Research Article

Simulation of high-temperature zirconium alloy oxidation in a nitrogen, oxygen and steam mixture[*]

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Abstract

The paper presents a correlation model of high-temperature zirconium alloy oxidation in a mixture of gases (steam, nitrogen and oxygen) for the weight gain calculation of the oxidized sample. The essence of the model consists in using the linear interpolation between the kinetic constants of oxidation in pure gases to describe the oxidation kinetics in gas mixtures. The approach allows one to describe the oxygen weight gain with different contents of gases in steam, nitrogen and oxygen mixtures. The model was validated against experimental data on oxidation in an air-steam mixture in a proportion of 50% to 50% of the volume. For temperatures of 1200 °C and 1400 °C, prior to the 625th second, the deviation between the experimental data and the simulation results is not more than 18%; for 800 °C, prior to the 14th hour, the deviation between the experimental data and the simulation results is not more than 40%. Besides the air-steam mixture, the paper presents the results of the weight gain calculation using the proposed model for oxidation in an oxygen-nitrogen mixture and in a steam-oxygen mixture at 800 °C and 1400 °C.

Keywords

zirconium alloy oxidation, gas mixtures, correlation model

Introduction

In conditions of design-basis and beyond-design-basis accidents in pressurized water reactors and spent fuel pools, as well as in RBMK reactors, there is a challenging issue of high-temperature oxidation of zirconium alloys leading to the generation of a large amount of heat and hydrogen. Experimentally, oxidation of zirconium alloys in a steam environment has been studied in reasonable detail both in Russia and in other countries. Normally, a mixture of a chemically active gas with an inert gas is used in experiments, which makes a part of the experimentation methodology. Inert gas, however, do not cause any major changes to the oxidation kinetics, so the mixture in question will be considered hereinafter as pure gas. Correlation models of oxidation in steam, air and oxygen have been developed for pure gases. Much fewer papers deal however with investigation of oxidation in mixtures of chemically active gases. No correlations can be found in the open literature that take into account fractions of chemically active gases in the oxidizing mixture. This paper proposes an approach to simulation of oxidation in a mixture of steam, oxygen and nitrogen based on a combination of correlations for oxidation in pure gases.

Model description

Oxidation of the zirconium alloy sample surface under the action of the environment, consisting of chemically active gases such as steam and air, or under the action of an aqueous environment leads to a multiphase structure formed within the sample. The phase boundaries are intricately shaped but, on the average, are parallel to the oxidized sample surface plane. Zirconium oxide, ZrO_2, is formed on the outside, followed by α-phase formed beneath it, oxygen-stabilized α-Zr(O), and further the zirconium β-phase with a variable oxygen content depending on depth. Some studies identify the ZrO phase (Kim et al. 2021) between ZrO_2 and α-Zr(O). There are no, however, explicit experimental data to prove it to exist. Still, an abrupt jump in the concentration on the boundary between the ZrO_2 and α-Zr(O) phases is attributed exactly to the existence of a thick ZrO layer highly resistant to diffusion.

In high-temperature conditions, prior to the loss of the phase structure integrity, the oxidation kinetics obeys the parabolic law. The phase structure integrity means the absence of cracks and delamination in the oxidized layer capable to accelerate the surface oxidation process. In other words, the parabolic law is observed prior to the kinetics breakaway (breakaway effect). The parabolic law for isothermal oxidation is written as follows

$$\frac{dm_O^2}{dt} = k, \tag{1}$$

where m_O is the specific mass of oxygen in the sample or, alternatively, weight gain in $[kg/m^2]$ units, and k is the reaction rate constant in $[kg^2/(m^4 \cdot s)]$ units. It has been shown experimentally that the Arrhenius law can be applied with a good accuracy for the reaction rate constant

$$k = Ae^{-\frac{B}{T}}, \tag{2}$$

where A $[kg^2/(m^4 \cdot s)]$ is the pre-exponential coefficient and B $[K]$ is the activation energy that are found experimentally.

