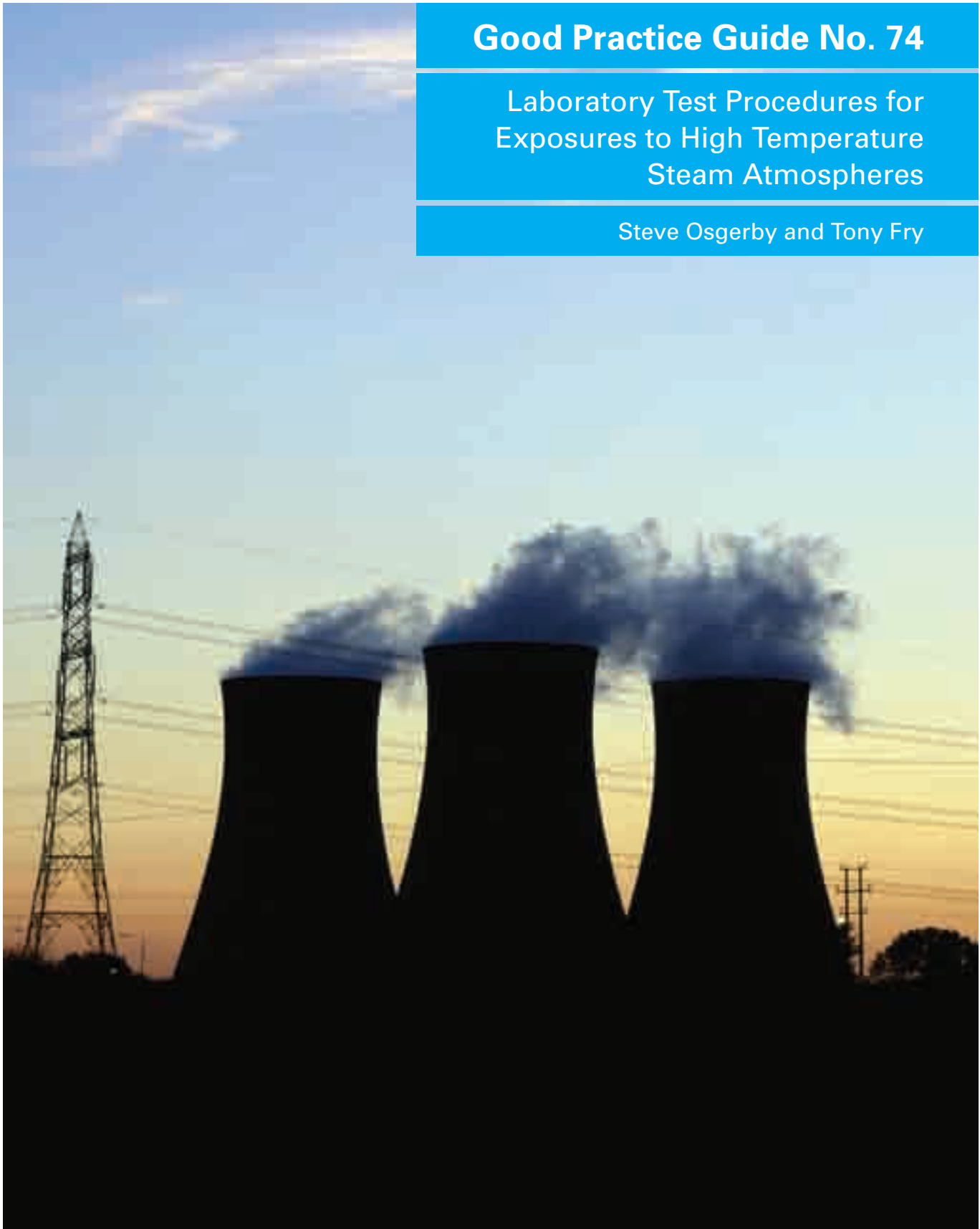


Good Practice Guide No. 74

Laboratory Test Procedures for
Exposures to High Temperature
Steam Atmospheres

Steve Osgerby and Tony Fry



Measurement Good Practice Guide No 74 (Issue2)

Laboratory Test Procedures for Exposures to High Temperature Steam Atmospheres

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Abstract

Laboratory exposures cannot reproduce all the features present in service conditions. The experimentalist is faced with the conflict between increasing the complexity of laboratory tests to replicate service more closely and keeping testing costs low by maintaining a simple procedure. The influence of various experimental parameters, which can be controlled in the laboratory, on the steam oxidation response of materials is discussed and recommendations for best practice are proposed.

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TITLE

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1 Introduction

The oxidation conditions that components experience in service, such as water chemistry, temperature excursions, pressure, heat flux and gas composition, are much more complex than those that can be reproduced in the laboratory. Consequently there is a conflict between performing laboratory exposures in as inexpensive a manner as possible and maintaining relevance to the industrial situation. Thus a key question that needs to be addressed is ‘which experimental/service parameters affect the growth kinetics and microstructure of oxide scales and thus need to be controlled (or at least reported) in laboratory studies’.

The influence of laboratory procedures on oxidation data was previously reviewed by Armitt et al [1] who made the following observations:

1. Oxidation behaviour appears to be insensitive to the direct effects of system pressure.
2. Metal loss rates appear to be unaffected by the impurity content of the steam.
3. Some experimental factors affect the tendency of Cr steels to form protective M_2O_3 scales rather than duplex oxides.
4. Spallation behaviour is particularly sensitive to scale morphology and composition. A good metallographic record is essential.

