

## **Quantifying High Temperature Corrosion**

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### **ABSTRACT**

Alloys designed for high temperature service can form a variety of surface oxides or scales based on the alloy composition, service temperature, gas environment, surface deposits, etc. The most severe environments, including molten salts and liquid metals can result in significant metal loss, void formation and/or pitting. Standard and evolving practices are discussed for measuring these types of degradation including measuring oxide scale thickness, internal oxidation and/or metal loss, correlating them to mass change and reporting the results. Manual and automated methodologies to measure oxide thickness and metal loss are reviewed and compared in order to provide a summary of techniques and identify the best practices for quantifying a variety of materials and damage mechanisms and producing statistically meaningful results. Such techniques create datasets useful for improved understanding of corrosion degradation mechanisms, potentially better predictive models and enhanced data analytics.

Key words: High temperature oxidation, liquid metals, molten salts, quantification

### **INTRODUCTION**

Research to develop high temperature corrosion solutions may include new environments and/or new materials, including coatings, surface modifications, etc. Often the first level of evaluation is specific specimen mass change. However, mass change may not be adequate to quantify the extent of attack if there are complications such as a non-uniform reaction front or to differentiate internal and external oxidation [1]. Likewise, characterization may be needed if there are two competing mechanisms (e.g. oxide formation and volatilization [2] or dissolution [3,4]) or involve complications with deposit-induced corrosion [5] due to the combined mass of the reaction products and residual deposits. In many cases, it is necessary to determine the depth of attack, thickness of the oxide scale, depth of subsurface precipitate dissolution and quantitatively report it in an accurate, useful and insightful manner. However, it is not always clear how to accomplish this reporting. Some current techniques are reviewed to begin

a conversation about the best practices and the increased use of automated optical imaging and/or image analysis [6-8] especially with regard to some complex issues like mechanistic studies of internal oxidation [9,10] and alloy compatibility in liquid metals and molten salts.

## EXPERIMENTAL PROCEDURE

A standard simple procedure for quantifying high temperature corrosion products is to use several representative images and manually taking ~10 measurements from each light or scanning electron microscopy (SEM) image or an open source software like ImageJ [11] to make the measurements. To avoid subjectivity in the measurements, equally-spaced vertical lines are drawn on the images to mark the locations where the scale is measured.

A more sophisticated approach is to use image analysis to make many measurements from each image. For example, a python-based script, AutoTracer, was developed to automatically measure the external scales in images. Figure 1a shows the duplex oxide scales formed on a commercially shot-peened S30409 tube after exposure to 1 atm steam for 1,000 h at 650°C [12]. The threshold was adjusted in the cropped light microscopy image (Figure 1a) to isolate the desired features (Figures 1b and 1c). The upper (magenta) and lower (blue) line boundaries of the individual features are defined by contours (Figures 1d and 1e). Steps are made along the lower boundaries where the linear shortest distance is found from the step point to a range of points on the upper boundary. The measured thicknesses are then outputted for analysis. Commercial software packages also perform similar image analysis [13].

A second script, CMAT, was developed to measure and quantify external and internal oxidation, including the depth and area fraction of internal oxides. Figure 2a is an SEM image of a model Ni-22wt.%Cr-2Al alloy [14] exposed for 500 h in air + 10% H<sub>2</sub>O at 950°C [15,16]. To prepare the image for analysis, white lines were manually drawn around the scales and internal oxidation zones to define the boundaries using ImageJ. Similar to the other script, thresholds were then manually adjusted, Figure 2b. Figure 2c shows the defined boundaries used for the measurements. For instance, the distance between lines 1 and 2 is used to calculate the thickness of the external scale, and the area between lines 2 and 3 is the internal oxidation zone, which can be used to estimate the area fraction of internal oxidation.

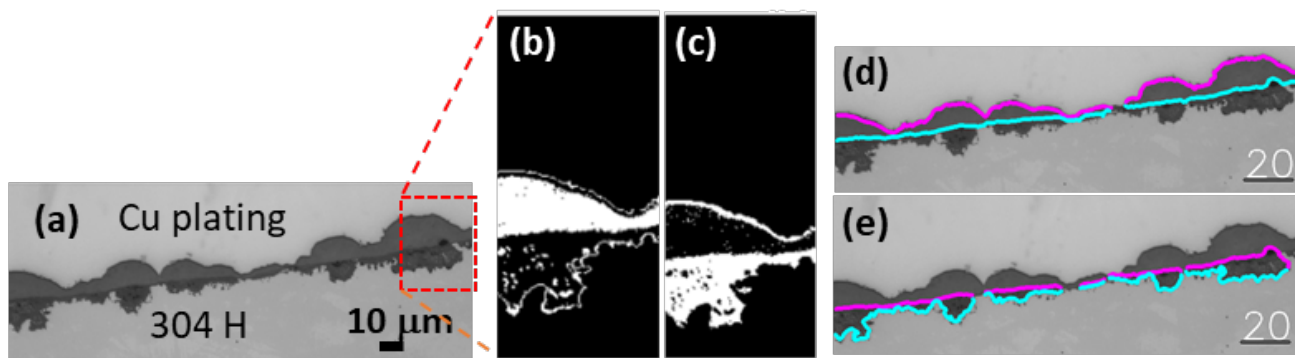


**Figure 1. (a) Cropped light microscopy image of a commercially shot peened S30409 tube after exposure to 1 atm steam for 1,000 h at 650°C, (b,c) a partial image of (a) is used to adjust the threshold to isolate the inner and outer scale, (d,e) select edges and define upper and lower boundaries.**

