

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

Irakli NAKHUTSRISHVILI\*  
Omar TKESHELASHVILI\*\*  
Andro CHANISHVILI\*\*\*

## 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)).

\* Ph.D, Senior Researcher of Institute of Cybernetics, Georgian Technical University, Tbilisi, Georgia.  
E-mail: gvipgirl@gmail.com

\*\* Leader Engineer of Institute of Cybernetics, Georgian Technical University, Tbilisi, Georgia.  
E-mail: ic@cybernet.ge

\*\*\* Ph.D, Head of Department of Institute of Cybernetics, Georgian Technical University, Tbilisi, Georgia.  
E-mail: achanishvili@yahoo.com

**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).

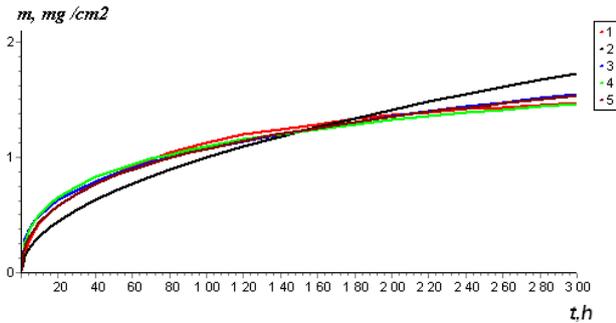


Figure 1. Experimental (1) and calculated (2, 3, 4 and 5) curves of mass gain plotted by the parabolic dependence, cubic dependence and the equations (2) and (4), respectively.

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  $\text{mg} / \text{cm}^2$  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.

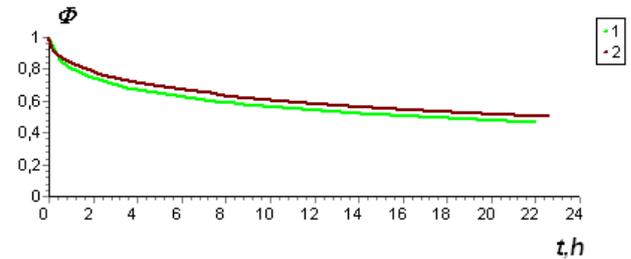


Figure 2. Reduction of  $\phi$ : 1 – by equation (6), 2 – by equation (8)

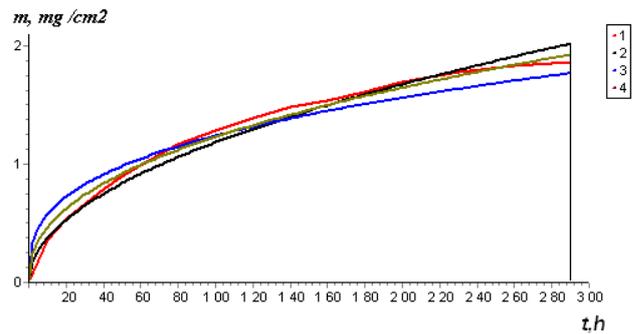


Figure 3. The part of experimental curve from Fig.1 (1); (2, 3 and 4) – the curves calculated using equation (9), parabolic and cubic dependences, respectively.

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  $\text{mg} / \text{cm}^2$  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.

