

Simulation of Steam Pipe Conditions Using Cyclic Oxidation Tests

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ABSTRACT

A new thermal cycling rig has been designed and built which provides the robustness to perform a wider range of thermal cycling tests under a range of possible atmospheres, temperatures, heating and cooling rates. Tests have been performed on a boiler steel using different thermal cycles to produce oxides scales which better reproduce those grown in service. These tests have shown that the combination of a relatively fast cycle time with a slow cool produces the best replication of service grown scale.

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Approved by Dr Markys Cain, Knowledge Leader, Materials Team

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1 Introduction

During service components in boilers and steam turbines are exposed to high pressure, high temperature flowing steam. The material used for these components are selected on the basis of service requirements, including mechanical loading, anticipated maximum temperature and cost. Traditionally the oxidation resistance is normally one of the last properties to be considered but it can prove to be the behaviour that limits component lifetime.

The general oxidation behaviour for a range of conventional alloys is well known and is presented in Figure 1 as a Larson-Miller plot in order to represent time and temperature as a single parameter. As this Figure shows, as the chromium content of steels is increased they become more oxidation resistant: Ni-base superalloys have similar chromium content to austenitic steels but are even more resistant to oxidation in steam atmospheres. However within each class of materials individual alloys exhibit oxidation resistance that is not totally explained purely by the chromium content, and so laboratory exposures are commonly used to evaluate the oxidation resistance of candidate materials.

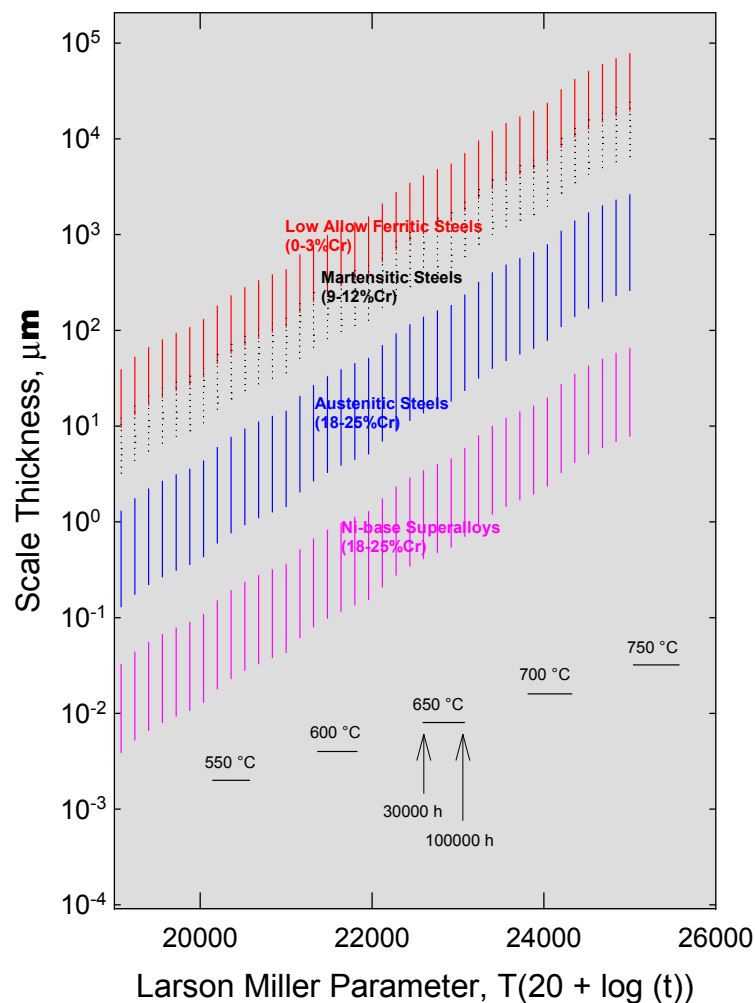


Figure 1 Approximate Scale Growth Rates for Alloys in Steam Environments, where T is the absolute temperature (K) and t is time (h) [4]

Whilst every attempt is made within the laboratory to reproduce the conditions these materials are exposed to in service, laboratory exposure cannot reproduce all the features present in service conditions. However, laboratory tests are performed and the data generated are used for material selection and lifetime prediction of components under such conditions and for the development of material models. Previous studies have shown that the details of laboratory testing procedures are important in characterising the oxidation behaviour. It has been observed that the whilst the growth kinetics for individual alloys are relatively unaffected by the exposure procedure the microstructure and consequently the spallation behaviour is dependant on the exposure procedure used [1-3].

Traditional laboratory tests are usually performed under well-controlled isothermal conditions. Whilst these are important in developing understanding of corrosion mechanisms and can be used to rank materials, they do not fully simulate plant conditions, or more importantly produce the oxide morphology seen in-service.

To better reproduce this morphology the use of thermal transients has been investigated. Thermal cycling is a test that has a multitude of possible combinations of experimental variables [4-5]. A facility has been developed to carry out cyclic oxidation in controlled gas atmospheres, and a series of tests performed to evaluate the effect discrete changes in the experimental procedure have on the kinetics and morphology of oxides.

2 Thermal Cycling

2.1 Apparatus

The tests as described in the following sections were performed using two different thermal cycling rigs. Initial tests were performed using the NPL 'Big Cycling Rig'. This consists of a large bore alumina tube housed within a second larger bore alumina tube. These tubes are sealed at both ends to provide a gas seal. The tubes run through a three-zone furnace. Within the tube is housed the specimen holder which can be mechanically pushed and pulled in and out of the three furnace zones. As the test programme continued it became clear that the alumina tubes were deteriorating due to the levels of water being used in the steam exposure tests. This deterioration ultimately resulted in the tube failing, and so a decision was made to develop a more robust system.

The second thermal cycling rig, which was developed during the course of the programme, consists of a split zone furnace mounted on horizontal and vertical drives which allow it to separate and move away from the work tube, as shown in Figure 2. The work tube used for this programme was a metallic tube (IN625). To one end of the tube was attached the steam inlet with the outlet at the other end. The control thermocouple for the furnace was placed inside the work tube. Compressed air lines were strategically placed around the outside of the work tube such that it could be cooled quicker during that phase of the thermal cycle.