The importance of controlling laboratory procedures is illustrated by the results of an intercomparison exercise carried out under the auspices of the COST522 collaborative programme in Europe [2]. Specimens from the same batch of P92 alloys were exposed at 600 and 650 °C for 1000 h at 9 different institutes each using their own current procedure. Two institutes carried out the exposures using two different exposure procedures to give a total matrix of 11 different exposure procedures. The results of the intercomparison are shown in Figure 1 where it can be seen that there is a wide variation in the scale thicknesses reported by the different laboratories – 60 to 100 μm at 600 °C and 40 to 240 μm at 650 °C. The differences in exposure conditions between the various laboratories are complex and the resultant scatter in the reported results arises from the summation of numerous individual effects of the exposure procedure on the steam oxidation behaviour.

In this guide the available information on the influence and criticality of each of these parameters on the data generated is reviewed. Analysis of this information allows the best practice for steam oxidation exposures in the laboratory to be proposed.

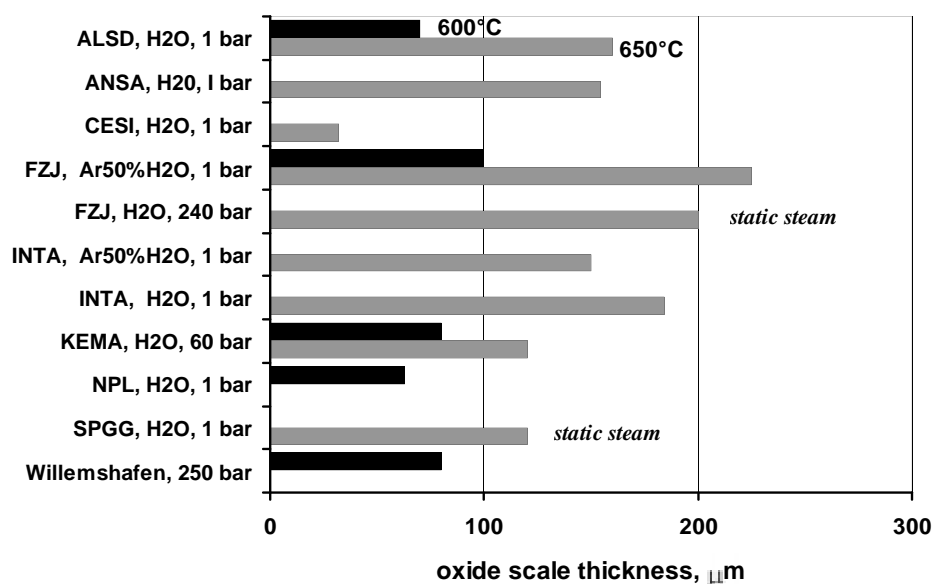


Figure 1 Intercomparison, by several European laboratories, of scale thickness measurement on P92 martensitic steel after exposure to ‘steam’ for 1000 h at 600 and 650 °C (After Ref [2])

2 Influence of Individual Exposure Parameters

As highlighted in the previous section the differences in exposure procedures between any two laboratories can be from a combination of changes in several individual control parameters, or just a change in one parameter. It is therefore important to understand the effect of these individual control parameters on the material response to the steam environment.

2.1 Once-through vs Recirculating Systems

The choice between using a ‘once-through’ or a recirculating steam system is complex and each system has advantages and disadvantages. A ‘once through’ system exhausts the furnace outlet to the atmosphere and is thus experimentally simple. However control of water chemistry is difficult unless a large reservoir of treated water can be produced in advance of exposure. This extra degree of control is simpler to achieve in a recirculating system. In addition the recirculating system is less prone to oxygen ingress by back diffusion from any orifice. The flow rate of the steam may also be limited by different factors for the two systems – for the ‘once-through’ system the limit for flow rate is the heat input required to raise the steam to the required exposure temperature whereas for the recirculating system there is an additional limitation of condensing the steam after exit from the furnace before recycling.

The recirculating system thus allows tighter control of some of the control parameters but may consequently impose restrictions on some of the others. Unfortunately there is no available information directly comparing these two types of system to allow a completely objective decision on whether the added complexity of recirculation is justified.

2.2 Specimen entry and removal

The effect of the method by which specimens are entered and removed from the furnace has been studied by Zurek et al [3] on both austenitic and ferritic steels. The respective specimens were either heated and cooled in the furnace under an argon atmosphere or removed from the furnace and cooled under air. In both cases the isothermal exposure was under an argon/50% H₂O atmosphere with the specimens removed at 250 h intervals. The effect of the different specimen handling procedures on the weight changes is shown in Figure 2 for an austenitic steel.

