AGH University of Science and Technology
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Fundamentals of High Temperature Corrosion

# Determination of the chemical diffusion coefficient of predominant point defects in oxides

## GOAL

The aim of this exercise is to get acquainted in practice with the research methodology used to determine the chemical diffusion coefficients of defects in metal oxides/sulphides exhibiting a deviation from stoichiometry.

## INTRODUCTION

Solid-state products of the reaction between a metal and oxidant (e.g. oxygen or sulphur vapours), which form the so-called scale that protects the metallic substrate against progressive destruction caused by high-temperature corrosion, should effectively isolate the substrate from the oxidant. Unfortunately, as a result of the scale-forming compounds demonstrating point defects in their crystalline structures due to lattice diffusion occurring at high temperatures, one or both reactants can be transported through this layer at a rate sufficient for further oxidation and, consequently, further destruction of the metallic substrate. From this it follows that mass transport in a metal-scale system is inextricably linked to the presence of point defects in the scale-crystalline lattice and their migration, the driving force of which is their concentration gradient. This process is called chemical diffusion, whereas the chemical diffusion coefficient is a direct measure of defect mobility in thermodynamic non-equilibrium conditions. Thus, in high-temperature corrosion studies, as well as physicochemical property investigations of oxides and sulphides at high temperatures, determining the degree of deviation from stoichiometry and the mobility of predominant defects is of fundamental importance. In the case of oxides (or sulphides) exhibiting a deviation from stoichiometric composition, this coefficient can be determined from the kinetics of sample mass change during transition from one equilibrium state to another.

One of the experimental methods used in these studies is the so-called re-equilibration method. The idea behind this method lies in the fact that, in the first stage of the experiment, a sample demonstrating deviation from stoichiometry, e.g. in the direction of real metal deficit (which means that the predominant disorder is observed in the cation sub-lattice, in the form of metal vacancies and can be represented by the formula: $Me_{1-y}X$ ), is heated at a given temperature under a predetermined oxidant partial pressure until thermodynamic equilibrium is achieved. In this state, the mass of the sample does not change. This means that a specific concentration of point defects in the sample and, subsequently, a specific deviation from stoichiometry, y, has been established. Then, the oxidant pressure in the reaction chamber is rapidly modified. As a result, the mass of the sample will also change gradually. This change, occurring as a function of time, is possible to register with the help of an appropriately sensitive microthermogravimetric apparatus. If the oxidant pressure was lowered, a reduction process will occur, resulting in a gradual loss of sample mass caused by oxidant transport to the gas phase. In the case of a $Me_{1-y}X$ compound, the electrons and cations released in this process will fill up electron holes and cation vacancies, respectively. Between the surface of the sample and its interior, a concentration gradient of electronic and ionic defects will be established, which will lead to ambipolar diffusion of these defects towards the surface of the studied material. As a consequence, the defect concentration, i.e. deviation from stoichiometry, will gradually decrease until a new equilibrium is established. When the oxidant pressure is rapidly raised (which will trigger the process opposite to that previously mentioned, i.e. oxidation), oxidant atoms will become bound to the surface of the sample by electrons and cations diffusing from the interior of the crystalline lattice. This will create an equivalent number of electron holes and cation vacancies inside the crystalline lattice of the investigated compound. As a result, the mass of the sample and hence the defect concentration (deviation from stoichiometry) will gradually increase.

In the case of compounds exhibiting real metal excess ($Me_{1+y}X$), i.e. when the predominant defects are interstitial cations and quasi-free electrons, the opposite situation is observed. During the "reduction" process (under reduced oxidant partial pressure), deviation from stoichiometry will increase, because the released cations and electrons will occupy interstitial positions. In the "oxidation" process, cations and electrons will diffuse from their interstitial positions towards the surface of the sample, taking up the correct lattice positions. As a consequence, deviation from stoichiometry of the material will decrease.

Oxidation and reduction processes occurring in compounds exhibiting predominant disorder within the anionic sub-lattice can be described the same way as above. Reduction of a compound demonstrating real oxidant excess ($MeX_{1+y}$) will lead to a decrease in defect concentration (interstitial anions and electron holes), and thus to a decrease in non-stoichiometry - as in the case of compounds exhibiting real metal deficit ($Me_{1-y}X$). On the other hand, the oxidation process will lead to an increase in non-stoichiometry. Finally, in the case of $MeX_{1-y}$-type compounds, the reduction and oxidation processes will cause an increase and decrease in the stoichiometric deviation, respectively, which is analogous to the behaviour of crystalline materials demonstrating real metal excess, $Me_{1+y}X$.

The activation energy of chemical reactions is generally much higher than the activation energy of diffusion processes that take place in a solid material. This means that, in the high temperature range, chemical reactions at the solid-gas interface are usually several times faster than solid-state diffusion. Consequently, the mass change rate of a non-stoichiometric compound during oxidation and reduction processes should be controlled by defect diffusion. Therefore, from re-equilibration kinetics, one can calculate the value of the chemical diffusion coefficient, which is a measure of defect mobility in non-equilibrium conditions (when a defect concentration gradient is present). The basic condition for accessing the reliability of the obtained results is to experimentally determine whether, in a particular case, the slowest partial process limiting the re-equilibration rate is diffusion of point defects. Such information can be received by repeating the oxidation and reduction processes under the same experimental conditions, i.e. changing the pressure of the oxidant within the same range, at a given reaction temperature. A lack of hysteresis in the obtained kinetic results and obtaining the same chemical diffusion coefficient values during reduction and oxidation will unequivocally prove that the re-equilibration process is determined by defect diffusion.

