

J. Malecka

*Opole University of Technology, Faculty of Mechanical Engineering, Department of Materials Engineering, Poland
j.malecka@po.opole.pl*

OXIDATION ACTIVATION ENERGY OF TITANIUM ALLOY BASED ON TiAl(γ) INTERMETALIC PHASE

ABSTRACT

The present paper deals with the analysis of the course of oxidation of the cyclic Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy in a hot air atmosphere in the temperature range of 875-975°C. The constant rates of the oxidation were determined (separately for the first and second stages of oxidation) and the energy of oxidation activation of the tested alloy was established. It was discovered that the oxidation process of the Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy develops according to the parabolic correlation, and it is only possible to determine the apparent energy of oxidation activation.

Keywords: titanium, intermetallic, oxidation, activation energy

INTRODUCTION

The development of the technology makes it necessary to increase the requirements of the construction materials. It is inextricably linked with the need to use materials that are characterized by improved mechanical properties, lower density, and greater resistance to high temperatures. In recent years a new group of advanced engineering materials based on titanium intermetallic phases have been formulated. They feature good practical properties, and most of all greater resistance to high temperature oxidation in comparison to conventional titanium alloys [1÷3]. This group of materials, which were researched in the 50-ties of 20th century, included alloys based on Ti₃Al(α_2) phase, alloys based on TiAl(γ) and based on TiAl₃ which shows high brittleness. The stimulus for research was the demand to produce light and rugged materials for aviation and space industry, and they were supposed to replace titanium alloys and nickel based alloys used in the construction of jet engines [2÷4].

Titanium alloys with the addition of intermetallic phases are rapidly developing materials and due to their attractive properties their popularity is growing. However, in order to assess the applicability of alloys on the basis of intermetallic phases at high temperatures, we need knowledge of the kinetics and mechanism of oxidation of this group of materials.

The course of oxidation of alloys and metals can be described by appropriate kinetic laws [5÷6], and the analyzed literature sources prove that the oxidation process of Ti-Al alloys

progresses according to the parabolic correlation [7÷10]. Nevertheless, the oxidation process of titanium alloys is characterized by the fact that along with the formation of scale, oxygen dissolves in the metallic solution, therefore the activation energy of oxidation of titanium alloys is a value composed of two partial energies: of the formation of scale and solid oxygen solution [11].

In this paper, oxidation rate constants of the Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy were determined and the energy of oxidation activation of the tested alloy was established.

Basics of oxidation theory

Regular and ordered research on the oxidation of metals and alloys were started in the 1920s by Pilling and Bedworth [12] Evans [13] and Tamm and Koster [14]. They provided a number of valuable information and helped to clarify the rules of metal oxidation. Later years also brought a series of studies and detailed descriptions of the basics of oxidation of metals can be found in books and publications by Kubaschewski and Hopkins [15], Kofstad [16 ÷ 19] as well as Rahmel [20]. However, the definite pioneer of modern science on high temperature corrosion in the 1950s was Wagner [21-22]. At this point the work of Gulbranssen and Andrew [23] Morton and Boldwin [24], Kinn and Knorr [25] and Jenkins [26] must be mentioned, which in the 1950s considered subjects in the field of oxidation of titanium, presenting often different points of view of the authors regarding the mechanisms of oxidation.

As a result of the oxidizing environment affecting the metal or alloy, phenomena occur that form reaction products that can be volatile, liquid or solid. Most often, products are formed on the surface, however, often the oxidation process also takes place in the metal phase as a result of the dissolution of the oxidant inside it [27]. In the simplest chemical reaction, the oxidation of metal M in the pure oxygen O₂ can be described by the following equation [27]:



In reality, however, high-temperature corrosion and oxidation processes are more complex, as they are composed of many elementary processes interlinked with one another [27]. Therefore, the oxidation of materials cannot be described with this simple formula. Mainly because of a big number of parameters and their different impact on the behavior of materials, depending on their type and oxidizing environment. Oxidation is not a desirable process, since the formation of oxide scale is associated with degradation of the material, still, the use of appropriate preventive measures allows using materials at high temperatures.

