On cooling rate dependent spallation behavior of \( \alpha \)-alumina scale grown by oxidation

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Abstract. It is hypothesized that dynamic and non-uniform plastic relaxation occurs in \( \alpha \)-Al\(_2\)O\(_3\) scale on Fe-Cr-Al substrate during cooling from high temperature, and furthermore, that the non-uniformity of plastic relaxation is related to (1) the variation of residual stress with respect to cooling rate; and (2) the rate of stress relaxation. Based on this hypothesis, a mechanical model is developed which gives accurate predictions for the cooling dependent spallation behavior of \( \alpha \)-Al\(_2\)O\(_3\) grown by oxidation.

Keywords: Alumina scale, Cooling rate, Pockets of energy concentration, Residual stress, Spallation.

1 Introduction

Tolpygo and Clarke [1,2] presented an excellent experimental study on the room temperature spallation failure of \( \alpha \)-alumina scale grown by oxidation on Fe-Cr-Al alloy substrate. Their observations are remarkable and thought-provoking. Refs. [1,2] convincingly demonstrate a thin scale spallation process with an unknown mechanism. To help readers understanding the work herein, a brief introduction to Refs. [1,2] is now given.

In Refs. [1,2], \( \alpha \)-Al\(_2\)O\(_3\) scales of different thicknesses were formed on the surface of Fe-Cr-Al heat-resistant alloy substrates of different thicknesses by oxidizing them at 1200 °C for different time periods. These scale-substrate material systems were then cooled to room temperature at different cooling rates. Cooling causes an increase of compressive in-plane residual stress in the \( \alpha \)-Al\(_2\)O\(_3\) scale due to thermal expansion mismatch with the substrate. The major observations were as follows: No separation or spallation failure occurs during cooling at any rate. For specimens cooled to room temperature at rates in the range 5–200 °C min\(^{-1}\), circular interfacial separations develop, apparently spontaneously, at a constant compressive residual stress far below the critical buckling stress: The separations nucleate, grow in separation distance and propagate...
radially. After a period of slow and stable growth, some of these separations then grow abruptly and the oxide spalls off. For specimens cooled at extremely slow cooling rates (≤2°C min⁻¹) and at very fast cooling rates (≥500°C min⁻¹), no separation or spallation occurs at any point. Various causes for the phenomenon were proposed and thoroughly and insightfully examined by Tolpygo and Clarke [1,2]. None of them, however, gives a completely satisfactory explanation.

Recent studies [3,4] hypothesize that pockets of energy concentration (PECs) in the scale-substrate material system exist due to dynamic and non-uniform plastic relaxation or creep during cooling. The energy in a PEC is essentially an extra strain energy in the scale-substrate material system in addition to the strain energy in the scale due to the biaxial in-plane compressive stress. PECs may be the cause of scale separation nucleation, growth and spallation at constant in-plane compressive stress after cooling to room temperature. When the separation process is regarded as the continuation of dynamic and non-uniform plastic relaxation, the time dependence of the process is apparent.

According to the hypothesis, PECs are formed during cooling and are randomly distributed. Their energy depends on cooling rate, scale thickness, substrate thickness, etc. In the case of fast cooling, nearly no plastic or creep relaxation due to cooling occurs in either the scale or the substrate and the mechanical process is closely thermo-elastic [1]. It is therefore reasonable to expect that very fast cooling results in uniform biaxial in-plane compressive stress in the scale and no interfacial stress except for in areas near to the edges of a specimen. In this case, therefore, there are no PECs formed in the oxide-substrate material system, even though the scale has the largest residual stress. In contrast, nearly complete plastic or creep relaxation will occur in both the scale and the substrate during extremely slow cooling. It is therefore again reasonable to expect that extremely slow cooling also results in uniform biaxial in-plane compressive stress in the scale and no interfacial stress except for in areas near to the edges of a specimen. In this case, therefore, there are also no PECs formed in the scale-substrate material system (with the scale having the smallest residual stress). Intermediate cooling rates, however, are unable to produce steady and uniform plastic relaxation.

A mechanical theory was developed in Refs. [3,4] based on the above PECs hypothesis which gives excellent predictions of some aspects of the spallation behavior, including the stable, unstable growth, and spallation sizes. In this work, a model is developed to explain and predict the cooling rate dependent spallation behavior.

