TEMPERATURE RESOLVED EVALUATION OF RESIDUAL STRESSES IN AN \(\alpha\)-\(\text{Al}_2\text{O}_3\) SCALE USING PARALLEL BEAM X-RAY DIFFRACTION

M. Groß, V. Kolarik, L. Singheiser*, W. Engel, N. Eisenreich

Fraunhofer-Institut für Chemische Technologie ICT, D-76327 Pfungtal, Germany
*Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

ABSTRACT

Residual Stresses in an \(\alpha\)-\(\text{Al}_2\text{O}_3\) scale on PM 2000 were examined by in situ X-ray diffraction during the growth of the oxide at 1060°C and during cooling and heating. At oxidation temperature small compressive stresses of less than -100 MPa were found, whereas larger compressive stresses built up during cooling, which reached about -4000 MPa at room temperature. Parallel beam geometry achieved on the laboratory source by a parabolic Göbel-mirror proved to be a useful tool to avoid measuring errors caused by inaccurate sample positioning due to the heating strip or non symmetric diffraction condition.

INTRODUCTION

Because the oxidation resistance of the high-temperature material PM 2000 is achieved by a protecting \(\alpha\)-\(\text{Al}_2\text{O}_3\) oxide scale, the adherence of the scale to the substrate and its stability are crucial for the life-time of the component [1]. Spallation of the scale leads to a loss of this protection and cracks in the oxide provide easy diffusion paths reducing the protection [2,3]. Even if the scale is healed by further oxidation, the ongoing process of damage and healing leads to a depletion of the oxide forming constituent aluminum in the upper region of the alloy. This results in less protective oxides being formed and an increase in oxidation rate [4]. Spallation and oxide cracking are caused by mechanical stresses in the oxide scale. Hence, the knowledge of such stresses is important for the development of high-temperature resistant materials.

Residual stresses in the oxide scale occur as growth stresses at oxidation temperature e.g. when inward diffusion of oxygen ions and outward diffusion of metal ions lead to further oxide formation within the scale or due to phase transformation. The major contribution to residual stresses at room temperature however are thermally induced stresses caused by different thermal expansion coefficients of oxide and alloy during cooling. As the knowledge of stress development and relaxation mechanisms is necessary for improving the adherence of oxide scales, in situ stress determinations are important.

Whereas X-ray diffraction stress analysis is a common tool for the determination of mechanical stresses at room temperature, few papers have been published of in situ X-ray stress analysis at high temperatures [5,6,7,8,9,10]. This is due to difficulties in tilting the samples while holding the temperature and maintaining the necessary precision in sample position. This study overcame the limitations by application of modern parallel beam geometry.
X-RAY STRESS ANALYSIS

X-ray stress analysis relies on the measurement of lattice strains \( \varepsilon \) or more precisely speaking of lattice plane distances \( d \). Due to the transverse strain the value of \( \varepsilon \) depends on the angle between \( \varepsilon \) and the applied stress \( \sigma \). Therefore in X-ray stress analysis the measured \( \varepsilon \) changes with the tilting angle \( \psi \) of the sample. In a flat, i.e. biaxial and surface-parallel stress state, which is likely in a thin oxide scale, the dependence curve of the strain \( \varepsilon \) to \( \sin^2 \psi \) is linear. In the case of a stress gradient perpendicular to the surface the curve is bent due to the dependence of the penetration depth on \( \psi \). In the case of texture the curve shows an oscillating appearance and in the case of a deviation from the flat stress state there are two curves: one for positive and one for negative \( \psi \).

