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THE KINETICS AND MECHANISM OF THE PROCESS OF NICKEL OXYDATION

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INTRODUCTION

Nickel oxidation is a heterogenous process and develops in more than one phase[1]. The kinetics of the process basically depends on the product (NiO) which is developing. As the molar volume[2] is greater(NiO) than the volume of Ni, so a compact coating is developing and this makes the diffusion process more difficult, or the general rate of the process undegroes to the difusion rate of the reacting components of the developed oxide, respectivelly.

For the study of nickel oxidation process with the use of the data obtained by thermal analysis, the method shown is the previous investigations were used[3]. The method consists of determination of reaction kinetics from one DTA or TG curve based on the identificated reaction mechanism by the results in isothermal conditions. Starting from the expresion for the reaction rate in nonisothermal conditipns:

$$\frac{d\alpha}{d\tau} = A.\exp - \frac{E}{RT(\tau)}. f(\alpha) \qquad (1)$$

Using the formerly determined reaction mechanism, e.g. the function $f(\alpha)$, as a linear heating rate program $T(\tau) = T_o + \phi\tau$, together with certain transformations by the approximation process, the function is obtained:

$$G_1 = \sum_{i=1}^{K} \left\| F(\alpha_i) - \frac{E.A}{R.\phi} \left\{ P \left| \frac{R(T_o + \phi\tau)}{E} \right| - P \left| \frac{R.T_o}{E} \right| \right\} \right\|^2 \qquad (2)$$

The solving, or the determination of kinetic parameter, respectively, has been calculated by computer by the "statistical gradient" method.

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EXPERIMENTAL

Experimental investigations have been carried out in isothermal and nonisothermal conditions. For the isothermal investigation thermoscale NETZCSH model 409 was used, and for nonisothermal investigation the DERIVATOGRAPH 1500°C, firm MOM, Budapest. As a sample nickel dust was used. The investigations were carried out with the starting mass 700.10^{-6}kg in the atmosphere with various heating rates.

RESULTS AND DISSCUSSION

In fig.1. DTA,DTG and TG curves for nickel oxidation process at the heating rate of $\emptyset$ = 5 K/min are shown. The first exoterm peak corresponds to nickel recrystalization, because it has no mass increase on the TG curve, while by the second peak the oxidation process is describe it is demonstratee on each curve.

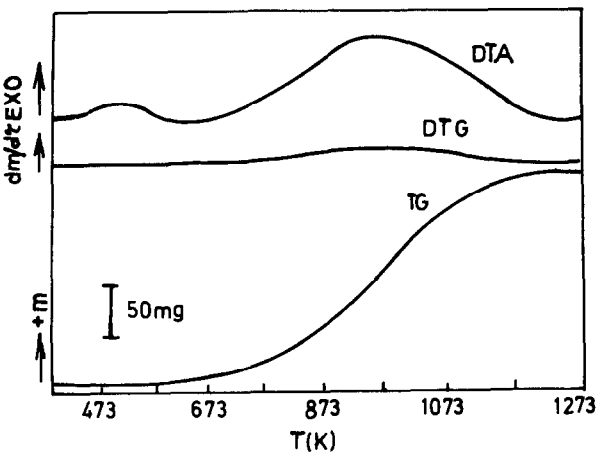

Fig.1.DTA,TG and DTG curve of the nickel oxidation process with heatin rate of 5 K/min ih the air athmosphere

It is evidently from DTA curve that the process is single staged (one-leveled) or that Ni oxidizes to NiO,respectively.

For determination of reaction kinetics of the oxidation,the data obtained in isothermal and nonisothermal conditions were used. Isothermal investigation results from the oxidation of Ni show that the influence of the temperature on the rate of the process is only slightly expressed, and it is characteristic for the reaction developing in diffusion region. The obtained isotherms at various temperatures are shown in the coordinate system $\alpha = f(\tau/\tau_{0,5})$ in fig.2, where it results in thier overlapping into one curve.

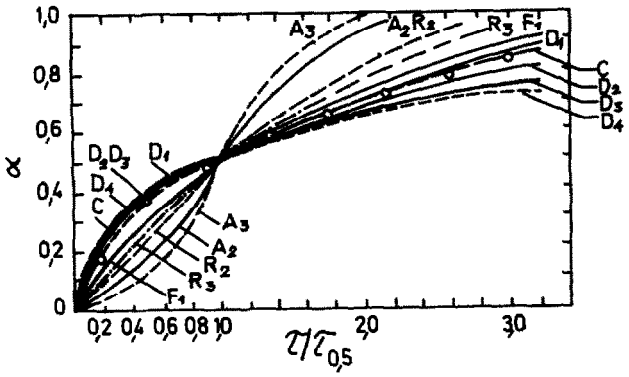

Fig.2. Depandance of the transformation level on the reduced time ($\tau/\tau_{0,5}$) for oxidation of Ni (C- experimental curve)