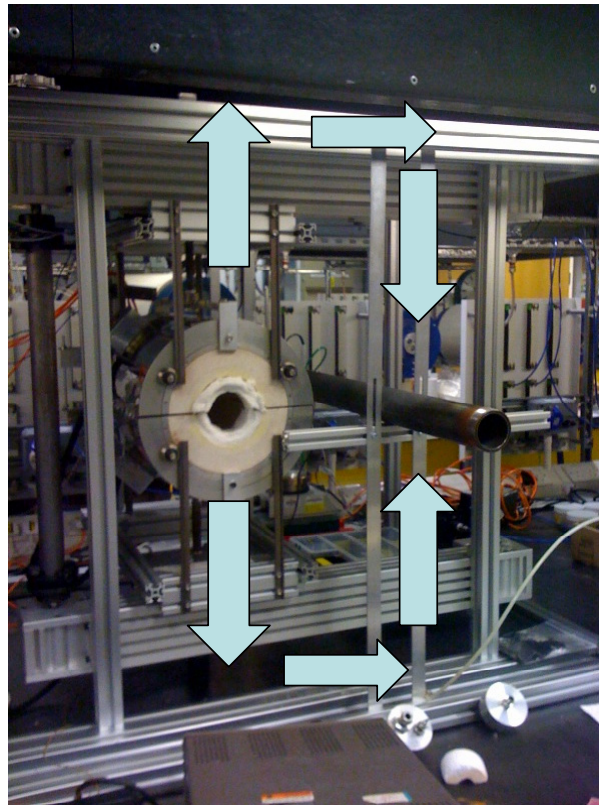


Figure 2 New thermal cycling apparatus

When developing the new thermal cycling rig it was imperative that the thermal cycles used in the 'Big Cycling' rig could be reproduced and that it could follow the guidelines being drafted by the ISO TC156 group, which are based on the COTEST code of practice. Figure 3 shows a typical thermal cycle with the recommended cooling times and timing points.

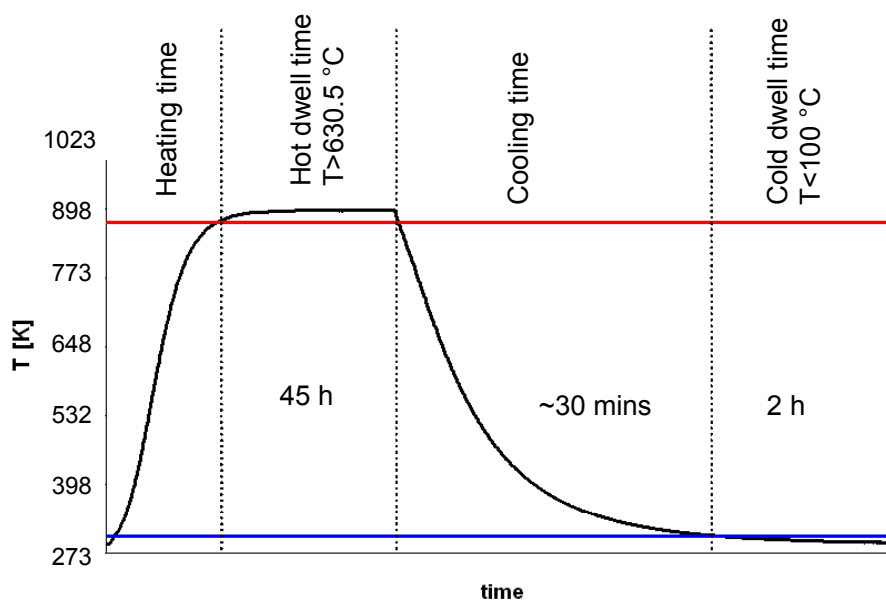


Figure 3 Schematic showing the thermal cycle and timing points

Thermal cycle traces from the old and new rigs has been collected and compares well, as shown in Figure 4.

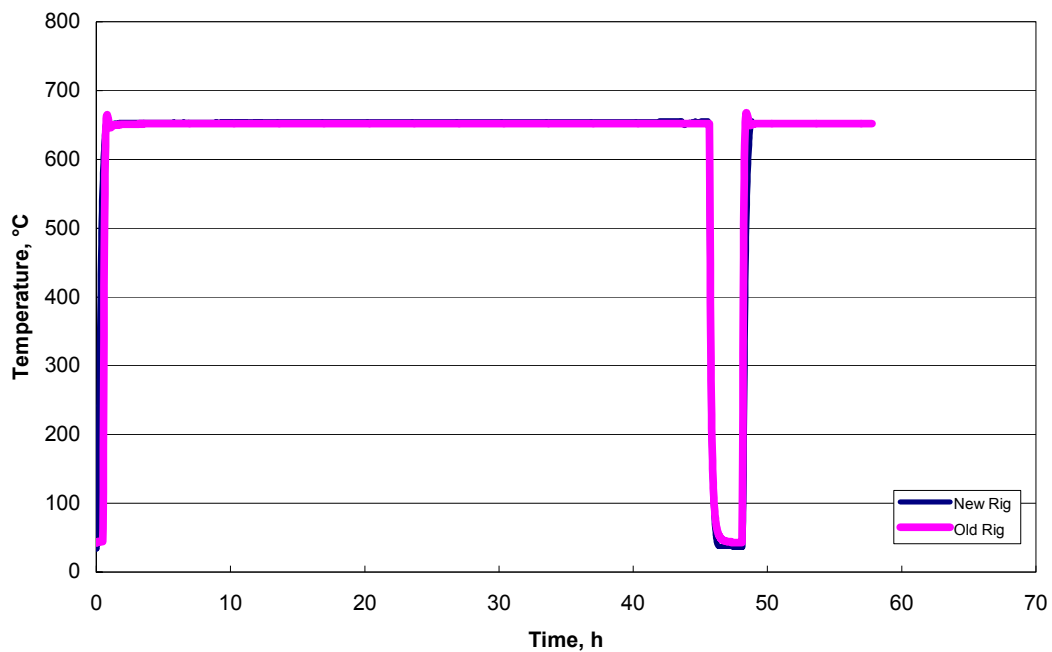


Figure 4 Comparison of the thermal cycle from the old NPL apparatus and the new apparatus

Figure 4 shows that the cycles from the two rigs agrees well, thus enabling data from both rigs to be compared. Closer inspection of the traces reveals there to be a subtle difference. The old rig would heat up faster since the specimen is being moved into a hot furnace and the thermal mass is low, compared with the furnace moving to encase a cold tube. However the heating and cooling times were still very encouraging with the specimen heating from 23°C to 650°C in 36 minutes and cooling from 650°C to 50°C in 33 minutes. Faster cooling rates were achieved for one series of tests by replacing the thick walled work tube with a thinner tube. The thermal cycle in this case is shown in Figure 5. Using this thin walled work tube the specimen temperature goes from 38°C to 632°C in 15 minutes and from 633°C to 50°C in 23 minutes thus enabling faster cycle times if required.

A thermostatically controlled water bath was placed at the inlet of both rigs such that a mixture of argon and steam could be used as the test atmosphere.

