action of the catalysts at a distance can be accounted for in the following way. Evidently the activated species are dissolved from the catalyst surface into the surrounding gas phase[114,126-128]. With increase of temperature, this is accompanied by a displacement of the dynamic equilibrium towards desorption. The desorbed species retain their activity for some time at a short distance from the catalyst surface, after which they recombine[126,127]. Contact of the catalyst with the specimen undergoing oxidation facilitates the transfer of active oxygen species from the catalyst to the oxide film. This is why the catalytic activity of the activated metals is greater on contact than at a distance.

V. SOME PRACTICAL APPLICATIONS

The results presented in the present review permit practical recommendations for the use of the titanium, silicon, germanium, and gallium arsenide oxidation reaction.

Determination of the kinetic parameters of reactions. The kinetic parameters of heterogeneous reactions involving the oxidation of metals and semiconductors, for example, the activation energy, are determined by the mathematical treatment of data obtained as a result of the visual observation of the changes in the interference colours of oxide films in the course of the interaction. It is then possible to establish the dependence of the kinetic parameters of the reactions on temperature, the thickness of the interference film, the nature of the material being oxidised, and other factors.

It is possible to use TiO_2, SiO_2, GeO_2, and Ga_2O_3 interference films as decorative and protective coatings on the surfaces of metals, alloys, and semiconductors.

The accelerated formation of oxide films in the course of the oxidation reaction is achieved by employing platinum, palladium, and silver catalysts which are either in contact with the surface of the specimens being oxidised or are at some distance from them. The employment of catalysts permits the formation of films with the required thickness over a short time interval and at a lower temperature than in the thermal oxidation in the absence of catalysts.

The comparative activities of catalysts are determined by comparing the times required for the formation of oxide films of identical thickness in the presence (τ_1) and absence (τ_2) of the catalyst. The increase of the rate of oxidation $K = \tau_2/\tau_1$ can serve as a measure of the activity of the catalyst. Furthermore, the activity of the catalyst can be estimated approximately from the diameter of the interference zone (in this case it is necessary to employ a catalyst carrier in the form of a needle). In addition, the activity of the catalyst can be inferred from the intensity of the exoelectron emission, since the intensity increases with increasing number of active centres on the catalyst surface.

The marking of articles. The use of catalysts (acting on contact or at a distance) makes it possible to mark titanium, silicon, germanium, and gallium arsenide with appropriate symbols[132]. Such marking does not affect the surface oxide layer on the article and is distinguished by an improved thermal and corrosion resistance in corrosive media. Furthermore, in forming the symbol, the surface of the marked article is not strongly acted upon. All these factors lead to good prospects for the practical employment of heterogeneous catalysis in the oxidation of metals, alloys and semiconductors.

