Influence of the simultaneous processes of scale evaporation and reaction surface reduction on the oxidation kinetics of chromia-forming alloys doped with rare-earth elements

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Abstract

The high-temperature oxidation of FeCr(La) and Cr(Ce) alloys was studied by thermogravimetry. The kinetic dependence of the FeCr(La) mass change has a specific form due to the simultaneous occurrence of scale evaporation and reduction of the reaction surface. The latter is due to the formation of diffusion barriers from lanthanum chromite. The kinetic dependence of the mass change of Cr(Ce) has an identical form. Based on this identity, it was suggested that diffusion barriers can also exist in the Cr(Ce) alloy, as is the case for the FeCr(La) alloy.

Keyword: *Oxidation of alloys, evaporation of scale, decrease of reaction surface.*

Introduction

To improve the composition, morphology and adherence of the scale of Cr_2O_3-forming heat-resistant alloys, these are doped with rare-earth elements (La, Y, Ce, etc.) [1,2]. During the high-temperature oxidation of these alloys, together with the basic oxide, there are also chromites formed on their surface (in particular, $LaCrO_3$, $YCrO_3$, $CeCrO_3$ [3-5]). In case of alloy FeCr(La) chromite is barrier for cation diffusion what is equipotent to the decrease of the effective area of the basic oxide formation reaction. This leads to the change of the parabolic kinetics of alloy oxidation to the logarithmic kinetics [3]. For the processes with the decreased reaction surface, U.R. Evans deduced the following ratio:

$$\varphi \equiv S/S_0 = e^{-km} \ , \tag{1}$$

where, S_0 is the initial area of metal or alloy surface, and S is the area free from the diffusion barriers of the surface of the specimen in case of mass gain m (i.e. its mass increase at the expense of the oxygen

entered into the reaction), k is the surface reduction coefficient. Based on Eq (1), one of the authors proposed an inexplicitly kinetic dependence of mass gain by time t:

$$t = \frac{2}{k^2 k_p}\left[e^{km}(km - 1) + 1\right],\tag{2}$$

where, k_p is a parabolic constant, which, alongside with the well-known Evans equation [3], m= $\frac{1}{k}\ln(k\sqrt{k_p t} + 1)$, can be applied to these processes considered. In particular, Eq (2) correctly described the kinetics of air oxidation of Al_2O_3 and Cr_2O_3 -forming alloys doped with lanthanum [3].
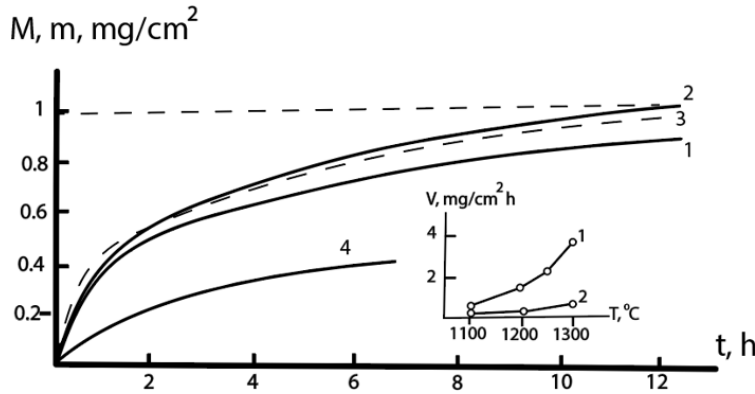
Results and discussion

Fig. 1. (1) Total mass change of the FeCr(La) alloy in air at 1200°C, (2) kinetic dependence of mass gain construed according to curve 1, (3) curve as per Eq.(2), (4) curve as per Eq.(4). The insert shows the evaporation rates (V) of (1) Cr_2O_3 and (2) $LaCrO_3$ within the range of 1100-1300°C.

