

Analisis of Kinetic Curves of Mass Change During the Interaction of Active Gases with Certain Metals and Compounds with Simultaneous Evaporation of the Product of Reaction

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Abstract

The influence of the secondary process of evaporation of the reaction product on the kinetics of interaction of gases (O_2 , Cl_2 , NH_3 , H_2O and N_2H_4 vapors) with the surface of some metals (Cr, Pb, Si, Ge) and compounds (BN, SiO_2 , SiC) is discussed. Also is considered the case when the growth of the scale is preceded by the process of gas etching of the metal surface. A general equation is given that describes the scale growth-evaporation kinetic (sample mass change - time) curves during the interaction of gases with the surface of metals and compounds. Special cases of parabolic, cubic and fourth degree processes are discussed. The kinetics of nitridation of the surface of single-crystalline germanium by ammonia and hydrazine vapors was studied in detail. By evaporating the nitride formed on the germanium surface, a film of germanium oxynitride is deposited on a substrate located in the cold zone of the reactor.

Keywords: Scale Growth-Evaporation, Germanium Nitride, Germanium Oxynitride Films

1. Introduction

This work is a continuation of, where the role of reduction of the reaction surface and evaporation of scale in the process of oxidation of chromium-containing alloys is considered [1]. Here we will consider in more detail the influence of the secondary process of evaporation (sublimation) on the formal kinetics (mass change - time) of the interaction of gases (O_2 , Cl_2 , NH_3 , H_2O and N_2H_4 vapors) with some metals and compounds. We used data from various works collected in, the results of the indicated author, as well as your data [2].

The process of scale formation with its simultaneous evaporation significantly changes the kinetics of the process. When the overall

kinetics is determined not by the rate of the chemical reaction itself, but by the diffusion of ions in the scale (volume diffusion), then the kinetics is parabolic and is called the Tedmon's process (although a similar case was discussed somewhat earlier [3-12]. In the case of short-circuit diffusion, cubic kinetics takes place, and in the case of local electric fields and volume charges, the kinetic law of the fourth degree is realized [13-17].

All of the above is clearly shown in the kinetic dependences of the mass gain, which are presented in the figure 1. Here M is total mass change per unit area at the time t and m is a specific mass gain of oxidized object due to reacted oxygen).

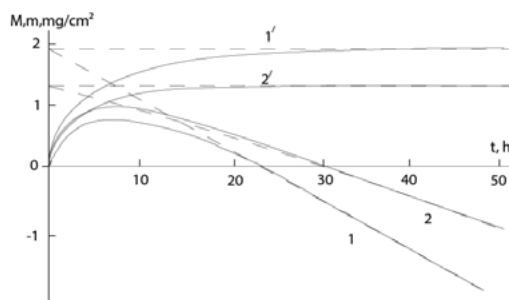


Figure 1: Kinetic Curves: (1) for Reaction $Cr + 2HCl = CrCl_2 + H_2$ at 750° and (2) $4Cr + 3O_2 = 2CrO_3$ at $1200^\circ C$ [18-19]; 1', 2' – dependences $m - t$

The slopes of the straight lines in Fig.1 corresponds to the rate of the mass decrease of the sample (v_m) due to the metallic component of the reaction product (Here we consider the coordinate systems $t - m$ and $t - M$; another coordinate system $t_w - W$ is considered in section 1.2.) To determine of reaction order (n), we can use the formula [20]:

$$n = \frac{\lg[(1-qk)(\bar{M}+v_m\bar{t})/pm_{\max}]}{\lg[(\bar{M}+v_m\bar{t})/m_{\max}]}, \quad (1)$$

where $q = v_m / v_g$, $p = (v_m + v_g) / v_g = q + 1$ (v_m is the speed of the system mass reduction due to the metal component of the evaporating part of the scale, v_g is the evaporation rate of reaction products by the gaseous component), k_r is rectilinear constant (dm/dt at the origin of coordinate system) and $k = v_g / (k_r - v_g)$. The tangents of the curves in Fig. 1 virtually coincide with ordinate axis at the origin of the coordinates: $k_r \rightarrow \infty \Rightarrow k \rightarrow 0$. In this case formula (1) is simplified as follows:

$$n = \frac{\lg[(\bar{M}+v_m\bar{t})/pm_{\max}]}{\lg[(\bar{M}+v_m\bar{t})/m_{\max}]}. \quad (2)$$

According to formula (2) for [18] it turns out $t_n \cong 2.02$, and for [19] $n \cong 3.75$, that are approaching to 2 [18-19]. Corresponding empirical expressions are: $t \cong -15.707\ln(1-0.554m)-8.693m$ and $t \cong 28.885\{[0.577 \arctg((1.424m)/(0.822m+2))] - [0.167\ln((1-0.822m)^2/(m^2+0.822m+1))]\} - 23.75m$, where m is in mg/cm^2 and t is in hours. The curves constructed using these equations on the scale used in Fig.1 practically coincide with the experimental curves.

