

## On the Kinetics of Scale Growth with the Change of the Effective Area of Diffusion

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**ABSTRACT.** On the basis of Evans' conceptual theory, a new equation of the growth of scale with the change of the effective area of diffusion has been tested and formulas obtained that allow constructing the kinetic curves of oxidation both for specific heat-resistant alloys and for possible, hypothetical subjects of research. © 2011 Bull. Georg. Natl. Acad. Sci.

**Key words:** oxidation kinetics, diffusion barriers, alumina.

Kinetic models of the oxidation processes of alloys could be considered as simplified diagrams of the ambient conditions in which they are located. A number of theories have been developed describing the kinetics of the indicated processes; for instance, according to Wagner's theory it becomes possible to correctly describe the process of the scale appearance, where the geometric dimensions and the structure of the interface alloy-scale remain constant in the course of the development of the reaction of oxidation [1]. At the same time, there is no doubt that the kinetics of growth of a not thin scale is mostly controlled by the components of its microstructure.

Occurrence in a protective oxide layer of the diffusion-impenetrable or less permeable phases, so-called diffusive barriers, reduces the effective area of diffusion since with the advent of the specified phases certain micro sites of scale cease to participate in the process of its growth. A theory, advanced by Evans [2], has proved most suitable for the description of the mechanism and kinetics of such scale, according to which

$$W = \frac{1}{k} \ln(k\sqrt{K_p\tau} + 1), \quad (1)$$

where  $W$  is a specific gain of oxidized object over time  $\tau$ ,  $k$  is a constant of reduction of the diffusive stream, and  $K_p$  is a constant of parabolic oxidation rate.

From Evans's equation (1) it follows that scale growth submits to the parabolic law  $W^2 = K_p \tau$  (2) at exponential reduction of the effective area of diffusion  $S = S_0 e^{-kw}$  (3), where  $S$  and  $S_0$  are current and initial sizes of diffusive section.

The majority of high-temperature heat resisting alloys of the system (Fe–Cr–Al) are oxidized by formation of an external layer of aluminum oxide, the slow growth of which protects the basic alloy from the continuous aggressive influence of the components of air.

The admixtures that are introduced into the growing scale can be of different origin. Some of them are technologically inevitable elements which are present, usually in small quantities, but may vary from test to test.

The source of admixtures, as a rule, is the basic metal (Fe, Ni, Co, Cr, and Al), taking root in the form of oxide at the initial stage of oxidation, and also specially deposited to alloy Y or La. The presence of oxides of these metals provides formation of diffusive barriers on borders of grains of the core oxide –  $\text{Al}_2\text{O}_3$  [3-5]. The growth of scale from  $\text{Al}_2\text{O}_3$  on the alloy not containing reactive elements -

Table

Values of factors  $k$  and  $K_p$  at 1200°C

№	Composition of alloy on the charge, % throughout the mass	Melting operation	Parameters of oxidation	
			$k, \text{cm}^2/\text{mg}$	$K_p, \text{mg}^2/\text{cm}^4\text{h}$
1	Fe+45Cr+4Al+0.3La	argon	2.16	0.20
2	Fe+45Cr+4Al+0.3La	air	1.126	0.089

(La, Y, Hf, Zr), is usually subordinated to the parabolic law of oxidation [5], while in the case of the presence of reactive elements in the alloy, the kinetics of its oxidation can be correctly described by Evans' equation [3,4].

Nonmetallic admixtures can also segregate on the growing interface of alloy/scale, as shown on the basis of the example of sulphur (S) [5]. Along with distribution of sulphur (S) in alloys NiAl and NiCrAl, its negative impact on the rate of oxidation has been also reported.

In the case when the admixtures, which in their slowly growing scale form easily permeable phases, serving as arteries for the diffusion mass transfer are located in heat resistant alloys, the kinetic equation of growth of such scale is deduced according to Evans' analogy

$$W = -\frac{1}{K} \ln(1 - K\sqrt{K_p\tau}), \quad (4)$$

where  $K$  is the constant of an exponential increase of the diffusion flow.

The obtained equation indicates the parabolic nature of the growth of scale at the exponential increase in the effective area of diffusion:

$$S = S_0 e^{KW} \quad (5)$$

where  $S > S_0$ .

