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Measurement of Growth Strain in Oxide Scales by Parallel Beam X-Ray Diffraction

Summary

This note is concerned with the measurement of growth strains in oxide scales. The proposed technique utilises a general X-ray diffraction facility with an attachment to collimate the reflected X-rays to increase the precision and speed of the measurement. The technique has been validated by comparison of results with two common methods of growth strain measurement viz the deflection test and the specimen extension test.

Background

During the oxidation process strains are introduced into the oxide scale as the volume of oxide formed by reaction between the substrate and the oxidising atmosphere differs from that of the substrate that it replaces. In most engineering alloys this strain is compressive in the oxide scale. If this strain is not relieved by substrate or oxide creep then eventually the oxide scale will fracture and the oxidation rate will be accelerated by loss of protection. A knowledge of the generation and relief of oxide growth stress is necessary in order to predict accurately the lifetime of high temperature components.

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Conventional X-Ray Diffraction Techniques

The principle behind the measurement of growth stresses by X-ray diffraction is that the spacing of interatomic planes in stressed material differs from that in unstressed material. Changes in the interatomic spacing can therefore be related to the *elastic* strain in the material and hence to the stress. The technique involves repeated scanning of a selected peak with the specimen orientated at an increasing angle, φ, to the incident beam. The geometry of the experimental set-up is shown in Figure 1. The shift in interatomic spacing as a function of φ gives the strain according to the expression:-

$$\frac{d_\varphi - d_0}{d_0} = \varepsilon_{el}\left(\frac{1+\nu}{1-\nu}\right)\sin^2\varphi$$

where

d_φ is the measured interatomic spacing at angle φ

d_0 is the measured interatomic spacing at φ=0

ε_{el} is the elastic strain in the specimen

ν is the Poisson's ratio of the oxide scale

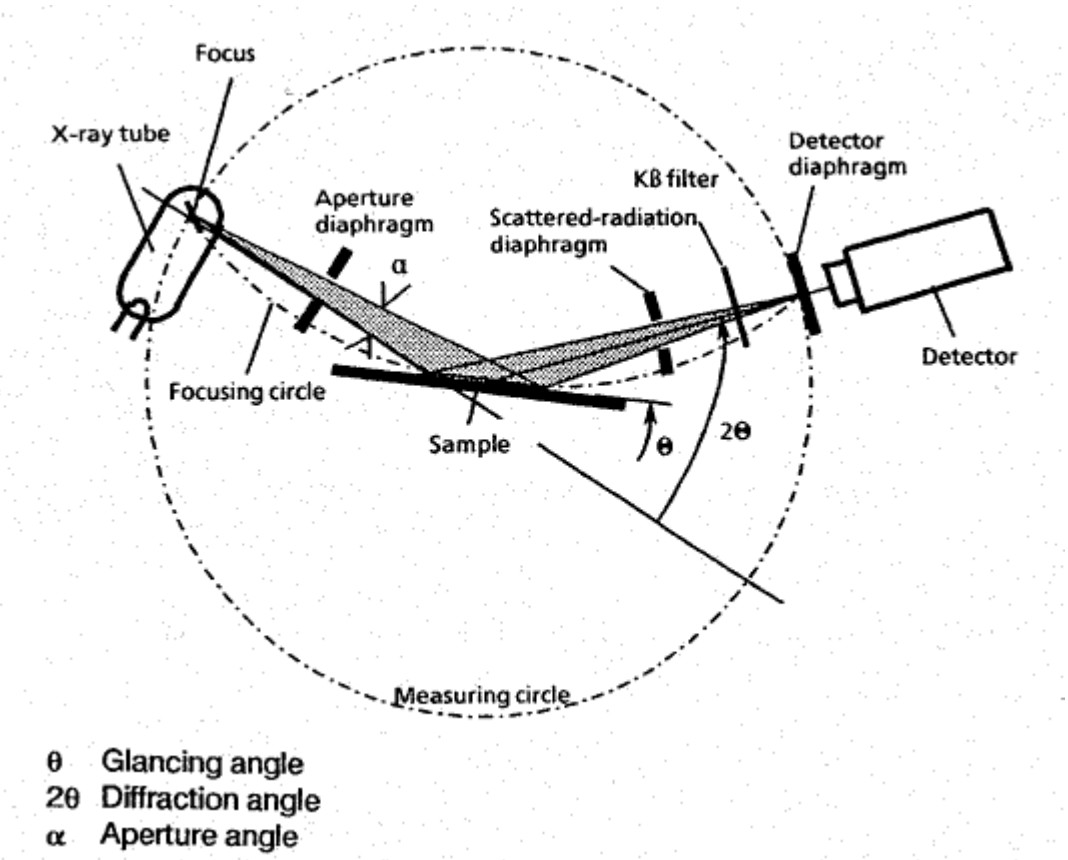

Figure 1 Schematic Representation of X-Ray Diffraction Apparatus used in Conventional Mode

Typically strains in the order of 0.05% can be resolved which gives stresses ~100 MPa [1].

