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The behaviour of amorphous silica coatings at high temperatures in aggressive environments

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Abstract. — Amorphous silica coatings produced by plasma assisted and laser chemical vapour deposition (PACVD and LCVD) on Incoloy 800H and 21/4 Cr 1 Mo ferritic steel were exposed in air and in simulated coal gasification atmospheres (CGA) for periods of up to two years at temperatures between 450 °C and 900 °C. In some cases interlayers of TiN were used to promote adhesion and to reduce interdiffusion between the coating and substrate. PACVD silica coatings deposited onto Incoloy 800H provided outstanding corrosion protection at 450 °C, but, at higher temperatures interaction with the substrate was observed which could be reduced by the presence of the TiN interlayer. However, these coatings would only adhere to the surface of 21/4 Cr steel in the presence of the TiN interlayer. Protection of both steels at 450 °C in the CGA using the LCVD silica coatings was dependent upon coating density, the presence of a TiN interlayer, and silica thickness in the range 0.35 – 3.5 μm . Adhesion of the silica layer to the Incoloy 800H substrates was good and, in this case, did not depend on the presence of a TiN interlayer. Differences between the individual coatings are interpreted in terms of residual stresses and interfacial chemistry.

1. Introduction.

There is considerable interest in the use of amorphous silica layers as protective coatings to resist high temperature corrosion [1-5]. These coatings provided long-term protection to 20/25 Nb steel exposed to CO₂-based gas mixtures at 700 °C and 825 °C [1, 5] and to Incoloy 800H exposed to aggressive sulphidising simulated coal gasification atmospheres (CGA) at 450 °C [2]. However, exposure at higher temperatures on other substrates (for example 21/4 Cr ferritic steel) resulted in some loss of protection due to crystallisation [3], interdiffusion or poor adhesion [4]. The work reported in this paper was undertaken to build upon the results of previous studies [4] on the use of interlayers to reduce these problems. Two different chemical vapour deposition (CVD) coating process routes were studied, plasma assisted (PACVD) and laser induced (LCVD).

2. Experimental procedures.

2.1 COATING PROCESSES. — The PACVD rig has been described previously [5]. Before depositing the silica, one of three different pretreatments was used: i) Incoloy 800H samples were pre-oxidized in CO₂, at 850 °C, to form a 1 μm thick chromium-rich oxide layer; ii) TiN

was deposited by PACVD using a $\text{TiCl}_4 - \text{H}_2 - \text{N}_2$ gas mixture; or iii) TiN was deposited by sputter ion plating (SIP). Silica coatings, 5-10 μm thick, were applied from $\text{SiH}_4 - \text{CO}_2$ gas mixtures to Incoloy 800H and 21/4 Cr steel substrates heated to about 800 °C by an RF coil. LCVD silica coatings were produced using an ArF excimer laser ($\lambda = 193$ nm, maximum pulse energy of 250 mJ) as previously described [6]. The LCVD reaction involved photo-induced oxidation of SiH_4 with N_2O in Ar. The laser beam was arranged to be parallel to the substrates, and was placed on a sample holder heated to 250 °C.

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) and 21/4 Cr ferritic steel (composition, wt%: 0.11 C, 0.21 Si, 0.47 Mn, 2.14 Cr, 0.92 Mo, 0.21 Cu, bal Fe) samples were used in the cold rolled state, ground to an 800 SiC grit finish and degreased in acetone and alcohol before coating.

2.2 COATING EVALUATION. — The thermal stability of the coatings was examined by exposure to oxidizing environments (air) at temperatures up to 900 °C, while a simulated coal gasification atmosphere (CGA) was used to determine the resistance of the coatings to sulphidation attack using procedures described elsewhere [7]. Briefly, a gas mixture containing, as vol%: 24.8 CO; 20.4 H_2 ; 3.93 CO_2 ; 6.3 H_2O ; 0.123 H_2S ; bal N_2 was used at 450 °C and 750 °C, which was sulphidising to the steel substrates. All corrosion tests were carried out using intermittent exposures and mass changes were monitored.