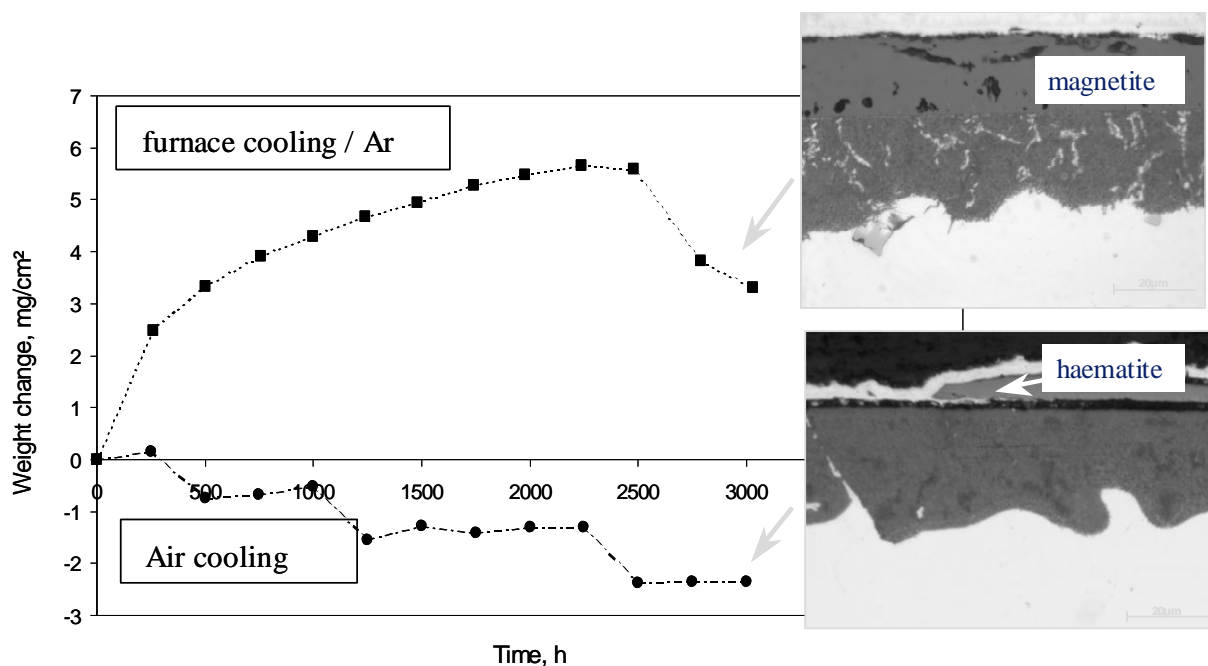


Figure 2 The influence of specimen entry/removal method on the steam oxidation behaviour of an austenitic steel during oxidation under argon/50 % H₂O at 600 °C (after ref [3])

The specimen that was furnace cooled under argon showed a continuous mass increase until 2500 h total exposure time. The microstructure of the scale formed was as expected with an outer magnetite layer and an inner spinel layer. In contrast the specimen that was removed from the furnace and air cooled showed spallation from the earliest stage of the exposure and also had an unusual microstructure with patches of haematite above the spinel. It is likely that the spallation is a result of the faster cooling rates achieved by withdrawal of the specimen from the furnace and that haematite formation occurs due to ingress of air into the furnace during the specimen withdrawal process. The effect was less pronounced in cases of steels that exhibit better scale adherence than the austenitic steels.

2.3 Water Chemistry

Power generation plants use complex chemical treatments in their water circuits to minimise corrosion damage and deposition problems. It is possible to simulate some of these treatments in the laboratory, however some laboratory systems only use very basic water treatment e.g. oxygen removal by gas displacement.

Little work has been carried out on the effect that water chemistry has on the steam oxidation but recent work by Nishimura et al [4] has suggested that there is little systematic effect on scale growth kinetics of P91 at temperatures between 600 and 700 °C and times up to 9939 h for high pressure steam exposures using two service water treatments.

The influence of a simple water treatment is illustrated in Figure 3. Specimens of P92 were exposed to a flowing 100% steam atmosphere for 1000 h at 650 °C. Little difference in the scale microstructure is observed with the exception that the specimen oxidised using the aerated water supply (not unsurprisingly) shows more haematite at the surface.

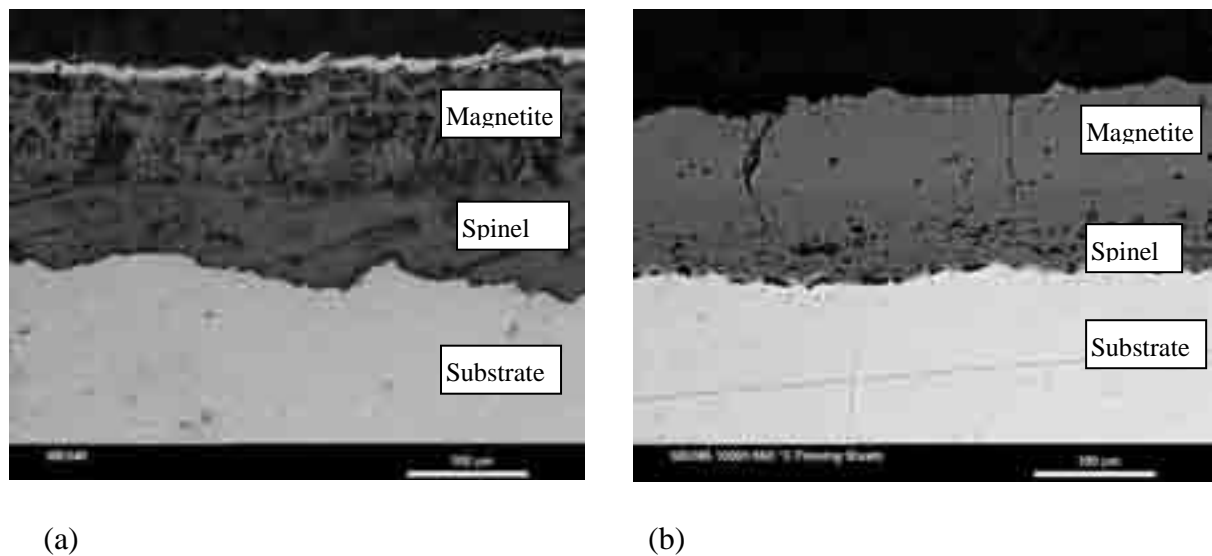


Figure 3 Micrographs of Scale Structure of P92 after exposure to flowing 100% steam at 650 °C for 1000 h (a) aerated water supply (b) water supply de-aerated by gas bubbling

2.4 Use of Carrier Gas

The two most common procedures used in the laboratory to expose materials to a steam atmosphere at ambient pressure are (i) 100% H₂O or (ii) 50% H₂O in an argon carrier gas. The latter atmosphere is achieved by passing argon through a suitable humidifier prior to entry into the furnace.