Comparing the flow of the experimental curve to theoretical curves[4], which are shown in the same diagram, it is evident that the Ni oxidation process completly corresponds to the reaction whose mechanism is a parabolic function $F(\alpha): \alpha^2 = K.\tau$ (theoretical curve $D_1(\alpha)$, or $f(\alpha) = 1/2\alpha$). It results that the total oxidation rate is limited by diffusion of the developed oxyde according to theoretical assumptions based on the state analysis of the product being developed. The previous investigations have already shown that the nickel oxidation process is shown by a parabolic curve[5].

The other data in the equation (2) have been obtained basing on the experimental measurements in nonisothermal conditions. Experiments were carried out the various heating rate, and that is:2,5;5;10and 20K/min. For calculating of transformation level (α), TG and DTA curve were used. The values of in the function of time for various heating rate are shown in fig.3.

Based on the previous investigations with the help of the starting equation by computer the values of kinetic parameters were determined. Un the table 1 the compared values of kinetic parameters obtained from DTA and TG curves are given.

The activation energy values are nearly the same, and the difference due to the limitation used for calculating transformational level from DTA curve are low. The low values of activation energy confirm the developing of nickel oxidation process in the diffusion region.

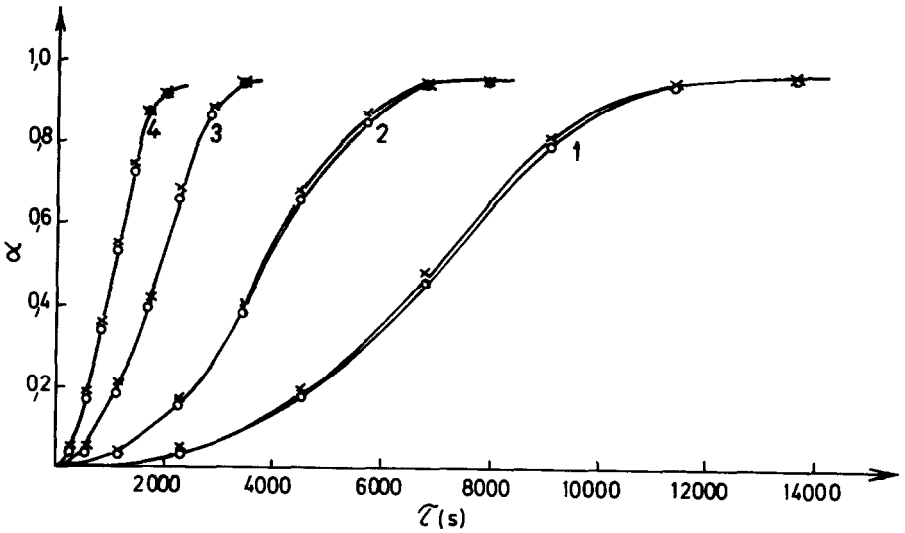

Fig.3. Kinetic curves $\alpha = f(\tau)$ for nickel oxidation process in nonisothermal conditions at various heating rate (1-2,5k/min;2-5K/min;3-10K/min;4-20K/min)
o - from TG curve; x - from DTA curve

Table 1. Values of kinetic parameters for nickel oxidation at various heating rate

Ø (K/min)	E (J/mol)		A	
	TG	DTA	TG	DTA
2,5	22 400	19 900	$1,51.10^{-3}$	$1,11.10^{-3}$
5,0	26 300	23 700	$3,84.10^{-3}$	$2,77.10^{-3}$
10,0	29 300	26 600	$15,37.10^{-3}$	$11,06.10^{-3}$
20,0	33 300	29 100	$18,58.10^{-3}$	$11,27.10^{-3}$

Second, with the increasing of the heating rate it has been noticed a slight increasing of activation energy, that could be explained by the fact that the increasing of the heating rate can influence the composition of the reaction agent because with a higher heating rate, the density of the defect could change and this could influence activation energy at the defect point.

Based on the previous analysis it could be concluded that the general nickel oxidation rate is determined by diffusion process of the reacting components through the layer of the developed oxide and that to each single heatin rate there corresponds an oxidation rate equation. So, for instance, kinetic law for nickel oxidation rate obtained from the TG data at the heating rate of $\emptyset = 5K/min$ states:

$$\frac{d\alpha}{d\tau} = 3,84.10^{-3}\exp\left(-\frac{3136}{630+5/60.\tau}\right)\frac{1}{2\alpha} \qquad (3)$$

In the same way can be formed the equat on for the other heating rates either by TG or by DTA data.

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