REFERENCES

1. L. S. Bai, D. I. Lainer, E. N. Slesareva, and M. I. Tsypin, "Okislenie Titana i Ego Splavov" (Oxidation of Titanium and Its Alloys), Izd. Metallurgiya, Moscow, 1970.
2. V. P. Chernetsov, "Titan i Ego Splavy" (Titanium and Its Alloys), Mashgiz, Leningrad, 1966.
3. P. V. Mikhailov-Mikheev, "Novyi Promyshlennyi Metall—Titan" (A New Industrial Metal—Titanium), Mashgiz, Moscow–Leningrad, 1958.
4. V. V. Glazova, "Legirovanie Titana" (The Alloying of Titanium), Izd. Metallurgiya, Moscow, 1966.
5. G. B. Luchinskii, "Khimiya Titana" (The Chemistry of Titanium), Izd. Khimiya, Moscow, 1971.
6. Ya. G. Goroshchenko, "Khimiya Titana" (The Chemistry of Titanium), Izd. Naukova Dumka, Kiev, 1970, Part 1.
7. N. M. Pul'tsin, "Titanovye Splavy i Ikh Primenenie v Mashinostroenii" (Titanium Alloys and Their Applications in Machine Engineering), Mashgiz, Moscow–Leingrad, 1962.
8. V. N. Eremenko, "Titan i Ego Splavy" (Titanium and Its Alloys), Izd. Akad. Nauk Ukrain. SSR, Kiev, 1955.
9. R. M. Burger and R. P. Donovan (Editors), "Fundamentals of Silicon Integrated Device Technology" Vol. 1, "Oxidation, Diffusion, and Epitaxy" (Translated into Russian), Izd. Mir, Moscow, 1969.
10. R. A. Gavrilov and A. M. Skvortsov, "Tekhnologiya Proizvodstva Poluprovodnikovykh Priborov" (The Technology of the Manufacture of Semiconductor Devices), Izd. Energiya Leningrad, 1968.
11. N. A. Kolobov and M. M. Samokhvalov, "Diffuziya i Okislenie Poluprovodnikov" (Diffusion and Oxidation of Semiconductors), Izd. Metallurgiya, Moscow, 1975.
12. V. A. Arslambekov, I. D. Kazarinova, and K. M. Gorbunova, Uspekhi Khim., **41**, 64 (1972).
13. B. A. Krasyuk and A. I. Gribov, "Poluprovodniki–Germanii i Kremnii" (Germanium and Silicon as Semiconductors), Izd. Lit. po Chernoi i Tsvetnoi Metallurgii, Moscow, 1961.
14. P. Kofstand, "Non-stoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides" (Translated into Russian), Izd. Mir, Moscow, 1975.
15. V. A. Roiter (Editor), "Problemy Teorii i Praktiki Issledovanii v Oblasti Kataliza" (Problems of the Theory and Practice of Research in the Field of Catalysis), Izd. Naukova Dumka, Kiev, 1973.
16. N. I. Il'chenko, Uspekhi Khim., **41**, 84 (1972) [Russ. Chem. Rev., No. 1 (1972)].
17. E. S. Vorontsov, V. K. Altukhov, A. N. Korneeva, and N. P. Peksheva, Uspekhi Khim., **42**, 1325 (1973) [Russ. Chem. Rev., No. 7 (1973)].
18. G. K. Boreskov, Kinetika i Kataliz, **14**, 7 (1973).
19. I. I. Kornilov and V. V. Glazova, "Vzaimodeistvie Tugoplavkikh Metallov Perekhodnykh Grupp s Kislorodom" (The Interaction of Refractory Transition Metals with Oxygen), Izd. Nauka, Moscow, 1967.
20. I. I. Kornilov and Yu. M. Vinogradov, "Novye Issledovaniye Titanovykh Splavov, Trudy VI Soveshchaniya po Metallokhimii, Metallovedeniyu i Primeneniyu Titana i Ego Splavov" (New Research into Titanium Alloys. Proceedings of the VIth Conference on the Metal Chemistry, Metallography, and Applications of Titanium and Its Alloys), Izd. Nauka, Moscow, 1965, p.102.
21. N. P. Peksheva and E. S. Vorontsov, Zashchita Metallov, 708 (1972).
22. N. P. Peksheva and E. S. Vorontsov, Zhur. Prikl. Khim., **46**, 1689 (1973).
23. N. P. Peksheva and E. S. Vorontsov, Zhur. Prikl. Khim., **48**, 1304 (1975).
24. N. P. Peksheva and E. S. Vorontsov, Zhur. Prikl. Khim., **48**, 2383 (1975).
25. N. P. Peksheva, E. S. Vorontsov, and K. S. Solov'ev, Symposium, "Poluchenie i Svoistva Tonkikh Plenok" (The Preparation and Properties of Thin Films), Izd. ONTI IPM Akad Nauk Ukrain. SSR, Kiev, 1976, p.79.