## References

- Chevalier, S. Formation and Growth of Protective Alumina Scale. In: Developments in High-Temperature corrosion and Protection of Materials (2008), Cambridge, England: Woodhead Publishing Limited, 290.
- Pint, B.A. Design Strategies for New Oxidation-Resistant High Temperature Alloys. *Ibid.*, 398.
- Heuer, A.H., Nakagawa, T., Azar, M.Z., Hovis, D.B., Smialek, GlesJ.L., Glesson, B., Hine, N.D.M., Guhl, H., Lee, H.-S., Tangney, P., Foulkes, W.M.C., Finnis, M.W. (2013). On the Growth of Al<sub>2</sub>O<sub>3</sub> Scales. *Acta Materialia*, 61 (18), 6670-6683.
- Saito Y., Effect of Rare Earth Elements on the High-Temperature-Oxidation of Heat-Resisting Alloys. In: Selected topics in high-temperature chemistry (1989), Amsterdam-Oxford-New-York-Tokyo: Elsevier, 227.
- Ishii, K., Kohno, M., Ishikawa, S., Satoh, S. (1997). Effect of Rare-Earth Elements on High-Temperature Oxidation Resistance of Fe-20Cr-5Al Alloy Foils. *Materials Transactions*, 38 (9), 787-792.
- Hou, P.Y. (2011). The Reactive Element Effect – Past, Present and Future. *Materials Science Forum*, 696, 39-44.
- Ozawa, M., Araki, K.-I. (2015). Effect of La Modification on the Stability of Coating Alumina Layer on FeCrAl Alloy Substrate. *Surface and Coatings Technology*, 271, 80-86.
- He, Y., Liu, J.H., Han, Z.B., Yang, B.F., Liu, J., Ji, Y.I. (2015). Effect of La on Mechanical Properties of FeCrAl Stainless Steel under High Temperature. *Continuous Casting*, 40 (4), 1-9.
- Chen, N., Ji, S., Yin, F., Zhao, L., Wang, W., Li, C., Liu, H. (2005). Preparation of LaAl<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/FeCrAl Catalyst and its Catalytic Performance for Methane Combustion. *Chinese Journal of Catalysis*, 26 (11), 1017-1021.
- Buscail, H., Nguyen, C.T., Cuff, R., Issartel, C., Riffard, F., Perrier, S. (2009). Effect of the La<sub>2</sub>O<sub>3</sub> Sol-Gel Coating on the Alumina Scale Adherence on a Model Fe-20Cr-5Al Alloy at 1100°C. *Materials Science*, 44 (15), 3968-3974.
- Nakatsuka, A., Ohtaka, O., Arima, H., Nakayama, N., Mizota, T. (2005). Cubic Phase of Single-Crystal LaAlO<sub>3</sub> Perovskite Synthesized at 4.5 GPa and 1273 K. *Acta Crystallographica*, E61, i148-i150.
- Boudali, A., Saadaoui, F., Zemouli, M., Khodja, M.D., Amara, K. (2013). Recalculate Structural, Elastic, Electronic and Thermal Properties in LaAlO<sub>3</sub> Rhombohedral Perovskites. *Advances in Materials Physics and Chemistry*, 3 (2), 146-152.
- Liu, Z., Gao, W., He, Y. (2000). Modeling of Oxidation Kinetics of Y-doped Fe-Cr-Al Alloys. *Oxidation of Metals*, 53 (3/4), 341-350.
- Badini, C., Laurella, F. (2001). Oxidation of FeCrAl Alloy: Influence of Temperature and Atmosphere on Scale Growth Rate and Mechanism. *Surface and coatings technology*, 135, 291-298.
- Zhang, Z.G., Gesmundo, F., Hou, P.Y., Niu, Y. (2006) Criteria for the Formation of Protective Al<sub>2</sub>O<sub>3</sub> Scales on Fe-10Al and FeCrAl Alloys. *Corrosion Science*, 48 (3), 741-765.
- Young, D.J., Naumenko, D., Niewalak, L., Wessel, E., Singheiser, L., Quadackers, W.J. (2010). Oxidation Kinetics of Y-doped FeCrAl Alloys in Low and High PO<sub>2</sub> Gases. *Materials and Corrosion*, 61 (10), 838-844.
- Othman, N.K., Zhang, J., Young, D.J. (2010). Water Vapour Effects on Fe-Cr Alloy Oxidation. *Oxidation of Metals*, 73 (1/2), 337-352.
- Tallman, D.J., Anasori, B., Barsoum M.W. (2013). A Critical Review of the Oxidation of Ti<sub>2</sub>AlC, Ti<sub>3</sub>AlC<sub>2</sub> and Cr<sub>2</sub>AlC in Air. *Materials Research Letters*, 1 (3), 115-125.
- Hellström, K., Israelsson, N., Mortazavi, N., Canovic, S., Halvarsson, M., Svensson, J.E., Johansson, L.-G. (2015). Oxidation of a Dispersion-Strengthened Powder Metallurgical FeCrAl Alloy in the Presence of O<sub>2</sub> at 1,100°C: The Influence of Water Vapour. *Oxidation of Metals*, 83, 533-558.
- Quadackers, W.J., Naumenko, D., Wessel, E., Kochubey, V., Singheiser, L. (2004). Growth Rates of Alumina Scales on Fe-Cr-Al alloys. *Oxidation of Metals*, 61 (1/2), 17-37.
- Chegroune, R., Salhi, E., Grisci, A., Wouters, Y., AGalerie, A. (2008). High-Temperature Corrosion of Dilute Chromium-Lanthanum Alloys. *Oxidation of Metals*, 70 (5/6), 331-350.
- Tavadze, F.N., Mikadze, O.I., Keshelava, N.P., Bulia, B.P. (1986). High-Temperature Corrosion of Low-Alloyed Chromium. *Oxidation of Metals*, 25 (5/6), 335-350.
- Pillis, M.F., Ramanathan, L.V. (2007). High-Temperature Oxidation Resistance of Rare Earth Chromite Coated Fe-20Cr and Fe-20Cr-4Al Alloys. *Materials Research*, 10 (3), 279-282.
- Evans, U.R. (1960). *The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications*, London: E. Arnold LTD, 272.
- Nakhutsrishvili, I.G. (2006). A New Kinetic Equation for the Scale Formation at the Reaction Surface Diminution. *Georgian Engineering News*, 4, 134-136.