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Low Temperature Oxidation of pure Iron : Growth kinetics and scale Morphologies

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Abstract. Isothermal oxidation of pure iron has been performed in air at atmospheric pressure between 260°C and 500°C. Growth kinetics are accurately analysed and scale morphologies are investigated by SEM and TEM observations. The calculation of the variations of the parabolic rate constant kp with scale thickness allows a better understanding of scale growth mechanisms involved at this intermediate temperature range, which have been poorly investigated up to now. These results are discussed with the objective of long term behaviour for long term interim storage of some nuclear waste containers.

Introduction

For high level nuclear waste containers in long term interim storage, dry oxidation will be the main degradation mode, because, for this kind of waste, the temperature at the surface of containers will be low (less than 300°C) but high enough to avoid any condensation phenomena for several hundreds of years. Low alloyed steels are some of the candidates for wastes containers [1]. Within the framework of research into the dry oxidation of metallic materials, iron is considered as a model material and is studied at low temperature (below 500°C) and under dry air or air with 2 vol% H_2O which can be considered as the typical atmosphere of the interim storage site. Indeed, iron oxide scales formed at low temperature have been poorly studied [2].

At any temperature below 570°C, at atmospheric pressure, only two iron oxides are stable : hematite (Fe_2O_3) and magnetite (Fe_3O_4). A duplex scale made of an inner magnetite layer thicker than the outer hematite layer is usually reported (Fig. 1).
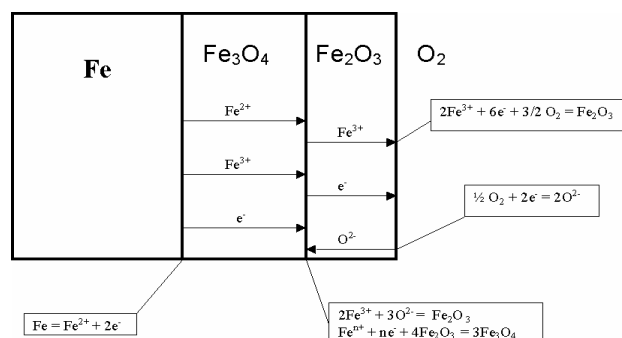

Fig. 1. Iron oxides duplex scale formed below 570°C : interfacial reactions and diffusion [3].

The structure of the magnetite layer favours cationic transport through the scale. However, Fe and O have similar diffusion coefficients in hematite, and it is not clear which species is likely to be rate controlling during film growth [4].

In order to model scale growth over long time, it is essential to characterise the nature, morphology and microstructure of the scales. Particular care has been brought to determine

grain sizes because at these low temperatures grain boundary diffusion could play an important role.

Several experimental means have been implemented. The oxidation tests have been performed in a thermobalance or in a classical furnace under a controlled atmosphere. Then, oxide scales formed have been characterised using SEM, TEM and X-Ray diffraction.

Experimental Procedure

Specimens Preparation. Every sample is taken from an ARMCO pure iron sheet, the composition is given in Table 1. These specimens ($30*10*2$ mm^3) were mechanically polished using 1200 grit SiC paper, then cleaned in alcohol , dried and left for about 3 days in an ambient atmosphere.

Table 1. Composition of pure iron samples used for experiments.

type	C	Mn	Si	S	P	Ni	Cr	Mo	Cu	Sn	Al	N
ARMCO [% weight]	0.001	0.05	0.01	0.003	0.004	0.019	0.013	0.001	0.005	0.002	0.001	0.003

Thermogravimetric Analysis. Oxidation treatments were performed in a "SETARAM TAG 24" thermobalance. The accuracy of this thermobalance is better than 5 µg at all temperatures. Furnace temperatures are controlled using Pt/Pt-Rh 10% thermocouples with an accuracy better than +/- 1 °C. The oxidation tests were performed between 260 and 500 °C under a mixture of dry air and H_2O vapour (2 vol%) flow. Furnace rising temperature speed is 10°C/min under reducing gas flow (He). After stabilization for 2 hours at the test temperature, the oxidant mixture flow rate is fixed at 2.3 l.hr^{-1}. One different test has been performed in the same conditions but using dry air as oxidation gas at the temperature of 400°C.