It would be impossible to use metallic materials at high temperatures for an elongated time, without learning and understanding the mechanisms that occur during oxidation.

Thermodynamics of oxidation

The occurrence of a specific corrosive reaction is dependent on the temperature and partial pressure of the oxidant in the oxidizing environment, and the main criterion in assessing the course of oxidation under the given temperature and pressure conditions is the negative or positive sign of free enthalpy ΔG [28-29]. Therefore, in terms of thermodynamics, the oxidation reaction can be described by the change of free enthalpy ΔG of the chemical reaction, i.e. the difference between the free enthalpy of the $M_x O_y$ reaction product and the M and O₂ reactants.

In the case where $\Delta G < 0$, the reaction develops in the considered direction (from metal to oxide), while for $\Delta G > 0$ there is a tendency to react in the opposite direction (reduction from oxide to metal). For $\Delta G = 0$, equilibrium conditions are fixed, so there are both reagents and reaction products [27]. As ΔG depends on the concentration of reagents and reaction products, they are usually replaced with the standard enthalpy of the chemical compound ΔG_0 , where the normal reaction state is defined when the activity of the M reagent and M_xO_y metal oxide are determined as one. In the case of most metals used in the industry, the standard enthalpy of chemical compound formation is negative, so oxides are stable in an environment with oxygen content, while the metals that form them are unstable. The enthalpy of formation is correlated with the standard enthalpy of the reaction ΔH , the entropy of the formation ΔS and the reaction temperature T:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

where :

$\Delta H, \frac{kJ}{mol}$ - enthalpy of the reaction

$\Delta S, \frac{J}{mol \cdot K}$ - entropy of the reaction,

T, K - absolute temperature

Because the formation of oxide reduces the entropy of the system, ΔG_0 increases, which results in a decrease of the stability of the oxide along with the increasing temperature. The standard enthalpy of oxide formation is dependent on temperature and correlated with the oxygen partial pressure p_{O_2} in the oxide according to:

$$\Delta G = RT \ln p_{O_2} \quad (3)$$

where

$R, \frac{J}{mol \cdot K}$ - gas constant

T, K - absolute temperature

The dissociation pressure denotes the partial pressure at which the oxide is still stable at a given temperature, and below this pressure, the oxide decomposes into metal and oxygen.

Thermodynamic data such as the standard enthalpy of formation of a compound or dissociation pressure allow predicting oxidation products. However, they do not provide knowledge about the rate of the reaction. In industrial systems, the formation of thermodynamically desirable phases may be so slow that less stable oxides are formed in the first place. Moreover, it should be added that if the activity of a single element in the alloy is less than unity, compounds can be formed or there is a total or limited miscibility in the solid state. Therefore, in many cases, assumptions for two-element alloys cannot be applied for more complex alloys [15, 16].

Concerning all chemical reactions, oxidation reactions are based on thermodynamic and kinetic factors. The equilibrium between the reaction and the stability of its products can be described by means of the rules of thermodynamics, while the time relation of the reaction belongs to the kinetics. There is a series of dependencies (kinetic laws of oxidation, Fig. 1)

describing the course of oxide scale growth as a function of time [5]. The linear course of the oxidation can be observed in the case of a reaction product being in a volatile or liquid state, and also when the solid oxidation product is characterized by the occurrence of numerous discontinuities.