The optical properties of the coatings were measured using silica deposited on (100) silicon wafers, which were produced simultaneously with the coated steel samples. Fourier transform infra-red spectroscopy (FTIR) was carried out using a Bomem model MB-100 spectrophotometer, an AutoE1 II ellipsometer (Rudolph Research) was used to measure the coating refractive index at a wavelength of 632.8 nm, and the density was established by mass and volume determinations. The mechanical properties of the coatings were evaluated using a nanoindenter (Nano Instruments Inc.), which measured load as a function of displacement during indentation with a Berkovitch diamond indenter. Experiments were carried out at a range of loads between 0.5 mN and 100 mN using multiple loading and unloading methods, as previously described [8]; five data sets were obtained for each load.

3. Results and discussion.

3.1 PROTECTIVENESS OF SILICA COATINGS.

3.1.1 PACVD silica. — Two types of silica coatings on Incoloy 800H were examined. The first comprised a pre-oxidized substrate with a single layer of silica, while the second was duplex TiN/ SiO_2 where the alloy/TiN and TiN/ SiO_2 interfaces were graded such that the TiN layer was in effect a Ti/TiN/Si triple layer with the Ti and Si layers being about 100 nm in thickness. In previous work [4] with similar duplex coatings on IN 939 the PACVD TiN was successfully used, but when applied to both Incoloy 800H and 21/4 Cr steel, and exposed at temperatures > 450 °C, its adhesion was poor. This was eventually attributed to trace amounts of chlorine present in the TiN and at low temperatures, where the coating was stable, the silica layer became opaque. TiN interlayers formed by the SIP process were, however, adherent, and so were used for the duplex layers to be discussed in the rest of this paper.

a) Incoloy 800H substrates. Figure 1 shows the results for the Incoloy 800H with a single-layer coating after long-term exposure at 450 °C in the CGA. The overall mass gains (Fig. 1a) were small, i.e. < 0.1 mg cm^{-2} , but at longer exposure times a slight mass loss was observed,

a)

b)

Fig. 1. — PACVD silica coated Incoloy 800H exposed in the CGA at 450 °C: a) mass change as a function of time and b) secondary electron micrograph of a cross-section after 16 280 h exposure.

which was associated with spallation. Examination of the sample cross-section (Fig. 1b) showed that the interface between the silica and the steel was completely stable even after 16000 h exposure. However, some areas showed coating fracture and spallation to about half the coating thickness; in isolated areas complete spallation had occurred but this did not lead to catastrophic attack. Coating/substrate interaction was observed for this type of coating on Incoloy 800H exposed at higher temperatures (Fig. 2).

Fig. 2. — Scanning secondary electron micrograph of a cross-section of PACVD silica coated Incoloy 800H after 8 540 h exposure in the CGA at 750 °C.

Use of the duplex TiN/SiO₂ system produced a stable coating for samples exposed in air at 900 °C (Fig. 3a), but in the more aggressive CGA environment some interaction was observed

Fig. 3. — Scanning secondary electron micrographs of cross-sections of PACVD silica-SiP TiN coated Incoloy 800H after a) 1 000 h exposure at 900 °C in air and b) 3 960 h exposure to the CGA at 750 °C.

within the coating although internal attack of the substrate was reduced by the TiN layer (Fig. 3b).

b) 21/4 Cr steel substrates. Adherent coatings could only be obtained in this case with the TiN interlayer, and figure 4 shows the results after 3000 h in the CGA at 450 °C. The low mass change and microstructure of the cross-section indicated that little substrate attack had occurred. Exposure in air for 12 500 h showed that this coating system was completely stable at 500 °C, but was less effective at 600 °C, although the overall attack was not extensive.

Fig. 4. — PACVD silica-SiP TiN coated 21/4 Cr steel exposed to the CGA at 450 °C: a) mass change as a function of time and b) scanning secondary electron micrograph of a cross-section after 3 000 h exposure.