Figure 4 shows a direct comparison of the scale growth kinetics observed using the two different atmospheres for two different steels, all other experimental parameters being unchanged between the two exposures. It can be seen that, although the 100% flowing steam atmosphere gives consistently higher scale thickness for both materials (except for P92 material after 1000 h where the data points superimpose on each other), the differences are small and within the expected experimental scatter.

The difference in the scale morphology observed after exposure to the two different atmospheres is illustrated in Figure 5. For both materials the amount of haematite that forms is higher in the 100% steam atmosphere than under the argon/50% H₂O environment. In addition the defect (pore) structure in the magnetite differs for the two atmospheres.

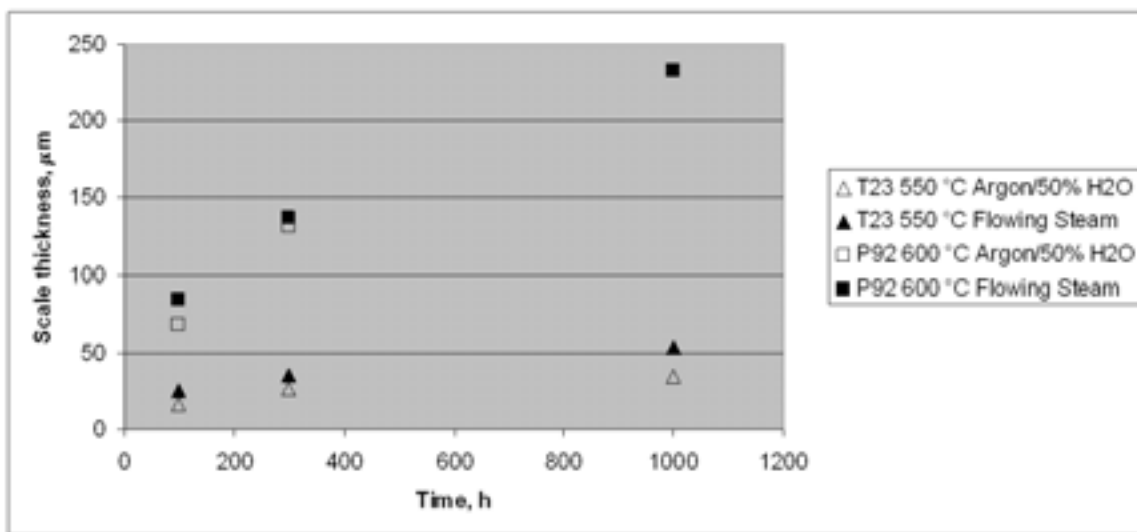


Figure 4 Oxide scale thickness as a function of time for T23 and P92 steels, oxidised under 100% H₂O and argon/50% H₂O