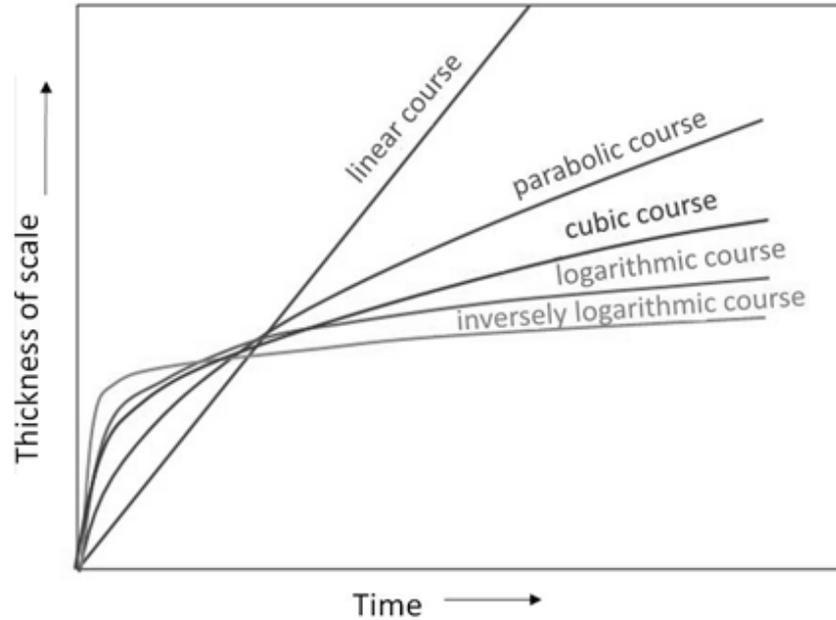


Fig. 1. Schematic of kinetic laws of oxidation [6]

If the forming scale is compact, then the rate of the oxidation course varies considerably and depending on the reaction time, temperature and pressure of the oxidizing environment, one of the processes may be decisive regarding the rate and nature of the scale formation. As a rule, during oxidation at low temperatures, the oxidation progresses according to the cubic law, while in the medium temperature range, it may develop according to exponential relations called logarithmic laws [5-6]. Within the high temperature range, for the diffusion-dependent growth of scale, the course of oxidation is parabolic and the rate of oxidation can be described by correlation [14]:

$$\frac{dx}{dt} = \frac{k'_p}{x} \quad (4)$$

or

$$x^2 = 2k'_p \cdot t + C \quad (5)$$

where:

x, cm - thickness of scale,

$k'_p, cm^2 \cdot s^{-1}$ - parabolic constant of reaction rate,

t, s - reaction time

C - integration constant.

However, in many cases, more complex or mixed growth rules can be observed. For example, when scale grows linearly after initial parabolic oxidation or when linear kinetics results in the formation of a protective layer leading to parabolic, cubic or logarithmic growth [5, 23]. Often, however, the parabolic constant of reaction rate k'_p is used to describe and

compare the resistance to oxidation of various materials, and knowing this constant allows determining the energy of oxidation activation. Since temperature is an important factor influencing the speed of the oxidation process, its impact can be described (in the area in which the given kinetic law is observed) with Arrhenius equation:

$$k'_p = A \cdot \exp\left(-\frac{E}{RT}\right) \quad (6)$$

where:

$E, \frac{J}{mol}$ - activation energy of the oxidation process,

$R, \frac{J}{mol \cdot K}$ - gas constant

T, K - absolute temperature

MATERIAL AND RESEARCH SCOPE

The material for testing was Ti-46Al-7Nb-0,7Cr-0,1Si-0,2Ni alloy with a plate structure consisting of intermetallic phase plates γ -TiAl and intermetallic phase α_2 -Ti₃Al. (Fig. 2).