The \( \varepsilon \) to \( \sin^2 \psi \) dependence for a flat stress state with additional rotational symmetry is

\[
\varepsilon_{\phi, \psi} = \frac{1}{2} s_2^{(hkl)} \sigma \sin^2 \psi + 2 \cdot s_1^{(hkl)} \sigma
\]

where \( \sigma \) is the surface-parallel stress and

\[
\frac{1}{2} s_2^{(hkl)} = \frac{\nu^{(hkl)} + 1}{E^{(hkl)}} \quad \text{and} \quad s_1^{(hkl)} = -\frac{\nu^{(hkl)}}{E^{(hkl)}},
\]


However, in X-ray stress analysis lattice plane distances are measured and the lattice strain has to be calculated according to

\[
\varepsilon = \frac{d - d_0}{d_0} \quad \text{where} \quad d_0 \quad \text{is the unstrained and} \quad d \quad \text{the strained lattice plane distance. It is difficult to get precise values for} \ d_0 \ \text{especially for higher temperatures. This can be overcome in the flat stress state with rotational symmetry where} \ \sigma \ \text{is determined by the gradient} \ m \ \text{and the intercept of the axis} \ b \ \text{of the} \ \sin^2 \psi \ \text{-diagram. This overdetermination allows to eliminate} \ d_0 \ \text{in the equations. A} \ d \ \text{to} \ \sin^2 \psi \ \text{-diagram is plotted, which in this case shows an equivalent linear behaviour}
\]

\[
d = m \sin^2 \psi + b.
\]

Comparison with the \( \varepsilon \) to \( \sin^2 \psi \)-dependence leads to the formula

\[
\sigma = \frac{1}{\frac{m}{s_2^{(hkl)}} \cdot \frac{h}{m} - 2 s_1^{(hkl)}}
\]

which was used to evaluate the measurements.

The \( \frac{1}{2} s_2^{(hkl)} \) were calculated for the hexagonal lattice of corundum according to the Reuss-model taken from Sarioglu et al. [9] using the single crystal elastic compliances of corundum given by Tefft [12] from room temperature to 600°C and estimated for values above 600°C. The values of \( s_1^{(hkl)} \) were taken from Eigenmann and Macherauch [13].
<table>
<thead>
<tr>
<th>X-ray reflection</th>
<th>(116)</th>
<th>(416)</th>
<th>(2 1 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>at room temperature</td>
<td>$\frac{1}{2}S_2^{[hk]}$</td>
<td>$3.30 \times 10^{-6}$ MPa</td>
<td>$3.09 \times 10^{-6}$ MPa</td>
</tr>
<tr>
<td></td>
<td>$S_1^{[hk]}$</td>
<td>$-0.66 \times 10^{-6}$ MPa</td>
<td>$-0.76 \times 10^{-6}$ MPa</td>
</tr>
<tr>
<td>at 1060°C</td>
<td>$\frac{1}{2}S_2^{[hk]}$</td>
<td>$4.13 \times 10^{-6}$ MPa</td>
<td>$3.87 \times 10^{-6}$ MPa</td>
</tr>
<tr>
<td></td>
<td>$S_1^{[hk]}$</td>
<td>$-0.79 \times 10^{-6}$ MPa</td>
<td>$-0.90 \times 10^{-6}$ MPa</td>
</tr>
</tbody>
</table>

Table 1: X-ray elastic constants of $\alpha$-Al$_2$O$_3$ used for stress evaluation.

MEASURING SYSTEM

The measuring system for temperature resolved X-ray stress analysis consists of an X-ray diffractometer D5000 by Bruker AXS combined with a high-temperature device by Paar and a programmable temperature controller as used for previous in situ high-temperature oxidation studies [14,15].

The sample tilting is achieved by asymmetric diffraction geometry, what is called the $\Omega$-setting (Figure 1). The restriction of the $\Omega$-setting is that the tilting angle $\psi$ is limited by the diffraction angle $2\theta$ to $|\psi| < 0$. Reflections with higher diffraction angles allow a larger range of $\psi$ and provide a higher accuracy in $d$, but are often weak in intensity. The choice of reflections is a compromise depending on measuring time available.

In the $\Omega$-setting the Bragg-Brentano focusing condition is not fulfilled due to the asymmetric geometry in contrast to the $\psi$-setting, where the sample tilting is achieved by an additional diffractometer circle. This leads to errors in the measured diffraction angles which are larger than the strain effects by a factor of up to ten and have to be corrected. However, a combination of the advantageous $\psi$-setting with a high-temperature device is not available.