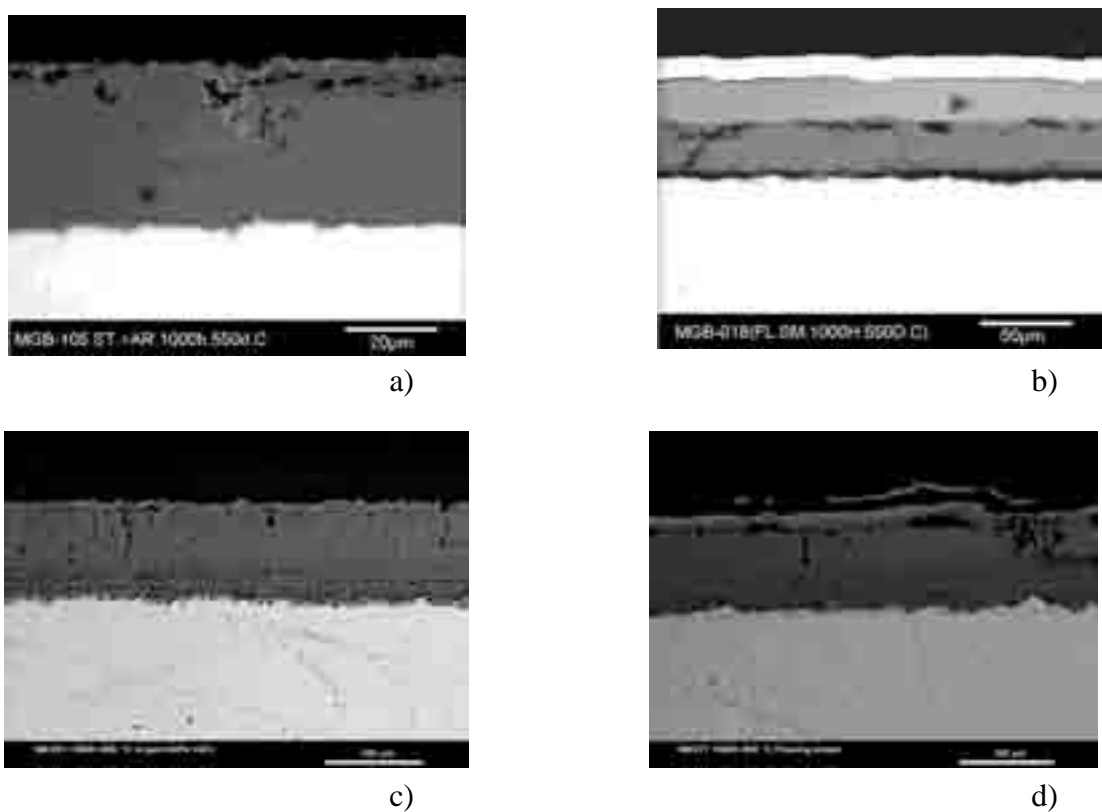


Figure 5 Micrographs of oxide scales grown for 1000 h (a) T23 under argon/50% H₂O at 550 °C (b) T23 under 100% H₂O at 550 °C (c) P92 under argon/50% H₂O at 600 °C (d) P92 under 100% H₂O at 600 °C

The difference in defect distribution in the magnetite may be expected to affect the spallation behaviour of the oxide scale. It has been shown [5] that the Rockwell indentation test can be used to measure the interfacial toughness of an oxide scale or coating. A qualitative measure of this parameter is the ratio of the radius of delaminated oxide to the radius of the indent causing the delamination. Figure 6 shows that, for oxide scales grown on P92 at 600 °C, the scale grown under argon/50% H₂O is less likely to spall (less damage around the indent) but that if it does spall then the individual flakes are likely to be larger (fewer radial cracks).

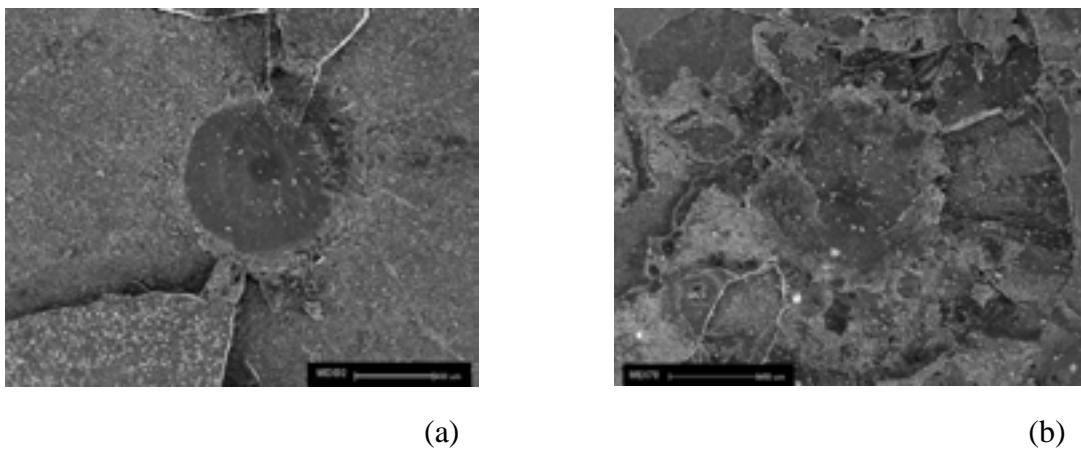


Figure 6 Rockwell indents on oxide scale grown on P92 for 1000 h at 600 °C (a) argon/50% H₂O (b) 100% H₂O

2.5 Amount of H₂O in Carrier Gas

The influence of oxygen and water content in the argon carrier gas has been investigated by Ehlers et al [6] and is summarised in Figure 7. In atmospheres that contain little oxygen a plateau in scale growth kinetics is reached with H₂O contents in the atmosphere $\geq 10\%$.

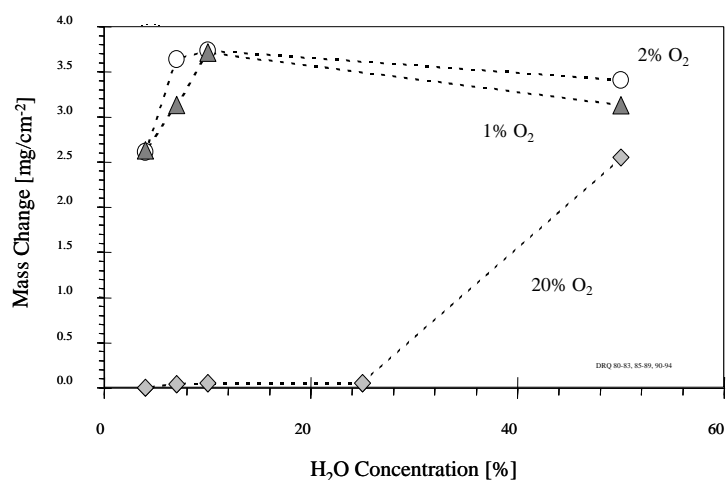


Figure 7 The influence of O₂ and H₂O content on oxide scale growth on P91 for 24h at 650 °C. Specimens were polished prior to exposure to suppress the incubation period of transient, protective oxide formation. (After Ref [6])

However with atmospheres containing a high (20%) level of oxygen the accelerating effect of H₂O on scale growth does not begin until the H₂O content is 25% and does not approach the same growth kinetics as in the environments containing low oxygen levels until the H₂O level is ~60%.

The influence of H₂O content in argon in the absence of added oxygen on scale growth on ferritic and martensitic steels. T22 and T23 were exposed to argon containing 15% and 50% H₂O at 550 °C and P22, Alloy 122 and X19 were exposed to the same atmospheres at 600 and 650 °C. In each case spallation of the oxide was observed after shorter times in the argon-15% H₂O atmosphere than under argon-50% H₂O although whilst the oxide was adherent there was no significant differences in the growth kinetics between the two atmospheres.