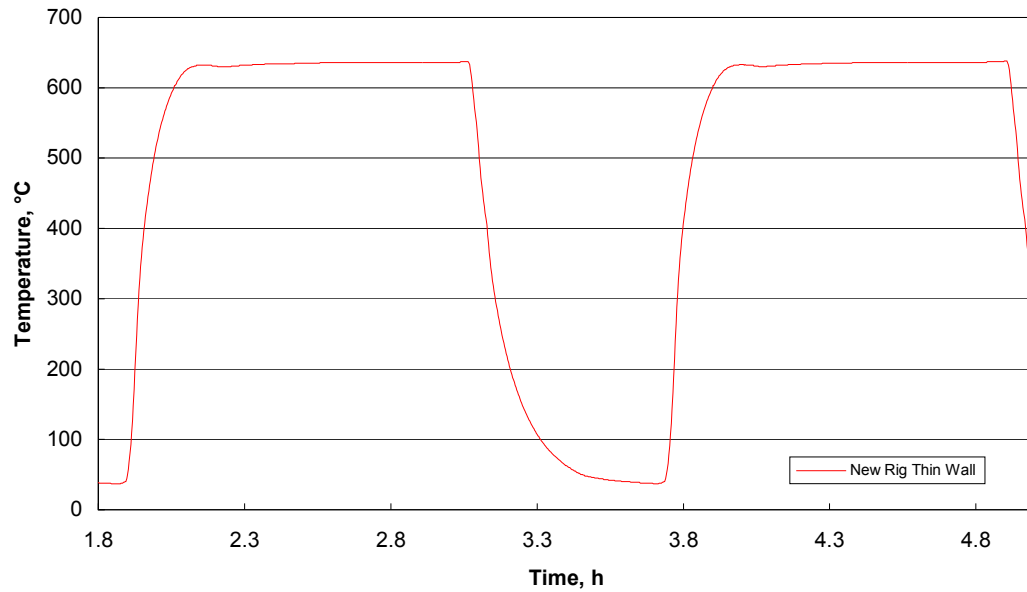


Figure 5 Thermal cycle achieved with a thin walled work tube

2.2 Test Programme

The tests were performed on specimens made from P92, a 9 wt%Cr martensitic alloy. The aim of the tests was to evaluate the relative effect of the cooling rate and thermal cycle on the oxidation kinetics and resultant scale morphology from changes in the test procedure. Thus a series of tests were conducted as summarised in Table I.

Table I Summary of test performed

Test No.	Steam mixture	Cooling	Hot dwell, h	Cold dwell, h	Heating / Cooling rate, °C min ⁻¹
1	50:50 Steam:Ar	Ambient	20	4	25 / 18
2	50:50 Steam:Ar	Ambient	45	2	17 / 18
3	50:50 Steam:Ar	Forced air	45	2	17 / 25
4	50:50 Steam:Ar	Forced air	16	2	40 / 25

3 Results

The results of the four different test setups are shown in Figures 6 and 7, showing the specific mass change and the average total oxide thickness for the tests.

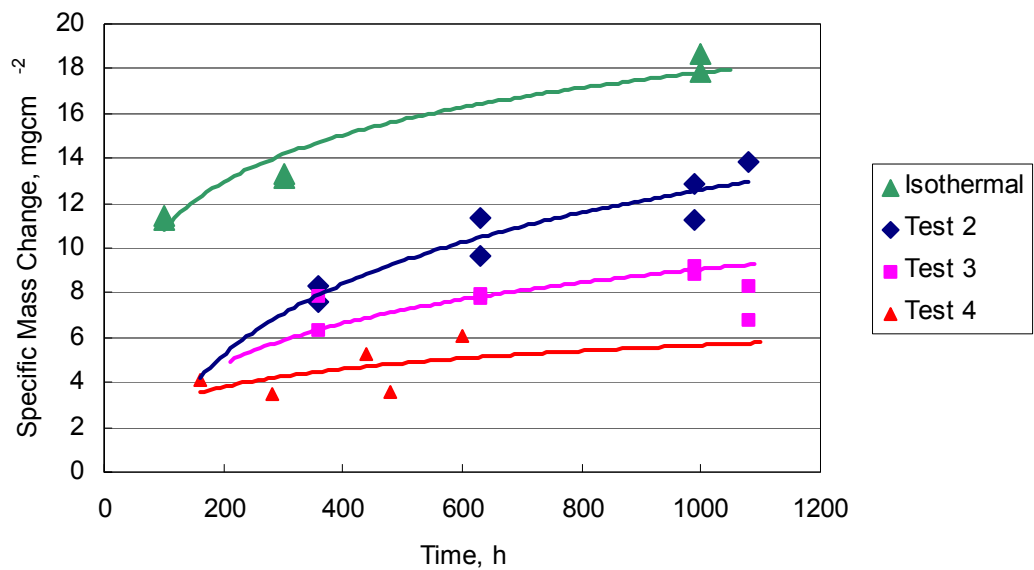


Figure 6 Specific mass change as a function of exposure time for P92 at 650°C under three different test setups as defined in Table I (test 1 excluded)

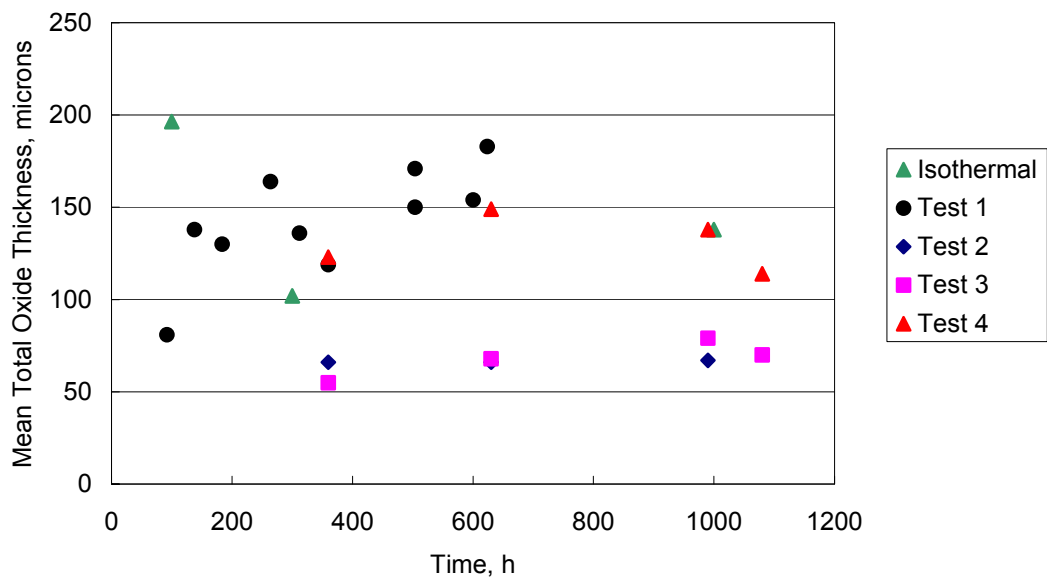


Figure 7 Average total oxide thickness as a function of exposure time for P92 at 650°C under four different test setups as defined in Table I

Figure 6 shows there is a difference in the specific mass change of the specimens used in tests 2 to 4 (test 1 has been excluded as the mass change data was not recorded) compared to isothermal tests. This figure shows that there is an effect from the both the cooling rate and the cycle time. This observation is not at all apparent when

considering the total oxide thickness as is shown in Figure 7. This figure indicates that the oxide reaches a certain threshold thickness past which further thickening does not occur, this is most likely due to spallation of the oxide. The number of cycles each specimen has will also critically affect the damage accumulation in the oxide and the degree of spallation. Consequently Figures 6 and 7 have been replotted to show the number of thermal cycles each specimen had, these are shown in Figures 8 and 9.