Fig.1 shows the kinetic curve of the general mass change (M) of Fe45Cr0.3La alloy in the air at 1200°C (curve 1). As simultaneously with the scale formation, its evaporation takes place, then $M = m - v_m t$, where v_m is the total rate of evaporation of Cr_2O_3 and $LaCrO_3$ for different metal components. By considering Eq.(2), the total mass change will take have the following parametric form:

$$M = m - \frac{2v_m}{k^2 k_p}\left[e^{km}(km - 1) + 1\right],\tag{3}$$

where, $m = M + v_m t$ plays the role of parameter. This means that first, t is calculated according to m by Eq (2), and then, M is calculated for the same value of m. The kinetic curve of the specimen mass change caused by the oxidation of oxygen entering into reaction (m = M+v_mt), is given in Fig. 1 (curve 2). Its processing using OriginPro8 software yielded the following values of constants: $k \cong 1.550$ cm²/mg and $k_p \cong 0.231$ mg²/cm⁴h. By considering these values, the estimate curve 3 according to Eq (2) (Fig. 1)

satisfactorily approximates the curve construed from the experimental one. It should be noted that the curve construed according to modified Tedmon's equation [6]:

$$t = -\frac{m_{max}}{v_g}\ln(1 - \frac{m}{m_{max}}) - \frac{m}{v_g} \qquad (4)$$

($m_{max} = \frac{k_p}{2v_g}$ is the limit value of mass change, $v_g = \frac{v_m}{q}$, $q = 3M_O / M_{cr} \cong 0.923$ is the rate of evaporation for the gaseous component of the scale (that's why the plan of evaporation of the basic oxide is: $4Cr + 3O_2 = 2Cr_2O_3$; $2Cr_2O_3 + 3O_2 = 4CrO_3$), and does not correspond to the experimental curve (see Fig.1). This is another argument of the presence of the diffusion barriers in the scale changing the kinetics of the process. By using expression (1), Eq.(2) will be as follows:

$$t = \frac{2}{k^2 k_p}\left[1 - \frac{1}{\varphi}\ln(e\varphi)\right], \qquad (5)$$

i.e. dependence $\varphi = f(t)$ can also be presented in an inexplicit form. Its graph, by considering the values of constants, is given in Fig.2.
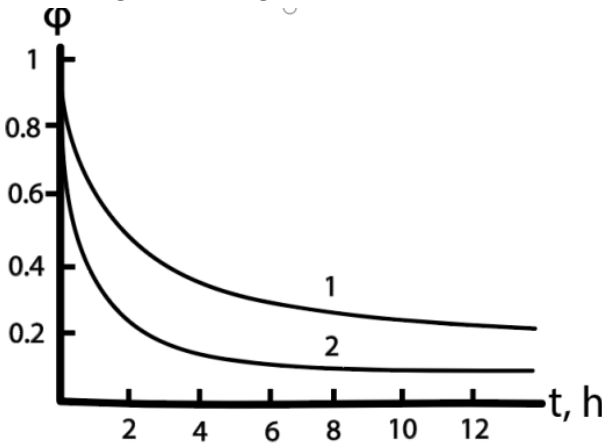

Fig.2 Dependences $\varphi = f(t)$: (1) FeCr(La) and (2) Cr(Ce).

The kinetic curve of the specimen mass change during oxidation of Cr0.5Ce alloy with oxygen ($P_{O_2} = 0.01$ atm, temperature 1100°C) totally repeats the form of typical curves of the Tedmon's process (initial increase of the mass of specimen, reaching the maximum value with a further decrease of mass) (Fig.3). However, as with FeCr(La) alloy, Eq.(4) yielded a big difference between the estimate and the experimental data (see Fig. 3).
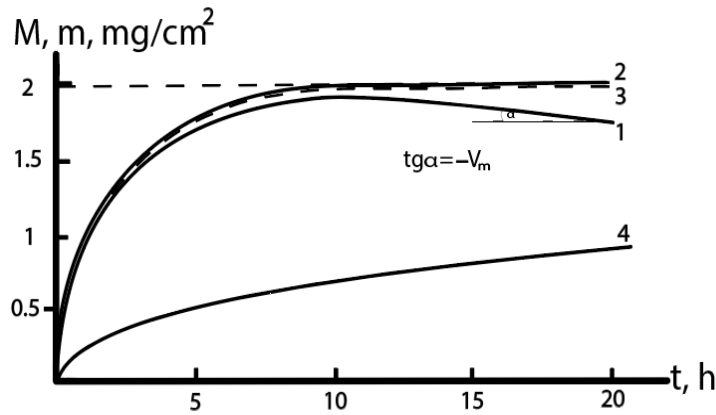
Fig.3. (1) Total mass change of alloy Cr(Ce) in oxygen at 1100℃, (2) kinetic dependence of mass change construed according to curve 1, (3) curve as per Eq.(2), (4) curve as per Eq.(4).

