

Measurement Note

NPL Report MN 5

Residual Stresses in Materials at High Temperature: The Link to Hardness and Scale Exfoliation.

Summary

This measurement note examines the links between hardness with residual stresses and growth stresses with exfoliation. Two examples are given where residual stress measurements have been used to show the effect of heat; the first for enhancing material properties and the second where high temperatures have degraded the material. The correlation between residual stress with hardness is discussed as is the use of stress measurements for the validation of a spallation model.

Introduction

Heat treatment has been used historically as a method for improving the strength of steels, by normalising and quenching. This can however result in undesirable residual stresses, which may in turn lead to cracking and distortion of the component being heat treated. This is well understood and remedial tempering processes can be used, if the problem is correctly identified. Still, it is clear that the control of heat input is fundamental to the production and processing of materials, but thermal aspects can also be important with regards to the application, performance and lifetime of the component. For example a heat exchanger tube within a coal fired power plant will be subjected to high temperature, high loads and aggressive environments during its lifetime. The oxidation under steam conditions of such pipe work is fundamental to its lifetime management in what is a safety critical environment. The combination of the atmosphere and high temperatures drive the oxidation rate which can impact on the creep life of the material and thermal performance of the component. Temperature fluctuations further complicate matters as they can lead to scale exfoliation. Modelling the scale growth and exfoliation is vital for understanding the material performance, stress is the driving force for this process and needs to be characterised.

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Residual stresses as a result of heat treatment

Depending on the thermodynamics and the rate of cooling it is possible to alter the mechanical properties of steel, through an annealing, normalising or hardening process. Slow furnace cooling will anneal the material removing any residual stresses and produce a 'soft' material. Normalisation is achieved through slightly faster cooling in air. This refines the grain structure of a material whose grains may have been deformed through cold work, and can lead to improved ductility and toughness through modification of the grain structure, thereby producing a much harder and tougher metal with normal tensile strength but not the maximum softness achieved by annealing. By cooling the material quickly in oil or water a martensitic transformation can occur and maximum hardening can be achieved in the steel.

The hardenability of steel can be measured using a Jominy end quench test, the British standard for which is BS EN ISO 642:1999. In this test a cylindrical bar with a diameter of 25 mm and length of 100 mm is normalized and then austenized. A jet of water is then quickly showered on the end of the specimen. The typical geometry and test schematic is shown in Figure 1.

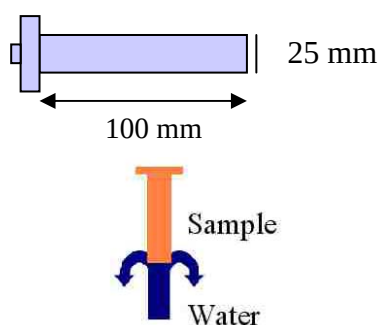


Figure 1. An example of a Jominy end quench bar, used in this work.

On cooling, hardness measurements can be made on parallel ground flats, and end-quench hardenability curves produced by plotting the hardness of the steel as a function of distance from the quenched end, as shown schematically in Figure 2. Knowledge of the hardenability properties of a material enables informed decisions regarding subsequent processing. If a material has a high hardenability, then a slower quench such as an oil quench can be used. This will not adversely effect the hardness and strength of the component because of its hardenability properties, but will reduce the distortion and residual stresses developed due to thermal gradients.

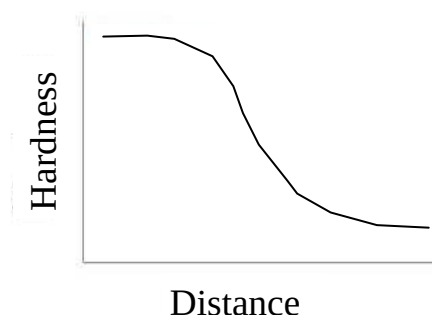


Figure 2. Hardness as a function of distance from the quenched end.

