

Mathematical Model of Thermogravimetric Curves of FeCrAl(La) Alloy Oxidation in Air

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Abstract

The oxidation process of FeCrAl(La) alloy at 1200°C in air is investigated. Alternative models of the thermogravimetric curve of this process are considered. This curve can be described by the cubic power dependence. A model of reaction area reduction for the formation of basic oxides can be used as well. This reduction can be explained by the formation of non-basic (barrier) compounds.

Keywords: FeCrAl(La), Oxidation, Mass Gain, Power Law, Reaction Area Reduction

Introduction

Nowadays, there are a great number of publications concentrating the FeCrAl alloy high-temperature oxidation study. In this process a protective film of alumina Al_2O_3 is formed [1-3]. To improve its adherence and the mechanical properties of FeCrAl in general, the alloying with rare-earth metals (REM) is used [4-8]. When using lanthanum for this aim, the formation of non-basic oxides and aluminates, particularly, $LaAlO_3$ was observed [9, 10]. This phase refers to perovskites [11, 12] and is diffusely hard-permeable.

During the FeAl, FeCrAl, FeCrAl(REM) oxidation and other similar reactions, the parabolic [13-19], sub-parabolic [19-21] or cubic [16, 18] law of kinetics is observed. According to these laws, the alloy mass change is described by the equation

$$(1) \quad m^n = k_n t$$

where m is the mass gain per specimen area unit, k_n is the process rate constant, t is time. Index n is equal to 2 or 3. As well, it can take another values, including fractional ones. In case of lanthanum, the perovskite phases must gradually reduce the reaction area for the basic oxides formation. A similar situation was observed during the oxidation of FeCr(La) and FeCrAl(La) with the chromite $LaAlO_3$ formation [22, 23]. This process resulted in the deviation of the mass gain from the power law [22]. U.R. Evans derived the following

equation for such processes [24]:

$$(2) \quad m = \frac{1}{k} \ln(k \sqrt{k_2 t} + 1)$$

where k is the reaction area reduction factor. This factor is introduced by the expression

$$(3) \quad \varnothing = \frac{S}{S_0} = e^{-km}$$

where S_0 is the initial alloy area, $S=S(t)$ is the area free of non-basic (barrier) compounds at the time point t . The implicit dependence was also derived [25]:

$$(4) \quad t = \frac{2}{k^2 k_2} [e^{km} (km - 1) + 1]$$

In this case, as well as for the Eq.(2) derivation, the mass gain rate expression was used [24]:

$$(5) \quad \frac{dm}{dt} = \frac{k_2}{2m} e^{-km}$$

From the Eqs.(3) and (5) it can be seen that in the absence of reaction area change ($\varnothing=1 \rightarrow k=0$) the mass gain follows the parabolic law ($n=2$ in Eq.(1)).

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Results

The oxidation process of the Fe44Cr4Al0.3La (the numbers indicate the mass.%) in air at 1200°C is considered in this report. The aim is to choose an optimal model for the experimental mass gain curve on the basis of Eqs.(1-4).

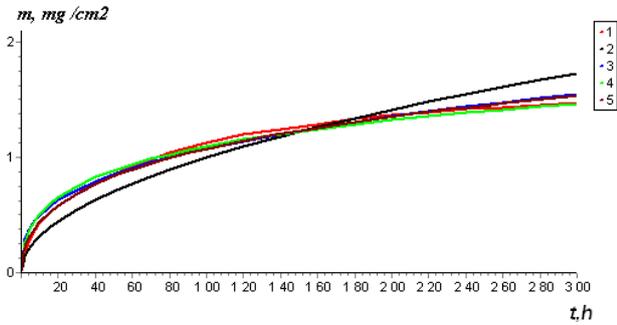


Figure 1. Experimental (1) and calculated (2, 3, 4 and 5) curves of mass gain plotted by the parabolic dependence, cubic dependence and the equations (2) and (4), respectively.

The experimental graph (the curve 1) and the graphs plotted in accordance with the Eq.1 are shown in Figure 1. The values of rate constant are: $k_2 \cong 1 \cdot 10^{-2} \text{ mg}^2 / \text{cm}^4 \text{ h}$ (the curve 2) and $k_3 \cong 1.125 \cdot 10^{-2} \text{ mg}^3 / \text{cm}^6 \text{ h}$ (the curve 3). It can be seen that the parabolic dependence differs significantly from the experimental curve, and the cubic one is fairly close to it. But let's consider the process also from the point of view of the reaction area reduction (Eqs.(2) and (4)). The treatment of these equations on the basis of the experimental dependence $m=m(t)$ gave the following value of reaction area reduction factor: $k \cong 1.126 \text{ cm}^2 / \text{mg}$. For the parabolic constant the values $k_2 \cong 4.7 \cdot 10^{-2} \text{ mg}^2 / \text{cm}^4 \text{ h}$ (Eq.2) and $k_3 \cong 2.7 \cdot 10^{-2} \text{ mg}^3 / \text{cm}^6 \text{ h}$ (Eq.4) were obtained. The corresponding empirical expressions are: $m = 0.888 \ln(0.244\sqrt{t} + 1)$ and $t = 58.424 [e^{1.126m} (1.126m - 1) + 1]$ where m is in mg / cm^2 and t is in hours. The curves plotted using these expressions are fairly close to the experimental curve (Figure 1).

