NEW APPROACH TO THE KINETIC MODELLING OF HIGH TEMPERATURE CORROSION OF METALS AND ALLOYS

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The kinetic modelling of the high temperature corrosion of metals and alloys is generally based on the identification of the rate-limiting step. Simple rate equations are frequently used as for example the parabolic or the linear rate law. However in some cases the experimental kinetic curves do not fit any of the usual rate equations, which suggests that the oxide growth proceeds through an alternative kinetic behaviour or model. In order to analyse such complex situations, we propose a new approach principally based on the verification of the kinetic assumptions that most of authors are using *a priori*. This is illustrated by two studies: the corrosion of zircaloy-4 by water vapour and the formation of MgO from oxidation of AlMg5% in the liquid state. It is also possible to apply it in the case of chemical transformations of powders (reduction of oxides by gases, thermal decompositions, …).

The mechanism of oxide scale growth is assumed to consist of a set of elementary steps; one of them is supposed to be rate controlling. This assumption implies that (i) the system is in a *pseudo*-steady state and (ii) that the oxidation rate can be expressed by equation [1]:

$$d\xi/dt \;=\; n_0\phi.E \qquad [1]$$

where n_0 is the initial amount in metal, ϕ is named the areic reactivity of growth of the oxide, (in $mol.s^{-1}.m^{-2}$), which depends on T, P_i (partial pressures), a_i (activities), and E a function (in $m^2.mol^{-1}$) characteristic of the extent of the reaction zone where occurs the rate-limiting step (it depends on time, sample shape, …).

In this paper, we show first that the two assumptions (i) and (ii) can be verified experimentally, then we propose a method of measurement of the variations of ϕ with T and P_i.

The first assumption (i) can be verified by recording simultaneously the rate of weight increase and the heat flow versus time at constant T by means of a TG-DSC 111 (Setaram). If the two signals can be superimposed, a steady state is really established (Fig.1).

The second assumption (ii) can be verified by experiments in which T or P_i is changed as suddenly as possible (T or P_i jumps). It comes out from equation [1] that if the ratio between the rates before and after the T or P_i change does not vary versus the weight gain (i.e. ξ), assumption (ii) is verified (Figs. 2 and 3).

The experimental method based on sudden jumps may also be used in order to obtain the variations of ϕ with T or P_i. For example, with the corrosion of zircaloy-4 by water vapour, only pressure jumps done after the kinetic transition (see Fig. 3) exhibited an accelerating influence of P_{H_2O} (ϕ was insensitive to P_{H_2O} jumps before the kinetic transition.).

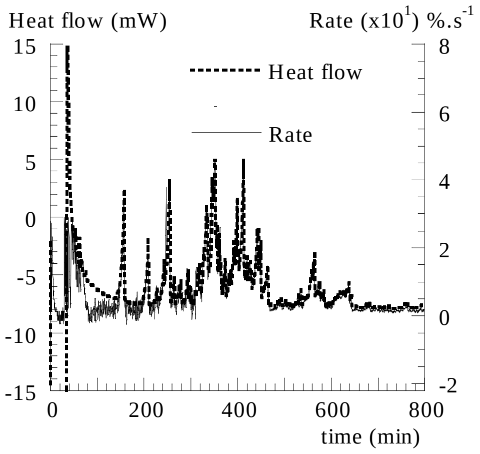

Fig.1. Verification of the steady-state assumption in the case of liquid AlMg5% oxidation by O_2 (200 hPa) at 700°C. (continuous line: weight gain rate).

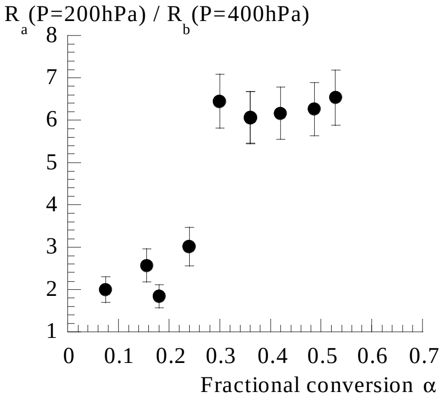

Fig.2. Verification of assumption $d\xi/dt \;=\; n_0\phi.E$ (or “ϕE test”) in the case of liquid AlMg5% oxidation at 700°C.from jumps in O_2 pressure (400 to 200 hPa). The results (two domains of constant ratios) indicate a change in the rate controlling step at $\alpha\approx0.3$.

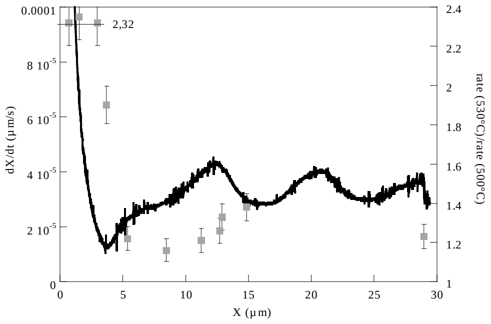

Fig. 3. Same legend than Fig.2 in the case of the corrosion of zircaloy-4 by H_2O (13 hPa) from temperature jumps 500-530°C (continuous line: rate of thickness increase). The results show that the rate limiting steps before and after the kinetic transition (near 3.5 µm) are different.