Oxidation tests in a classical furnace. The furnace design allows the exposure of several samples to a controlled atmosphere at the same time. Specimens are introduced in a quartz tube in a furnace through which a 15 l.hr^{-1} continuous flow of a mixture of air + 2 vol% H_2O. Oxide scales were fractured and their morphologies were investigated using SEM.

Determination of parabolic rate constant k_p. Assuming that the oxide scale growth follows a parabolic law, the parabolic rate constant (k_p) has been evaluated from weight gain measurement by using the most general expression for parabolic kinetics [5]:

$$t = a + b\,\Delta m + c\,\Delta m^2 \tag{1}$$

where Δm is the weight-gain per unit area (mg.cm^{-2}) and t the time (s). In Equation (1), the coefficient c is equal to the reciprocal of the parabolic rate constant k_p (mg^2.cm^{-4}.s^{-1}), independent of the initial condition for integration of the rate equation [5]. Equation (1) could be fitted to the entire set of (t, Δm) data to get a global value of k_p. Moreover, Equation (1) could also be fitted only to a smaller part of (t, Δm) data to determine the instantaneous k_p values, representative of given time or scale thickness interval. Therefore variations of k_p as a function of time or scale thickness could be studied. For this last calculation, the size of the mass-gain interval fit was increased proportionally to the time squared in order to keep a constant noise/signal ratio. Equation (1) could also be fitted on the final part of (t, Δm) data where ($\sqrt{t}$, Δm) is linear, to get the final parabolic rate constant k_p that is used to make a long term provision and to determine the life time of pure iron samples.

Results

Long-time thermogravimetric treatments (about 250 hours) have been performed at four distinct temperatures: 260, 300, 400 and 500°C. All experiments have been done in a mixture of dry air and 2% (vol) H_2O. An additional thermogravimetry analysis has been performed in dry air at 400°C.

Growth kinetics. Fig. 2 compares weight gain per unit area versus time for 2 samples exposed 260 hours at 400°C in different atmospheres : dry air and air with 2 vol% H_2O. In both cases, the curve appears to be parabolic but the oxidation seems faster in dry air.
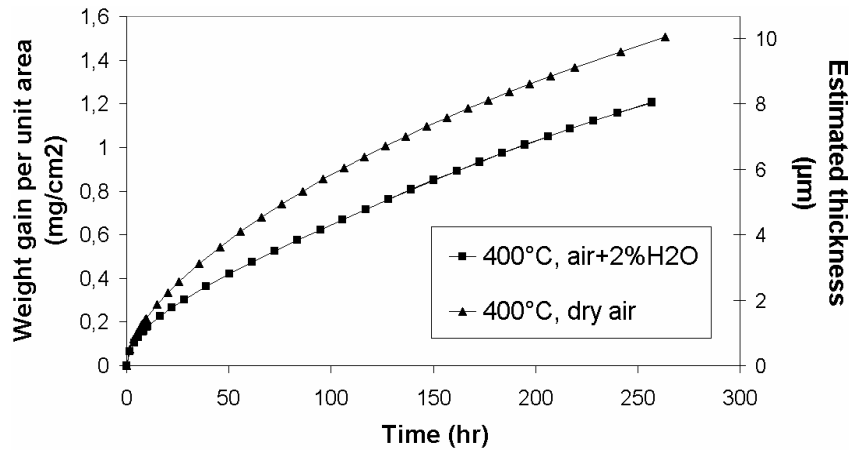

Fig. 2. Weight gain curves obtained during isothermal oxidation at 400°C under two different atmospheres: air + 2 vol% H_2O and dry air.

The evaluation of parabolic rate constant (k_p) is made as described previously. Calculated values after the transitory stage of faster oxidation kinetics are summarised in Table 2. These values are compared with those from the literature in the Arrhenius plot presented Fig. 3.

Table 2. Parabolic rate constants evaluated for iron oxidation at four temperatures and in two atmospheres.