26. V. M. Strukov and E. S. Vorontsov, Kinetika i Kataliz, 17, 797 (1976).
27. V. M. Strukov and E. S. Vorontsov, Zhur. Prikl. Khim., **49**, 978 (1976).
28. G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovskii, "Sprovochnik Termodinamicheskikh Velichin" (Handbook of Thermodynamic Data), Atomizdat, Moscow, 1971.
29. N. P. Peksheva and E. S. Vorontsov, Zhur. Fiz. Khim., 50, 1524 (1976) [Russ. J. Phys. Chem., No. 6 (1976)].
30. N. P. Peksheva and E. S. Vorontsov, "Sbornik Nauchnykh Trudov Yaroslavskogo Politekhnicheskogo Instituta, Fizicheskaya Khimiya" (Collected Scientific Reports from the Yaroslavl' Polytechnic Institute, Physical Chemistry), Yaroslavl, 1974, p.79.
31. I. V. Tananaev and M. Ya. Shpirt, "Khimiya Germaniya" (The Chemistry of Germanium), Izd. Khimiya, Leningrad, 1967.
32. V. M. Strukov and E. S. Vorontsov, Zhur. Prikl. Khim., **49**, 1687 (1976).
33. H. T. Minden, J. Electrochem. Soc., **109**, 733 (1962).
34. S. N. Fainshtein, "Obrabotka Poverkhnosti Poluprovodnikovykh Priborov" (The Treatment of the Surfaces of Semiconductor Devices), Izd. Energiya, Moscow–Leningrad, 1966.
35. A. S. Medvedev, "Vvedenie v Tekhnologiyu Poluprovodnikovykh Materialov" (Introduction to the Technology of Semiconducting Materials), Izd. Vysshaya Shkola, Moscow, 1970.
36. Ya. A. Ugai, "Vvedenie v Khimiyu Poluprovodnikov" (Introduction to the Chemistry of Semiconductors), Izd. Vysshaya Shkola, Moscow, 1975.
37. N. G. Ryabtsev, "Materialy Kvantovoi Elektroniki" (Materials for Quantum Electronics), Izd. Sovetskoe Ratio, Moscow, 1972.
38. J. Bernard (Editor), "Oxydation des Metaux" (Translated into Russian), Izd. Metallurgiya, Moscow, 1968, Vol. 1.
39. P. Kofstad, "High-Temperature Oxidation of Metals" (Translated into Russian), Izd. Mir, Moscow, 1969.
40. N. D. Tomashov, "Teoriya Korrozii i Zashchity Metallov" (Theory of the Corrosion and Protection of Metals), Izd. Akad. Nauk SSSR, Moscow, 1960.
41. N. P. Zhuk, "Kurs Teorii Korrozii i Zashchity Metallov" (A Course on the Theory of Corrosion and Metal Protection), Izd. Metallurgiya, 1976.
42. K. Hauffe, "Reaktionen in und an festen Stoffen" (Translated into Russian), Inostr. Lit., Moscow, 1963, Part II.
43. O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys" (Translated into Russian), Izd. Metallurgiya, Moscow, 1965.
44. A. D. McQuillan and M. K. McQuillan, "Metallurgy of the Rarer Metals: Titanium" (Translated into Russian), Metallurgizdat, Moscow, 1958.
45. J. L. Everhart, "Titanium and Titanium Alloys" (Translated into Russian), Metallurgizdat, Moscow, 1956.
46. I. N. Frantsevich, R. F. Voitovich, and V. A. Lavrenko, "Vysokotemperaturnoe Okislenie Metallov i Splavov" (High-Temperature Oxidation of Metals and Alloys), Gostekhizdat, Kiev, 1963.
47. D. I. Lainer and M. I. Tsypin, "Metallurgiya i Toplivo" (Metallurgy and Fuel), Izd. Akad. Nauk SSSR, Otd. Tekh. Nauk, 1959, p.131.