Care must be exercised to select a peak which is unambiguously identified with the oxide under investigation and is sufficiently defined to allow reliable measurement of the interatomic spacings at the different φ. The equipment must also be calibrated by scanning a suitable stress-free (eg powder) sample to identify any peak shift arising from misalignment in the test equipment.

Specimen heating is preferably achieved by direct resistance heating of conducting specimens and monitored by a calibrated thermocouple attached directly to the specimen. Care must be taken to ensure that the thermocouple does not interfere with the X-ray path.

The typical time taken for a scan at growth temperatures is ~2 hours and the minimum thickness of scale that can be measured is 2–3 μm.

Parallel Beam X-Ray Diffraction

The experimental set up required to modify X-ray diffraction facilities to parallel beam operation is shown in Figure 2. The technique was originally developed to characterise thin layers of single crystal deposited upon various substrates and used very low angles of incidence for the X-ray beam - so called glancing angle X-ray diffraction. It has been claimed that using the facility in glancing angle mode then films of thickness ~1 μm can be characterised [2].

Glancing incidence angles cannot be used to measure residual strain in oxide layers as insufficient values of the angle φ can be generated; however the modified equipment does offer considerable advantages over conventional X-ray diffraction apparatus in terms of enhanced intensity of the diffracted beam resulting in more rapid scanning of the individual peaks and the ability to detect and measure peaks on thinner scales.

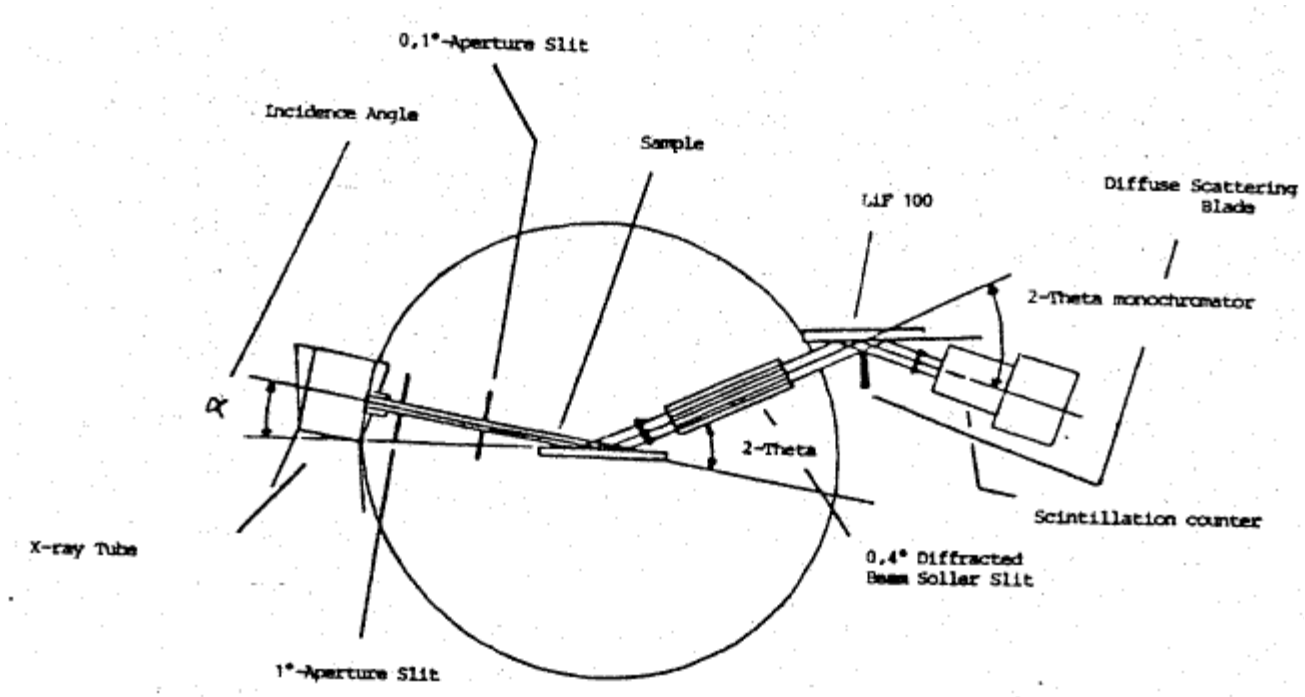

Figure 2 Schematic Representation of XRD Apparatus Configured for Parallel Beam Configuration

Validation Experiments

Parallel Beam X-Ray Diffraction

A matrix of tests to measure growth stresses on materials that form Al_2O_3 has been carried out. Two substrates, Fecralloy and PM2000, were chosen that exhibited low and high creep strength respectively at the oxide growth temperatures, 1000 and 1100°C.