2.6 Flow Rate

The influence of flow rate on steam oxidation of P91 was investigated by Zurek et al [7]. A series of specimens were exposed at 650 °C in a quartz tube with an inner diameter of 10 mm. The test atmospheres were argon-H₂O mixtures in which the water vapour contents varied between 4 and 50%. The exposure times ranged from 10 minutes to 5 hours and the gas flow rate was varied between 1 and 15 l h⁻¹.

After the various exposures the specimens in all studied cases exhibited macroscopically visible flow patterns on their surfaces and generally the scale thickness decreased in the flow direction. It was shown that this effect was not related

to limitations in oxygen supply; in all studied cases the oxygen supply rate was substantially larger than the amount of oxygen required to form the oxide of the thickness found at the front end of the specimen (i.e. at the side where the gas entered the reaction tube). Here the thickness of the oxide scale did not clearly vary as a function of water vapour content or gas flow rate. Clear differences in scale thickness, morphology and composition as a function of these parameters were, however, found at the specimen end; here the scale thickness tended to decrease with decreasing water vapour content and/or flow rate. Also, the tendency for outer haematite formation was far less pronounced at the specimen end than at the front edge of the specimen. It was proposed [7] that these experimental findings are related to the formation of hydrogen as a result of the reaction between the water vapour and the steel. As the gas starts to react at the front edge of the specimen, hydrogen is produced such that the end of the specimen is exposed to a Ar/H₂/H₂O gas mixture. It is easy to derive that here, the H₂O/H₂-ratio and thus the equilibrium oxygen partial pressure will increase with increasing initial H₂O content and/or gas flow rate. The decrease in oxygen partial pressure in gas flow direction leads to the suppression of outer haematite formation and a decreasing growth rate of the magnetite based layer, in agreement with the experimental findings.

2.7 Steam Pressure

Data regarding the influence of pressure on steam oxidation behaviour show a considerable amount of variation. Therefore it is difficult to determine any consistent effect of pressure. Ootoguro et al [8] measured the maximum scale thickness on 4 austenitic alloys (SUS347HTB, 17/14CuMo, 20Cr/25Ni and 22Cr/35Ni) after exposure to steam for 500 h at 650 and 700 °C and pressures up to 35 MPa. Figure 8 shows that, on increasing the pressure at 650 °C, two of the alloys investigated showed a decrease in scale growth rate of approximately 20%, one of the alloys showed no influence of pressure on the scale thickness and one alloy showed an increase in scale thickness by a factor of 4. The same trend in results was observed at 700 °C.

Montgomery and Karlsson [9] have summarised data on the influence of pressure on scale growth kinetics during exposure of martensitic steels to steam environments. Data for two materials, HCM12 and P92, are shown in Figure 9. The high pressure data for HCM12 lie below the mean line implying a decrease in scale growth rate with increasing pressure whereas the high pressure data for P92 straddle the mean line implying either no effect of pressure or a change in the pressure effect with temperature depending on interpretation.

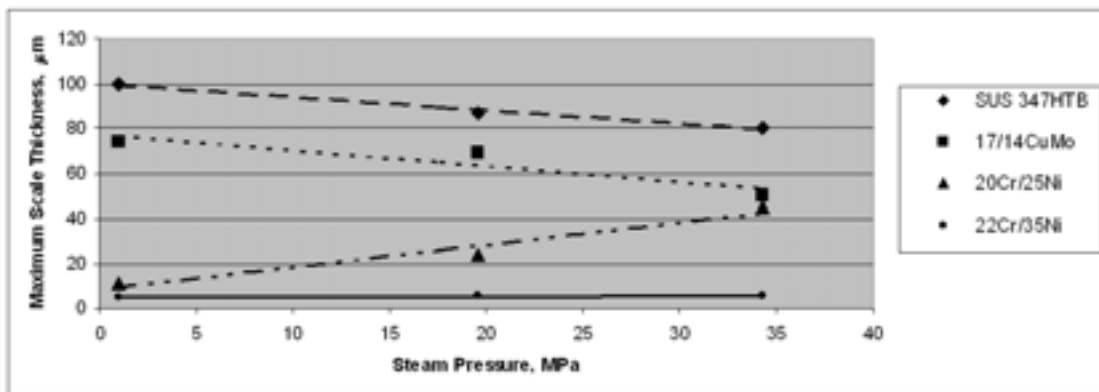
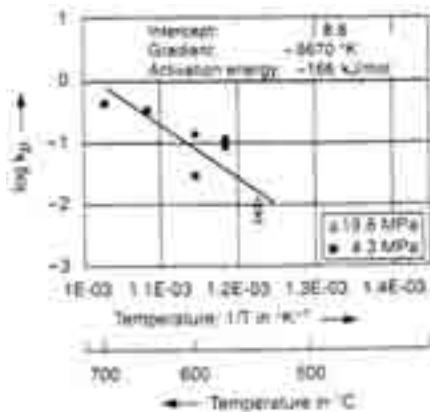
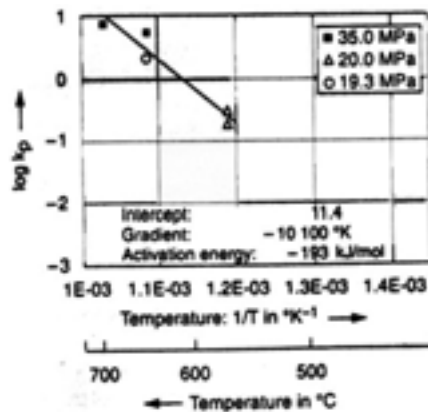


