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## Automatic evaluation of the performance of corrosion resistant LCVD silica coatings

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**Abstract.** — A new method for the automatic evaluation of the corrosion resistance of coatings is described which is based on automatic feature detection combined with chemical classification (AFDCC) using an X-ray microanalysis system and scanning electron microscope. The results of this evaluation procedure are compared with conventional gravimetric analysis, and the AFDCC method is shown to have a number of advantages: i) greater sensitivity; ii) partially coated samples can be studied; iii) coating defect growth rate can be monitored and iv) corrosion product characterisation is an integral part of the evaluation procedure. The combination of i) and ii) rise to a rapid method for optimising coating performance and can eliminate the need for long-term testing during the optimisation phase of coating development.

### 1. Introduction.

Previous work on the dependence of the properties of excimer laser chemical vapour deposition (LCVD) silica coatings on the process variables indicated that precise control of film characteristics was possible [1, 2]. This unusual capability in a CVD system is a powerful tool and allowed selection of many process parameter combinations resulting in different coating properties. There was a requirement, therefore, to develop test methods that would allow rapid discrimination between different coatings with nominally "good" performance so that coating optimisation could be carried out efficiently on a short timescale.

The conventional method of determining the protective nature of coatings is to expose the material to the working environment and measure mass change as a function of exposure time. For coatings which are generally protective long exposure times are often needed to determine which are the more resistant to attack, since only very small mass changes may occur. Furthermore, with a coating system, the attack may be highly localised around small defects in the coating and thus the failure process will have already been initiated, but again only small changes in mass would be associated with these localised failure events. These defects may be isolated pinholes in the coating or failure could occur largely at edges and corners where stress gradients can lead to premature coating failure.

Examination of the samples using optical or scanning electron microscopes (SEM) is, of course, possible but the information obtained in this way is usually only qualitative. Recent developments in X-ray microanalysis software now allow quantitative image analysis combined with chemical classification. The application of this method has been explored in this work to assess coating performance, and the results obtained compared to the conventional mass gain measurements.

## 2. Experimental procedures.

**2.1 COATING PROCEDURE.** — Silica coatings were produced using an ArF excimer laser ( $\lambda = 193$  nm, maximum pulse energy of 250 mJ), several optical elements, and a reaction chamber connected to the vacuum and gas supply system, as described previously [1]. The LCVD reaction using ultra high purity gases involved photo-induced oxidation of  $\text{SiH}_4$  with  $\text{N}_2\text{O}$  in Ar. The laser beam was focused by a lens placed just before the beam entered the reaction chamber thus obtaining an energy density of 120 - 200 mJ cm<sup>-2</sup> in the chamber. Substrates were placed parallel to the beam on a temperature controlled sample holder, which permitted fine control of the beam to substrate distance. Incoloy 800H (nominal composition, wt%: 20.6 Cr, 31.4 Ni, 0.68 Mn, 0.43 Si, 0.29 Al, 0.23 Ti, bal Fe) substrates were used which were cut from cold-rolled sheet, ground to an 800 grade SiC finish and degreased with acetone and alcohol in an ultrasonic bath.

**2.2 CORROSION TESTING.** — Sulphidation tests were carried out in a simulated coal gasification atmosphere (CGA) at 450 °C and 750 °C. The gas mixture employed had the following composition, vol%: 24.8 CO, 20.4 H<sub>2</sub>, 3.93 CO<sub>2</sub>, 6.3 H<sub>2</sub>O, 0.123 H<sub>2</sub>S, bal N<sub>2</sub>. Previous work [3] indicated that gas equilibration did not occur at the lower temperature so that  $p(\text{O}_2)$  and  $p(\text{S}_2)$  were considered to be established by the H<sub>2</sub>/H<sub>2</sub>O and the H<sub>2</sub>/H<sub>2</sub>S ratios, respectively, giving  $p(\text{O}_2)$  and  $p(\text{S}_2)$  values of  $10^{-26}$  and  $5 \times 10^{-7}$  Pa, respectively. At the higher temperature equilibrium was achieved and the corresponding values were  $5 \times 10^{-17}$  and  $6 \times 10^{-6}$  Pa. Pre-mixed dry gases were used and water was added by passing the gas over a water saturator held at 37 °C. Specimens were introduced into the furnace *via* an air-lock, and mass change during the test was determined by weighing the samples before and after exposure.