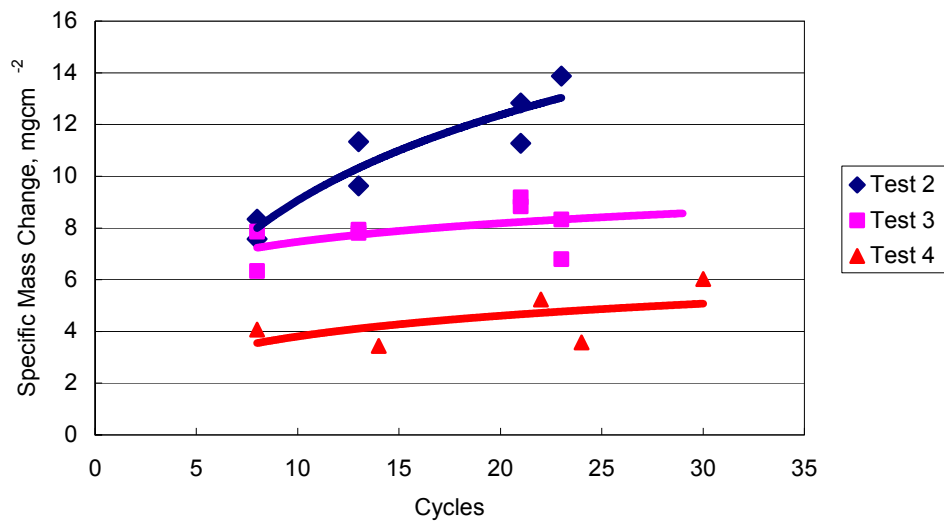


Figure 8 Specific mass change as a function of thermal cycles for P92 at 650°C under three different test setups as defined in Table I (test 1 excluded)

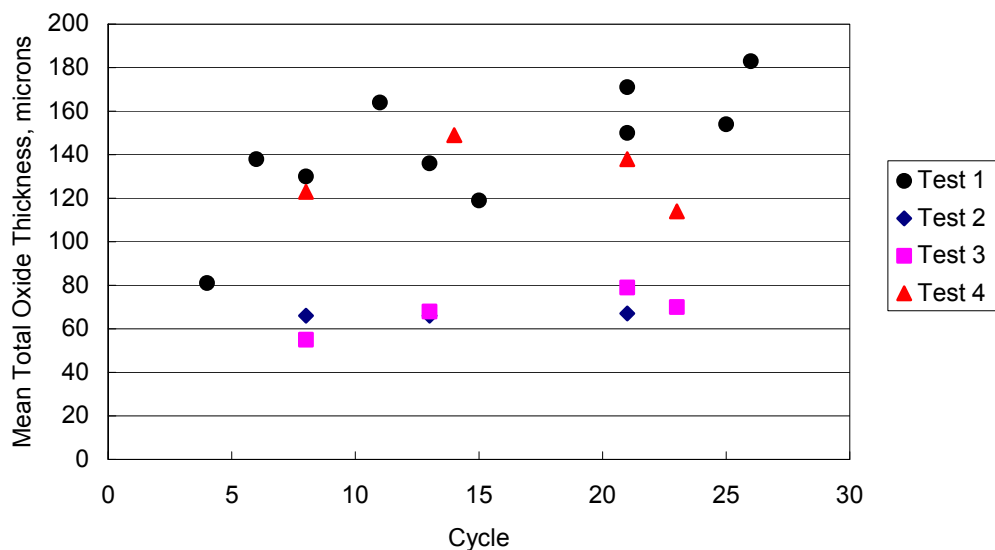


Figure 9 Mean total oxide thickness as a function of thermal cycles for P92 at 650°C under four different test setups as defined in Table I

To fully understand the differences in the tests it is important to look at the morphology of the oxide scale. Figures 10 to 13 show the cross sections of the specimens exposed to thermal cycling, Figure 14 shows the scale formed in an isothermal test.

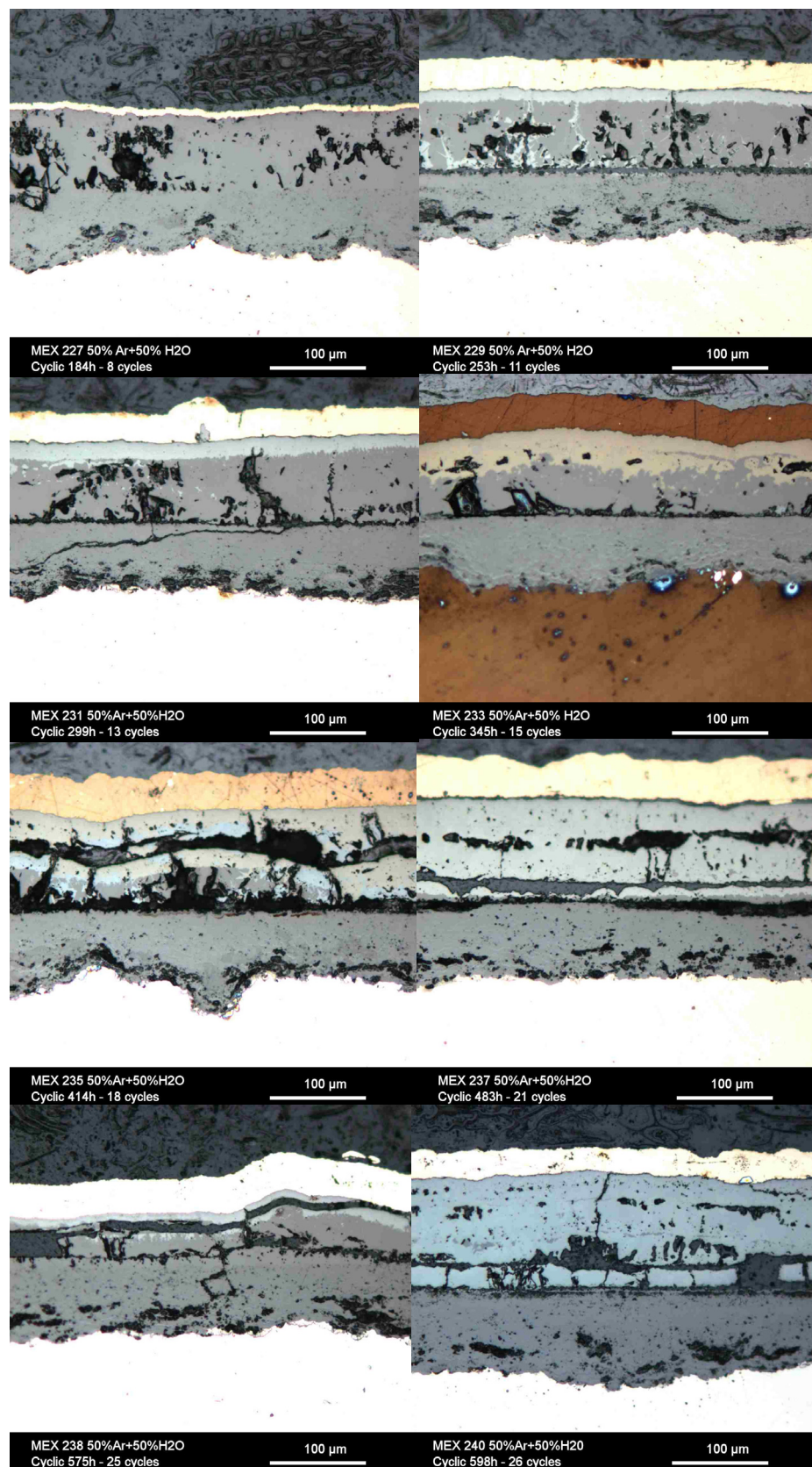


Figure 10 P92 exposed to flowing 50%Ar+50%H₂O at 650°C, thermal cycle consisted of 20h hot dwell and a 2h cold dwell