Therefore, particular caution is needed when assuming the possible reduction of the reaction surface and using Eq.(2). Since the dependence M=f(t) cannot be given as elementary functions (both, explicitly and inexplicitly), contribution v_m to the total mass change should be disregarded and dependence m = f(t) should be plotted. This can be done graphically (curve 2, Fig. 3). In this case, Eq.(2) can be used again (values of constants: $k \cong 1.177 cm^2/mg$ and $k_p \cong 2.648$ mg^2/cm^4h). Kinetic curve 3 calculated by this equation in the given scale virtually coincides with the curve plotted according to the experimental one (Fig. 3); while dependence $\varphi = f(t)$ for alloy Cr(Ce) plotted using Eq.(5) is given in Fig. 2.

Clearly, all the above-mentioned is not a full argument to justify the presence of diffusion barriers in alloy Cr(Ce) and the question of possible formation of $CeCrO_3$ during Cr(Ce) oxidation should be further investigated by using direct physical methods.

To conclude the given communication, we would like to note that Eqs. (2) and (5) can be presented more generally:

$$t = \frac{2}{k^2 k_p}\left[e^{km}(km - 1) + 1\right] + \frac{1}{kk_r}\left(e^{km} - 1\right), \tag{2'}$$

$$t = \frac{2}{k^2 k_p}\left[1 - \frac{1}{\varphi}\ln(e\varphi)\right] + \frac{1}{kk_r}\left(\frac{1}{\varphi} - 1\right), \tag{5'}$$

where, $k_r = \left(\frac{dm}{dt}\right)_{t=0, m=0}$ is a rectilinear constant. Consequently, other expressions change as well, e.g., $m_{max} = \frac{(k_r - v_g)k_p}{2v_g k_r}$. When $k_r \to \infty$, Eqs. (2') and (5') are transformed into Eqs. (2) and (5) respectively. In our case, for alloys FeCr(La) and Cr(Ce), $k_r \cong 18.898$ and 15.928 mg/cm²h, respectively. High values of this constant allow using Eqs. (2) and (5) processing the experimental data with high accuracy.

Conclusion

So, the study of the oxidation processes of alloy Fe45Cr0.3La in air at 1200°C and alloy Cr0.5Ce in oxygen (pressure 0.01 atm) at 1100°C has shown similar kinetics of these processes. Since there are diffusion barriers in alloy FeCr(La) as chromite LaCrO3, the presence of CeCrO3 in alloy Cr(Ce) can also be assumed, which should be further investigated by direct physical methods.

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ხენჯის აორთქლებისა და სარეაქციო ზედაპირის შემცირების ერთდროული პროცესების გავლენა იშვიათმიწა ელემენტებით დაპირებული ქრომია-წარმომქმნელი შენადნობების ოქსიდირების კინეტიკაზე

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საქართველოს ტექნიკური უნივერსიტეტის კიბერნეტიკის ინსტიტუტი

რეზიუმე

თერმოგრავიმეტრული მეთოდით შესწავლილია FeCr(La) და Cr(Ce) შენადნობების მაღალტემპერატურული ოქსიდირების კინეტიკა. FeCr(La)-ს მასის ცვლილების კინეტიკურ დამოკიდებულებებს გააჩნიათ სპეციფიური ფორმა ხენჯის აორთქლებისა და სარეაქციო ზედაპირის შემცირების პროცესების ერთდროული მიმდინარეობის გამო. ამასთან ერთად, ადგილი აქვს დიფუზიური ბარიერების წარმოქმნას ლანთანის ქრომიტისაგან (LaCrO₃). FeCr(Ce)-ს მასის ცვლილების კინეტიკურ დამოკიდებულებებს გააჩნიათ იდენტურ ფორმა. ამ იდენტურობის საფუძველზე გამოთქმულია ვარაუდი, რომ Cr(Ce) შენადნობში შესაძლებელია არსებობდეს დიფუზიური ბარიერები, როგორც ამას ადგილი აქვს FeCr(La) შენადნობისათვის.

საკვანძო სიტყვები: *შენადნობთა ოქსიდირება, ხენჯის აორთქლება, სარეაქციო ზედაპირის შემცირება.*