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Early stages of oxidation observed by in situ thermogravimetry in low pressure atmospheres

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ABSTRACT

A highly sensitive set-up for in situ mass-gain measurements during high temperature reaction is presented. By removing the inert gas components of a corrosive atmosphere and keeping the flows and partial pressures of the reactive species constant, the experiment is preformed in a low-pressure environment. A better signal-to-noise ratio which increases sensitivity down to 10 μg/cm^2 is achieved. The random behaviour of the mass-gain signal, caused by turbulences in the gas stream, could be reduced by a factor of 10.

Compared to theoretical simulations, the mass-change during oxidation in binary iron-based model alloys is slower than expected from pure bulk diffusion behaviour.

1. Introduction

High temperature reactions represent a highly important and intensively investigated field of research. Especially for steel industry, a fundamental understanding of oxide formation kinetics during alloy production [1], sheet-manufacture [2–4] or under working conditions of the final workpiece (e.g. turbine blades, and boiler steels for steam power plants [5–7]) becomes essential to invent novel strategies for corrosion protection. Here, the formation and stability of an outer oxide layer hinders further corrosive attack and protects the material from further degradation at elevated temperatures [8–13]. Nowadays, in situ thermogravimetry under well-defined atmospheric conditions, mimicking a large variety of corrosive environments, has proven to be most successful to provide kinetic data for long term exposures of several hours [14,15]. Enhanced throughput by simultaneously measuring several samples in the gas stream [16], measurements in extremely corrosive environments containing sulphur or fluorine [17,18] and the use of thermogravimetry for determining the temperature dependent solubility of gases in metals [19] are reported. Atmospheric turbulences near the sample surface, either caused by high gas flows or rapid sample heating [20,21], lead to an up-and-down motion of the free hanging sample on the thermobalance. As a consequence, the recorded mass change signal of the experiment behaves random (so-called "buoyancy effect"), which limit the applicability of this technique. Hence, short-term annealing cycles of less than 2 min and mass changes during the initial stages of corrosion could not be accessed so far [22]. To overcome this problem, this work represents a novel approach for a highly sensitive in situ thermogravimetry set-up, by just using the amounts of reactive gas species in a low pressure environment. The approach of "substituting" the inert gas by vacuum not only enhances the signal-to-noise ratio but also allows to investigate the initial stages of corrosion due to a drastic reduction of buoyancy effects, caused by rapid heating [23].

2. Experimental

Pure iron and binary cast alloy samples of iron with 1 wt.% Al, Cr, Mn, Si or 0.8 wt.%C were cut into square shaped pieces of 10 mm × 10 mm × 1 mm in size. A small hole was drilled to mount each sample on the quartz hook of the thermobalance (±0.1 μg Microbalance, CI Precision, United Kingdom). All surfaces of the samples were mechanically ground by using grinding papers from 400 down to 2500 grit size to ensure an optimal compromise between sample roughness and the efficiency of sample heating in an infra-red furnace (so-called "optical heating") [24]. Prior to exposure, the samples were ultrasonically cleaned in ethanol and dried in a cold stream of dry air.

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Selective oxidation experiments were carried out at 800 °C for 60 min in an infra-red heated furnace, equipped with a thermobalance, as shown in Fig. 1. For the experiments at ambient pressure, mixtures of $Ar/H_2/H_2O$ (4 vol.% H_2, 1.94 vol.% H_2O; +17 °C dew point) with a total flow of 30 L h^{-1} at 25 °C and 1.4 bar were used, as well as H_2/H_2O (67.6/32.4, v/v; +71 °C dew point) with a flow of 1.5 L h^{-1} at 57–60 mbar in the reaction chamber for the sub-atmospheric pressure conditions. Both gas mixtures possess similar partial pressures and flow of the reactive species in the reaction chamber. Furthermore, the calculated oxygen partial pressure of 1.03×10^{-19} bar O_2 in both atmospheres is sufficient for the formation of all thermodynamically stable oxides underneath an outer scale layer but insufficiently low for the formation of wuestite (2.23×10^{-19} bar O_2 at 800 °C; +23 °C dew point for the $Ar/H_2/H_2O$ atmosphere [25]). After the heat treatment, the furnace was turned off and the samples were left to cool down to room temperature in the flowing gas stream.

An accurate temperature control during the heat treatment was realised by mounting a pure iron sample of identical dimensions and surface preparation on the thermocouple of the furnace in close proximity to the sample alloy on the thermobalance (see Fig. 1). A membrane-type vacuum pump (PC3000 VARIO, Vacuubrand, Germany) was used to evacuate the reaction chamber. A heated bypass valve and the pump valve (both type SS-SS2-D-VH, Swagelok, Germany) were used to regulate the gas flow and total pressure in the reaction chamber, respectively (Fig. 1). Flow calibration curves for the used valve type can be found in Fig. 6a in Appendix A. All process parameters (temperature, gas humidity, mass change, pressure, etc.) were recorded automatically and stored in a protocol file during the heat treatment, by using an in-house written software routine [26]. After exposure, the samples were cross sectioned and investigated by LOM, SEM and EDX. The iron–carbon alloy was etched in 1% HNO_3/ethanol for 15 s to better visualise the carbon-rich phases [20,27].