The rate of mass increase due to the reacted gas in the general case is:

$$\frac{dm}{dt} = \frac{k_n/n}{m^{n-1} + (k_n/nr_r)} - v_g, \quad (3)$$

where $n=2, 3$ or 4 ; $k_r \equiv dm/dt$ (at point $t=0, m=0$) is rectilinear constant; k_n is the power-law constant. Its integral form is as follows:

$$t = (1+k) \frac{m_{\max}^{n-1}}{v_g} \int \frac{dm}{m_{\max}^{n-1} - m^{n-1}} - \frac{m}{v_g}, \quad (4)$$

where $k = v_g / (k_r - v_g)$, and $m_{\max} = (k_n / nk_r k)^{1/(n-1)}$ is the maximum mass gain of the system at the expense of active gas. Boundary condition for solving of Eq. (2) for different n is $t = 0, m = 0$.

The Tedmon-Wajsel equation ($n = 2$) in our notation will be:

$$t = -(1+k) \frac{m_{\max}}{v_g} \ln \frac{m_{\max} - m}{m_{\max}} - \frac{m}{v_g}. \quad (5)$$

For $n=3$ and 4 we will have:

$$t = (1+k) \frac{m_{\max}}{2v_g} \ln \frac{m_{\max} + m}{m_{\max} - m} - \frac{m}{v_g}, \quad (6)$$

$$t = (1+k) \frac{m_{\max}}{v_g} \left[\frac{1}{\sqrt{3}} \arctg \frac{\sqrt{3}m}{m+2m_{\max}} - \frac{1}{6} \ln \frac{(m_{\max}-m)^2}{m^2 + mm_{\max} + m_{\max}^2} \right] - \frac{m}{v_g}, \quad (7)$$

respectively [20]. For the total mass change will be:

$$M = m - v_m t. \quad (8)$$

Such containing maxima curves were obtained in a number of works, in works collected in, and others [2]. Here we will look at graphs in which this maximum is clearly expressed and from which reliable information can be obtained (some graphs, which are not considered here, give unrealistic values of kinetic parameters) [18-28].

2. Experimental

In the experiments, we used plates of single-crystalline germanium of N-type conductivity and with concentration of charge carriers $n = 2 \cdot 10^{20} m^{-3}$. They were successively degreased in boiling toluene, dried in the air, etched in a liquid etchant CP-4A ($HF : HNO_3 : CH_3COOH = 1:15:1$) for (4-5) min and, washed in running distilled water, followed by drying. Ammonia (freezing point $-33.4^\circ C$) was dried by slowly passing it through a trap cooled with a mixture of liquid nitrogen and alcohol or ice with NaCl. The pressure of ammonia was $P_{NH_3} = 2.7 \cdot 10^3 Pa$, and pressure of hydrazine $P_{N_2H_4} = 2 \cdot 10^3 Pa$ (saturated vapor pressure of N_2H_4 at room temperature). In the case of ammonia, water vapor was deliberately introduced into the reactor: $P \equiv P_{H_2O} / P_{NH_3} \cong 2$ and 5% . The nitridation temperature was $(680-820)^\circ C$. The temperature of the electric heater was regulated using a high-precision regulator $\mathcal{Z}(\mathcal{V})\mathcal{R}\mathcal{T}$ -3 with an accuracy of $\pm 0.5^\circ C$. Kinetic measurements were carried out by continuously weighing the samples during the oxidation process. For this purpose, a homemade microbalance built into a vacuum unit was used (sensitivity $\cong 10^{-6} g$). Electromagnetic compensation for changes in the sample mass was carried out automatically.

3. Results and Discussion

3.1. Analysis of kinetic curves of mass change during the interaction of active gases with the surface of certain metals and compounds with simultaneous evaporation of the products of reaction

3.1.1. Kinetic Curves of the Total Mass Change, Having a Maximum

As mentioned above, kinetic curves containing a maximum are presented in many works. Most of them are curves corresponding to parabolic kinetics ($n = 2$); there is little data for $n = 4$; but for $n = 3$ we did not find such data, although cubic processes (with curves without maxima) are considered in a fairly large number of works.