3.1.2 LCVD silica. — Gravimetric measurements provided a measure of the performance when the specimen was completely coated, but, in most cases only one surface was coated, and automatic feature detection combined with chemical classification (AFDCC) [9] was used to quantify sulphide formation within a 2 mm² area of the coating surface following exposure to the CGA at 450 °C.

Performance was studied as a function of coating density, which was controlled by the beam/substrate distance, and the presence of TiN interlayers. Coatings with density values corresponding to thermally formed silica (2.1 g cm⁻³) (Type 1) cracked when heated to temperatures > 200 °C above that during deposition (Fig. 5), whereas silica films of lower density (1.49 g cm⁻³) (Type 2) were able to tolerate the tensile stresses involved in heating to 900 °C [8].

Fig. 5. — Histogram showing the cracking behaviour of LCVD silica coatings on Incoloy 800H.

a) Incoloy 800H substrates. Adherent silica layers between 0.35 and 3.5 μm thick deposited on Incoloy 800H without interlayers. TiN interlayers did not prevent cracking of the Type 1 silica when exposed to temperatures greater than 450 °C. Corrosion protection increased with increasing Type 2 coating thickness, and additional benefits were obtained if a thin layer of Type 1 silica was present on the outer surface (Tab. I). The Type 2 coating was equally as effective as the PACVD coatings at 450 °C in affording long-term corrosion protection to this alloy in CGA (cf Figs. 1a and 6).

b) 21/4 Cr Steel Substrates. Less work has been carried out with the 21/4 Cr steel but the results were similar to those detailed for Incoloy 800H. In contrast to the PACVD coatings, silica could be deposited directly on to the alloy without the need for any pretreatment. Corrosion resistance to sulphidising atmospheres increased with increasing Type 2 coating thickness up to 3.5 μm. Type 1 silica did not crack on heating to 450 °C if deposited on a TiN interlayer.

3.2 PROPERTIES OF SILICA COATINGS. — A detailed study was undertaken of the effect of changing processing conditions on the properties of LCVD silica coatings and the consequent effect on corrosion protection. A similar, but less detailed, study was also carried out with the PACVD silica coatings.

Table I. — Sulphidation resistance determined by AFDCC of LCVD silica coated Incoloy 800H following 120 h exposure in CGA at 450 °C.

Coating Material	System Thickness, μm	% Sulphide in Analysed area
Type 2 SiO_2	0.35	0.393
Type 2 SiO_2	2.35	0.051
Type 1 SiO_2 + Type 2 SiO_2	0.35 2.00	0.014
Type 2 SiO_2	3.50	0.008

Fig. 6. — Mass change as a function of time for Incoloy 800H uncoated and coated with 1.2 μm thick Type 2 LCVD silica during exposure at 450 °C in the CGA.

3.2.1 LCVD silica. — The refractive index, infra-red spectrum and density of the two types of coating produced was determined (Tab. II). There was a direct relationship between coating density and the beam/substrate distance during deposition, while the refractive index decreased with decreasing coating density. The infra-red spectra showed that the frequency of the Si-O stretching mode was independent of coating deposition conditions, but that the full width at half maximum height of that peak (FWHM) increased with decreasing coating density.

The stoichiometry of the film was estimated from an empirical correlation between the Si-O stretching mode wavenumber, ν , and Rutherford backscattering analysis of the LCVD coatings [10], which established that values of $\nu = 1070 \text{ cm}^{-1}$ corresponded to a SiO_x stoichiometry where $x = 2$. Thus, it can be seen from table II that both types of LCVD silica coating were approximately stoichiometric in composition. Density was calculated using the relationship proposed by Lucovsky [11] based upon the refractive index and FWHM of the infra-red peak assuming that the coatings have the same stoichiometry. As can be seen from table II good agreement was obtained with the directly measured values. The density of

Table II. — *Properties of PACVD and LCVD silica coatings.*

Coating Type/ /Coating Property	Type 1 LCVD	Type 2 LCVD	PACVD
Beam/substrate distance, mm	2.1	0.6	—
Refractive index	1.46	1.31	n/a
Density (calc), g cm ⁻³	2.1	1.5	
Density, g cm ⁻³	2.089	1.492	n/a
Si-O stretching mode wavenumber, cm ⁻¹	1070	1073	1083
FWHM, cm ⁻¹	75	90	83

Type 1 silica coating was approximately the same as that for thermally formed silica, while for the corresponding Type 2 coating the density values were about 28% lower.