To describe the oxidation kinetics in a mixture of oxygen and nitrogen, it has been proposed to use a linear interpolation of the mixture reaction rate constant, $k_{O_2\text{-}N_2}$, based on the volume fraction of nitrogen between the oxygen reaction rate constant for oxygen, k_{O_2}, and the oxidation reaction rate constant for air, k_{air}

$$k_{O_2\text{-}\mathbb{N}_2} = k_{O_2} + \frac{x(k_{air} - k_{O_2})}{x_{N_2}}, \tag{3}$$

where x is the volume fraction of nitrogen in an oxygen-nitrogen mixture, and $x_{N_2} = 0{,}78$ is the volume fraction of nitrogen in air. When the ideal gas approximation is used, the volume fraction in normal conditions is equal to the molar fraction, and, hence, to the ratio of the partial pressure of nitrogen to the total pressure of oxygen and nitrogen in the preset conditions. The proposed method allows, therefore, taking into account a more aggressive action of the environment in terms of corrosion in conditions of the nitrogen concentration growth, since the reaction rate constant, $k_{O_2\text{-}N_2}$, increases as the nitrogen concentration grows. To a certain extent, as noted in Gestin et al. 2019, nitrogen is the oxidation process catalyst. Hence, it is important that models take into account the effect caused by nitrogen.

When the volume fraction of nitrogen exceeds $x > x_{N_2}$ in a mixture of nitrogen and oxygen, the use of extrapolation may fail to reflect the reality, since high concentrations of nitrogen do not lead to its weight gain increase changing greatly the oxidation kinetics. Due to this, with $x > x_{N_2}$, $k_{O_2\text{-}N_2}(x_{N_2}) = k_{air}$ may be adopted for the reaction rate constant.

To calculate the reaction rate constant, k_{mix}, for the oxidation reaction rate in a mixture of oxygen, nitrogen and steam, the steam fraction, a_{steam}, and the oxygen/nitrogen mixture fraction, $a_{O_2\text{-}N_2}$, in a steam, nitrogen and oxygen mixture are taken into account:

$$k_{mix} = a_{steam}k_{steam} + a_{O_2-N_2}k_{O_2-N_2}, \tag{4}$$

where k_{steam} is the oxidation reaction rate constant in pure steam.

Noteworthy is that, with inert gases present in the oxidizing atmosphere, their fraction is not taken into account in the reaction constant calculation. This is evidenced by experimental studies, e.g. Steinbruck and Bottcher 2021, which show that that the presence of inert gases in tolerable amounts does not have a major effect on the oxidation process. In an experimental study, therefore, oxidation, e.g. in pure air, means oxidation in a mixture of air and inert gas. Naturally, the oxidation process will slow down with very small concentrations of chemically active gases in an inert gas. This requires allowances to be introduced to take into account the fraction of inert gases, while these effects are beyond the scope of this paper.

A drawback of the considered approach to describing the oxidation reaction rate constant in a mixture of gases is that it does not make it possible to take into account the oxidation kinetics acceleration with the nitrogen fraction growth in a steam-nitrogen mixture, that is, when there is no oxygen component altogether. However, it has been shown experimentally that the presence of nitrogen in steam leads to the kinetics acceleration (Steinbruck et al. 2017). The effect is essentially nonlinear, since the nitrogen weight gain, in the event of large nitrogen concentrations, leads to a drop in the oxidation rate while the weight gain in the nitrogen content, in the event of small nitrogen concentrations, leads to a growth in the oxidation kinetics.

The approach considered can also be used to calculate the reaction rate constant in the event of linear oxidation kinetics

$$\frac{dm_o}{dt} = k. \tag{5}$$

It is possible to construct, as discussed, the reaction rate constant for the oxidation kinetics of the same order. Thus, for example, oxidation by steam under low temperatures can be of a cubic nature while oxidation by air at the same temperature is parabolic. More complex models need to be built to describe oxidation of such a nature. As the "breakaway' effect occurs, that is when the layer integrity is lost, the acceleration of oxidation takes place for all components. In this case, no oxidation can have linear kinetics for one component and parabolic kinetics for another.

