AGH University of Science and Technology
Faculty of Materials Science and Ceramics
Department of Physical Chemistry and Modelling

**Fundamentals of High Temperature Corrosion**

**Temperature and Pressure Dependence of the Oxidation Rate of Metals**

## GOAL

The goal of the exercise is to determine the kinetic law according to which copper oxidation takes place, as well as temperature and oxidant pressure influence on the oxidation rate, and to determine the activation energy of the process carried out in isobaric conditions.

## INTRODUCTION

Basically, all metals subjected to oxygen-containing environments will undergo an oxidation reaction and form their respective oxides. In most cases, the reaction product is a solid and deposits itself on the surface of the reacting metal. If this process proceeds under the effects of a high temperature, then we classify this as high-temperature (or gas) corrosion. Gas corrosion has a special significance in the case of thermal devices, which include all types of engines that operate at increasingly higher temperatures, in aggressive combustion gas atmospheres. Therefore, researching, among other things, oxidation process rates are especially important for designing machines and selecting materials foreseen for high-temperature operation.

Currently, the most popular way of studying high-temperature oxidation kinetics is to use the thermogravimetric method, which consists of measuring the mass change of a studied metal sample as a function of time in selected thermodynamic conditions. In the case of oxides, these types of studies can now be carried out with great precision thanks to the possibility of using modern, automatic thermobalances that enable continuous measurement of sample mass changes at a high temperature under a selected oxygen pressure with accuracy the order of $10^{-7}$ g. Such great measurement precision allows for studying even very slow oxidation reactions. The sample mass gain is registered by a microthermobalance, in the case where the forming scale is a solid, does not evaporate or spall off the metallic core. This mass gain is equal to the mass of the oxidant that bonds with the metal to form the reaction product. Depending on the type of metal and thermodynamic conditions, in which the oxidation

reaction takes place, the procedure of the process can be described by several kinetics laws. The most common are the: linear, parabolic, cubic, exponential, logarithmic and inversely logarithmic rate laws. During oxidation kinetics studies performed on a given metal, the fundamental task is to determine the kinetic law, according to which the metal oxidation takes place, as well as the reaction rate constant for the process, and also analyze the influence of factors such as temperature and oxidant pressure.

Because the oxidation rate depends to a large degree on temperature, in the temperature region in which a given kinetic law is maintained, the correlation between reaction rate and temperature can be described by the Arrhenius equation. The activation energy determined by measurements of kinetics is the activation energy of the slowest partial process that determines the scale growth rate. Thus, in the case of e.g. a parabolic oxidation process, this value denotes the activation energy for the diffusion of components that take part in the scale formation reaction.

## PERFORMING THE EXERCISE

**Note: during this exercise, be especially careful due to the high temperature (inside the furnace and its casing).**

The idea behind this exercise is to determine copper oxidation kinetics in air atmosphere, the correlations between the oxidation rate and temperature and partial oxidant pressure, as well as the process activation energy. In order to carry this out, oxidation of a copper sample must be performed in three temperatures selected by the laboratory instructor. Before this, purify the sample from organic impurities, determine its initial mass and surface area. The studied sample will be oxidized without interrupting the process in three subsequent temperatures (750, 800 and 850ºC), changed abruptly in intervals chosen by the laboratory instructor (e.g. every 40 minutes). During oxidation, sample mass changes will be continuously registered by using an automatic microthermogravimetric apparatus.

After the sample is oxidized at the highest temperature, studies on the influence of oxidant partial pressure on the copper oxidation rate must be carried out. In order to perform this task, while maintaining a constant temperature of 800ºC, modify the oxidant pressure value by changing the settings on the flowmeters that control the gas flow throughout the

reaction chamber of the apparatus. The parameters for the settings are chosen by the laboratory instructor.

After finishing the oxidation process, stop the measurement of mass change in the Labweigh program, lower and turn off the furnace. After the reaction tube cools down to room temperature stop the gas flows. Measurement results are saved in .dat files.


**ELABORATION OF RESULTS**


In order to determine the reaction kinetics, for each oxidation stage (in increasingly higher temperatures), prepare a table according to the one provided below (tab.1.).


Tab. 1. Comparison of data for elaboration of metal oxidation kinetics measurements at high temperatures.

| $t$ [s] | $m$ [mg] | $\Delta t$ [min] | $\Delta m$ [g] | $\Delta m/q$ [g·cm$^{-2}$] | $\log t$ [-] | $\log (\Delta m/q)$ [-] | $(\Delta m/q)^2$ [g$^2$·cm$^{-4}$] |
|---|---|---|---|---|---|---|---|
| | | 0 | 0 | | | | |
| | | ... | ... | | | | |

note:

$\Delta m = m - m_0$

where: $m_0$ – initial sample mass.


„$t$" and „$m$" columns contain experimental data: reaction time and mass registered by the thermobalance, respectively. On the basis of the results listed in the previously prepared tables, first draw the correlation $\log (\Delta m/q) = f(\log(t))$ (where: $\Delta m/q$ – sample mass change per unit area, $t$ – duration of the process). If a straight line is obtained, then the value of the exponent $n$ in the equation below can be calculated:

$$\left(\frac{\Delta m}{q}\right)^n = k_n{''} \cdot t + C$$

assuming that C = 0. If the calculated $n$ values are approximatly 2, determine the $k_p$ value for each series of measurements carried out at a constant temperature. In order to do this, present the results in the following plot: $(\Delta m/q)^2 = f(t)$ and calculate $k_p$ from the tangent of the inclination angle of the straight line. After calculating the $k_p$ values from the three experiments, determine the activation energy of the oxidation process from the tangent of the

inclination angle of the straight line in the plot *log $k_p$ = f(1/T)*, where *T* denotes temperature in K.

In order to determine the influence of oxidant partial pressure on oxidation reaction rate similar considerations as those above must be carried out, but this time based on data obtained at 800°C for several oxygen pressure values.

**Literatura**

1. S. Mrowec, Metal Oxidation Kinetics and Mechanism, Katowice 1982.
2. N. Birks, G.H. Meier, F.S. Pettit, Introduction to the high-temperature oxidation of metals. Second edition. Cambridge University Press 2006.