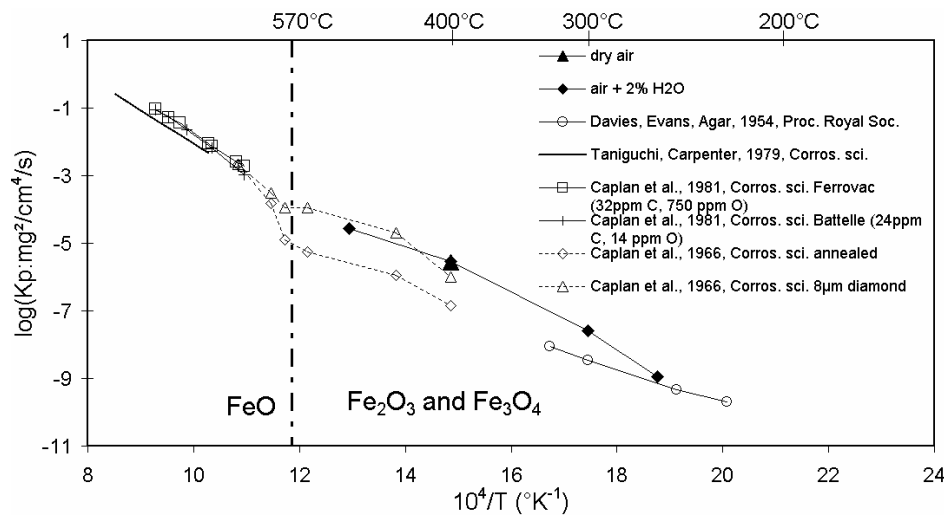| Temperature [°C]	260	300	400	400	500
Duration [hr]	280	260	260	260	28.4
Atmosphere	Air + 2% H_2O	Air + 2% H_2O	Air + 2% H_2O	Dry air	Air + 2% H_2O
k_p [$mg^2/cm^4/s$]	$1.14\ 10^{-9}$	$2.58\ 10^{-8}$	$2.95\ 10^{-6}$	$2.71\ 10^{-6}$	$2.68\ 10^{-5}$

Fig. 3. Comparison of parabolic rate constants as a function of test temperatures (called "dry air" and "air + 2% H_2O") with those from the literature [6, 7, 8, 9].

Even if the weight gain curve of iron oxidation in dry air is higher than the one obtained in air with 2 vol% H_2O, k_p values are close.

Parabolic rate constants obtained in this work are in good agreement with data published by Caplan et al. in 1966 for polished specimens [9] and Davies et al. in 1954 at 260°C[6]. And it seems that annealed specimens lead to slower kinetics between 300 and 600°C. Moreover Davies et al. underline that only their kinetics obtained at 350°C follow a parabolic law.

To assess a basic model for long time prediction based on the extrapolation of mass gains using measured parabolic rate constants [10], the thermogravimetric experiment performed at

300°C has been extended over a 800 hours duration and local k_p analysis proposed in [5] has been used to analyse the mass gain curve (**Fig. 4**).
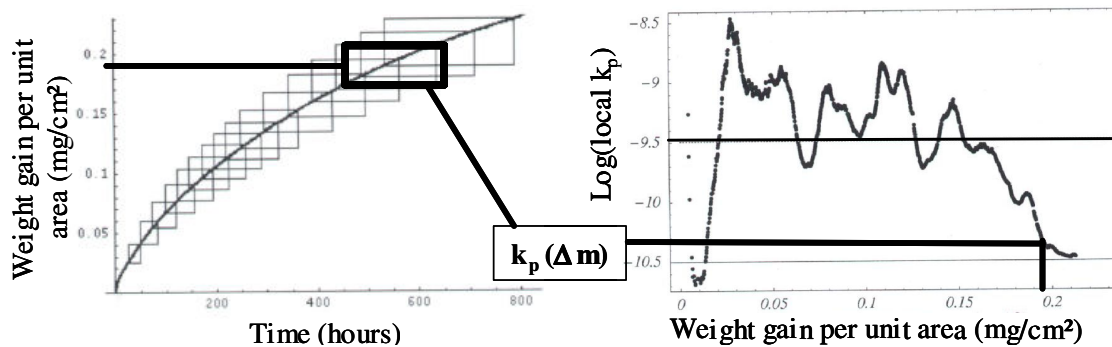

Fig. 4. On the left: weight gain curve during long time isothermal oxidation of iron at 300°C, and on the right: evolution of local k_p versus weight gain.