Table 1. Typical composition of EN8

Typical Analysis, wt%					
C	Si	Mn	S	P	Fe
0.40	0.25	0.80	0.05	0.05	bal

To examine the link between hardness and residual stress a sample of EN8, an unalloyed medium carbon steel the composition of which is shown in Table 1, was used in a Jominy end quench test. This consisted of normalising the material at 850 °C before performing the end quench test. The sample was then sectioned for metallographic, hardness and X-ray examination. Figure 3 shows the hardness measurements for the

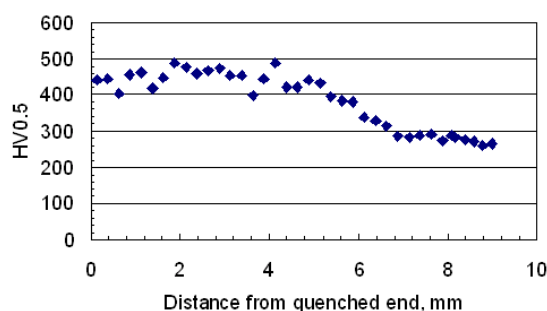


Figure 3. Microhardness of the Jominy bar as a function of distance from the quenched end.

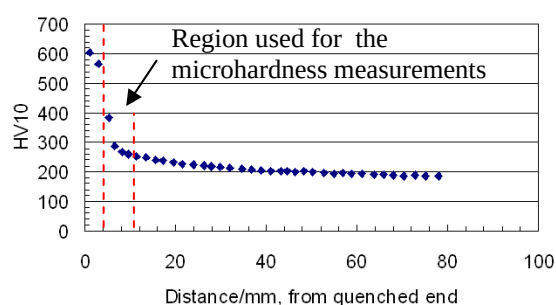


Figure 4. Macrohardness of the Jominy bar as a function of distance from the quenched end.

Jominy end quenched specimen as a function of distance from the quenched end. The hardness in the first 5 mm from the quenched end was of the order of 450 HV0.5, this then drops and the material becomes softer reaching a second plateau at around 7 mm from the quenched end. Figure 4 shows comparative measurement of macrohardness (HV10) measured along the whole length of the Jominy bar, showing how the material becomes softer with decreasing cooling rate. The dashed line indicates the comparative position of the start point of the microhardness measurements. This shift of around 2 mm was due to material being removed during the sectioning and mounting process. Figures 3 and 4 therefore are in good agreement as to the hardness profile along the specimen.

Residual stress measurements were then made on the sectioned sample using a Bruker D8 Discover diffractometer. This consisted of Cr- $k\alpha$ radiation collimated

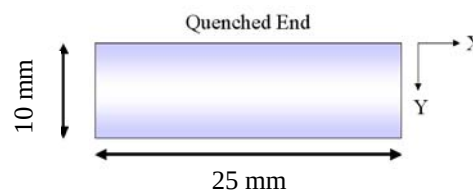


Figure 5. Schematic showing the measurement orientation with respect to the quenched end.

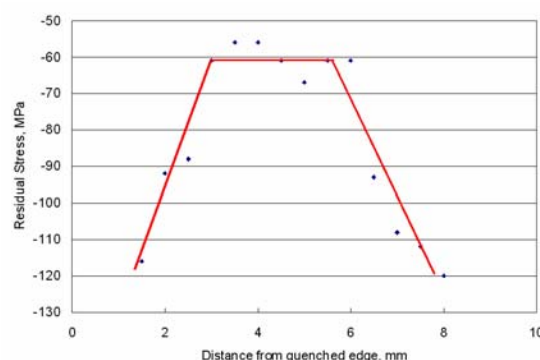


Figure 6. Residual stress in the Y direction as a function of distance from the quenched end.

using a 1 mm 'snout'. The residual stress was calculated using the iso-inclination method on diffraction data from the [211] Iron plane. The first measurement was made 2 mm from the quenched end, with subsequent measurements being performed every 0.5 mm along the width of the specimen as shown in Figure 5. The stress was analysed in both the X and Y directions, and the results for the Y direction are presented in Figure 6. The data shows that close to the quenched end, high compressive stresses can be found in the quenching direction. This compressive stress then decreases in magnitude up to a point approximately 4 mm from the quenched end, it then increases again at a distance of 6 mm from the quenched surface.