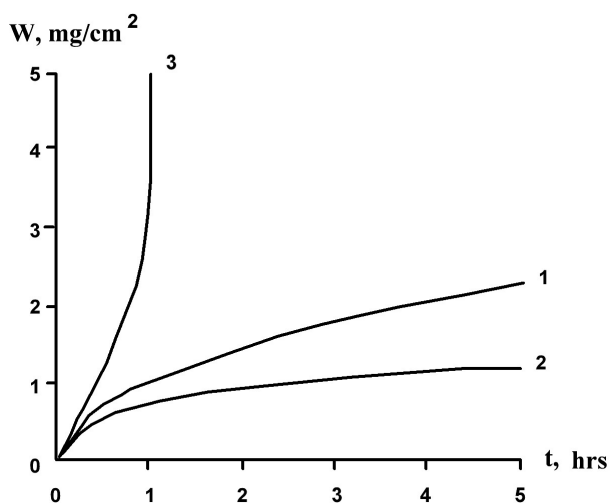


Fig. 1. Temporal dependence of weight gain, computed by relevant equations: 1 – Wagner's equation; 2 – Evans' equation; 3 – New equation;

In order to describe the kinetics of oxidation of a particular heat resisting alloy and compare theoretical curves with experimental ones an alloy of optimum composition containing 0.3 % of lanthanum was selected in the system Fe–Cr–Al.

Melting operations were conducted in the air and in inert atmosphere. The oxidation of samples was investigated by the method of continuous weighing in the air at 1200°C for 10 hours. The values of the parameters of oxidation of the alloy under investigation, calculated according to the experimental data, are represented in Table.

For an abstract description of the high-temperature oxidation process of the material three equations were used:

$$1. W^2 = K_p \tau, \quad 2. W = \frac{1}{k} \ln(k\sqrt{K_p\tau} + 1);$$

$$3. W = -\frac{1}{K} \ln(1 - K\sqrt{K_p\tau}),$$

Fig. 1 shows the temporary time dependence of the specific gain, calculated by relevant equations  $W=f(\tau)$ ; at the same time, for the purpose of simplification in calculations, it was accepted that  $K_p=k=K=1$ . The abstract nature of these calculations disappears for Wagner's equation which describes the initial stages of the oxidation

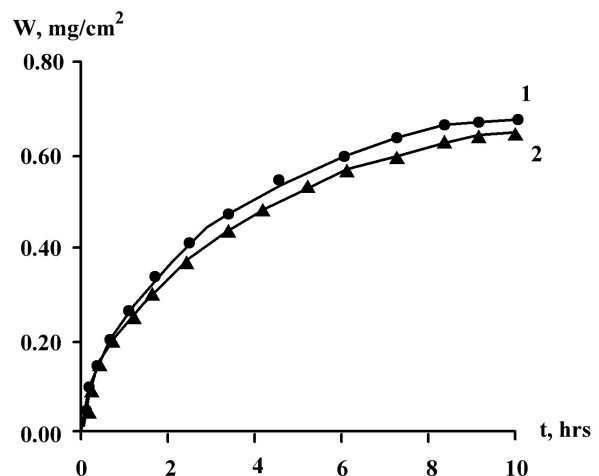


Fig. 2. Oxidation kinetics of alloys 1 and 2: Continuous curves are experimental curves, circles and triangles on them represent the calculated data

process in elementary form, prior to the appearance of diffusion barriers in the structure of heat-resistant alloys with a decreasing effective area of diffusion, while Evans' equation proved to be very good for the clarification of the increase in scale at the subsequent stages of oxidation.

As for the new equation with the increasing effective area of diffusion (4), we can only assume that it describes a short period of transition to linear oxidation at the end of the operational resource of the material.

As is evident from the Table, the parameters of oxidation of alloys having identical chemical composition of the metallic charge differ significantly, depending on the

method of melting. However, the values of specific weight gain and the nature of their changes in these alloys are quite close (Fig. 2).

Calculation formulas for the construction of theoretical curves of oxidation are obtained by introduction of tabulated data of the parameters of oxidation into the kinetic equations.

It should be added to the foregoing that the theoretical and experimental kinetic curves of oxidation of the heat-resistant alloys under study are practically identical. Consequently, the tested equations can be used for predicting the high-temperature properties of  $Al_2O_3$  forming heat-resistant alloys.

### მასალათმცოდნეობა

## ოქსიდური ხენჯის ზრდის კინეტიკა დიფუზიის ეფექტური ზედაპირის ცვლილებისას

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ევანსის კონცეპტუალური თეორიის საფუძველზე მოსინჯულია დიფუზიის ეფექტური ზედაპირის ცვლილების პირობებში ოქსიდური ხენჯის ზრდის ახალი განტოლება და მიღებულია საანგარიშო ფორმულები როგორც კონკრეტული მხურვალემდეგი შენადნობების, ასევე კვლევის ჰიპოთეზური ობიექტების ჟანგვის კინეტიკური მრუდების ასაგებად.

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