In both materials the growth stresses were compressive. The stresses in PM2000 (~1 - 2 GPa at both temperatures) are greater than in the Fecralloy (400-700 MPa). This observation is a result of relaxation in the metallic substrate being much more rapid in the weaker Fecralloy than in PM2000.

Specimen Extension Tests

Where the cross section of the oxidising specimen is small, the stresses evolving in the oxide and resultant stresses in the substrate can act to produce plastic strain in the substrate, leading to a uniform extension of the specimen which can be measured after cooling to room temperature. This extension can then be used to calculate the average stresses that developed in scale and substrate during oxidation. The only requirement for independent data is that the creep properties of the substrate are also known. Creep rate,ε dot, can be expressed in the form:-

$$\dot{\varepsilon} = A\,\sigma^{n}\,\exp\text{-}\left(\frac{Q}{RT}\right)$$

where

A is a constant
σ is the stress acting on the substrate
n is the stress exponent
Q is the activation energy
R is the gas constant
T is the absolute temperature

Analysis of the stress distribution [2] leads to the expression for the stress in the oxide scale, σ_{ox1} thus:

$$\sigma_{ox} = -\frac{h}{2\xi}\left(\frac{\dot{\varepsilon}}{A\exp\left(\frac{Q}{RT}\right)}\right)^{\frac{1}{n}}$$

where

h is the thickness of the substrate

ξ is the oxide scale thickness

The lower limit of strain that can be measured is ~0.01%. This corresponds to a mean creep rate of 10^{-9} s^{-1} on a 24 h exposure.

Thin specimens of PM2000 and Fecralloy have been exposed at 1000 and 1100°C for 8, 16 and 24 h. The length of each specimen was measured before and after the exposure using a travelling microscope. The specimens were then sectioned and the oxide thickness measured under the optical microscope.

The creep laws used for the two materials are as follows:

Fecralloy

$$\dot{\varepsilon} = 5.96 \times 10^{-27} \sigma^{5.5} \exp\left(\frac{-47136}{T}\right),\ s^{-1}$$

(σ measured in Pa)

PM2000 at 1100°C

$$\dot{\varepsilon} = 1.08 \times 10^{-27} \sigma^{11},\ s^{-1}\ (\sigma \text{ measured in MPa})$$

Using the above analysis, growth stresses were calculated for the two alloys. Again the growth stresses decay with increasing oxidation time and those generated in PM2000 (2-5 GPA) are an order of magnitude greater than those generated in Fecralloy (100-400 MPa).

The calculation of growth stress using this method is critically dependent upon the creep laws for the substrate material. Creep data for PM2000 shows a very high degree of scatter and data for Fecralloy is sparse at these temperatures. Caution must therefore be used in placing too great an emphasis on the precision of these data.

Deflection Tests

This approach utilises thin rectangular specimens whose length is much greater than their width or thickness - typical dimensions are 50 x 10 x 0.2 mm. The specimen is protected from oxidation on one face eg by deposition of a protective coating. Oxidation of the remaining large surface causes bending in the sample resulting in a measurable deflection. The test relies upon the corrosion resistance of the coating to prevent all but minimal oxidation of the protected surface. A schematic representation of the experimental apparatus is shown in Figure 3.