Interestingly, the plateau of the residual stresses in the quenching direction corresponds to the region where the hardness of the material begins to drop. Similar behaviour is observed in the FWHM values of the diffraction peaks,

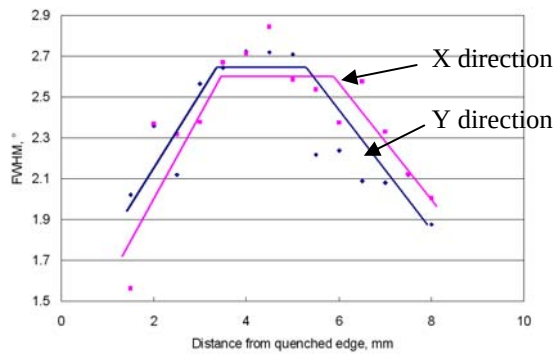


Figure 7. FWHM plotted as a function of distance from the quenched surface.

as shown in Figure 7. This shows that close to the quenched face the peaks are well defined with a narrow peak width. Moving away from the quenched surface the peaks become broader, indicating increased plastic deformation. The peak width is a maximum at a distance of around 4-5 mm, and then begins to narrow again past this point.

The relationship of hardness with residual stress has been previously examined and explanations vary depending on the materials and the stress states being considered. For example Coupard et al [1] showed a clear relationship between the hardness of induction hardened steels and the compressive residual stress profile and the FWHM of the diffraction peaks. Tanner and Robinson [2] also show a good correlation between compressive residual stresses and hardness, in this case in aluminium alloys. However, they showed that the change in hardness was not a direct effect of the residual stresses, but was due to precipitation in the alloys. Tensile residual stress as a results of grinding have been studied by Blehaut et al [3], again showing a relationship between the hardness, residual stress and FWHM in ground samples of A42 steel and 316L stainless steel.

The results presented in Figure 6 for the residual stresses can be rationalised by