Whereas a high precision in 20-measurement is required for stress determination, the use of a long heating strip for high temperature measurement which can easily be bent can result in a deviation from Bragg-Brentano focusing condition, leading to errors in the detection of diffraction angles. An alignment prior to the oxidation experiment using substrate reflections is hindered by variable lattice parameters depending on composition and can be altered by thermal expansion of the strip on heating.

In this work the effects of asymmetric geometry and of sample displacement were overcome by a parallel beam X-ray geometry. This was achieved by using a Göbel mirror in the incident beam, which is a parabolically bent multilayer with an appropriate gradient in the layer thickness designed to parallelize divergent X-rays [16]. Using the Göbel mirror instead of a parallizing the radiation with a collimator pipe avoids losses in intensity. It was shown that parallel beam geometry with a Göbel mirror enables correct angle detection despite asymmetric diffraction and sample displacement [17]. Copper K$_\alpha$ was used due to the construction of the Göbel mirror. The experimental setup used is shown in Figure 1.
Using parallel beam geometry a soller slit is necessary in front of the scintillation counter for a correct angle detection. Because of the fluorescence of the iron containing sample in the copper radiation a LiF secondary monochromator was used. The wavelength bandwidth of the monochromator is determined by the divergence of the incident radiation. Therefore the use of the fine 0.14° soller slit led to too low intensities and a combination of secondary monochromator with 0.4° soller slit proved to be an appropriate combination.

Figure 1: Geometry of the parallel beam Ω-diffractometer using a Göbel mirror.

MATERIAL

For the experiments the oxide-dispersion-strengthened superalloy PM 2000 was chosen, since it forms a homogenous α-Al₂O₃-scale at temperatures above 1000°C. It was developed by PM Hochtemperatur-Metall GmbH / Plansee AG [18] in a series of powder metalurgical materials for us in the temperature-range between 900 and 1350°C. Applications among others are heating elements, combustion chambers of gas turbines and moulds for glass press work.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>Y₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PM 2000</strong></td>
<td>bal</td>
<td>19</td>
<td>5.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 2: Composition of PM 2000 in weight percent.

EXPERIMENT

The PM 2000 sample was 10 x 10 x 1 mm in size, polished to 1 µm, fixed onto the heating strip with a high temperature ceramic glue and cleaned with alcohol immediately prior to the experiment. After the sample was oxidized at 1060°C for 100h, it was cooled to room
temperature, reheated to 1060°C and cooled to room temperature again, each cooling or heating phase lasting for 4 h. At oxidation temperature and room temperature precise stress measurements in the alumina layer were carried out using the (416) and (2 1 10) reflection. The stress development during oxidation, during cooling and during heating was monitored with fast measurements using the intense (116) reflection.

RESULTS AND DISCUSSION

Figure 2 and Figure 3 show the sin²ψ-diagrams of the (416) reflection of α-Al₂O₃ at oxidation temperature and after cooling to room temperature. The linear functions confirm the assumption of a stress state without texture and gradient. The diagrams are equally scaled to show the difference in stress between oxidation temperature and room temperature. The stresses measured at 1060°C are shown in Table 3, those measured at room temperature in Table 4. Figure 4 contains the stress development during oxidation and Figure 5 the stress development during cooling and reheating.

![Figure 2: sin²ψ-diagram of the (416)-reflection of α-Al₂O₃ on PM 2000 at 1060°C.](image)

At 1060°C small compressive growth stresses were found in the oxide scale by in situ X-ray diffraction, which were caused by the formation of new oxide within the layer grown before due to counter diffusion of aluminum and oxygen. Within the first few hours of oxidation the growth stresses were higher, but were reduced to about -80 MPa within 30 h by relaxation (Figure 4).