**2.3 COATING CHARACTERISATION USING AFDCC.** — The analysis of samples was carried out using a Camscan series 2 SEM with stage control and automatic feature detection with chemical classification implemented using proprietary software ("Spectra" and "Digiscan", respectively) developed by Link Analytical for use on the AN 10000 microanalytical system. Alternatively, the Cambridge S360 SEM combined with the Link eXL microanalysis system using software packages "Autopoint" and "Featurescan" for stage control and chemical classification, respectively, was used for some of the work involving chromium-containing particles because of the ability of the software to include or exclude particles touching the edge of the field of view.

A grid of 105 equi-spaced SEM stage co-ordinates within an area of 2 × 1 mm was stored and at each of these stage positions an area 17.2 × 17.2 μm was imaged; thus within the area examined 1.6% of the surface was analysed. The imaging mode was selected to resolve the features of interest, and, for example, figure 1 shows (at a similar magnification to that used during the analysis) typical areas of LCVD silica coated incoloy 800H testpieces after exposure to sulphidising atmospheres at 450 °C and 750 °C. Both secondary and backscattered images are shown where, respectively, sulphur- or silicon- and chromium-containing particles are resolved. Figure 2 shows the corresponding X-ray images confirming the chemical discrimination achieved by these different imaging methods.

Chemical classification ranges were determined by spot analyses of a few particles of interest and the unattacked coating. Appropriate files were then set-up to store the particle size and analytical data in the selected composition ranges. For the current work particles containing > 2% sulphur were defined as "sulphides", "silica" contained < 2% sulphur, "unclassified" refers to particles that apparently have negative sulphur content due to an artefact