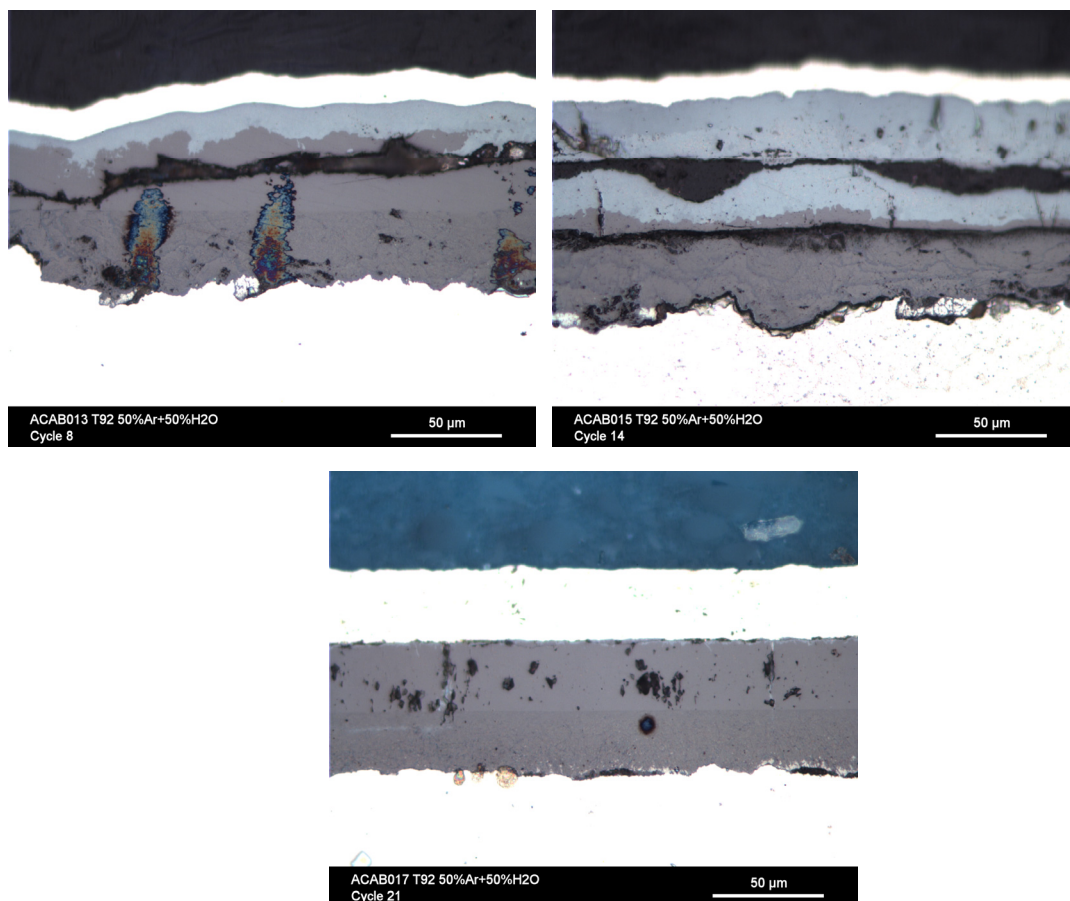


Figure 11 T92 exposed to flowing 50%Ar+50%H2O at 650°C, thermal cycle consisted of 45h hot dwell and a 2h cold dwell

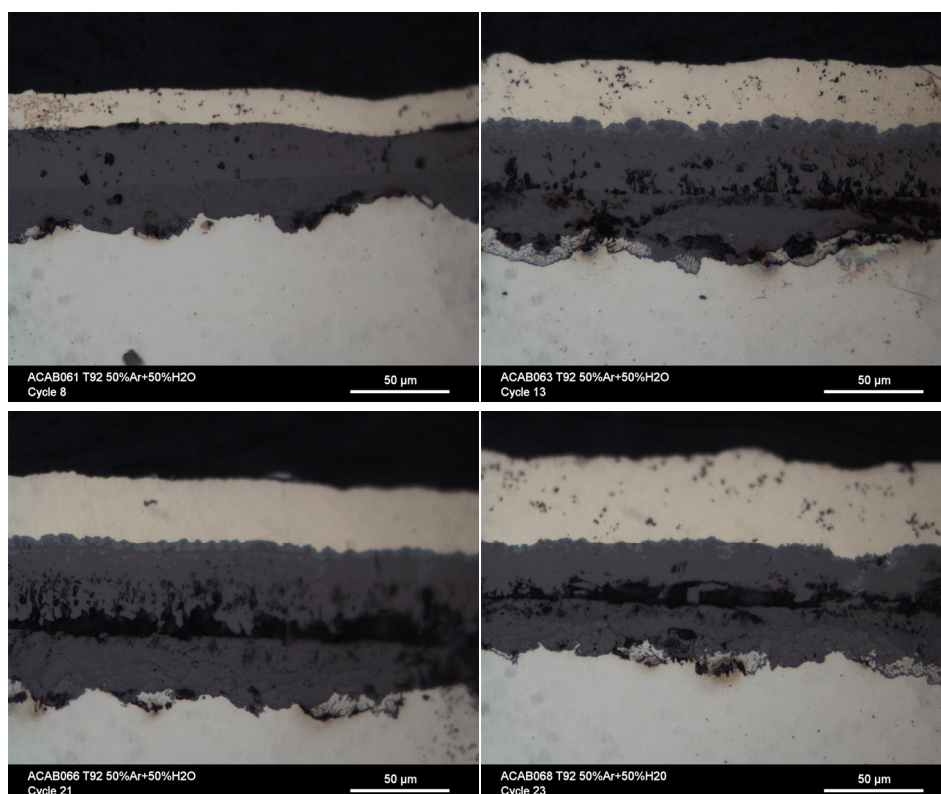


Figure 12 T92 exposed to flowing 50%Ar+50%H2O at 650°C, thermal cycle consisted of 45h hot dwell and a 2h cold dwell forced cooled