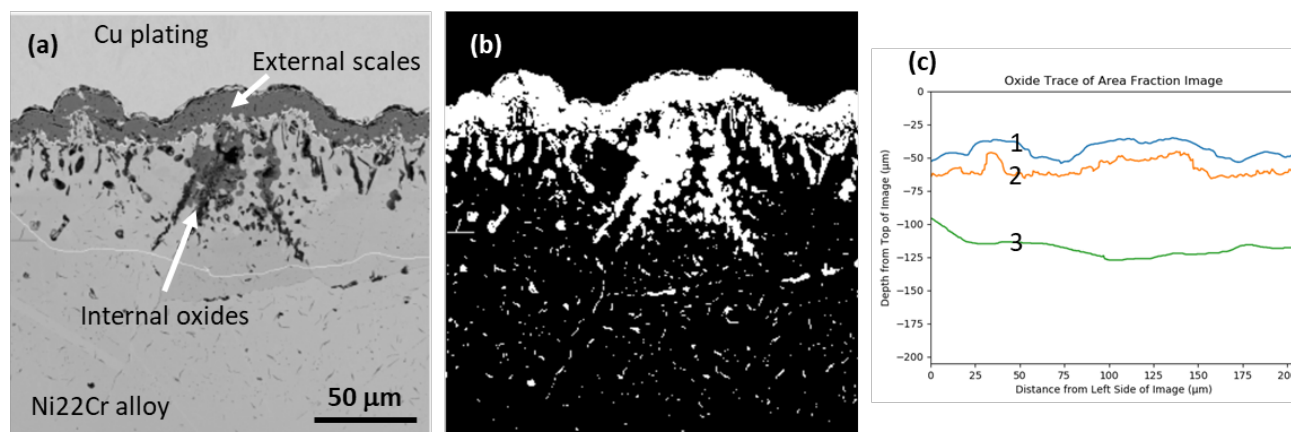


**Figure 2. SEM image of a model alloy Ni-22Cr-2Al tested in air + 10% H<sub>2</sub>O at 950°C is used for automated image analysis for internal oxidation: (a) draw white boundaries around scales/zones, (b) adjust threshold, (c) distance between line 1 and 2 is used to calculate the thickness of external scales, between line 2 and line 3 is defined as internal oxidation zone.**

## RESULTS

Figure 3 shows an example of fairly uniform oxide scales formed on K90901 (T91) steel after 500 h in 300 bar (30 MPa) CO<sub>2</sub> at three different temperatures. The method and number of oxide measurements are not important in the case of a fairly uniform reaction product. For Figure 3a, which has an inner and outer oxide layer, Figure 4 shows the box and whisker plots [12,14,17] of the inner oxide layer and total oxide scale thickness. The boxes are defined by the first and third quartile with the median value (line in box) shown. The whiskers show the minimum and maximum values measured using the ImageJ method with 30 values measured on 3 images. In some studies, authors prefer to report the maximum attack, especially for internal oxidation [18,19] so the whiskers provide those values. Figure 4 also shows the total oxide scale thickness from the image in Figure 1a, where 180 values were automatically measured by the AutoTracer script. Figure 4 also shows the average values from these data sets with the whiskers showing one standard deviation. For the uniform scale in Figure 3a the average values are not significantly different from the median values. However, for the irregular scale in Figure 1a, the median and average values are quite different with the average value being affected by thicker areas. In the case of a non-normal distribution, the median value may be more relevant than the average oxide thickness. Also, the standard deviation doesn't capture the entire distribution like the boxplots.

Figure 5 shows another example of an irregular oxide scale formed on shot-peened S30409 tube, exposed for 1000 h at 600°C in 1 atm steam [12]. Figure 6 shows a comparison of the ImageJ and