Simulation of oxidation in a mixture of gases

To simulate the oxidation process using the method under consideration, correlation Leistikow and Schanz 1985 was chosen for high-temperature oxidation in steam, correlation Uetsuka and Hofmann 1985 for oxidation in oxygen, and correlation Stempniewicz 2016 for oxidation in air. There are multiple correlations for oxidation in steam while computations show that it is the correlation discussed that has been studied to the greatest extent. This correlation performs well enough in a broad range of temperatures for different alloys.

Fig. 1 presents the result of simulating an experiment for the oxidation of Zircaloy-4 alloy under different temperatures in a mixture of steam and air in a ratio of 50% to 50% of the volume.
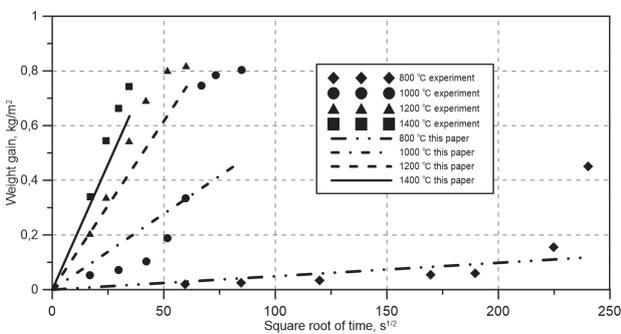
Figure 1. Simulation results versus experimental data Steinbruck 2009 for oxidation in a mixture of steam and air in a ratio of 50% to 50% (vol.).

Simulation gives for a good fit between the calculation results and experimental data at the initial oxidation stages in a mixture of steam and air: for temperatures of 1200 °C and 1400 °C, until the time point of 625 s, the experimental data differ from the calculated values by not more than 18%, and for 800 °C, until the time point of 14 h, the experimental data differ from the calculated values by not more than 40%. Rather a high percentage of deviation for 800 °C is explained by the small weight gain values in terms of absolute quantity. For 800 °C, until the time point of 14 h, the oxidation kinetics accelerates

which evidences of its breakaway (breakaway effect). Specific for high temperatures of 1200 °C and 1400 °C, after the time point of 625 s, is a certain downward bias in the calculated results against the experimental data, and it can be seen from the curve nature that the experimental points fail to agree with strictly parabolic kinetics.

It should be noted that the proposed approach leads to rather an accurate description of the experimental data with small times: for temperatures in excess of 1200 °C, until the time point of $\approx$ 290 s, and for 800 °C, until the time point of $\approx$ 3600 s, experimental points lie practically on the theoretical curve.

The most difficult problem for simulation is to describe oxidation of zirconium alloys at 1000 °C, since the kinetics behavior at this temperature has a complex nature. A possible explanation is the existence of a transition zone at the phase diagram of zirconium alloys including both α- and β-phases. Nonspecific behavior of the Zircaloy-4 oxidation kinetics in steam at 1000 °C was observed in experimental study Leistikow and Schanz 1985, where, after a particular time point, a marked deviation from parabolic kinetics took place, which required additional investigations as part of the study. A temperature of 1000 °C stands apart in the oxidation kinetics for the E110 and E125 alloys as well. It is noted in experimental study Asmolov et al. 2013 that it is exactly at temperatures of 900 °C to 1000 °C that the E110 and E125 oxidation kinetics in steam differs greatly.