48. T. N. Arzhanyi, Symposium, "Titan i Ego Splavy" (Titanium and Its Alloys), Izd. Akad. Nauk SSSR, 1958, No. 1, p.82.
49. C. Wagner, Z. phys. Chem., **21**, 25 (1933).
50. C. Wagner, Z. phys. Chem., **32**, 447 (1936).
51. N. Cabrera and N. Mott, Rep. Progr. Phys., 12, 163 (1949).
52. K. Hauffe and B. Ilschner, Z. Elektrochem., 58, 382, 467 (1954).
53. A. T. Fromhold, J. Phys. Chem. Solids, **24**, 1081 (1963).
54. A. T. Fromhold, J. Phys. Chem. Solids, **24**, 1309 (1963).
55. P. J. Jorgensen, J. Chem. Phys., 37, 874 (1962).
56. S. J. Laverty and W. D. Ryen, Intewat. J. Electronics, **26**, 519 (1969).
57. D. P. Miller, J. G. Garper, and T. R. Perry, J. Electrochem. Soc., 108, 1123 (1961).
58. U. R. Evans, "The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications" (Translated into Russian), Mashgiz, Moscow, 1962.
59. V. I. Arkharov, Symposium, "Mekhanizm Vzaimodeistviya Metallov s Gazami" (The Mechanism of the Interaction of Metals with Gases), Izd. Nauka, Moscow, 1964, p.24.
60. P. D. Dankov, Dokl. Akad. Nauk SSSR, **26**, No. 5 (1952).
61. K. Navratil, Czech. J. Phys., 18, 266 (1968).
62. A. K. Jenkins, J. Inst. Metals, **82**, No. 1, 213 (1953–54).
63. N. D. Tomashov, "Korroziya i Zashchita Metallov" (The Corrosion and Protection of Metals), Metallurgizdat, Moscow, 1952, Part 1.
64. G. G. Bykhvalov and A. V. Turkovskaya, "Korroziya i Zashchita Metallov" (The Corrosion and Protection of Metals), Metallurgizdat, Moscow, 1947.
65. G. V. Akimov, "Teoriya i Metody Issledovaniya Korrozii Metallov" (Theory and Methods for the Investigation of Metal Corrosion), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1945.
66. L. I. Kadaner, "Zashchitnye Plenki na Metallakh" (Protective Films and Metals), Izd. Khar'kov. Univ., Kharkov, 1956.
67. E. S. Vorontsov, Uspekhi Khim., 34, 2020 (1965) [Russ. Chem. Rev., No. 11 (1965)].
68. E. S. Vorontsov, Uspekhi Khim., 37, 167 (1968) [Russ. Chem. Rev., No. 1 (1968)].
69. E. S. Vorontsov, Izv. Akad. Nauk SSSR, Metally, No. 3, 51 (1968).
70. G. I. Chufarov and E. S. Vorontsov, Izv. Vys. Ucheb. Zaved., Chernaya Metallurgiya, No. 9, 5 (1969).
71. E. S. Vorontsov and K. A. Koshkina, Kinetika i Kataliz, 11, 246 (1970).
72. E. S. Vorontsov and V. A. Kozheurov, Izv. Akad. Nauk SSSR, Metally, No. 1, 230 (1971).
73. K. A. Koshina and E. S. Vorontsov, Zhur. Prikl. Khim., **44**, 209 (1971).
74. E. S. Vorontsov and A. N. Korneeva, Izv. Vys. Ucheb. Zaved., Chernaya Metallurgiya, No. 7, 8 (1971).
75. E. S. Vorontsov, N. P. Peksheva, and V. V. Peshkov, Zhur. Fiz. Khim., **48**, 970 (1974) [Russ. J. Phys. Chem., No. 2 (1974)].
76. O. A. Esin and P. V. Gel'd, "Fizicheskaya Khimiya Pirometallurgicheskikh Protsessov" (Physical Chemistry of Pyrometallurgical Processes), Metallurgizdat, Sverdlovsk, 1962, Part. 1.