As can be seen in Fig. 4 during the first steps of the oxidation process, the local parabolic rate constant has a large increase. It could be the effect of the transitory state. Then local k_p oscillates around a global k_p value represented by the horizontal line on the right of Fig. 4. Finally, after about 350 hours, the local k_p decreases.

Such an evolution of the parabolic rate constant could be due to an evolution of cross scale diffusion parameters. That is why it seems very useful to observe oxidized samples and study the evolution of scales morphologies with oxidation temperature and time of exposure to the oxidation gas.

Scale Morphologies.
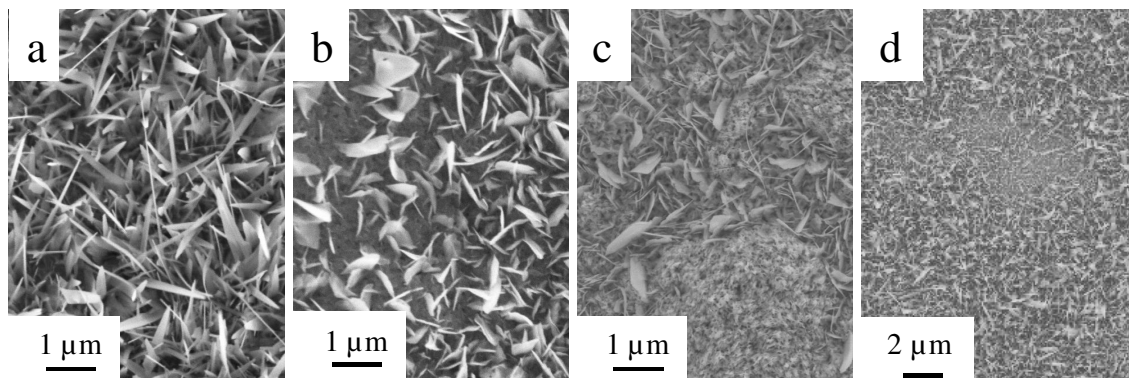
Surface scale morphologies.

Fig. 5. Evolution of iron oxide surface morphology formed in air + 2 vol% H_2O at different temperatures : (a) 300°C, 260hr, (b) 400°C, 260hr, (c) 500°C, 28hr, (d) 300°C, 1000hr.

Fig. 5 shows the evolution of the surface morphology of scales formed at temperatures between 300 and 500°C in air + 2 vol% H_2O. On samples treated at 300 and 400°C in wet air for 260 hours, there are many whiskers all over the surface. Voss and al. have observed such structures on iron oxides and shown the presence of a superdislocation or of a tunnel in some whiskers giving an easier way for cation diffusion to the surface [11]. Moreover, according to Rapp, whiskers formation is favoured in wet atmospheres and at low temperatures because surface diffusion needs to be faster than volume diffusion and oxidant molecule dissociation. Then this dissociation rate controls whiskers growth. At 400°C there are some areas where the whisker density is lower. At 300°C, the whiskers are longer but thinner than at 400°C. Diffraction in a TEM on a specimen oxidised at 300°C for 260 hours has shown that whiskers have a hematite structure [12]. The surface of the scale obtained at 500°C in wet air presents two different morphologies: areas with whiskers as seen at lower temperature, and areas

where crystallites are round-shaped. The observation of a sample oxidized at 300°C for 1000 hours in wet air (Fig. 5(d)) exhibits two different morphologies as seen on sample oxidised 28 hours at 500°C.

The observation of the surface of a specimen oxidized at 400°C in dry air shows that the main difference between the 2 atmospheres (dry air and air + 2 vol% H_2O) at 400°C is the total absence of whiskers on the surface of the scale obtained in dry air.

Microstructure of fractured oxide scales. Some observations of fractured cross-sections of iron oxides formed at 400°C are given in Fig. 6. At 300, 400 and 500°C, whatever is the atmosphere, three-layered scales exhibit three distinct microstructures. Table 3 summarises the microstructural characteristics of each of the three layers for the different specimens.