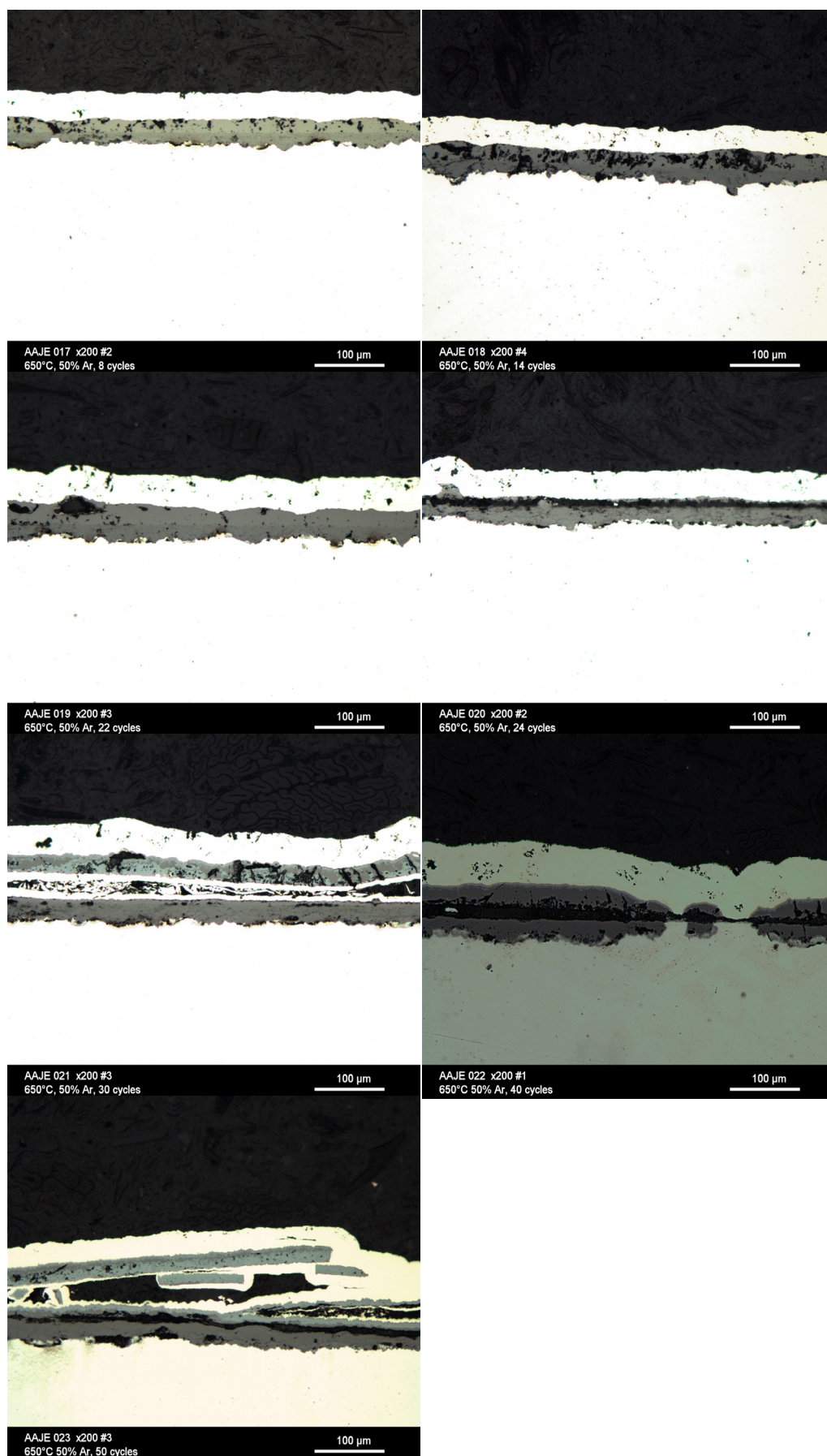


Figure 13 T92 exposed to flowing 50%Ar+50%H₂O at 650°C, thermal cycle consisted of 16h hot dwell and a 2h cold dwell forced cooled

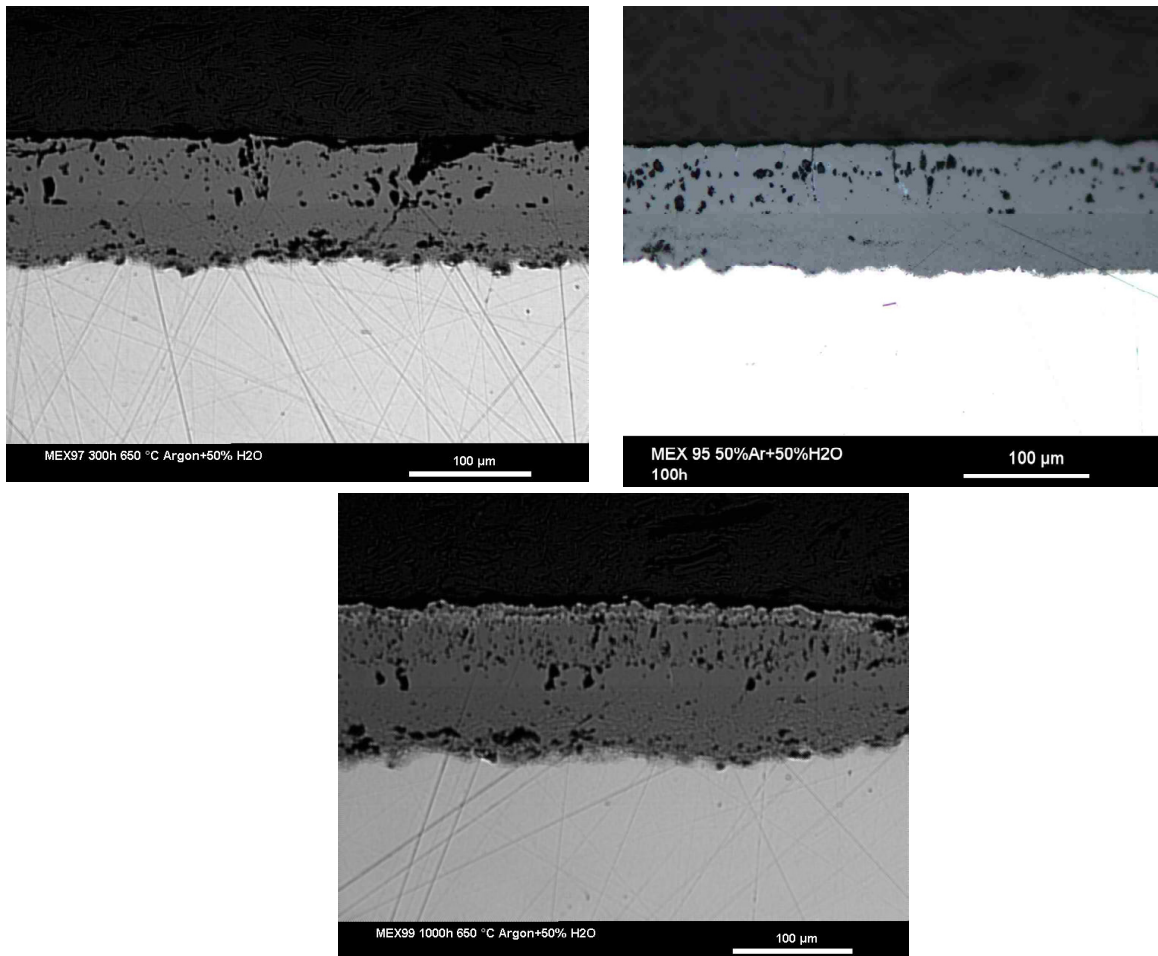


Figure 14 P92 exposed to flowing 50%Ar+50%H₂O at 650°C, isothermal test

4 Discussion

Under isothermal conditions the alloy initially forms a two-layered oxide consisting of an outward growing layer of magnetite (Fe_3O_4) and an inward growing layer consisting of an iron chromium spinel ($\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$). The thickness of these two layers is approximately the same (theory would suggest that the ratio of these two layers should be 1.2, see below). As the oxide grows any differences in the ratio of the two thicknesses is indicative of oxide spallation. The rationale for this has been explained by Knödler [6] and is as follows.