The compressive stresses increased linearly during cooling such that the room temperature stresses were dominated by thermal stresses (Figure 5). To judge this statement the expected
thermal stress was calculated from average values over the temperature range of the thermal expansion coefficients of PM 2000 and alumina in the approximation for a thin scale using [19]

\[
\sigma = -E_{\text{ox}} \cdot \Delta T \cdot (\alpha_{\text{met}} - \alpha_{\text{ox}}) \cdot \frac{1 - \nu_{\text{ox}}}{T_0 - T_1}
\]

Figure 3: \(\sin^2 \psi\)-diagram of the (416)-reflection of \(\alpha\)-Al\(_2\)O\(_3\) on PM 2000 at room temperature.

<table>
<thead>
<tr>
<th>at 1060°C</th>
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<th>(416)</th>
<th>(2 1 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before reheating</td>
<td>measuring time</td>
<td>2 h</td>
<td>15 h</td>
<td>14 h</td>
</tr>
<tr>
<td>residual stress</td>
<td>-85 MPa</td>
<td>-59 MPa</td>
<td>-134 MPa</td>
<td></td>
</tr>
<tr>
<td>after reheating</td>
<td>measuring time</td>
<td>12 min</td>
<td>71 min</td>
<td>-</td>
</tr>
<tr>
<td>residual stress</td>
<td>-81 MPa</td>
<td>-18 MPa</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Residual stresses in \(\alpha\)-Al\(_2\)O\(_3\) on PM 2000 at 1060°C before and after reheating.

<table>
<thead>
<tr>
<th>at room temperature</th>
<th>X-ray reflection</th>
<th>(116)</th>
<th>(416)</th>
<th>(2 1 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before reheating</td>
<td>measuring time</td>
<td>2 h</td>
<td>9 h</td>
<td>-</td>
</tr>
<tr>
<td>residual stress</td>
<td>-4138 MPa</td>
<td>-3852 MPa</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>after reheating</td>
<td>measuring time</td>
<td>1 h</td>
<td>8 h</td>
<td>5 h</td>
</tr>
<tr>
<td>residual stress</td>
<td>-4142 MPa</td>
<td>-3813 MPa</td>
<td>-3792 MPa</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Residual stresses in \(\alpha\)-Al\(_2\)O\(_3\) on PM 2000 at room temperature before and after reheating.
Figure 4: Development of residual stress in $\alpha$-$\text{Al}_2\text{O}_3$ on PM 2000 at 1060°C measured using the (116) reflection.

Figure 5: Development of residual stress in $\alpha$-$\text{Al}_2\text{O}_3$ on PM 2000 on cooling, reheating and second cooling between 1060°C and room temperature measured using the (116) reflection.
For the cooling from 1060°C to room temperature a thermal stress of -2400 MPa was estimated, which is lower than the measured results. The difference might be due to an uncertainty in the thermal expansion coefficient of PM 2000. For this calculation a value given by the manufacturer [18] was used, which is smaller than comparable literature values. An alternative explanation is an alteration of the thermal expansion coefficient of the oxide by solid solution of Fe or Cr ions in the \( \alpha-Al_2O_3 \)-scale.

The reversibility of the thermal stress on reheating and second cooling indicates that there are no inelastic relaxation mechanisms on cooling (Figure 5).

The results show that temperature resolved stress measurements with in situ X-ray diffraction are possible and provide insights into stress formation and relaxation. The stress development with time and temperature and the similarity of results before and after reheating demonstrate a high relative precision. While the uncertainty of the small stress values at oxidation temperature is about as large as the values themselves, the fact that no positive stress values were found in all experiments confirms the existence of a small compressive stress state (Table 3). At room temperature the stresses measured using the (416) and (2 1 10) reflection are in good agreement, whereas the values determined by the (116) reflection are less reliable due to the smaller \( \psi \)-range and the higher errors at smaller diffraction angle 2\( \theta \) (Table 4).

Parallel beam geometry proved to be an important tool for in situ stress determination. The use of the Göbel mirror and the arrangement described above allowed correct lattice strain measurements all through the range of positive tilting angles \( \psi \) and despite shifts in the heating strip height due to thermal expansion. The measurements with negative \( \psi \) were less accurate, because their high penetration depth yielded too low reflection intensities of the 4 \( \mu \)m thin oxide scale.

REFERENCES