Both specimens oxidized at 300 and 400°C for 260 hours show columnar grains in the middle of their scales. Even if there is a great difference between the scale thickness, the microstructures are similar, but with a typical grain size of 100 nm at 300°C and of about 200 nm at 400°C. Tests performed at 400 and 500°C allow the comparison of the microstructures of scales of the same thickness despite the different temperatures. In this case, the outer layer is thin (300 to 500 nm) and composed of equiaxed grains. The middle layer is made of columnar grains of about 400 nm diameter showing porosities of about 100 nm in the upper part of this intermediate layer. This is illustrated on Fig. 6(c). The inner scale is composed of smaller columnar grains than the middle layer (Fig. 6(b)).

Table 3. Characteristics of iron oxide scales formed during different oxidation treatments.

	300°C 260 hours air + 2% H_2O	400°C 260 hours air + 2% H_2O	400°C 260 hours dry air	500°C 28.4 hours air + 2% H_2O
Surface morphology	Whiskers	Whiskers	Round crystallites	Whiskers + round crystallites
Outer layer of the scale	Fine grains e~150 nm	Equiaxed grains d~100 nm e~300 nm	Equiaxed grains d~100 nm e~300 nm	Equiaxed grains 100<d<300 nm e~800 nm
Middle layer of the scale	Small columnar grains d~100 nm e~650 nm	Columnar grains Porosity in the upper half part d~300-600 nm e~10 µm	Columnar grains Porosity in the upper half part d~400 nm e~12 µm	Columnar grains Porosity in the upper half part d~500 nm e~10 µm
Inner layer of the scale	Fine grains e~200 nm	Fine columnar grains e~1 µm	Fine columnar grains e~1 µm	Fine columnar grains e~1.8 µm
Scale thickness measured on micrographs	~ 1 µm	~ 10 - 13 µm	~ 13 - 14 µm	~ 11 - 13 µm
Scale thickness estimated from mass gain	1 µm	9 µm	10 µm	14.4 µm

A decohesion between the inner and middle layers has been observed several times on 300 and 400°C oxidized samples. The origin of this phenomenon has not yet been investigated but it does not seem to be due to the fracture of specimens for observation because it has also been observed on polished cross sections. This could happen during the furnace cooling or be due to growth stress during oxide scale growth. An alternative explanation could be an accumulation of vacancies at this particular interface.

At 400°C, contrary to surface morphologies, there is not much difference between samples oxidized in wet or in dry air in scale fracture morphologies.

X-Ray diffraction analyses made on different samples with two incidence angles shows that hematite layer is laying over the magnetite layer. Considering the microstructure of scales and previous studies it seems reasonable that the two inner layers made of columnar grains

are magnetite and that the outer layer made of equiaxed grains is hematite, as verified by diffraction on isolated whiskers.
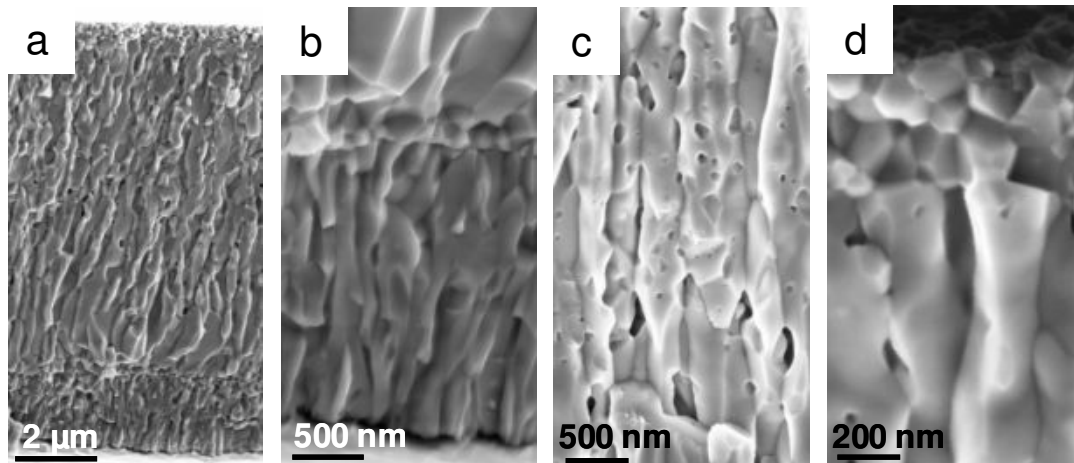