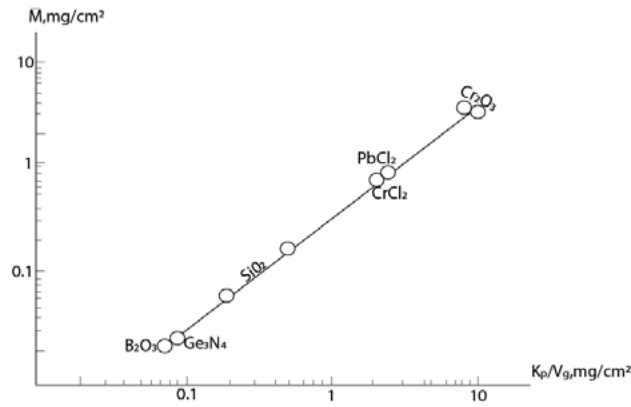


Figure 2: dependence $\bar{m} - kp / v_g$ for different samples in logarithmic coordinates.

Figure 2 shows the dependence in coordinates $\lg(kp/v_g) - \lg \bar{m}$ for different samples from [2]. The following reactions are considered here: $2Cr + 3O_2 = Cr_2O_3$, $Pb + Cl_2 = PbCl_2$, $Si + O_2 = SiO_2$, $SiC + 2O_2 = SiO_2 + CO_2$, $Si_3N_4 + 3O_2 = 3SiO_2 + 2N_2$ and $4BN + 3O_2 = 2B_2O_3 + 2N_2$ (for all reactions the kinetics are parabolic: kp - power-law constant at $n=2$). We have added data for reactions $Cr + 2HCl = CrCl_2 + H_2$ and $3Ge + 4NH_3 = Ge_3N_4 + 6H_2$ (also with parabolic kinetics). This data fit well into this dependence.

3.1.2. Consideration of Preliminary Mass Reduction

In some cases the growth of scale is preceded by other processes, for example, gas etching of the surface of the metal or alloy (initial section of curve 1 in coordinate system $t-W$). In this case, to describe the $m - t$ dependence, it is necessary to solve the differential equation (1) with the boundary condition $t = 0, m = m_0$.

For $n = 2, 3$ and 4 these solutions have the form:

$$t = -(1 + k) \frac{m_{\max}}{v_g} \ln \frac{m_{\max} - m}{m_{\max} - m_0} - \frac{m - m_0}{v_g}, \quad (9)$$

$$t = (1 + k) \frac{m_{\max}}{2v_g} \ln \frac{(m_{\max} + m)(m_{\max} - m_0)}{(m_{\max} - m)(m_{\max} + m_0)} - \frac{m - m_0}{v_g}, \quad (10)$$

$$t = (1 + k) \frac{m_{\max}}{v_g} \left[\frac{1}{\sqrt{3}} \arctg \frac{\sqrt{3}m(m - m_0)}{m + 2m_{\max}} - \frac{1}{6} \ln \frac{(m_{\max} - m)^2 (m_0^2 + m_0 m_{\max} + m_{\max}^2)}{(m_{\max} - m_0)^2 (m^2 + m m_{\max} + m_{\max}^2)} \right] - \frac{m - m_0}{v_g}, \quad (11)$$

respectively. To demonstrate, we present data on the interaction of single-crystalline Ge with $NH_3 + H_2O$ and N_2H_4 vapors.