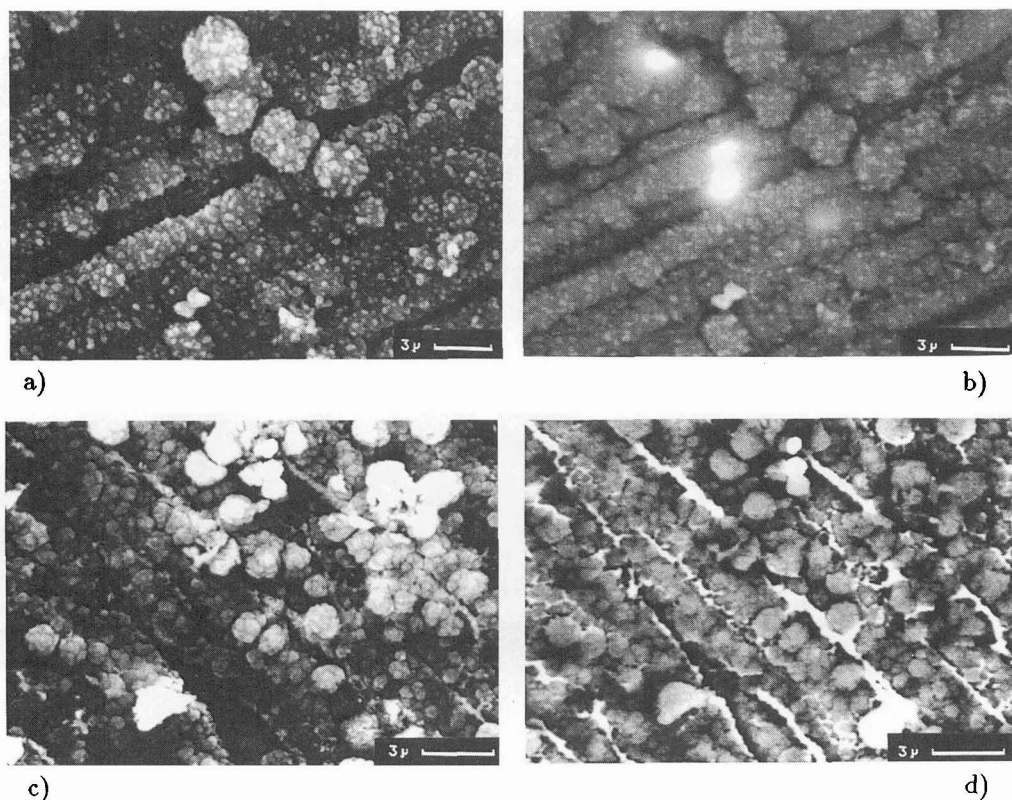


Fig. 1. — Secondary (a and c) and backscattered (b and d) electron images of silica coated Incoloy 800H exposed at 450 °C (a and b) and 750 °C (c and d) in the CGA.

of the analysis and thus should be considered as silica particles. The percentage composition refers to the uncorrected net integral of the peak in question relative to the total of all peaks in the spectrum likewise chromium-containing particles were classified using a composition of > 35% chromium.

Grey level thresholds were set for each specimen to discriminate particles from the unattacked coating, and figure 3 shows the discrimination achieved with silicon- and sulphur-containing particles. During the analysis "Digiscan" (or "Featurescan") then automatically sized particles using the thresholded image and finally the beam was driven to scan each particle in order to determine the chemical analysis. Thus complete analysis proceeded by examining each particle within the field of view, and then automatically selecting the next predetermined area until all 105 areas had been analysed.

Analytical conditions chosen for this work were a beam energy of 20 keV with a dwell time of 10 seconds during the analysis of each particle. Working distance was set at a compromise value of 25 mm so that reasonable imaging and analysis could be obtained. It was very important to ensure that the electron beam was stable before starting an analytical run, and usually an hour's operation prior to the start was sufficient. The time taken to complete analysis of one specimen was, of course, dependent upon the number of particles identified