Fig. 6. Fractured cross-section of iron oxides formed at 400°C in 260 hours : (a) global view of the scale, wet air, (b) inner layer, wet air, (c) middle layer, dry air, (d) outer layer, dry air.
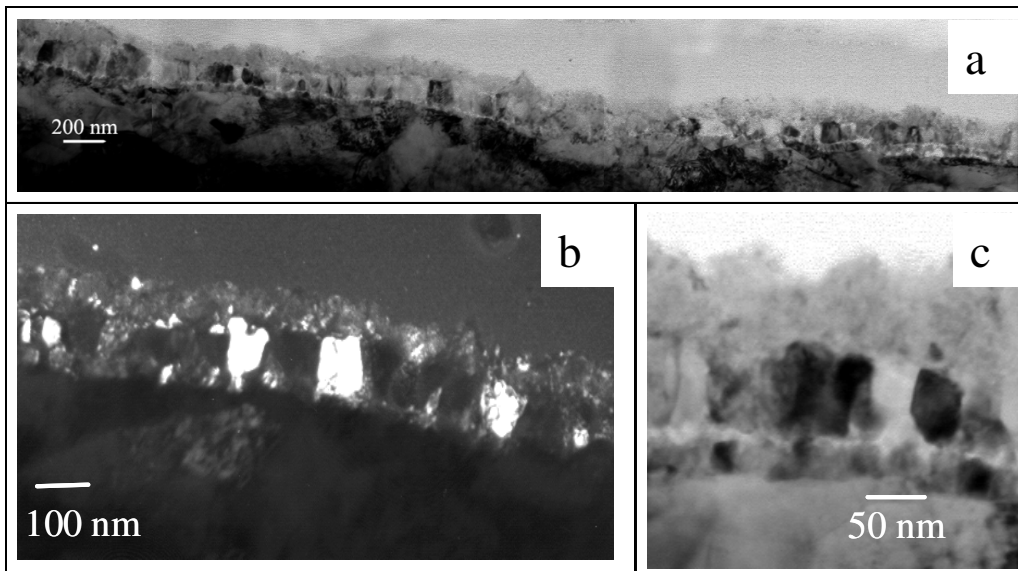
Investigations of thin oxide scale (TEM).

Fig. 7. TEM observations of iron oxide cross-section formed during 96 hours at 260°C.

In order to get an idea of the evolution of oxide scale microstructure as a function of time and temperature, an additional test has been performed at 260°C for 96 hours. Then the oxide scale has been observed in cross-section using a TEM. The morphology of the oxide scale is given on Fig. 7, the oxide thickness is about 140 to 200 nm, divided in three distinct layers. The inner one close to the metal/oxide interface is about 25 to 30 nm thick and composed of fine grains. The second layer is about 50 to 80 nm thick and is constituted of columnar grains. Finally, the external layer is the thickest one (100 nm) and shows very fine grains.

Discussion.

Parabolic rate constants. At the highest temperatures tested in this work, parabolic rate constant evaluations are in relatively good agreement with those presented in the literature, particularly those published by Caplan et al. [9]. Then, the discrepancy with published data at lower temperature may be due to differences in sample preparation. Indeed, Davies' iron samples were annealed before oxidation treatment [6], and that leads generally to slower

oxidation [2, 6]. Moreover, comparisons are difficult because of differences in experiment durations as it has been illustrated previously with the kinetic analysis of the oxidation experiment performed at 300°C for 800 hours.