77. N. F. Mott, Trans. Faraday Soc., **35**, 1175 (1939).
78. H. J. Engell, K. Hauffe, and B. Ilschner, Z. Elektrochem. Ber. Bunsenges. Phys. Chem., **58**, 478 (1954).
79. N. D. Tomashov and R. M. Al'tovskii, "Korroziya i Zashchita Titana" (The Corrosion and Protection of Titanium), Mashgiz, Moscow, 1963.
80. V. I. Arkharov and G. P. Luchkin, Dokl. Akad. Nauk SSSR, **83**, 837 (1952).
81. W. Kinna and W. Knorr, Z. Metallk., **47**, 594 (1956).
82. L. S. Moroz, B. B. Chechulin, I. V. Polin, L. V. Butalov, S. M. Shul'kin, and N. P. Goryachev, "Titan i Egov Splavy" (Titanium and Its Alloys), Vol. 1, "Tekhnicheski Chistyi Titan" (Technically Pure Titanium), Sudpromgiz, 1960.
83. E. S. Vorontsov, N. P. Peksheva, V. V. Peshkov, and A. N. Korneeva, Symposium, "Vliyanie Fiziko-Khimicheskoi Sredy na Zharoprochnost' Metallicheskikh Materialov" (The Influence of the Physicochemical Medium on the Heat Resistance of Metallic Materials), Izd. Nauka, Moscow, 1974, p.94.
84. N. P. Peksheva, Zhur. Prikl. Khim., **49**, 2168 (1976).
85. N. P. Peksheva and E. S. Vorontsov, Symposium, "Poluchenie i Svoistva Tonkikh Plenok" (The Preparation and Properties of Thin Films), Izd. ONTI IPM Akad. Nauk Ukrain. SSR, Kiev, 1976, p.82.
86. N. P. Peksheva and E. S. Vorontsov, Symposium, "Fizicheskaya Khimiya Neorganicheskikh Plenok i Pokrytii" (Physical Chemistry of Inorganic Films and Coatings), Voronezh Politekh Inst., Voronezh, 1973, No. 1, p.30.
87. N. P. Peksheva and E. S. Vorontsov, Zhur. Fiz. Khim., **51**, 1088 (1977) [Russ. J. Phys. Chem., No. 5 (1977)].
88. N. P. Peksheva and E. S. Vorontsov, "Rasshirennye Tezisy Dokladov VI Vsesoyuznogo Soveshchaniya po Kinetike i Mekhanizmu Khimicheskikh Reaktsii v Tverdom Tela, Minsk, 1975" (Extended Abstracts of Reports at the VIth All-Union Conference on the Kinetics and Mechanisms of Solid-Phase Chemical Reactions, Minsk, 1975), p.171.
89. N. P. Peksheva, Zhur. Prikl. Khim., **49**, 744 (1976).
90. N. P. Peksheva, V. M. Strukov, and E. S. Vorontsov, Kinetika i Kataliz, **17**, 542 (1976); article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No. 3403-75, 1975).
91. V. M. Strukov and N. P. Peksheva, article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No. 2384–77, 1977).
92. E. S. Vorontsov, N. P. Peksheva, and V. M. Strukov, Symposium, "Poluchenie i Svoistva Tonkikh Plenok" (The Preparation and Properties of Thin Films), Izd. ONTI IPM Akad. Nauk Ukrain. SSR, Kiev, 1976, p.143.
93. N. P. Peksheva and E. S. Vorontsov, Symposium, "Voprosy Fiziki Tverdogo Tela" (Problems of Solid State Physics), Voronezh Politekh Inst., Voronezh, 1973, No. 3, p.150.
94. N. P. Peksheva and E. S. Vorontsov, Zhur. Prikl. Khim., 49, 494 (1976).
95. G. P. Luchkin and G. G. Il'in, Fiz. Metall. i Metallov., **2**, 521 (1956).
96. D. I. Lainer and M. I. Tsypin, Symposium, "Metallovedenie i Obrabotka Tsvetnykh Metallov i Splavov" (Metallography and Treatment of Non-Ferrous Metals and Alloys), Metallurgizdat, 1961, No. 20, p.42.