To illustrate the growth in the oxidation kinetics with the change in the steam and air component ratios in a mixture, Fig. 2 presents dependences of the weight gain for 800 °C, accumulated for 12 h of oxidation, in an assumption that there is no breakaway effect within the preset time interval.
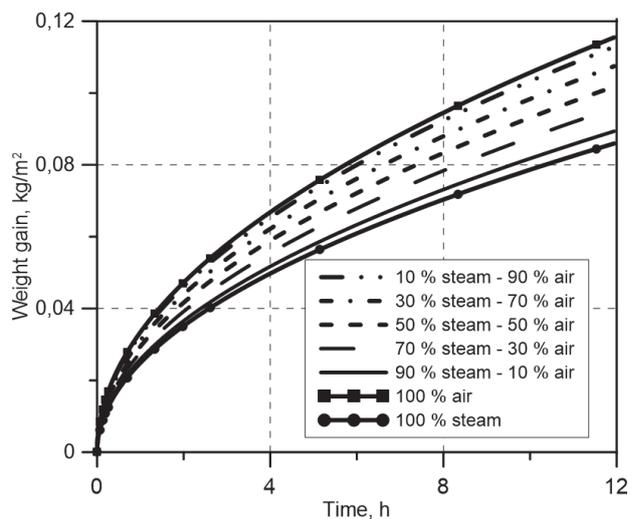
Figure 2. Weight gain behavior for oxidation in mixtures with different steam and air ratios at 800 °C.

It can be seen from Fig. 2 that the air content growth leads to the kinetics acceleration. As of the time point of 12 h, the relative difference between the adjoining weight

gain curves, in the event of mixtures, is 5 to 7% with a greater difference with smaller contents of air with a 20% increase in the steam content.

Fig. 3 presents the dependence of the weight gain on the oxidation time for a mixture of oxygen and nitrogen at different temperatures. There are not data on the weight gain measurement for such conditions in open literature. The calculation results obtained using the proposed model may serve a guide in the kinetics of oxidation in this mixture with different ratios of components.

Noteworthy is how markedly the oxidation rate changes as the content of nitrogen in the mixture grows. And with oxygen fraction increasing, the more oxygen fraction is in the mixture, the less oxidation rate increase occurs. By the time point of 12 h at 800 °C, as well as by the time

point of 15 min at 1400 °C, the weight gain during oxidation in air exceeds by about a factor of three the weight gain during oxidation in oxygen.

The model also makes it possible to describe the kinetics of oxidation in a mixture of steam and oxygen in the absence of nitrogen. Fig. 4 presents the calculation results for such mixture with different contents of components for different temperature with no comparison against experimental data, since there are no such data in the open literature.