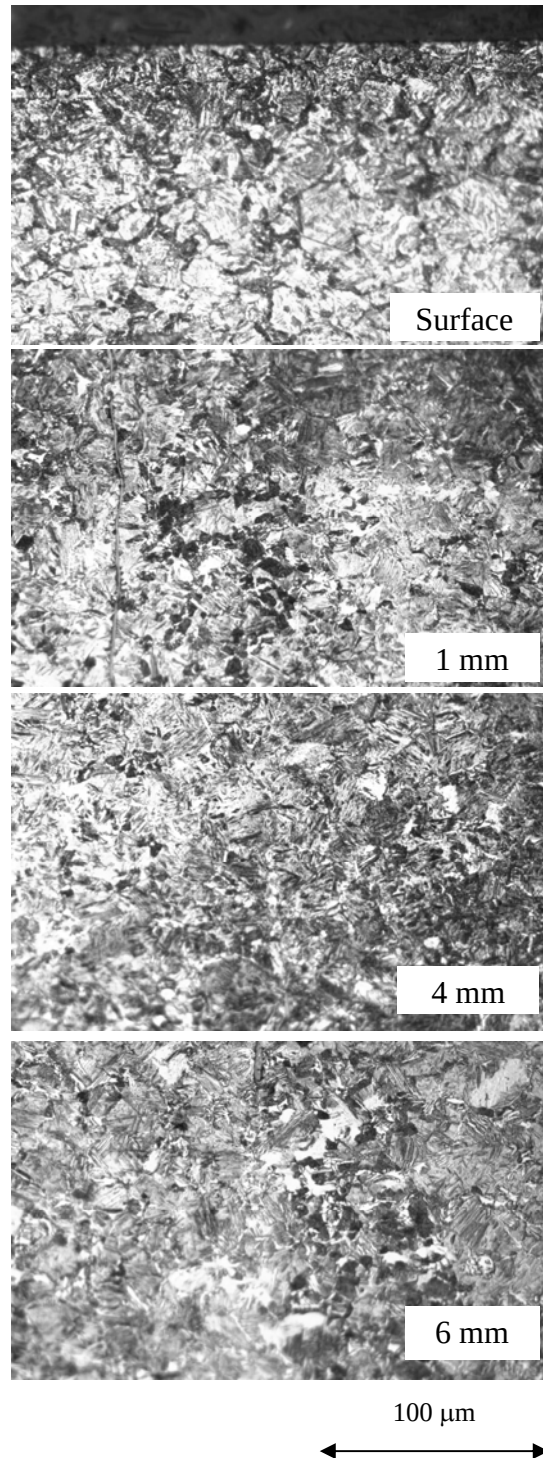


Figure 8. Microstructure of the Jominy bar sample at set points away from the quenched surface, as indicated in the images.

considering the transition between a martensitic and a bainitic/pearlitic microstructure. Transformation stresses arise from volume changes associated with the formation of certain phases. For

example, when austenite transforms to martensite in a 1% carbon steel, there is an increase in volume of 4%, while the transformation to pearlite results in an increase of 2.4% [4]. This transition can be seen in Figure 8, which shows optical micrographs of the measured surface, and at points 1, 4 and 6 mm away from the quenched surface. The area near the quenched end appears to have a martensitic microstructure as would be expected. Moving away from the quenched end we seen ferrite forming and a decrease in the amount of martensite. Moving further away from the quenched surface the microstructure changes again, with a decrease in ferrite and the appearance of bainite with bands of pearlite. This transition is gradual but there does appear to be a clear change at around 4 - 6 mm. This correlates with the transition seen in the hardness plots and is also the point at which the residual stress plateaus.

By considering the transformation stresses, an explanation for the distribution seen in Figure 6 can be postulated. Close to the quenched surface a martensitic transformation has occurred. The volume change from this causes the surrounding material to be under additional compressive stress. Moving away from the quenched surface the amount of martensite decreases, whilst at the same time ferrite forms. The ferrite is much softer than the martensite and so plastically deforms. Thus the compressive stress can be accommodated, and the hence the magnitude decreases. The decrease in stress can be seen in Figure 6, and the increase in plasticity shown in the FWHM plots in Figure 7. Moving further away from the quenched surface, there is a decrease in the amount of ferrite, and an increase in the volume of bainite and pearlite. The decrease in ferrite means that there is less easily deformable material

and hence a decrease in the plasticity is observed in Figure 7 with a corresponding increase in the compressive residual stresses, shown in Figure 6. The shape of the stress profile whilst unexpected, can be explained from microstructural observations. Comparing the hardness profile and the stress profile, in Figure 9, does show that the plateau in the stress profile does correspond to the softening point in the hardness data. Whilst in this case no clear direct relationship between the residual stress and hardness is seen there are trends which with further work could be used and numerical relationships between hardness and residual stress developed. This is likely to require including changes in the microstresses. This is a subject for further work and development in a new DIUS funded project.

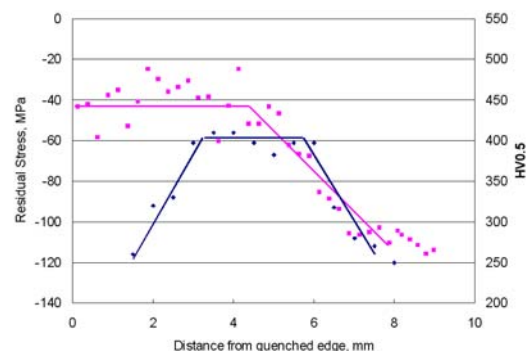


Figure 9. Residual stress and the microhardness of an end quenched sample.