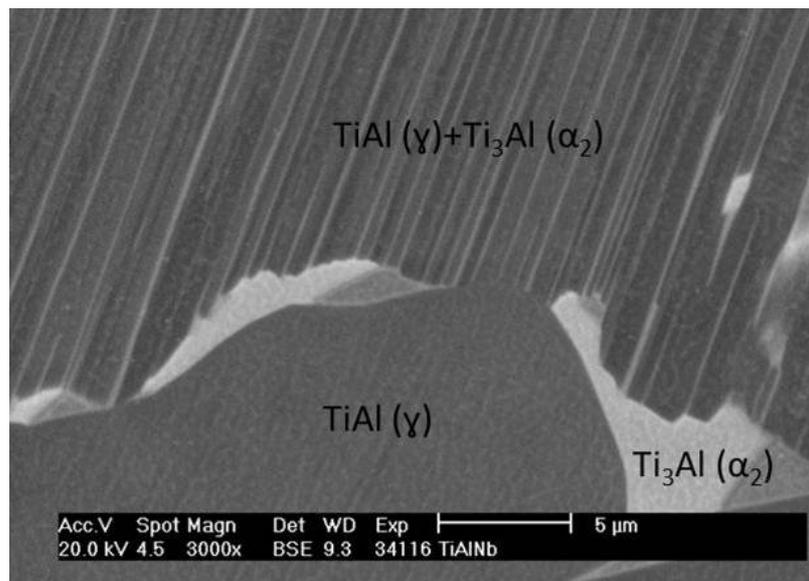


Fig. 2. Scanned images (BSE) of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni

The aim of the research was to determine the energy of oxidation activation of the tested alloy. This aim was achieved by carrying out periodical corrosion tests in the air in the temperature range between 875-975°C during 60 hours (Fig. 3). Based on the obtained empirical data, the values of oxidation rate constants were determined and the oxidation activation energy of the tested alloy was established.

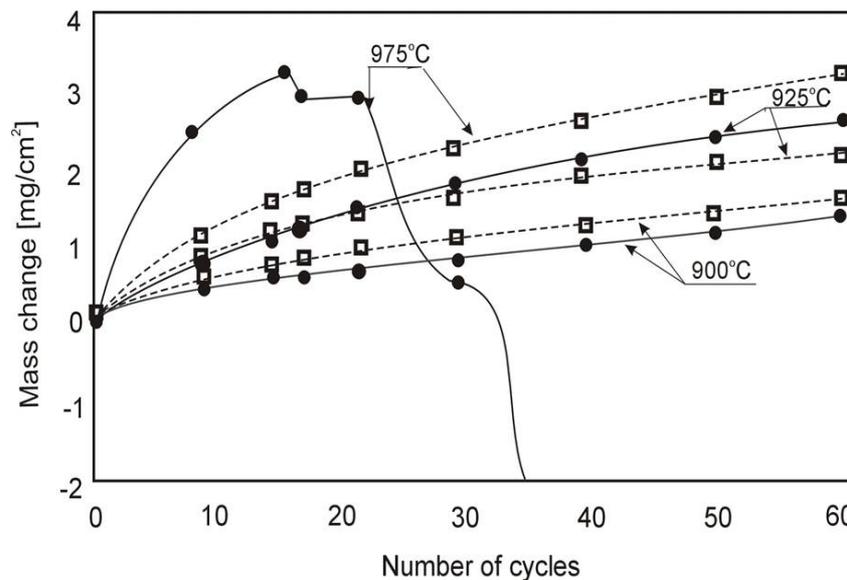


Fig. 3. Course of cyclic oxidation of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni

The oxidation in 875°C, 900°C and 925°C during 60 cycles only causes mass gain, which, however, increases significantly past 900°C. The oxidation at 950°C and 975°C only causes mass gain in initial cycles, which then turns into dominant mass loss due to chipping in the cooling cycle. For the temperature of 950°C, this takes place after approximately 30 cycles of oxidation, and for 975°C after the 14th oxidation cycle. At the temperature of 975°C after the 32nd oxidation cycle, the sample reaches a mass similar to the initial one while during further cycles only the mass loss occurs (Fig. 3).

Analysis of the test results

Using the classical isobaric-isothermal method that allows the determination of the mass increments of oxidized metals or alloys, the oxidation behavior can be described by appropriate kinetic laws [5-6]. In many publications concerning Ti-Al alloys based on intermetallic phases, it is proved that their oxidation develops according to the parabolic relationship.