Figure 8 The influence of steam pressure on the maximum scale thickness of 4 austenitic alloys after exposure to steam at 650 °C for 500 h (Data from Ref [8])



(a)



(b)

Figure 9 The influence of temperature and steam pressure on the oxidation rate constant of martensitic steels (a) HCM12 (b) P92

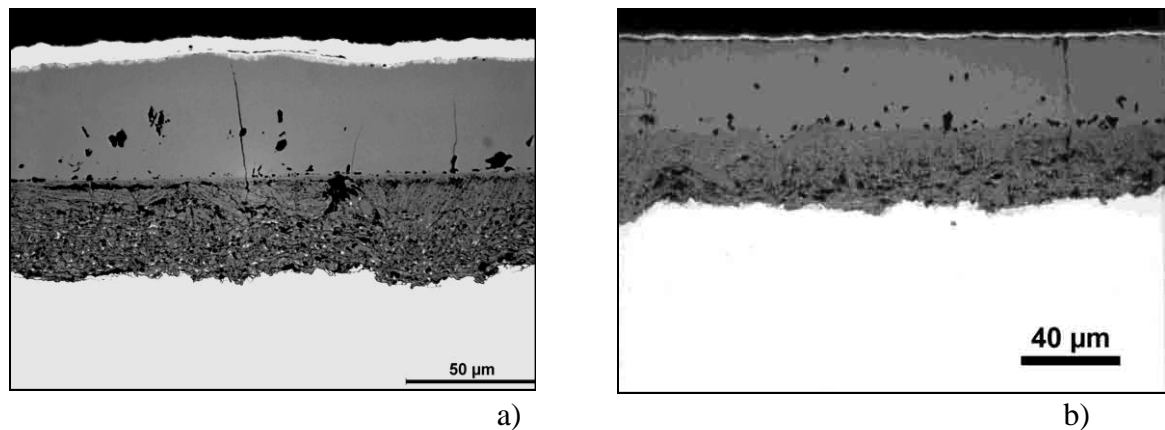


Figure 10 Micrographs of 10Cr1.5Mo martensitic steel after exposure to steam atmospheres for 250 h at 650 °C (a) flowing argon/50% H₂O at ambient pressure (b) static 100% steam at 300 bar

The apparent influence of steam pressure on the scale morphology is illustrated in Figure 10 for martensitic 10Cr1.5Mo steel oxidised for 250 h at 650 °C. When exposed to argon/50% H₂O at ambient pressure much more haematite forms on the surface (Figure 10a). However the high pressure exposure was carried out in an autoclave and the observed effect is probably due to a build up of hydrogen in the sealed system. This leads to a decrease in oxygen partial pressure, thus inhibiting haematite formation. This observation shows that information obtained from exposures carried out in sealed systems must be treated with caution.

2.8 Heat Flux

The presence of heat flux is a major difference between most laboratory exposure procedures and service conditions. The influence of this parameter has been studied by Griess and his co-workers [10] who demonstrated a significant influence of heat flux on scale growth rate.

Figure 11 shows the average metal loss of 2¼Cr1Mo steel as a function of exposure time to superheated steam, with and without the presence of a heat flux. The isothermal exposure showed the lowest metal loss rate even though the temperature was higher than in the exposures where heat flux was present. Griess also noted that the scales that formed in the presence of heat flux were less adherent than those that were produced in isothermal exposures.

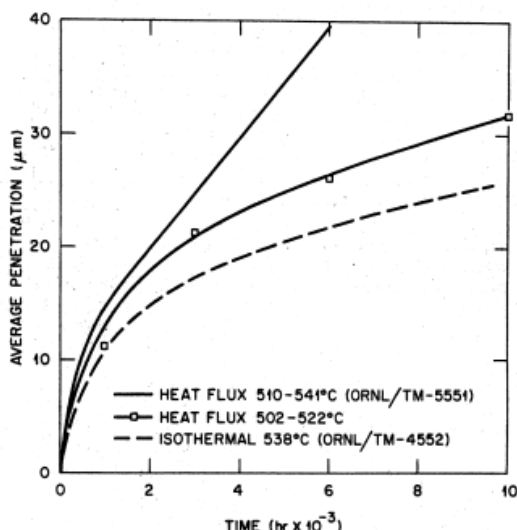


Figure 11 The influence of heat flux on the scale growth kinetics of a ferritic steel in superheated steam (after Ref [10])

3 Comparison of Laboratory and Plant Data

After all the discussion of the limitations of laboratory exposure procedures it may be suspected that comparisons between data that are generated in the laboratory and in service do not correlate well. On the contrary, measurements of scale growth show good agreement between scales produced in the two environments.

Figure 12 compares the scale thickness as a function of time for several martensitic steels exposed to steam-containing atmospheres in the laboratory at 625 °C (open symbols) or plant (filled symbols) at a steam temperature of 600 °C. Differences in the scale growth kinetics are minor and within the variation expected between different casts of the same alloy.