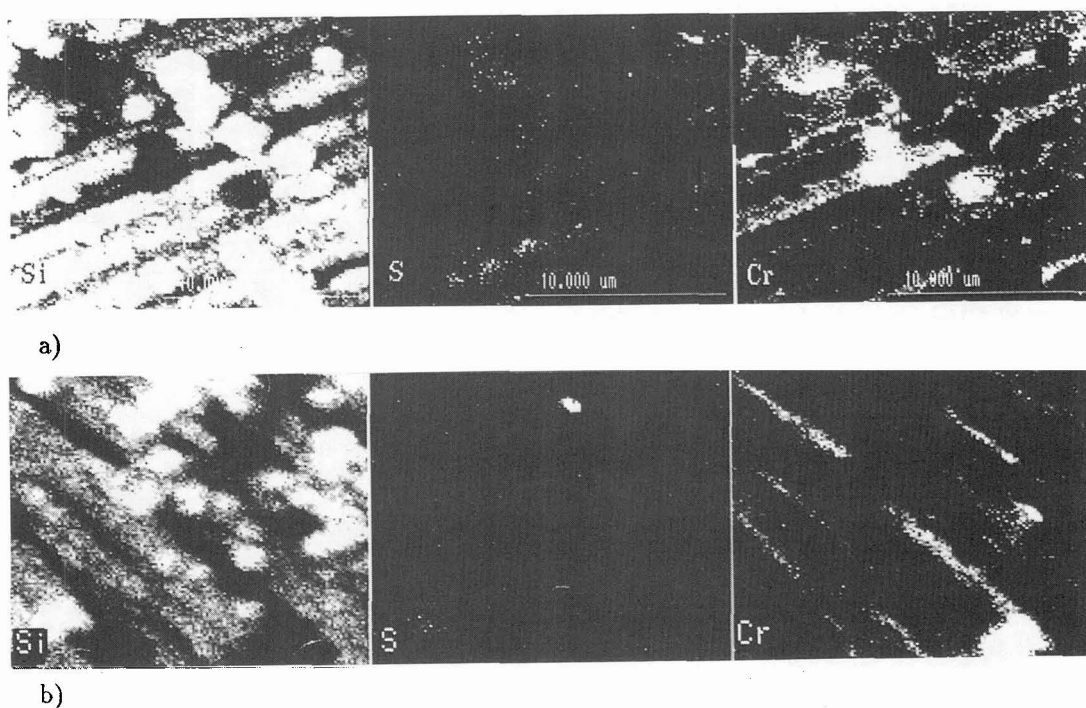


Fig. 2. — X-ray images of LCVD silica coated Incoloy 800H exposed for a) 1486 h at 450 °C and b) 962 h at 750 °C in the CGA.

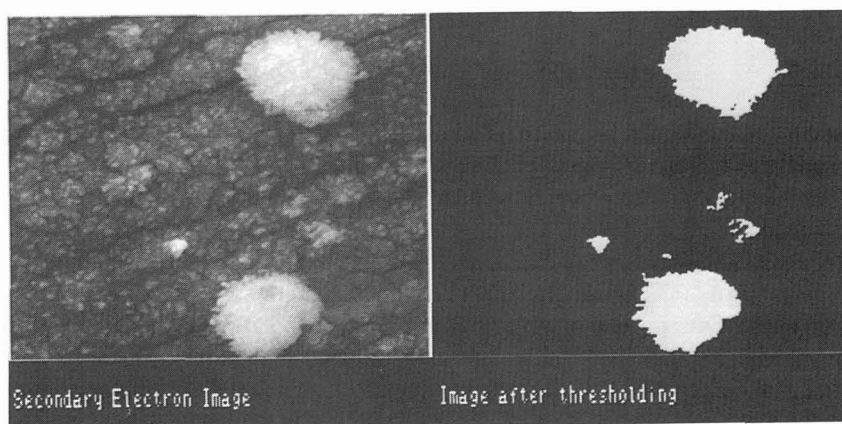


Fig. 3. — Example of thresholding a secondary electron image of a silica coated sample.

in the individual images, but typically for these samples this ranged from 2 - 4 h, although some analyses took up to 20 h where many particles were detected, thus it was convenient to carry out the work overnight. As a check on beam stability, an image of the final area

analysed was stored, and if discrimination of particles departed significantly from the original conditions the analysis was ignored; it was found, however, that beam instability during the course of this work was not a problem.

### 3. Results and discussion.

**3.1 COATING OPTIMISATION.** — LCVD coating is a line of sight process and during coating development it was convenient to coat only one surface, so that testing using gravimetric methods would not be applicable. Thus the AFDCC method was used to examine several slightly different coatings applied to only one surface of Incoloy 800H where processing conditions were altered such that coating thickness and type were varied; Type 1 silica had normal density and Type 2 silica was of reduced density. Several such coatings 0.35-3.5  $\mu\text{m}$  in thickness were exposed for only 66 h to the sulphidation test environment at 450 °C, and figures 1 and 2 are examples of the type of structure and particle distribution observed. Using the automatic AFDCC system it was possible rank the performance of the coatings by comparing the relative surface coverage with sulphide particles. Figure 4 is a typical histogram obtained from this analysis showing the number of particles classified according to size and chemical composition. From this information the area fraction covered with sulphide particles was computed, and as shown in table I significant differences in sulphide formation were observed, thus allowing selection of the best coatings.

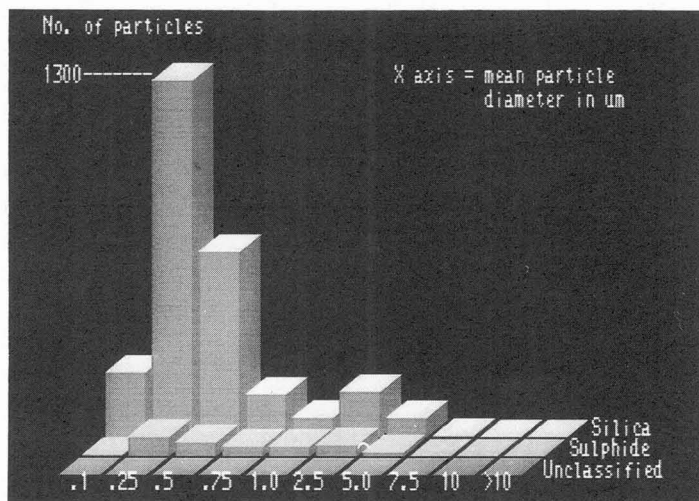


Fig. 4. — Typical histogram obtained from AFDCC analysis showing particle size and chemical classification.