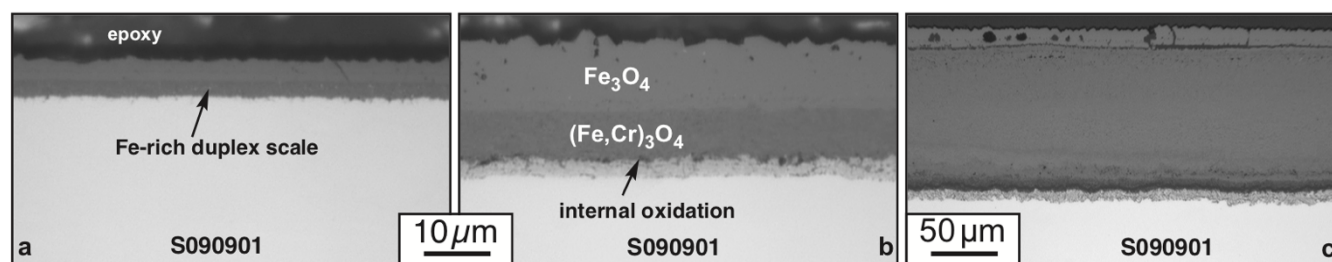


**Figure 3. Light microscopy of polished cross-sections of S90901 after 500 h in 30MPa sCO<sub>2</sub> at (a) 450°C, (b) 550°C, and (c) 650°C.**

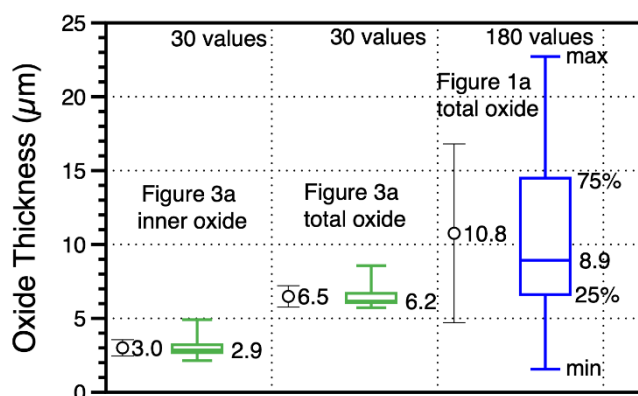


**Figure 4. Box and whisker plot of oxide thicknesses measured from Figures 1a and 3a compared to traditional average (black color?) and standard deviation values from same data sets. For Figure 1a, the script measured 180 total oxide thickness values. For Figure 3a the inner oxide and total oxide were measured by ImageJ.**

script data sets for the three images in Figure 5. For the 33 measurements done by hand, the mean was larger than the median by ~25%. For the 614 measurements from the AutoTracer script, the mean value was ~35% higher than the median from the manual measurements and is in good agreement with the median for this measurement technique.

Irregular reaction products can also present a problem in terms of sampling bias. Whether by hand or by script the measurements assume representative images. Figure 7 shows examples from another shot-peened S30409 tube, which was exposed in 1 atm steam at 625°C, with the formation of relatively few nodules. Low magnification images are shown in Figures 7a-7e and the measurements are shown in Figure 7f. The median values vary significantly with the exposure time and do not show a continuously increasing oxide scale thickness as expected. One explanation is that the measurements were made on images which contain too many (or too few) nodules. For example, in Figure 7b, the nodules are infrequent, yet the 15.5 μm median value suggests a much thicker oxide. Likewise, the very large nodule shown in Figure 7e was not sampled in the measurements shown in Figure 7f. Other issues can arise such as a gap between the copper coating and specimen (Figure 7c) or the oxide scale being damaged during preparation (Figure 7d). The solution to an irregular oxide scale may be to have more random image sampling or take more images that can be quickly quantified using the AutoTracer script. Automated stages for light microscopes and even SEMs with autofocus capability are becoming more common, and the acquisition of a hundred pictures from a single specimen can be achieved in a cost effective manner.

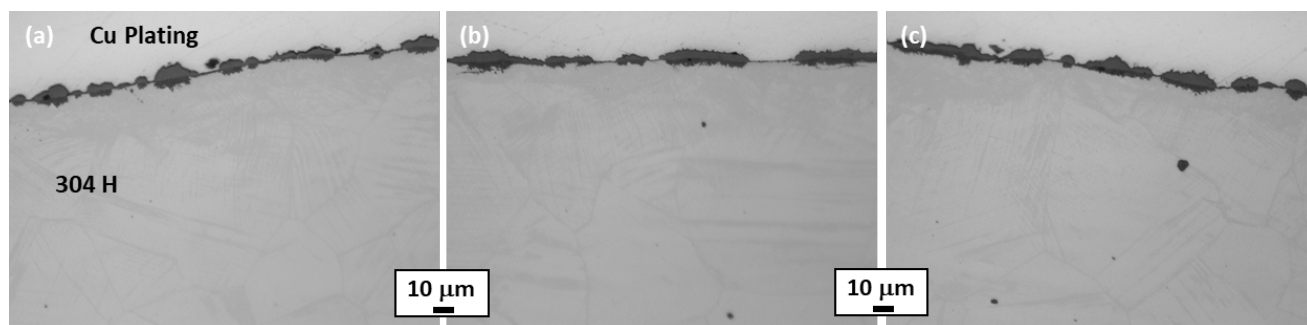


**Figure 5. (a), (b) and (c) are light microscopy images of a commercially shot peened type 304 H tube after exposing to one bar steam for 1000 h at 650°C.**