When determining the oxidation activation energy of titanium alloys, including the so-called intermetals, several processes must be considered. The most important one is that the growth in reaction products takes place at both phase boundaries, i.e. at the product-oxidant interface and at the product-metal substrate interface. The process rate depends on the degree of defect of both the cationic subnetwork and the anionic subnetwork of the forming rutile. Another process consists in the oxidant being "consumed" not only to form the product, but also dissolving in the metallic substrate. In the case of the alloys based on the γ -TiAl phase, solid solutions of oxygen and nitrogen are formed in the metallic substrate. It also needs to be taken into consideration that the reaction product being formed (oxide layer) is not mono-phase and the various phases formed are dispersed in a mixture of $\text{TiO}_2 + \alpha\text{Al}_2\text{O}_3$ with different concentrations of rutile or corundum.

Therefore, the knowledge of these limitations allows the presumption that it is only possible to determine the apparent energy of activation. So, it was assumed that the oxidation process of the tested alloys in the analyzed temperature range is subject to the general power law

$$x^n = k' \cdot \tau + C \quad (7)$$

where:

x - the thickness of the reaction product layer after time τ ,

k' - oxidation rate constant,

C - integration constant.

Due to the fact that the thickness of the product layer is directly proportional to the mass of the oxidant bonded per unit area (the layer thickness is additionally influenced by the pore distribution, and the mass gain Δm is influenced also by whether Al or Ti are bonded in a greater amount, which produces oxides of different density), hence the general power equation (7) can be formulated, when using the gravimetric method, in the following form

$$\left(\frac{\Delta m}{s}\right)^n = k' \cdot \tau + C \quad (8)$$

where:

Δm - mass gain [mg] of the sample during time τ [min],

s - initial area [cm²],

k' - reaction rate constants [mg² cm⁻⁴ min⁻¹].

Based on the experimental data of oxidation from equation (8), the values of oxidation rate constants can be determined, assuming, based on literature [7, 9], that $n=2$, and thereby the process proceeds according to a parabolic correlation.

Determining the oxidation activation energy of Ti-Al alloys on the intermetallic phases, it should be noted that the growth of oxidation products takes place both at the interface of product-oxidant as well as the product-substrate interface. The fact that the forming oxide layer is not mono-phase is also significant. For this reason, it is only possible to determine the apparent energy of oxidation activation. Nevertheless, when calculating oxidation constants, it was noticed that for shorter isothermal oxidation times (up to approximately 10 hours) they are different than for long times. Therefore, parabolic oxidation constants were determined separately for the first stage and separately for the second oxidation stage (Tab. 1).

The determination of the value of activation energy by a graphical method is possible when the measurement points of the constant k'_p in the $\ln k'_p - 1/T$ system produce a linear correlation resulting from the Arrhenius equation (9):

$$k = k_0 \exp\left(-\frac{Q}{RT}\right) \quad (9)$$

$Q, \frac{J}{mol}$ - activation energy of the oxidation process,

$R, \frac{J}{mol \cdot K}$ - gas constant

T, K - absolute temperature

After the using logarithm in the Arrhenius equation (10) the following is obtained:

$$\ln(k'_p) = \ln(A) - \frac{Q}{RT} \quad (10)$$

Table 1. Parabolic oxidation rate constants [$\text{mg}^2 \text{cm}^{-4} \text{min}^{-1}$] of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni 2Ni alloy cyclically oxidized in air atmosphere

		Temperature, °C				
		875	900	925	950	975
first oxidation stage		$3.45 \cdot 10^{-4}$	$5.66 \cdot 10^{-4}$	$1.22 \cdot 10^{-3}$		
second oxidation stage		$5.3 \cdot 10^{-4}$	$1.17 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$3.8 \cdot 10^{-3}$	$7.1 \cdot 10^{-3}$