**3.2 COATING DEGRADATION.** — Optimised coatings were developed by the procedures defined above, and entire specimens coated so that it would be possible to compare the AFDCC method with gravimetric tests. Sulphidation tests were conducted at two temperatures (450 °C

and 750 °C) in which coating failure was evidenced by formation of sulphide or chromium oxide, respectively, with lesser amounts of sulphide at the defects in the coating. The coating performance was assessed by monitoring mass change and sulphide or chromium oxide area fraction as a function of exposure time. Examination of the development of particle size and number gives additional information that cannot be obtained from the gravimetric tests. For example, an increase in mass could be associated with formation of a new defect site or simply growth of corrosion product associated with a constant number of defects, but the dominant process could be readily determined from the AFDCC technique.

Figure 5 shows the mass gain data of the samples exposed at the two test temperatures, and figure 6a shows the area fraction and number of sulphide particles as a function of time for the samples exposed at 450 °C. It can be seen that both number and area fraction of the sulphide particles has increased with increasing time, while mass gains were negligible and/or very small mass loss occurred which may be attributable to loss of water or was simply the weighing errors. Figure 6b shows similar data plotted for the 750 °C tests which indicates both the number and area fraction of sulphides was much reduced compared with the behaviour at the lower temperature, and that while the area fraction of sulphides increased with increasing exposure time the number of sulphide particles remained constant. Compared with the mass gain data and the corresponding behaviour at 450 °C, it is clear that the mass gain cannot be accounted for by sulphide formation since the mass gains were much greater on the samples exposed at the higher temperature. The number of chromium-containing particles and their area fraction was determined after 962 h exposure at 750 °C, and was 2322 and 3.95 %, respectively, thus the reason for this discrepancy is the formation of chromium oxide particles which, as can be seen in figure 1, are aligned with the grinding marks replicated in the silica coating. The number and area fraction of chromium oxide particles is about an order of magnitude greater than that of the sulphides, so that the chromium oxide formation completely dominated the mass changes observed.

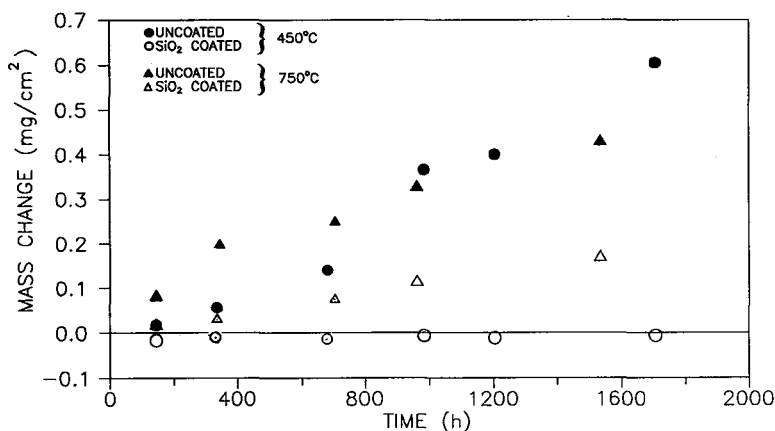


Fig. 5. — Mass change data for uncoated and silica coated Incoloy 800H samples exposed at 450 °C and 750 °C in the CGA.