- The inner layer grows inside the steel via oxygen diffusion, with the oxygen replacing the original iron.
- The outer layer grows via iron diffusion consisting of the iron atoms displaced by the oxygen atoms of the inner layer.
- There is no net loss in iron unless spallation occurs, hence the sum of the iron in alloy and the outer and the inner scales must be constant.

- Inner oxide:
 - 1 cm³ is equivalent to 8 g Fe
 - 1 cm³ of oxide is equivalent to 5 g of oxide
 - Loss of 3 gcm⁻³ due to the formation of the inner oxide
- Outer oxide:
 - 1 cm³ of oxide is equivalent to 5 g of oxide
 - Gain of 5 gcm⁻³ due to the formation of the outer oxide

In the case of the inner scale in 1 g of oxide there is 0.72 g of iron. Assuming an oxide density of 5 gcm⁻³ this is equivalent to a volume of inner scale of 0.2 cm³. Now consider the outer scale, the iron content before oxidation was 1.6 g in 0.2 cm³, it is now 0.72 g, therefore there is a 0.88 g difference. This amount of iron has to have moved to the outer scale forming an oxide of 1.2 g, which corresponds to a volume of 0.24 cm³ of oxide. Therefore the ratio of outer to inner scale should be 0.24/0.2 = 1.2, assuming no spallation has occurred. Using this relationship it is possible to estimate the degree of spallation using Equation 1, as shown in Figure 15.

$$W = \frac{\mu_{tot}}{(1+k)} (0.5k - 0.3) \quad 1$$

where W is the mass change, μ_{tot} is the total scale thickness and k is the ratio of the inner scale thickness to the outer scale thickness.

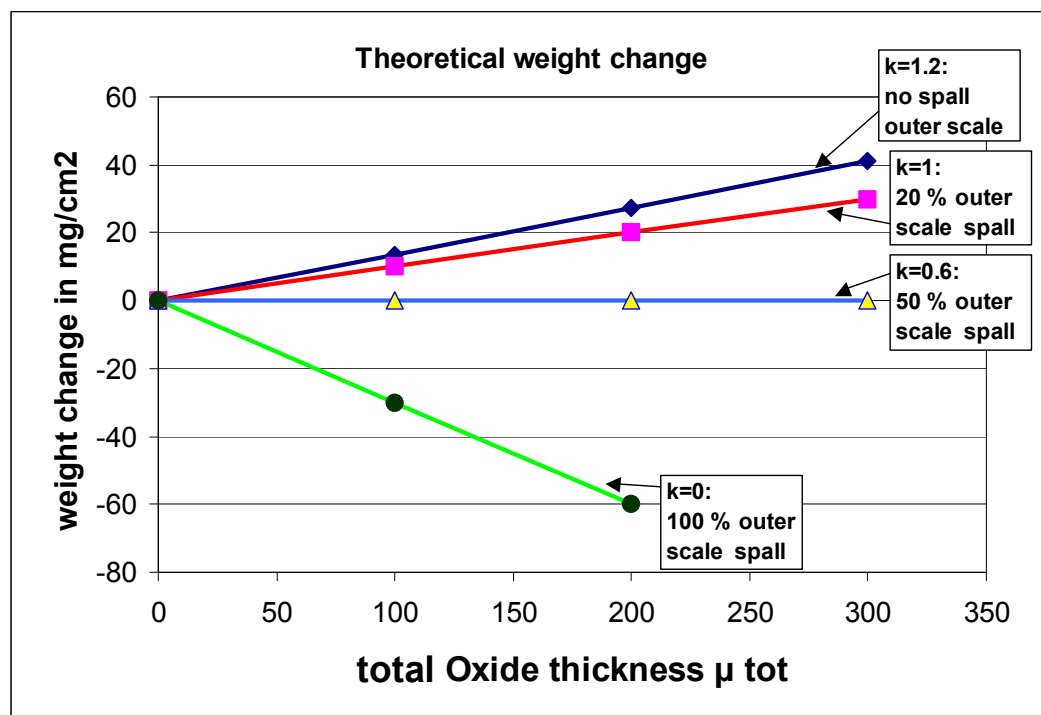


Figure 15 Plot of weight change with total oxide thickness showing the percentage spallation [6]

As the oxide scale thickens defects can become larger and diffusion of additional iron atoms slows and stops. Thermodynamics will lead to the transformation of magnetite to haematite (Fe_2O_3), which will decorate the outer surface, cracks, and pores of the oxide, as shown in Figure 14. Under cyclic conditions damage can accumulate at a much faster rate due to thermal strains and growth strains in the scale, the severity of these strains will be dependant on, amongst other things, nature of the thermal cycle and the rate of heating and cooling. Using the above analysis method the degree of spallation has been calculated and is presented in Table II.

Table II Calculation of percentage-spalled oxide from the thermal cycling tests

Test ID	Time, h	Cycles	% Spallation
1	92	4	NA
	138	6	NA
	184	8	NA
	264	11	NA
	312	13	NA
	360	15	NA
	504	21	NA
	504	21	NA
	600	25	NA
	624	26	NA
2	360	8	6
	630	13	-6 ⁽¹⁾
	990	21	-21 ⁽²⁾
	1080	23	NA
3	360	8	12
	630	13	11
	990	21	12
	1080	23	10
4	160	8	11
	280	14	38
	360	22	3
	440	24	20
	630	30	1 ⁽³⁾

(1) Haematite forming producing a thicker outer scale

(2) Dense oxide being retained

(3) Spalling occurred but oxide retained

Consider now the micrographs of the thermal cycling specimens, these show quite distinct behaviour between the four different thermal cycles. Consider first tests 2 and 3 which were both conducted with a 45 hour hot dwell and a 2 hour cold dwell, but with test 3 cooled faster using forced cooling. The total oxide thickness between the two tests is comparable, as shown in Figure 9. The specific mass change is initially the same but as the specimens go through more thermal cycles the mass change for test 2, where the specimens cool slower, increases whilst the mass change for test 3 increases at a slower rate and eventually losses mass. Examination of the scale morphology shows that under the faster cooling rate the oxide appears to have more defects in the

form of porosity within it. In both cases there is evidence of interlaminar fracture and transformation of magnetite to haematite, as shown in Figures 11 and 12. Comparing test 4 with test 1 which had similar hot dwells (16 hours and 20 hours respectively) but with test 4 having forced cooling it is clear from Figure 9 that the two sets of specimens showed similar increases in total oxide thickness. Data on the specific mass change for test 1 is not available so no comparison on mass change is possible. Examination of the micrographs shown in Figures 10 and 13 show both tests produced extensive damage to the oxide scale, in the case of test 1 this was evident after 11 cycles and in the case of test 4 after 22 cycles. The damage in the oxide accumulates until interlaminar separation of the magnetite and the spinel occurs, transformation of the magnetite to haematite then proceeds, eventually transforming the whole magnetite layer into haematite.