Residual stresses in growing oxides

Spallation of oxides is a critical issue within heat exchanger tubes used in the power generation industry, and can have important consequences such as the loss of tube wall thickness, loss of flow rate caused by blockages from spalled oxide and increases in creep rate caused by local overheating of the tube as a result

of the blockage. The mechanism for the spallation of the oxide scale is believed to be driven by the increase in interfacial residual strains caused by thermal transients and differences in the coefficients of thermal expansion. The development of a crack and spalled particle is shown in the optical micrographs in Figure 10.

A model for the spallation of steam grown oxides on 9-12% Cr materials has been developed and is described in Refs 5 and 6. The modelling tool developed is made up of a number of steps, the first two being related to the development of residual growth stresses in the oxide and substrate. Initially the model predicts the rate of oxide growth as a function of alloy composition, time and temperature. A cooling cycle is then used to generate the through thickness stresses within the constituent oxide layers due to mismatch in the coefficients of thermal expansion. This can then lead to through thickness and interfacial cracking of the oxide scale.

The development of the stress build up and subsequent cracking of the oxide scale has been followed using XRD residual stress measurements on samples of a 9% Cr steel used in heat exchanger tubing. These samples were oxidised within a high temperature environment (650 °C) with a mixture of 50% Ar and 50% H₂O passing over them. The samples were held at temperature for 20 hours and then allowed to cool to room temperature for 4 hours before being heated again to 650 °C. Samples were removed periodically for mass change and XRD measurements; the samples were sectioned and the oxide thickness measured optically. The total test duration was 600 hours, with samples extracted at 200, 250, 300, 350, 400, 575 and 600 hours for use in XRD stress measurements. The oxide thickness of both the outward growing magnetite layer and

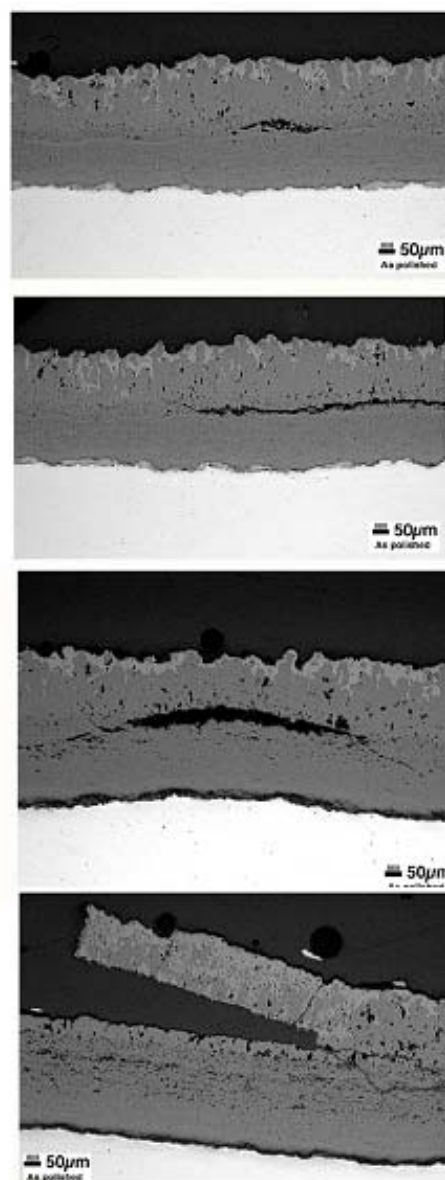


Figure 10. Micrographs showing the spallation mechanism from isothermal tests: Initial oxidation, interfacial crack forms between the magnetite and spinel layers, crack growth and final spallation.

inward growing Fe-Cr spinel with time is shown in Figure 11, a trend line has been added for clarity. Micrographs of the sample at various cumulative thermal cycles are presented in Figure 12. The micrographs clearly show how initially a porous magnetite and Fe-Cr spinel forms, with further cycling a third layer forms which has been identified as haematite.