2 Cooling rate dependent spallation behaviour

In Refs. [1,2], commercial Kanthal A-1 alloy samples (Fe-21.2%Cr5.6%Al in wt.%) with thickness of 0.53 mm, 1.05 mm, 2.00 mm and 2.65 mm were prepared, polished to a 3-µm surface finish and cleaned in acetone. Then all the samples were oxidized at 1200 °C in ambient air for durations in the range 0.5–100 h to produce alumina scales with different thickness. Figure 1 shows the specimens that were oxidized for 25 h. The randomly distributed white spots are spallation sites. Note that separation nucleation, growth and spallation of the α-alumina scales occurred at room temperature and under constant compressive residual stress. The substrate thickness of the samples shown in
Figs. 1a–f is 1.05 mm. It is seen that no spallation occurs when the cooling rate is 2°C min⁻¹ as complete plastic relaxation is achieved at any temperature during cooling resulting in no PECs. When the cooling rate is 500°C min⁻¹, also no spallation is observed as the cooling process is purely thermo-elastic resulting in no PECs. Spallation is observed, however, at intermediate cooling rates, with it being most prevalent at about 20°C min⁻¹. Furthermore, Figs. 1g–i shows that the spallation behavior also depends on the substrate’s thickness as more spallation observed on the thinner substrate.

As mentioned earlier, recent studies [3,4] hypothesized that dynamic and non-uniform plastic relaxation from intermediate cooling rates results in pockets of tensile stress on the interface and its adjacent material. These pockets of stresses result in PECs and cause scale separation nucleation, growth and spallation. In this work, it is further hypothesized that the non-uniformity of plastic relaxation from intermediate cooling rates is related to (1) the variation of residual stress with respect to cooling rate; and (2) the rate of stress relaxation. In the following, a model is developed based on this hypothesis.

Figure 2 shows the compressive residual stresses measured at room temperature in α-alumina scales grown on Kanthal samples of various thickness after 25 h oxidation at 1200°C and cooling at various rates. The experimental data [1,2] (also shown in Fig.
1) show that the cooling rate that produces the most prevalent spallation is within this range.

![Fig. 2. The compressive residual stresses in α-alumina scales grown on Kanthal samples of various thickness and at various cooling rates.](image)

Table 1. Values of parameters $a$, $b$ and $c$ in Eq. (1).

<table>
<thead>
<tr>
<th>$h_i$ [mm]</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\sigma_0^*$ [GPa]</th>
<th>$\tilde{R}$ [°C/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.53</td>
<td>0.67</td>
<td>26.75</td>
<td>3.11</td>
<td>4.55</td>
<td>22.35</td>
</tr>
<tr>
<td>1.05</td>
<td>0.80</td>
<td>31.97</td>
<td>3.65</td>
<td>5.06</td>
<td>25.72</td>
</tr>
<tr>
<td>2.00</td>
<td>0.73</td>
<td>23.95</td>
<td>4.26</td>
<td>5.21</td>
<td>17.91</td>
</tr>
<tr>
<td>2.65</td>
<td>0.84</td>
<td>9.82</td>
<td>4.26</td>
<td>5.21</td>
<td>7.05</td>
</tr>
</tbody>
</table>

Each curve in Fig. 2 can be approximated by the following formula:

$$\sigma_0 = ae^{-bR} + c,$$

where $R$ represents the cooling rate in °C min$^{-1}$, and the parameters $a$, $b$ and $c$ can be determined by finding the best fit to the experimental data, which are tabulated in Table 1. The quantity $\sigma_0^*$ in Table 1 is the maximum compressive residual stress measured at very fast cooling rates (≥500°C min$^{-1}$) for which no plastic relaxation occurs. Based on the hypothesis above, a function $F(R)$ which represents the non-uniformity of plastic relaxation is defined as

$$F(R) = \frac{d\sigma_0}{dR} = \frac{d\sigma_0^R}{dt} = \frac{ab}{R} e^{-bR} \cdot \frac{\sigma_0^* - \sigma_0}{\Delta T},$$

where $\sigma_0^R$ represents the stress relaxation and $\Delta T$ is the temperature drop.

Figure 3 shows the variation of $F(R)$ with respect to cooling rate for the experimental cases shown in Fig. 2. Note that the cooling rate for the maximum $F(R)$ is represented by $\tilde{R}$ which is recorded in Table 1. Two important observations are seen...
in Fig. 3: (1) the value of $\bar{R}$ is around 20 °C min$^{-1}$ for the first three cases, which is in excellent agreement with the experimental data [1,2] (also shown in Fig. 1), and (2) the values of $F(R)$ for the two cases with thicker substrates are considerably smaller than those for the two cases with thinner substrates. This indicates that more spallation occurs in the samples with thinner substrates, which again agrees with the experimental observations in Refs. [1,2] (also shown in Fig. 1).

![Figure 3](image)

**Fig. 3.** The variation of $F(R)$ in Eq. (2) with respect to the cooling rate.

## 3 Conclusion

A mechanical model is developed to quantify the non-uniformity of plastic relaxation in the $\alpha$-Al$_2$O$_3$ scales on Fe-Cr-Al alloy substrates during cooling at various cooling rates. This work reveals two important factors which affect the relaxation and spallation behavior of alumina scales. They are: (1) the variation of residual stress with respect to cooling rate; and (2) the rate of stress relaxation. The predictions from the analytical model are in very good agreement with the experimental observations in Refs. [1,2].

## 4 References