Table II shows the calculated theoretical percentage spallation. Whilst this calculation is not available for Test 1 it can be applied to the three other tests. The table indicates that more severe spallation occurred when forced cooling was applied, this is consistent with our understanding regarding the strain development in scales during temperature transients. It is curious that the calculated spallation for the specimens exposed in Test 2 shows a negative trend; this is likely due to the magnetite transforming to haematite where the addition of extra oxygen atoms has the potential to increase the mass gain by 32 atomic mass units for every oxygen molecule whilst reducing the volume thereby producing a more dense oxide.

Table II shows that there is increased spallation for Test 4 when compared with Test 3, which both employed forced cooling. The difference between the two tests is that Test 4 had a much faster cycle time, thereby introducing greater damage in the thinner oxide scales. Whilst the oxide in Test 3 was allowed to grow for longer and become denser, thereby it could be postulated, imparting more strength to the scale and providing more resistance to spalling. The micrographs in Figure 12 would attest to the intrinsic strength of the scale as even though delamination has occurred the oxide is retained.

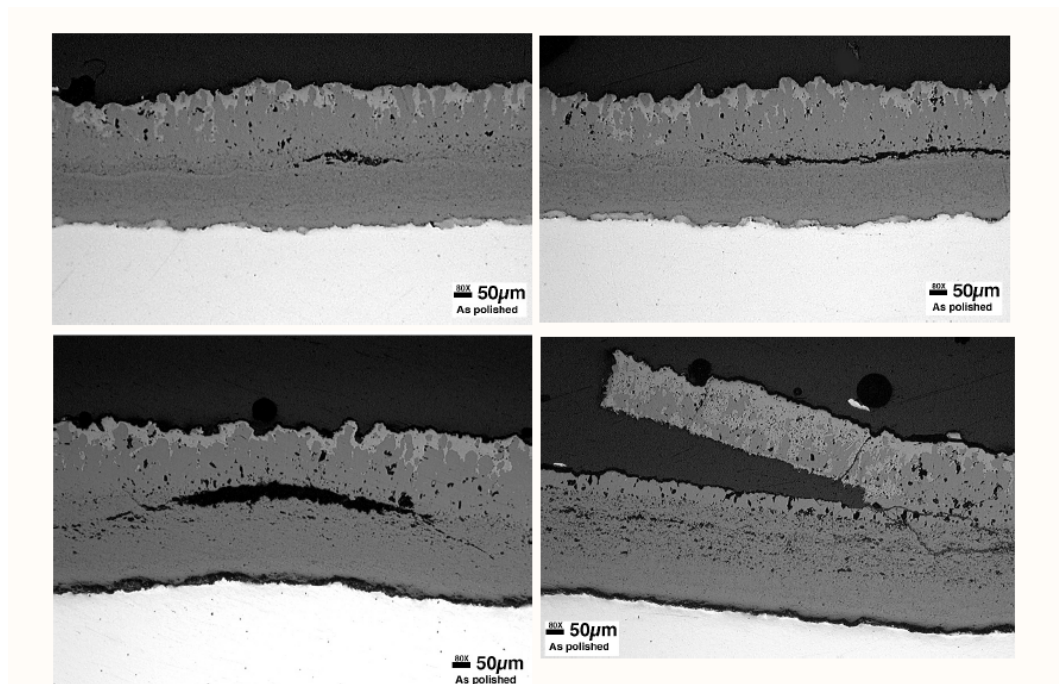


Figure 16 T91, 61kh at 566°C, 138 bar (courtesy of Ian Wright, ORNL)

The aim of this work was to produce a test that would generate scales which simulated plant scales more accurately. Figure 16 shows four micrographs from a section of T91 tubing exposed at 566°C for 61 kh at 138 bar. The images show the spallation sequence as it progresses. The issue with regards to the thermal cycling test is which condition best simulates the scale formed. Examination of Figures 10 to 13 would indicate that tests 1 and 4 best replicate the defect structure, with test 3 showing signs that the correct structure is being formed although in this case spallation is not seen optically and haematite is not as prevalent, evidence of spallation is seen in the calculation shown in Table II however. Thus the results show that the hot dwell time and number of cycles is a more dominant factor than the cooling rates used in this work to generate the correct oxide scale morphology. The dwell times needs to be sufficient to grow the oxide and the cooling rate slow enough to accommodate strain redistribution. Hence in this case the combination of a fast cycle, i.e. 20h hot 4h cold, coupled with a slow cooling rate, i.e. ambient cooling of 18°C/min has produced the best comparison to plant grown scale.

5 Conclusions

- A new thermal cycling rig has been designed and built which provides the robustness to perform a wider range of thermal cycling tests under a range of possible atmospheres, temperatures, heating and cooling rates.
- This new rig has been shown to be comparable to the old NPL thermal cycling apparatus but with improved robustness brought about by the use of metallic work tubes rather than ceramic.
- Tests have been performed on a number of P92 specimens to investigate the effect of two critical test parameters, namely the cycle time and the rate of cooling.
- The results have shown that collection of mass change data is vital for these types of test as this parameter is more sensitive and a better discriminator between the four tests conducted as part of this study. This data shows that there is an effect from both the cooling rate and cycle time, which is not wholly apparent when purely considering the total oxide thickness data.
- The results indicate that there is an upper limit to the oxide thickness, beyond which further oxidation is restricted and spallation becomes energetically favourable. The precise value is dependant on the cycle but would appear to have an upper limit of 200 microns.
- The more severe the thermal cycle, in terms of cooling rate the greater the amount of damage developed in the oxide. This is because the oxide layers do not have sufficient time for the thermal strains to relax through creep.
- Examination of the oxide micrographs show that under the faster cooling rates the oxide has more defects and porosity. It is this porosity that leads to accelerated spallation and interlaminar cracking. This cracking also leads to the formation of haematite as the test progresses.
- The combination of a relatively fast cycle time with a slow cool produces the best replication of service grown scale. In this work this was seen with the 24h cycle with ambient cooling, future work looking at the combination of a 24h cycle with forced cooling and an 18h cycle with ambient cooling would also be of benefit to examine more discreet changes in the test parameters.

6 Acknowledgement

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