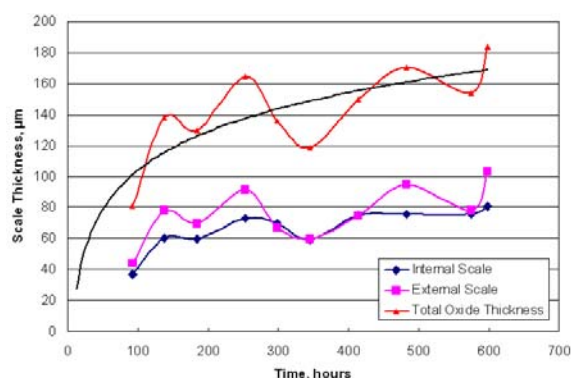


Figure 11. Oxide scale thickness with respect to time for the inward and outward growing scale.

This forms on the surface of the sample and penetrates down through the cracks and decorates the pores in the magnetite layer. With further cycling the size of the pores increases with some pores coalescing and interfacial cracking appearing at the magnetite-spinel interface. Cracks are also seen extending into the spinel layer, an observation not usually present in isothermal oxidation tests. The amount of cracking increases with additional cycling with clear evidence of material loss and repair. This is seen in both the optical images (Figure 12) and the scale thickness measurements (Figure 11).

Residual stress measurements were conducted using a Siemens D500 diffractometer with Cr- α radiation. Measurement were made using the $\sin^2\psi$ technique with the goniometer in Bragg Brentano geometry. The residual stress in the magnetite layer of the oxide was measured. This layer was then removed and the residual stress in the spinel/substrate measured. When measuring the residual stresses in oxide scales care should be taken to ensure that sufficient areas are being measured so that localised debonding does not skew the results. Care is also needed in handling these delicate samples to avoid damage to the oxide during the measurement. It is also important to take into