Scales morphologies. The aim of the experiments was to investigate the evolution of scale morphologies (surface and cross-section) versus time (or total oxide scale thickness) and atmosphere composition. The test performed at 500°C is shorter in order to get the same thickness as the scale obtained at 400°C and to determine the role of temperature. At 400°C, the whole surface of the iron oxide obtained in the mixture of air and 2 vol%. H_2O for 260 hours, is covered by whiskers. At 500°C, the scale surface exhibits two distinct morphologies: whiskers and round-shaped grains. It appears that locally the whiskers are embedded by the growing scale. Thus, it seems that at 500°C, even if the total average thickness is the same as at 400°C, the surface morphology achieves faster a more advanced evolution stage. A quite similar result has been observed at 300°C: the surface oxide formed for 260 hours is also totally covered with whiskers. But, after 1000 hour oxidation treatment, the scale surface exhibits the same morphology as the scale obtained after 28 hours at 500°C.

The only difference observed between surfaces of the sample oxidised at 400°C for 260 hours in wet and dry air is the total covering of the surface with whiskers in the case of oxidation in wet air, and the total absence of these whiskers when the atmosphere is dry. This is in agreement with Rapp [13]: whisker formation is controlled by oxidant dissociation and water dissociation is easier than oxygen dissociation.

At all temperatures, in wet and dry air, and for all scale thickness encountered ranging from 150 nm to 14 µm, the oxide scale is three-layered. The thickest scales are comprised of an inner fine columnar-grained layer, a coarser columnar-grained layer and a thin outer equiaxed-grained layer. A similar description has been previously reported by Chen and Yuen [2] who describe the two inner layers as a duplex magnetite layer. The fine columnar grained layer was believed to form via an oxide dissociation [14]. However, the formation of the hematite equiaxed grained layer is not clear. According to Chen and Yuen, TEM analysis made by Groswami in 1965 [15] revealed that the hematite layer appears at the end of the oxidation process in the following stages: $Fe \rightarrow Fe_3O_4 \rightarrow \alpha\text{-}Fe_2O_3$. On the contrary, Davies et al. published in 1954 results where the hematite layer appeared first and only after a few hours magnetite could germinate and spread locally below the hematite oxide film [6]. From our results, we can only conclude that even in the case of very thin oxide thickness, about 150 nm, a three-layered scale has been observed. Furthermore, this thin scale appears to have similar but finer microstructures to the ones observed on thicker scales. However, the relative thicknesses of the three layers are very different from what can be observed on thicker scales, and this shows that the thin scales formed at lower temperature cannot be simply seen as the reduction of thicker scales formed at high temperature. At higher temperature, it seems that the outer layer composed of equiaxed grains and the inner layer composed of fine grains develop in the early stage of oxidation but they grow much slower than the middle one. For a 1 µm thick scale, the middle layer is already the thickest one but the inner and the outer layers still have important proportions (about ten times the proportion they will have in thick scales). On the thickest scales observed (about 10 µm), obtained at 400 and 500°C, the proportions of the different layers do not seem to depend on the temperature.

Conclusions

Long duration oxidation experiments have been performed on iron at low temperature in dry air and wet air. The parabolic rate constants measured are in relatively good agreement with previous studies and differences have been attributed to the effect of sample preparation (no annealing prior to oxidation). The local analysis of parabolic rate constants made on a very long duration TGA experiment (800 hours) shows that local k_p is not stable and decreases

during the second half part of the experiment. A comparison of iron oxidation in dry air and in a mixture of air with 2% vol. H_2O at 400°C shows that the weight gain is greater in dry air. This phenomenon is probably due to the transitory states because parabolic rate constants are similar. Evolution of iron oxide scale surface morphology has been studied as a function of experiment duration and temperature. The surface of oxide formed in dry air shows no whiskers. At every temperature, oxides obtained in wet air are covered by whiskers but there is an evolution: first, the whole surface is covered and then it seems that the oxide scale grows between the whiskers so that there are two distinct morphologies on the surface of iron oxide scales: whiskers and round-shaped crystallites. Whatever the temperature and the total scale thickness, in wet and dry air, the iron oxide scales are three-layered composed of an equiaxed grained outer layer probably made of hematite, a thick middle layer and a thin inner one, both made of columnar grains forming a magnetite duplex scale. It seems that the two extreme layers develop first, but this must be investigated further.

Acknowledgments

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