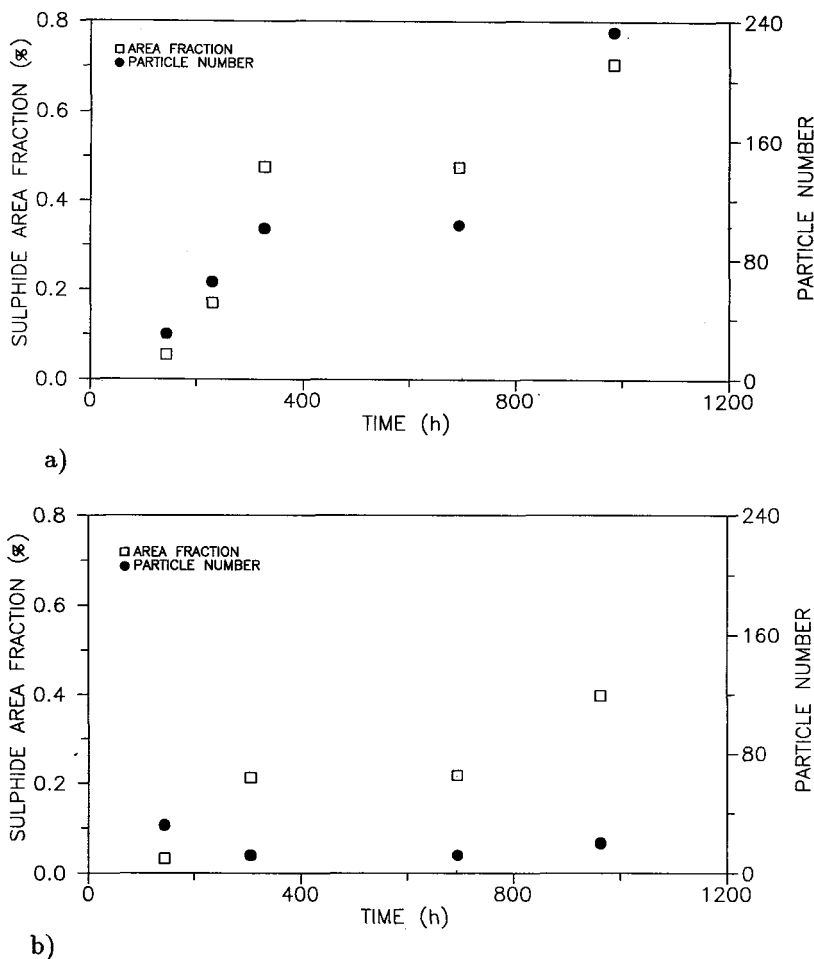


Fig. 6. — Sulphide area fraction and particle number as a function of time after exposing silica coated samples to the CGA at: a) 450 °C and b) 750 °C.

**3.3 GENERAL DISCUSSION.** — This method of analysis has a few problems in its present data of development. For example, when using Digiscan particles touching the edge of the frame were not included in the analysis and thus the absolute number of particles and their area fraction will have been slightly underestimated during this work. Furthermore, as can be seen by comparison of figures 1 and 2 not all of the sulphides formed at 450 °C were identified in the secondary electron image, thus again an underestimate would result. Use of Featurescan, which only became available toward the end of the work, has overcome the difficulty of particles at the edge of the frame, but the lack of an appropriate imaging mode to select *all* particles of interest is likely to remain a fundamental problem and particle numbers will always be underestimated. It is believed that this problem may also be eventually overcome by using the X-ray image itself to select particles for analysis and sizing. Nevertheless this work has demonstrated the usefulness of the analytical procedure to obtain a semi-quantitative assessment of coating performance that has many advantages over gravimetry.



#### 4. Conclusions.

The AFDCC method has been shown to have a number of advantages over gravimetry in the evaluation of performance of corrosion resistant coatings:

- i) Defect detection in coatings can be readily carried out on a quantitative basis;
- ii) The method allows the study of partially coated material, thereby facilitating coating development, particularly in the case of line of sight coating processes;
- iii) Defect number can be monitored and thereby additional information can be obtained about coating degradation;
- iv) The method is considerably more sensitive than gravimetry and thus facilitates rapid testing of coatings that would otherwise require long periods of exposure to the corrosive environment.

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