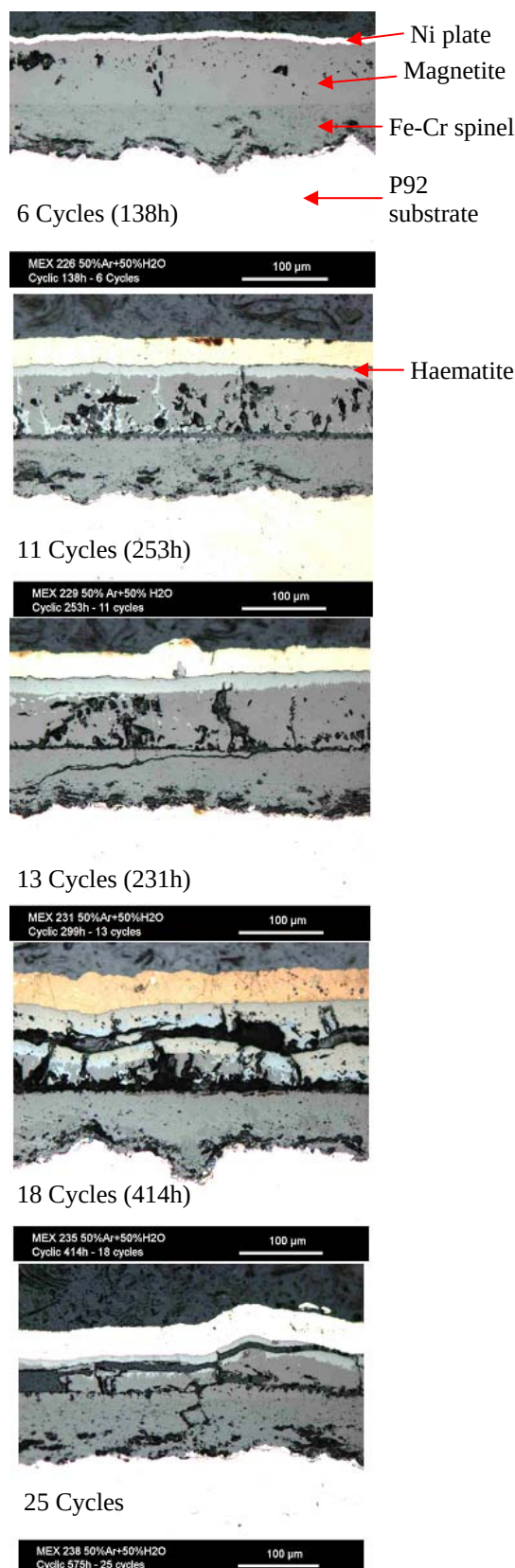


Figure 12. Micrographs of the oxide morphology after thermal cycling, clearly showing the crack formation.

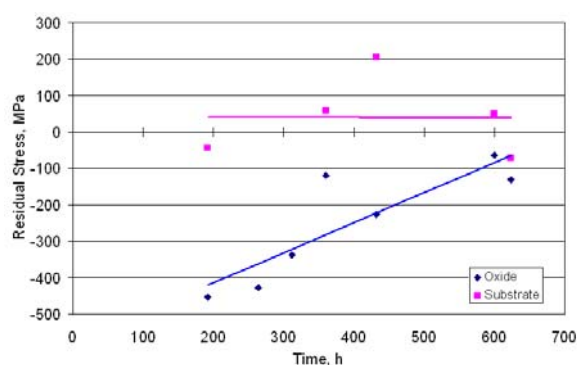


Figure 13. Residual stress of the oxide scale and substrate as a function of thermal cycles.

consideration the penetration depths of the X-rays, since only the top 20 - 30 microns of oxide will be measured. Hence whilst fresh oxide will grow and new cracks will emerge in the surface layers, the increasing distance from the magnetite/spinel interface means that the transfer of this interfacial stress to the outer magnetite surface is reduced, and it is likely that the remaining stresses being measured are much smaller than those still developing at the interface. Creep relaxation may also occur in the oxides, and so storage of sample is also another important consideration.

The results for measurements made after 200, 250, 300, 350, 400, 575 and 600 hours are presented in Figure 13. This shows how the stress level in the substrate remains fairly constant, generally fluctuating between ± 50 MPa, which is the typical uncertainty of the XRD technique, with a mean value of approximately 50 MPa. The residual stresses in the oxide layer are more self consistent than those found in the substrate. These show that the residual stress in the oxide after 6 cycles is highly compressive, in the order of -450 MPa. This corresponds to a dense oxide structure with some slight porosity. The residual stress in the oxide remains at this level for another 5 thermal cycles but then starts to relax

faster as the oxide develops more cracks and porosity. This is evident from the stress measurements and micrographs for the period between 13 to 25 thermal cycles. After 600 hours exposure the oxide scale continues to grow and strains are likely to still develop at the interface.

It is clear from the results of the residual stress measurements that during thermal cycling there is a stress build up which develops within the oxide. This originates from the differences in thermal expansion coefficients. Large stresses have been shown to be generated, which are more than capable of cracking the oxide and causing spallation. Further measurements are required to establish the repeatability of this stress build up, but it is feasible that a relationship between temperature, cooling rates and oxide thickness can be developed and included in the modelling tool to give an improved prediction of stress build up and oxide spallation. This could then be used to aid lifetime management of plant, and help schedule maintenance periods.

Conclusions

It has been shown that residual stress measurements can identify regions of improved properties and be used to map the extent of these regions, although consideration of growth and/or transformation stresses is also required. Heat, or rather thermal transients, have also been shown to effect the function of components, in this case a heat exchanger. Measurements of the residual stresses in the oxide layer formed has shown how the stress develops in the scale, thereby supplying the stored energy required to produce cracking and lead to scale exfoliation.

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