97. I. P. Bardin and A. V. Revyakin, Symposium, "Titan i Ego Splavy" (Titanium and Its Alloys), 1961, No. 2, p.119.
98. S. S. Gorelik, L. N. Rastoroguv, and Yu. A. Skakov, "Rentgenograficheskii i Elektronograficheskii Analiz" (X-Ray Diffraction and Electron-Diffraction Analysis), Izd. Metallurgiya, Moscow, 1970.
99. K. W. Andrews, D. J. Dyson, and S. R. Keown, "Interpretation of Electron Diffraction Patterns" (Translated into Russian), Izd. Mir, Moscow, 1971.
100. V. I. Lainer (Editor), "Spravochnoi Rukovodstvo po Gal'vanotekhnike" (Manual of Electroplating Techniques), Izd. Metallurgiya, Moscow, 1969.
101. N. P. Peksheva and E. S. Vorontsov, USSR P 370 271 (1972); Byul. Izobret., No. 1, 86 (1973).
102. N. P. Peksheva and E. S. Vorontsov, Zavod. Lab., 1488 (1974).
103. N. P. Peksheva and E. S. Vorontsov, Zhur. Prikl. Khim., **48**, 224 (1975).
104. L. Ya. Popilov and L. P. Zaitseva, "Elektropolirovanie i Elektrotravlenie Metallograficheskikh Shlifov" (Electropolishing and Electroetching of Metallographic Sections), Metallurgizdat, Moscow, 1963.
105. V. V. Romanov, "Metody Izzledovaniya Korrozii Metallov" (Methods for the Investigation of Metal Corrosion), Izd. Metallurgiya, Moscow, 1965.
106. N. P. Fedot'ev and S. Ya. Grillikhes, "Elektrokhimicheskoi Travlenie, Polirovanie i Oksidirovinie Metallov" (Electrochemical Etching, Polishing, and Oxidation of Metals), Mashgiz, Moscow-Leningrad, 1957.
107. S. Ya. Grillikhes, "Polirovanie, Travlenie i Obezzhirivanie Metallov" (Polishing, Etching, and Degreasing of Metals), Izd. Mashinostroenie, Leningrad, 1971.
108. P. K. Lavorko, "Oksidnye Pokrytiya Metallov" (Oxide Coatings on Metals), Mashgiz, Moscow, 1963.
109. V. M. Strukov, A. N. Korneeva, and E. S. Vorontsov, "Materialy II Vsesoyuznoi Konferentsiyan po Nitevidnym Kristallam i Tonkin Plenkam" (Proceedings of the IInd All-Union Conference on Filamental Crystals and Films), Voronezh Politekh Inst., Voronezh, 1975, Part 2, p.389.
110. V. M. Strukov and E. S. Vorontsov, "Rasshirennye Tezisy Dokladov VI Vsesoyuznogo Soveshchaniya po Kinetike i Mekhanizmu Khimicheskikh Reaktsii v Tverdom Tele, Minsk, 1975" (Extended Abstracts of Reports at the VIth All-Union Conference on the Kinetics and Mechanisms of Solid-Phase Chemical Reactions, Minsk, 1975), p.169.
111. F. F. Vol'kenshtein, "Elektronnaya Teoriya Kataliza na Poluprovodnikakh" (Electronic Theory of Catalysis on Semiconductors), Izd. Fiz.-Mat. Lit., Moscow, 1960.
112. A. A. Balandin, "Sovremennoe Sostoyanie Mul'-tipletnoi Teorii Geterogennogo Kataliza" (The Present State of the Multiplet Theory of Heterogeneous Catalysis), Izd. Nauka, Moscow, 1968.
113. V. A. Roiter and G. I. Golodets, "Vvedenie v Teoriyu Kinetiki i Kataliza" (Introduction to the Theory of Kinetics and Catalysis), Izd. Naukova Dumka, Kiev, 1971.
114. S. G. Roginskii, "Elektronnye Yavleniya v Geterogennon Katalize" (Electronic Phenomena in Heterogeneous Catalysis), Izd. Nauka, Moscow, 1975.