3. Mathematical modelling

Transport calculations by assuming local chemical equilibrium conditions were used to determine the total oxidation depth and local distribution of stable oxide phases. A detailed description of the method has been given in [28]. Calculations for an ambient pressure decarburisation experiment have already been performed in [20]. A subsequent two-step finite element algorithm was applied to derive (1) element transport by solving the set of diffusion equations for each mobile species (i.e. iron, oxygen and the alloy element), and (2) phase stability, assuming local thermodynamic equilibrium conditions [29,30]. A constant oxygen concentration, depending on the oxygen partial pressure in the reactive atmosphere was used for the boundary conditions at the sample surface. This corresponds to the constant source approach, firstly proposed by Wagner [31]. Insulating boundary conditions for the element transport were set at a depth of 0.5 mm, to account for the expected symmetry of the concentration distributions and mimicking a total sample thickness of 1 mm. The calculation of the diffusion was carried out for small time intervals. The results after each calculation step were used to derive the local concentrations of each phase with the thermodynamic subroutine ChemApp (GTT-Technologies, Germany). The amount of each phase from the equilibrium calculation was set as the starting value for the diffusion calculation in the next time step. After the last simulation step, the results were displayed as a one-dimensional concentration map – similar to a line scan of a cross sectioned specimen – indicating the amount and spatial distribution of each phase.

Results of the thermogravimetry behaviour have been derived by integrating the total amounts of oxide phases MO_y (with y being the stoichiometric coefficient of oxygen) in the sample and converting the molar amounts into the weight gain of the sample per surface area Δm by using the formula:

$$\Delta m = \frac{d}{2 n_{Fe} V^m_{Fe}} M_{oxygen} \sum_{all\ oxides} y \times n_{MO_y} \quad (1)$$

Here, d is the sample thickness, M_{oxygen} the molar mass of oxygen (15.999 g mol^{-1}), n are the molar amounts of the corresponding phases in the calculations and V^m_{Fe} stands for the molar volume of ferrite at 25 °C ($V^m_{Fe} = 7.09 \times 10^{-6}$ m^3 mol^{-1}). Results of the mass change over time are plotted together with the experimental values to better allow for comparisons and to discuss deviations that may be caused by defects and/or grain boundaries in the real sample microstructure.

Carefully selected bulk diffusion values for element transport and the oxygen solubility, used for the calculations, are listed in Table 1.

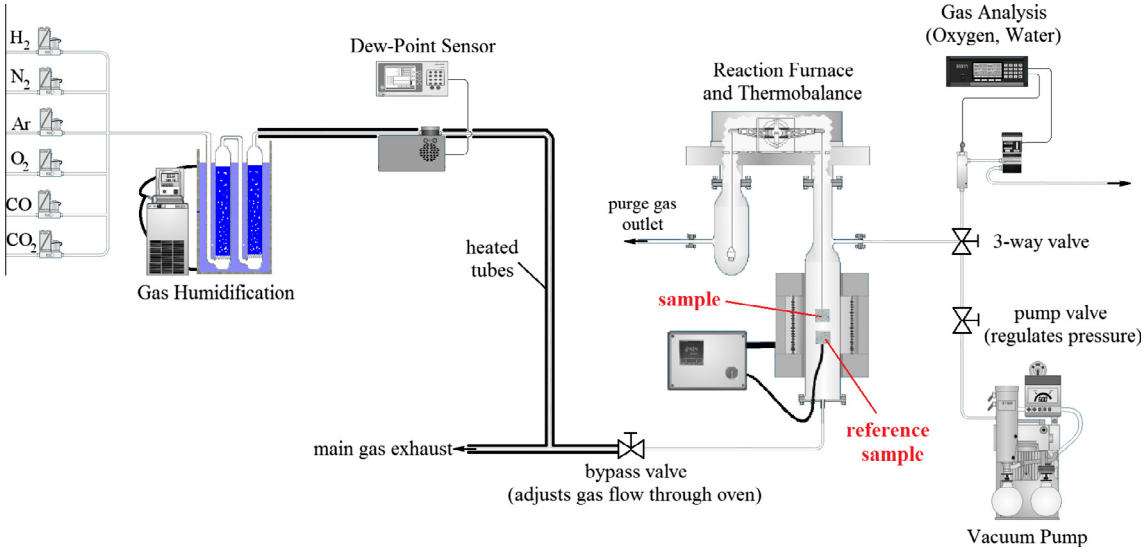

Fig. 1. Schematic picture of the experimental set-up for low pressure thermogravimetry.

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