According to the above, Fig. 4 shows the dependence of $\ln(k)$ as a function of $1/T$ for the alloy Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni cyclically oxidized in air atmosphere. The obtained results indicate that in the scope of the first stage of oxidation and the second stage, it is possible to determine the energy of activation of oxidation. According to Fig. 4, the calculated activation energy of the oxidation equals to:

- for the first oxidation stage $Q_I=291$ [kJ/mol]
- for the second oxidation stage $Q_{II}=304$ [kJ/mol]

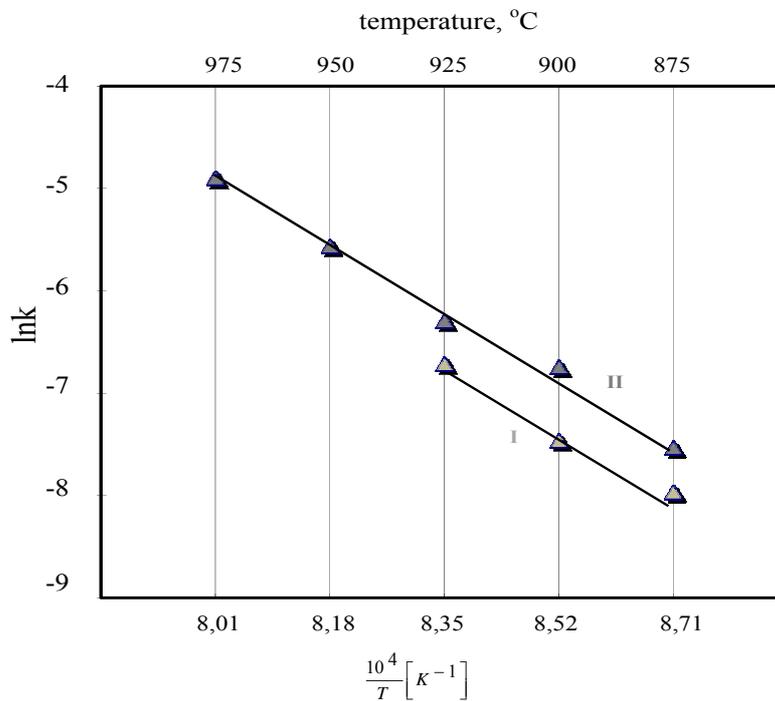


Fig. 4. The dependence of parabolic oxidation constants of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy in the air atmosphere in the Arrhenius system $\ln k - 1/T$: I) according to data for the first oxidation stage, II) according to data for the second the oxidation stage

SUMMARY

When determining the oxidation activation energy of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy, it should be taken into account that the reaction product growth occurs in a twofold manner: at the product-oxidant interface and at the product-substrate interface, and moreover, the reaction product is not a mono-phase product but forms a variety of phases. It is assumed that the 5 temperature ranges of oxidation and thus the high concentration of points in the Arrhenius system are the basis for the correct determination of the diffusion activation energy of the tested alloy. However, in the analyzed case, there is no compact, single phase product formed during the oxidation, but multiphase scale, so the determined value of activation energy is only an "apparent" energy of oxidation activation.