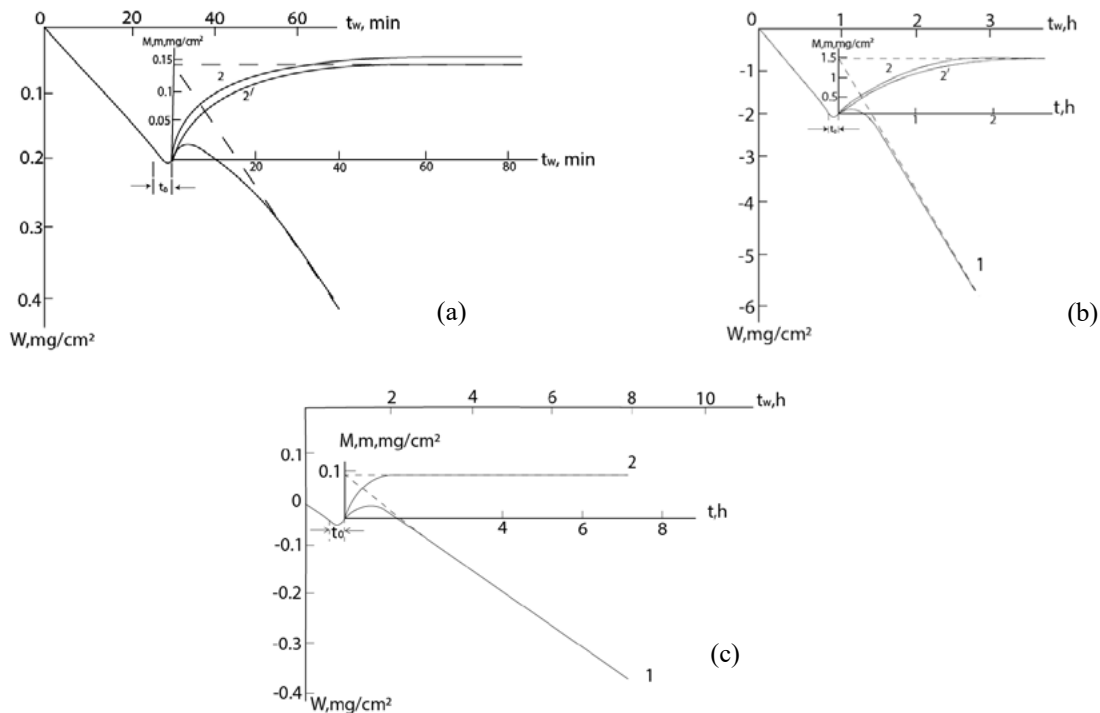


Figure 3: Kinetic Dependences of Interaction of Ge: with $NH_3 + H_2O$ at (a) $P = 2\%$, $820^\circ C$, (b) $P = 5\%$, $800^\circ C$, ($P \equiv PH_2O / PNH_3$); and (c) with N_2H_4 ($PN_2H_4 = 2 \cdot 10^3 Pa$) at $720^\circ C$ – (1) dependences $W - t$, (2) – dependences $m - t$; 2' – calculated curves (in the scale of the figure (c), the experimental and calculated curves practically coincide with each other)

On these curves, the initial decrease of mass is due to the etching of the germanium surface by water vapor, which is contained in small quantities also in concentrated hydrazine (volatile GeO is formed here: $\text{GeO} + \text{H}_2\text{O} = \text{GeO} + \text{H}_2$) [29-30]. Also it is obvious that the formation of nitride on the germanium surface will begin before the zero point in the $t - m$ coordinate system. But from the presented model it follows that the $m - t$ dependences are convex in the positive direction. Time shifts between equations (3) and (9), (4) and (10), (5) and (11) are:

$$t_0 = (1+k) \frac{m_{\max}}{v_g} \ln \frac{m_{\max} - m_0}{m_{\max}} + \frac{m_0}{v_g}, \quad (9')$$

$$t_0 = (1+k) \frac{m_{\max}}{2v_g} \ln \frac{m_{\max} + m_0}{m_{\max} - m_0} + \frac{m_0}{v_g}, \quad (10')$$

and

$$t_0 = (1+k) \frac{m_{\max}}{v_g} \left[\frac{1}{6} \ln \frac{(m_{\max} - m_0)^2}{m_0^2 + m_0 m_{\max} + m_{\max}^2} + \frac{1}{\sqrt{3}} \arctg \frac{\sqrt{3} m_0}{m_0 + 2m_{\max}} \right] + \frac{m_0}{v_g}, \quad (11')$$

respectively. Thus, the values of m_0 can be estimated by solving of transcendental equations (9')-(11') by substituting the values of k , m_{\max} , v_g , and t_0 determined from experimental data. The main difficulty is the accurate determination of t_0 in the initial section of the curves - conducting an additional experiment of short duration would lead to even larger errors.

According to the experimental data presented in Fig.3, one can estimate $t_0 \approx -3$ min, -0.14 h, and -0.33 h, respectively with Figs(a), (b) and (c). Then the values of m_0 will be ≈ 0.3 , 0.05 and 0.03 mg/cm^2 . As you can see, m_0 makes up (20-34)% of corresponding m_{\max} (0.145, 1.42, 0.092 mg/cm^2 , respectively) and this cannot be ignored when conducting an experiment using the gravimetric method.

Footnote

When active gases interact with metal or alloy surface, processes often occur in which compounds of doping impurities are formed. These compounds can create diffusion barriers that prevent the main reaction from occurring. This is equivalent to a decrease in the area of the reaction surface. The corresponding kinetic equations have been derived for such processes. The situation is complicated by the simultaneous occurrence of the processes of evaporation of the main compound and a decrease in the reaction surface. In paper 1, it is indicated that the solution of the corresponding differential equation cannot be expressed using elementary functions. It would be possible to compile tables similar to some known functions, but this would be of interest only for the problem under consideration. Moreover, at present it is possible to construct the necessary graphs using computer programs without considering mathematical formulas.

4. Conclusion

A general equation is given that describes the scale growth- evaporation kinetic (sample mass change - time) curves during the interaction of gases with the surface of metals and compounds. Special cases of parabolic, cubic and fourth degree processes are discussed. Equations are also given for the case when scale formation is preceded by the process of gas etching of the metal surface. By evaporating the nitride formed on the germanium surface (along with the formation of volatile monoxide), a film of germanium oxynitride is deposited on a substrate located in the cold zone of the reactor.

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