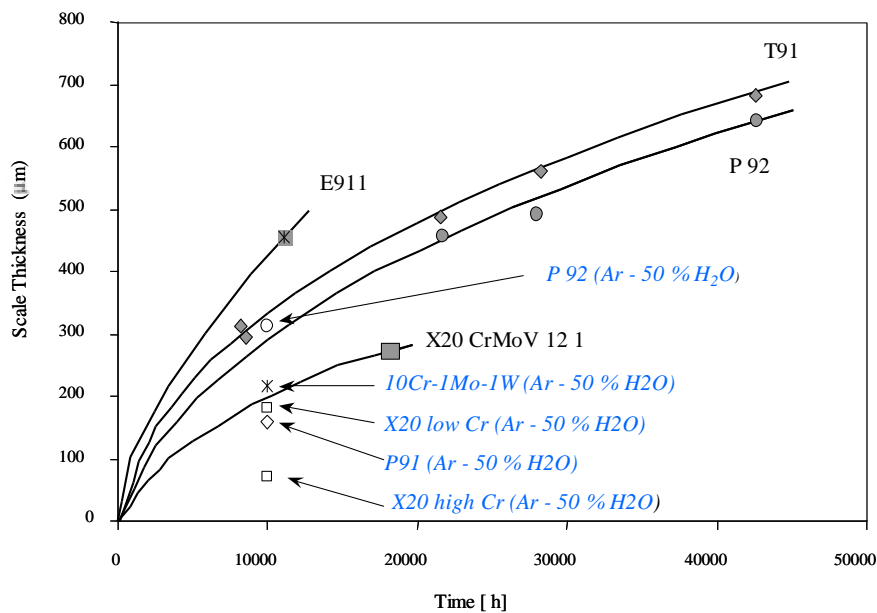


Figure 12 Comparison of Laboratory and Plant Scale Growth Rates for Martensitic Steels (After Ref [6])

4 Conclusions

The factors that affect scale growth kinetics and scale morphology during laboratory exposures have been critically reviewed. The main parameter that requires control to achieve scale growth rates comparable to plant experience is heat flux. It is also prudent to control the system pressure, although consistent data on the effect of pressure are lacking. Additional parameters that require control to reproduce the relevant scale morphology are water chemistry and flow rate as well as heating/cooling conditions.

5 Recommendations for Laboratory Exposures

5.1 Specimen Preparation

Specimens for exposures should have an exposed surface area $>500 \text{ mm}^2$. Either disc or plate specimens are acceptable. The surface of the specimens should be prepared by grinding using 1200 grit paper or alternatively should be representative of service.

5.2 Apparatus Layout

The apparatus is generally composed of (i) a temperature regulating device for heating the test piece uniformly at a constant temperature, (ii) a chamber which separates the test piece from outside air, and (iii) a mechanism for supplying continuously the test atmosphere. The test piece chamber shall not be composed of a material that reacts with the test atmosphere during the test to a degree that it changes the composition of the atmosphere. The furnace shall be characterised prior to the testing to determine the length of the isothermal zone inside the furnace and the set point of the apparatus. A common method is by the use of an independent moveable thermocouple.

5.3 Control of Water Chemistry

The water from which steam is generated should either (i) be as 'pure' as possible or (ii) reproduce specific industrial treatments. If 'pure' water is used this should be de-ionised either by the use of resin exchange columns or by boiling. In addition dissolved oxygen should be removed from the water by bubbling a suitable gas eg nitrogen, through the reservoir. It is possible to reproduce industrial water treatments in the laboratory but this requires relatively large volumes to be treated and stored in reservoirs prior to testing.

5.4 Use of Carrier Gas

The use of a carrier gas e.g. argon, is permitted but it must be established that the fraction of water vapour in the gas mixture is sufficient that the kinetics of scale growth approach that observed for the material in 100% steam at the same temperature. In the absence of significant amounts of oxygen, 50% argon/50 % H₂O is generally suitable.

5.5 Flow Rate

The gas flow rate over the surface of the testpiece should be high enough to ensure that no depletion of reaction species will occur. At the same time the gas flow shall be slow enough to allow the gas mixture to preheat and not disturb the temperature of the testpiece. In practice a linear flow rate in the range 1-10 mm s⁻¹ is suitable.

5.6 Testpiece Entry and Removal

Testpieces and their supports should be entered into the furnace whilst it is at temperature and the test atmosphere is flowing. Correspondingly testpieces and their supports should be removed from the hot zone and cooled whilst still under the test

atmosphere where possible. The use of an air-lock system to prevent oxygen ingress during specimen transfer is recommended.

5.7 Temperature Control

Temperature during the test shall be maintained within the limits shown in Table I.

Table I Temperature Limits For Laboratory Steam Exposures

| $\leq 573 \text{ K}$ | $573 \text{ K} < T \leq 873 \text{ K}$ | $873 \text{ K} < T \leq 1073 \text{ K}$ | $1073 \text{ K} < T \leq 1273 \text{ K}$ | $> 1273 \text{ K}$ |
|----------------------|----------------------------------------|-----------------------------------------|------------------------------------------|--------------------|
| ± 2 | ± 3 | ± 4 | ± 5 | ± 7 |

5.8 Steam Pressure

Exposures under supercritical steam environments are specialised tests and outside the scope of this guide. There is as yet insufficient evidence to make definitive statements regarding best practice for steam pressure during testing however some general guidelines can be stated:

- The use of sealed autoclaves containing static steam is not recommended.
- Pressures slightly above ambient reduce the risk of oxygen ingress due to leaks in the test chamber.
- The pressure of the exposure should be reported.

5.9 Heat Flux

Testing under an imposed heat flux is not commonly carried out. If this specialised exposure is used then the heat flux should be maintained constant and reported.

5.10 Testpiece Examination

After exposure the initial measure of oxidation is mass change. However it is strongly recommended that testpieces are also examined metallographically using agreed procedures [11] to determine scale thickness and metal loss. The structure of the oxide scale should be compared with scales on similar materials that have been exposed in service.

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