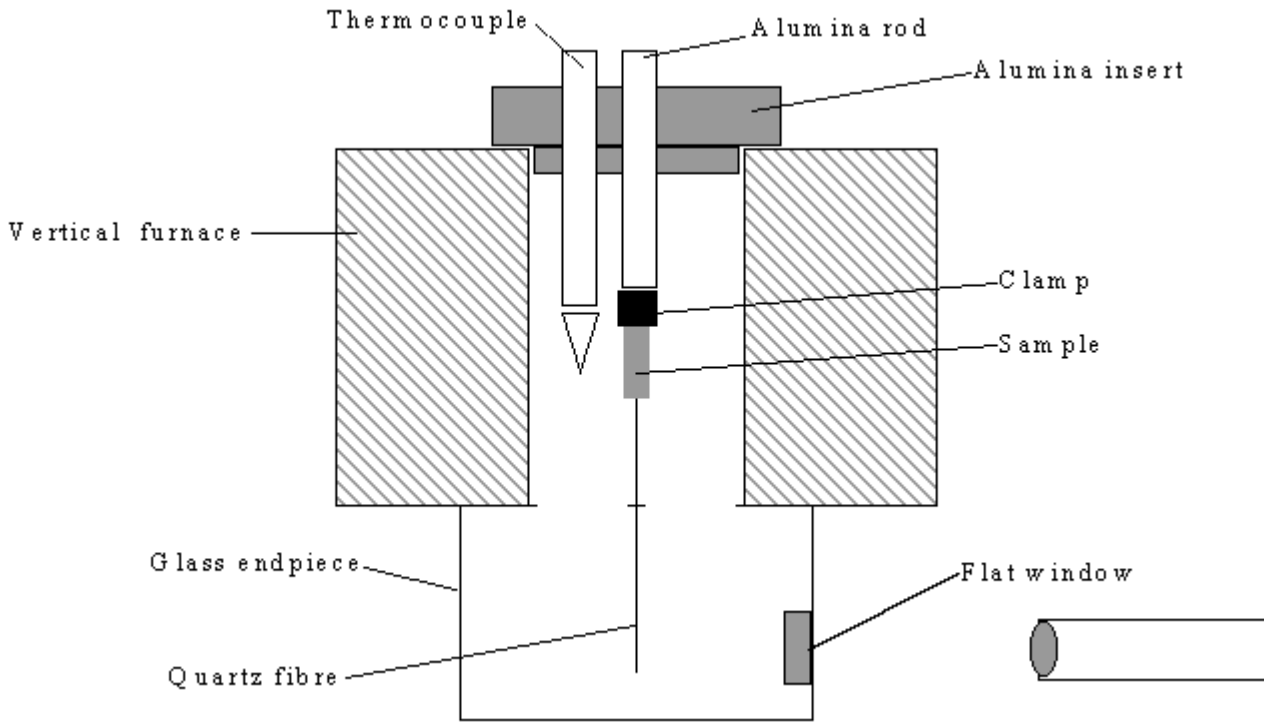

Figure 3

Analysis of the experiment is complex and requires measurement of the rate of change of curvature of the substrate and oxide. The analysis, which requires knowledge of the creep properties of test sample and numerical solution of a pair of simultaneous equations, has been described fully in work published previously [3].

One series of growth stress measurements has been carried out on Fecralloy at 1000°C and the results are presented in Figure 4. The growth stresses again decay with increasing oxidation time and are consistent with those measured using the other techniques.

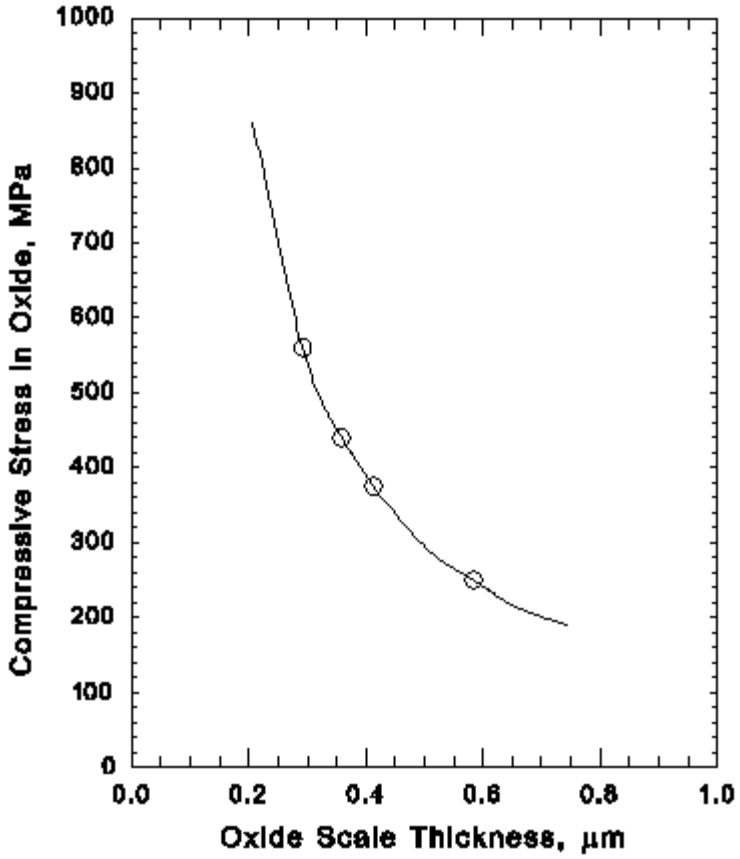

Figure 4

Summary and Conclusions

Growth stresses have been measured on alloys which form an alumina scale, using three techniques. The techniques give results which are broadly consistent and indicate clearly that growth stresses are substantially relaxed by creep of the substrate - growth stresses in an oxide of a given thickness are reduced when the substrate is weakened either by an increase in oxidation temperature or when the inherent substrate strength is low.

Parallel beam X-ray diffraction has the advantage over the other techniques investigated in that it requires fewer independent data inputs. The other two techniques both require creep data for the substrate material which may not be available or, even if it does exist, may show considerable scatter, thereby introducing uncertainties into the calculated growth stress.

Acknowledgements

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