Because the process of binding oxidant atoms to the surface of the sample (i.e. the occurrence of a chemical reaction) proceeds much faster than solid-state diffusion, defect concentration in the surface layer of the studied material instantly reaches a new thermodynamic equilibrium. Due to the appearance of a defect concentration gradient, cation vacancies - constantly generated at the surface of the sample - diffuse into the material. As a result, their concentration increases in gradually deeper parts of the sample. The fact that, while in the initial stages of the re-equilibration process, defect concentration only changes in the near-surface layer of the sample, whereas it remains unmodified in the interior of the material, is particularly noteworthy. Then, in the later stages of the reaction, changes occur throughout the entire material.

The following solution to Fick's second law can be applied to interpret the kinetics of the re-equilibration process:

$$\frac{\Delta m_t}{\Delta m_k}=1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2\pi^2\tilde{D}t}{4a^2}\right) \tag{1}$$

where: $\Delta m_t$ – change in the mass of the sample after time $t$, $\Delta m_k$ – total change in the mass of the sample obtained after reaching a new thermodynamic equilibrium, $a$ – half of the sample's thickness, $\tilde{D}$- chemical diffusion coefficient.

The chemical diffusion coefficient can be calculated numerically by applying equation (1) to the obtained experimental results. However, this equation can be reduced to a simpler form by taking into account only the first part of the sum on the right side of the expression, i.e. for n = 0.

$$1-\frac{\Delta m_t}{\Delta m_k}=1-\frac{8}{\pi^2}\exp\left(\frac{-\tilde{D}\pi^2 t}{4a^2}\right) \tag{2}$$

The calculation results obtained by both the first and the second method remain consistent for longer experimental durations, after a new oxidant pressure is set. Practically identical chemical diffusion coefficient values can also be obtained in an easier way using the logarithmic form of equation (2):

$$\log\left(1-\frac{\Delta m_t}{\Delta m_k}\right)=\log\frac{8}{\pi^2}-\frac{\pi^2\tilde{D}t}{4\cdot 2.303\,a^2} \tag{3}$$

assuming that $\tilde{D}t/a^2>0.2$.

Mass change measurements performed on the tested material, obtained during the re-equilibration process and presented in a semi-logarithmic system of coordinates as a function of time, will follow a straight line. The chemical diffusion coefficient can then be determined from the inclination angle.

## PERFORMING THE EXERCISE

### The re-equilibration method

The sample indicated by the instructor should be measured (thickness), weighed on a laboratory scale, and then placed in a thermogravimetric apparatus. Next, the apparatus must be reset (setting initial registered sample mass as 0) and calibrated. Begin heating the furnace to a given temperature and introduce an atmosphere with a specified oxidant partial pressure (also indicated by the instructor) into the reaction chamber. Heating should be performed until the studied sample achieves a constant mass. In accordance with the assumptions of the re-equilibration method, perform a series of changes concerning the oxidant partial pressure in the reaction atmosphere introduced into the microthermogravimetric system. Oxidant pressure changes are carried out by selecting appropriate flow rate values for both the oxidizing gas and the inert gas (helium or argon) that mixes itself together with the oxidant in the reaction chamber. Repeat the changes from high to low oxidant partial pressure values several times and vice versa, each time setting the same values as before. All modifications to experimental conditions should be written down in a table, the template of which is shown below.

| Experiment duration [hour: min] | Oxidant set-point [%] | Noble gas set-point [%] | Oxidant partial pressure [Pa, atm] | Reaction temperature [$^oC$] |
|---|---|---|---|---|
| | | | | |
| | | | | |

After the experiment, the degree of non-stoichiometry in the studied compound, as well as the diffusion coefficient of predominant defects, should be determined on the basis of the collected data.

### Determining deviation from stoichiometry

Using the correlation between stoichiometric coefficients in the compound formula $Me_aX_b$, formed under certain oxidation conditions, and the amount of metal and oxidant involved in the reaction, the degree of deviation in stoichiometry can be determined:

$$\frac{m_{Me}/M_{Me}}{m_X/M_X}=\frac{a}{b} \qquad (4)$$

where: $m_{Me}$ – initial mass of the metal (before the reaction), $M_{Me}$ – molar mass of the metal, $m_X$ – oxidant mass bound to the metal during the reaction (equivalent to the increase in sample mass), $M_X$ – molar mass of the oxidant.

Depending on the type of defect present in the investigated compound, the occurrence of non-stoichiometry, y (a±y or b±y), should be taken into account in formula (4). The oxidant mass, $m_X$, should be read from the m = f(t) plot recorded by the thermobalance. As the starting point for determining the weight gain, assume a constant level indicating the mass of the sample before beginning the oxidation process. Mass changes in each subsequent stage of the experiment (oxidation or reduction) should be read in relation to this initial level. Describe the correlation between deviation from stoichiometry exhibited by the studied compound and oxidant partial pressure $y=f\left(\log\left(p_{O_2}\right)\right)$.

## Determining the chemical diffusion coefficient

In order to determine the diffusion coefficient of the predominant defects in the investigated compound, the kinetics recorded as the sample achieves a new equilibrium state during each change in oxidant pressure inside the reaction chamber of the microthermogravimetric apparatus should be used. For this purpose, plots should be prepared for each of the oxidant pressure changes that illustrate the following correlation:

$$\log\left(1-\frac{\Delta m_t}{\Delta m_k}\right)=f(t)$$

based on equation 3. The slope of the line obtained in this semi-logarithmic system of coordinates should then be used to calculate the $\widetilde{D}$ value.

## References

Lectures 4 & 5: Defect structure and transport properties of oxides (http://home.agh.edu.pl/~grzesik/FHTC/04_05_Defect%20structures%20in%20oxides.pdf)