REFERENCES

1. Appel F., Paul J. D. H., Oehring M., Gamma titanium aluminide alloys, Wiley-VCH Verlag GmbH (2011).
2. Loria A.: Gamma titanium aluminides as prospective structural materials, *Intermetallics* 8 (2000) 1339–1345.
3. Szkliniarz W., The alloys from the binary system of Ti-Al, Z. Bojar, W. Przetakiewicz, (Eds.), *Metallic materials with the participation of intermetallic phases*, Technical Military Academy, Warsaw (2006) 66–88 (Chapter 2.2, in Polish).
4. Kumpfert J., Leyens C.: *Titanium and Titanium Alloys, Fundamentals and Applications*. Edited by Christoph Leyens, Manfred Peters, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (2003).
5. Mrowec S., Werber T.: *Gas Corrosion of Metals*, Katowice (1975) (in Polish).
6. Mrowec S., Werber T.: *Gas Corrosion*, WNT, Katowice (1965) (in Polish).
7. Kakare S.A., Toney J.B., Aswath P.B., Oxidation of Ductile Particulate Reinforced Ti-48Al Composite, *Metallurgical and Materials Transactions*, 26A (1995) 1835-1845.
8. Woo J.C., Varmas.K., Mahapatra R.N., Effect of Ta and Zr additions on the oxidation characteristics of Ti-44Al-xNb alloy, *Gamma Titanium Aluminides*, (2003) 585-589.
9. Singheiser L., Quadackers W.J., Shemet V., Isothermal and cyclic oxidation behavior of titanium aluminides, *Gamma Titanium Aluminides*, (1999) 743-752.
10. Reddy R.G., Wen X., Okafor I.C.I., Interdiffusion in the TiO₂ oxidation product of Ti₃Al, *Metallurgical and Materials Transactions A*, 32A (2001) 491-495.
11. Król S., Mechanism and kinetics of oxidation titanium and selected titanium alloys, ??? 82, Opole (1994) (in Polish)
12. Pilling N., Bedworth B., The oxidation of metals at high temperatures, *Journal of the Institute of Metals*, 29 (1923) 529-534.
13. Evans U.: *Transaction Electrochemical Society*, 46 (1924) 267.
14. Tammann G., Koster W.: Die Geschwindigkeit der Einwirkung von Sauerstoff, Schwefelwasserstoff und Halogenen auf Metalle, *Zeitschrift für anorganische und allgemeine Chemie*, 123 (1922) 196-224.
15. Kubaschewski O., Hopkins B.E., *Oxidation of Metals and Alloys*, London: Butterworths (1962).
16. Kofstad P., *Nonstoichiometry, diffusion and electric conductivity in binary metal oxides* (1983), Malabar, Florida: R. E. Krieger Publishing Company.
17. Kofstad P., *High Temperature Corrosion*, Elsevier Applied Science, London, New York (1988).

18. Kofstad P., Fundamental aspects of corrosion by hot gases, *Materials Science and Engineering A120* (1989) 25–29.
19. Kofstad P.: Defects and Transport Properties of Metal Oxides, *Oxidation of Metals* 1/2, 44 (1995) 3–27.
20. Rahmel A., ed. Aufbau von Oxidschichten auf Hochtemperaturwerkstoffen und ihre technische Bedeutung, Deutsche Gesellschaft für Materialkunde e.V.: Oberursel (1983).
21. Wagner C., Formation of composite scales consisting of oxides of different metals, *Journal of the Electrochemical Society* 103(11) (1956) 627–633.
22. Wagner C., Reaktionstypen bei der oxydation von legierungen, *Elektrochemie* 63 (1959) 772–782.
23. Gulbransen E.A., Andrew K.F., Kinetics of the reactions of titanium with O₂, N₂ and H₂, *Metals Transactions* 185 (1949) 741-748.
24. Morton P.H., Baldwin W.M., The scale of titanium in air, *Transactions of the American Society for Metals* 44 (1952) 1004-1029
25. Kinna W., Knorr W., Über die oxidation von Titan, *Z. Metallkunde* 47 (1956) 594-598.
26. Jenkins A.E., The oxidation of titanium at high temperatures in an atmosphere of pure oxygen, *Journal of the Institute of Metals* 82 (1954) 213-221.
27. Mrowec S., Werber T., Kinetics and mechanism oxidation of metal, Katowice (1982) (in Polish)
28. Kubaschewski O., Evans E., Alcock C.B., *Metallurgical thermochemistry*, Pergamon Press, London (1968).
29. Krupkowski A., *Laws of thermodynamics*, PWN, Cracow (1958) (in Polish).