Among the gases considered, the weakest oxidation kinetics is observed for pure oxygen. Oxidation is faster with the growth in the steam content in a steam-oxygen mixture. By the time point of 12 h at 800 °C, and by the time point of 15 min at 1400 °C, the weight gain during oxidation in steam and oxygen differs by about a factor of two.
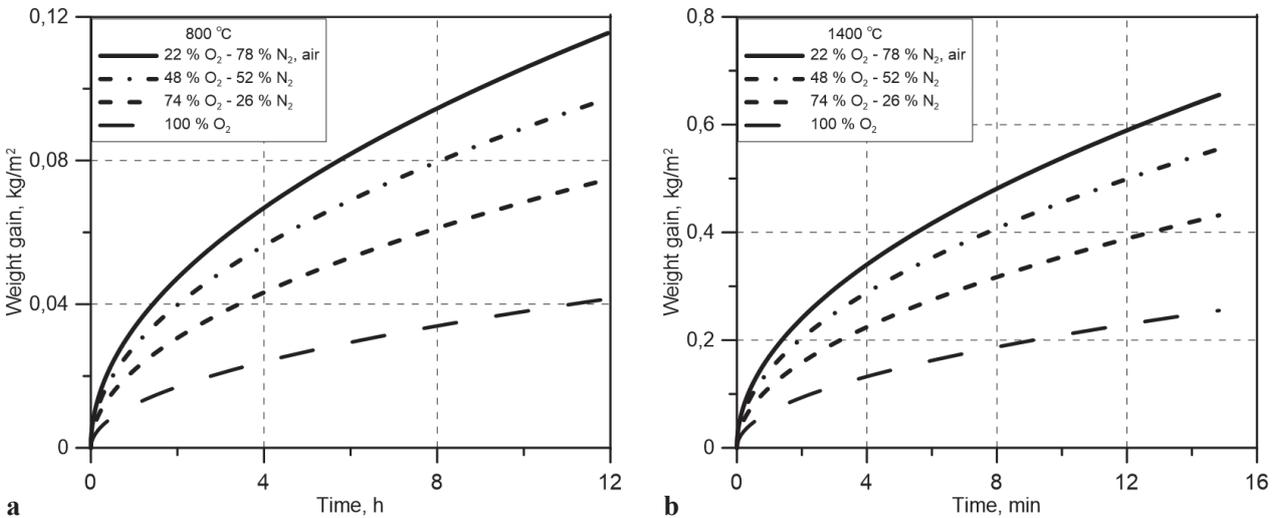
Figure 3. Weight gain behavior for oxidation in mixtures with different oxygen and nitrogen ratios at **a.** 800 °C and **b.** 1400 °C.
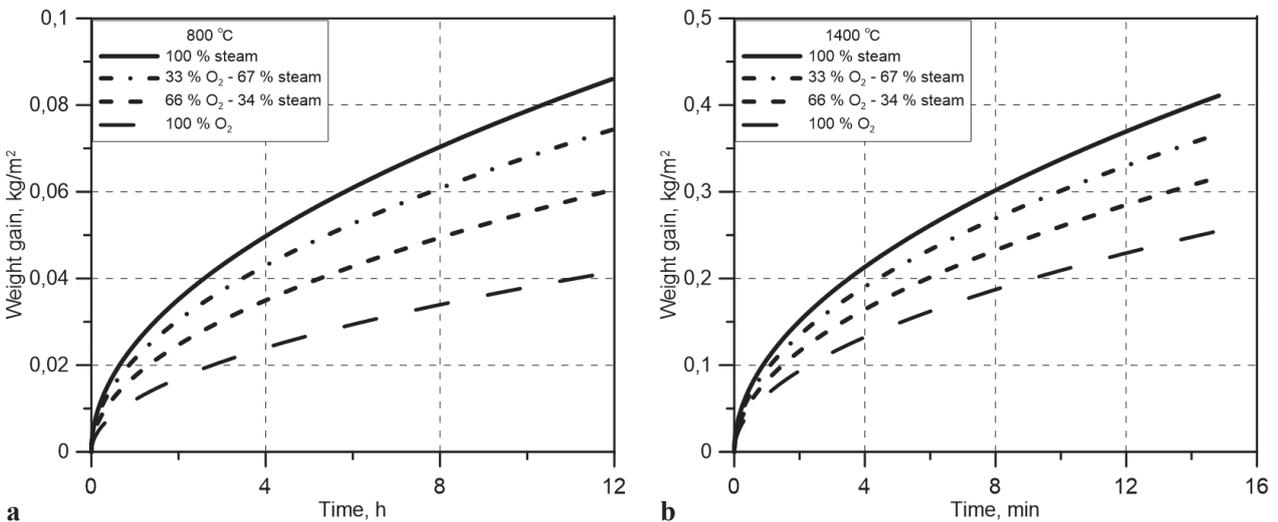
Figure 4. Weight gain behavior for oxidation in mixtures with different steam and oxygen ratios at **a.** 800 °C and **b.** 1400 °C.

Conclusions

The paper presents a correlation model of the oxidation kinetics in mixtures of chemically active gases, such as steam, oxygen and nitrogen. A comparison of the cal-

culated weight gain data based on the presented model with experimental data on oxidation in a mixture of air and steam makes it possible to conclude that, with small times, the proposed approach allows an exact description of oxidation in the above mixture. With reduced

temperatures (800 °C) and longer times, the model leads to a somewhat high result as compared with the experimental values, and there is a downward bias observed for the calculation curve at higher temperatures (> 1200 °C). The most complex description of the oxidation kinetics is at 1000 °C, which can be explained by this being within the transition zone in the zirconium alloy phase diagram. Calculations are presented for nitrogen-oxygen mixtures, as well as for steam and oxygen without comparing their results against the experimental data, since there are no such data in the open literature. However, the model can serve a sort of a guide when estimating the behavior of oxidation for such mixtures.

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