115. B. V. Erofeev, "Perekhodnye Metally i Ikh Kataliticheskie Svoistva" (Transition Metals and Their Catalytic Properties), Izd. Znanie, Moscow, 1966.
116. V. A. Roiter (Editor), "Kataliticheskie Svoistva Veshchestv" (Catalytic Properties of Substances), Izv. Naukova Dumka, Kiev, 1968.
117. E. S. Vorontsov and V. M. Strukov, Kinetika i Kataliz, **16**, 1075 (1975).
118. V. M. Strukov and E. S. Vorontsov, Izv. Akad. Nauk SSSR, Neorg. Materialy, 2056 (1976).
119. V. M. Strukov, E. S. Vorontsov, and I. A. Ozaulenko, Elektronnaya Tekhnika, Materialy, No. 2, 83 (1976).
120. N. I. Kobozev (Editor), "Ekzoelektronaya Emissiya" (Exoelectron Emission), Inostr. Lit., Moscow, 1962.
121. A. S. Shashkov, V. M. Mozzhukhina, I. V. Krylova, and N. I. Kobozev, Zhur. Fiz. Khim., 40, 250 (1966). [Russ. J. Phys. Chem., No. 2 (1966)].
122. I. A. Rakhmatullina and I. V. Krylova, Zhur. Fiz. Khim., 42, 2654 (1968) [Russ. J. Phys. Chem., No. 10 (1968)].
123. I. V. Krylova, Kh. Minchev, and V. Penchev, Zhur. Fiz. Chem., 45, 1546 (1971) [Russ. J. Phys. Chem., No. 6 (1971)].
124. Yu. F. Balalaev and O. V. Devochkin, Symposium, "Voprosy Fiziki Tverdogo Tela", (Problems of Solid State Physics), Voronezh. Politekh. Inst., Voronezh, 1971, No. 2, p.178.
125. A. Ya. Rozovskii, "Kinetika Topokhimicheskikh Reaktsii" (Kinetics of Topochemical Reactions), Izd. Khimiya, Moscow, 1974.
126. M. M. Pavlyuchenko and E. A. Prodan, (Editors), "Geterogennye Khimicheskie Reaktsii i Reaktsionnaya Sposobnost'" v. (Heterogeneous Chemical Reactions and Reactivity), Izd. Nauka i Tekhnika, Minsk, 1975.
127. M. M. Pavlyuchenko, Izv. Akad. Nauk Beloruss. SSR, Ser. Khim. Nauk, No. 1, 128 (1972).
128. G. M. Panchenkov and V. P. Lebedev, "Khimicheskaya Kinetika i Kataliz" (Chemical Kinetics and Catalysis), Izd. Khimiya, Moscow, 1974.
129. V. M. Strukov and E. S. Vorontsov, Kinetika i Kataliz, **17**, 1606 (1976).
130. N. P. Peksheva, Candidate's Thesis, Voronezh Polytechnic Institute, Voronezh, 1973.
131. V. M. Strukov, E. S. Vorontsov, and I. A. Ozaulenko, Zhur. Fiz. Khim., 51, 595 (1977) [Russ. J. Phys. Chem., No. 3 (1977)].
132. E. L. Petrikovskii and V. F. Krasnikov, "Markirovanie Izdelii v Radio- i Elektronnoi Promyshlennosti" (The Marking of Articles in Radio and Electronics Industry), Izd. Energiya, Moscow, 1974.
133. V. M. Strukov, Candidate's Thesis, Voronezh Polytechnic Institute, Voronezh, 1978.

Department of General Chemistry,
Voronezh Polytechnic Institute