From the Eqs. (3) and (5) it can be seen that as a first approximation, $d\phi / dt \rightarrow 0$ when $m \rightarrow 1/2k$. Accordingly, by considering the model, in the oxidation process when $\phi = e^{-1/2} \approx 0.6$ the formation of barrier compound must be completed.

Let us transform the Eqs.(2) and (4) using the Eq.(3):

$$(6) \quad \phi = (k\sqrt{k_2 t} + 1)^{-1}$$

or

$$(7) \quad t = \frac{1}{k_2} \left(\frac{\phi^{-1} - 1}{k} \right)^2$$

and

$$(8) \quad t = \frac{2}{k^2 k_3} [1 - \phi^{-1} \ln(e\phi)].$$

Introducing $\phi = e^{-1/2}$ and the values of constants into Eqs.(7) and (8) we will get $t \cong 7.1$ and 10.3 h respectively. Thus, it can be considered that the surface of alloy where the basic oxides build-up takes place-, in approximately 10 hours it practically becomes unchanging again. After introducing the values of constants into Eqs. (6) and (8) the kinetic dependences of the reaction area reduction takes the form: $\phi = (0.244\sqrt{t} + 1)^{-1}$ and $t = 58.424 [1 - \phi^{-1} \ln(e\phi)]$ where t is in hours. Their graphs are shown in Figure 2.

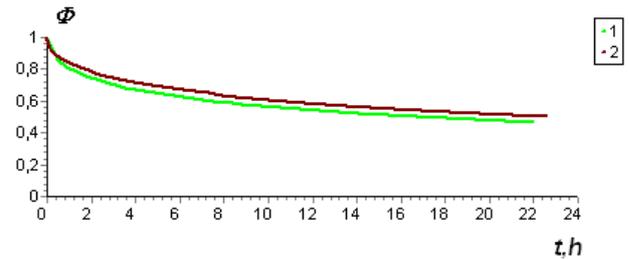


Figure 2. Reduction of ϕ : 1 – by equation (6), 2 – by equation (8)

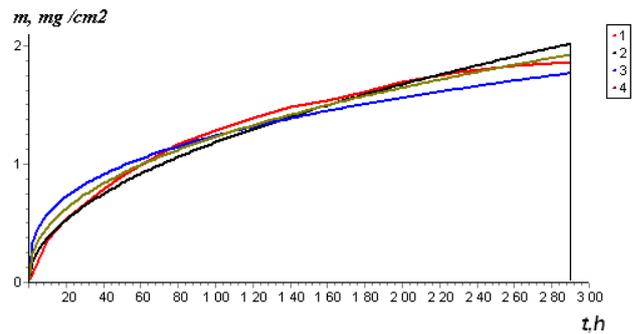


Figure 3. The part of experimental curve from Fig.1 (1); (2, 3 and 4) – the curves calculated using equation (9), parabolic and cubic dependences, respectively.

In Figure 3 a part of the experimental curve from Figure 1 is shown. 10-300 hours of oxidation are allocated taking into account the reduced surface area of the alloy. This part can be described by the equation

$$(9) \quad m^{2.38} \cong 0.0165 \cdot t$$

where m is in mg / cm^2 and t is in hours. The Eq.(9) is closer to the parabolic dependence ($k_2 \cong 1.41 \cdot 10^{-2} \text{ mg}^2 / \text{cm}^4 \text{ h}$) than to the cubic one ($k_3 \cong 1.92 \cdot 10^{-2} \text{ mg}^3 / \text{cm}^6 \text{ h}$).

At the end it must be mentioned that – from the Eq.(2), when expansion of logarithm in series, it comes out: $m^2 \approx k_2 t$ and from Eq.(4) when expansion of exponent in series we will have: $m^2 \approx k_2 t / 2$. Thus, the parabolic constant in Eq.(2) is $0.047 / 0.027 \cong 1.74 \approx 2$ times greater than that in Eq.(4).

Conclusion

Kinetics of the alloy oxidation process can be described by the change of sample weight. But the formal mathematical description of this change may lead to ambiguous conclusions. The oxidation process of a widely used in industry and technology heat-resistant alloy FeCrAl is described by a power law. In most cases this law is used also in the presence of barrier oxides, chromites and aluminates at the alloy surface. The data given in this short report show that the cubic law can be used in the case of high temperature oxidation of FeCrAl(La). As well, a significant reduction of the alloy active surface due to the barrier compounds formation can be accounted. For such a case non-power kinetic dependences, namely, the Evans's equation and the implicit kinetic equation have been applied. These equations have their application limits. But in the case of FeCrAl(La) high-temperature oxidation, both of them satisfactorily describe the increase in weight of the sample. In conclusion, we can assume that for the studied process the model with reaction area reduction is more acceptable than the model with power law.

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