Figure 7 shows Young's modulus as a function of indentation depth for Types 1 and 2 LCVD silica coatings, 1.2 μm in thickness and, for reference purposes, bulk fused silica. Both LCVD silica coating types had lower modulus values than fused silica at small indentation depths but were higher at larger indentation depths. The lower modulus of Type 2 silica was consistent with its higher strain tolerance. Only at the shallow indentation depths (< about 150 nm) did the measured values reflect the coating properties without substrate interference [12].

Fig. 7. — Young's modulus as a function of indentation depth for bulk fused silica and LCVD silica coatings on Incoloy 800H.

3.2.2 PACVD silica. — Infra-red spectra were obtained on the PACVD silica coatings after thinning with HF to permit use of this technique (Tab. II). These proved to be similar to Type 1 LCVD coatings giving a similar wavenumber and FWHM for the Si-O stretching mode, suggesting that the coating was stoichiometric and that it was of a high density type (Tab. II). Measurements of Young's modulus again provided similar values to the LCVD coatings. However, since these coatings had a rough surface a large scatter in values was observed due to underestimation from indents on peaks (no lateral constraint) on the silica surface and overestimation on slopes due to larger contact areas.

3.3 OVERALL COMPARISON OF THE BEHAVIOUR OF PACVD AND LCVD COATINGS.

3.3.1 Strain tolerance. — A fundamental difference in the behaviour of the silica coatings produced by the two different CVD processes was their response to thermally imposed strains. The PACVD coatings were mechanically stable under all conditions, whereas some of the LCVD coatings were susceptible to tensile cracking when exposed at temperatures 200 °C above the processing temperature (250 °C). The PACVD silica coatings were produced at ~800 °C and thus were in compression on cooling to lower temperatures and did not crack. When exposed at higher temperatures than the process temperature the coating was mechanically stable, even although it was subjected to similar tensile strains that caused the LCVD silica coatings to crack. It is believed that viscoelastic stress relaxation occurred at these temperatures, thereby, preventing tensile cracking.

The thermal behaviour of the LCVD silica coatings was much more complex. Although tensile cracking was observed for the Type 1 coating when heated to about 200 °C above the processing temperature, the behaviour could be modified by the presence of interlayers, coating density, substrate and process conditions. It is believed that use of the TiN interlayer successfully eliminated tensile cracking of Type 1 silica coated 21/4 Cr steel but not for Incoloy 800H because of the lower expansion coefficient of the low chromium ferritic steel.

Generally CVD processes do not introduce significant stress into the coating during deposition, so that it can be assumed that the residual strain results from thermal expansion coefficient mis-match. Thus, the effect of depositing at 250 °C and heating to 450 °C is to subject the silica to a 200 °C temperature increment which, given the published values of expansion coefficients, would result in 2.9% tensile strain. Using the measured high temperature modulus values for low loads (Fig. 7) and assuming only elastic behaviour, the maximum failure stress of Type 1 coatings was 1.25 GPa, while a Type 2 silica coating was able to withstand a stress of 0.85 GPa at 450 °C without cracking. These coatings also did not crack when 500 °C and 650 °C thermal cycles were imposed, and, again assuming only elastic behaviour, the stresses were of the order of 2.25 and 2.7 GPa, respectively, however, it is likely that some visco-elastic stress relaxation would have occurred.

3.3.2 Coating adhesion. — There was a significant difference between the adhesion of the silica coatings. Generally the PACVD process produced layers requiring substrate pretreatments for the formation of adherent coatings, whereas the LCVD coatings could be applied directly to both steel substrates. It is proposed that this behaviour is related to the different residual compressive stresses in each type of coating. The PACVD layers would have much larger compressive stresses due to the higher processing temperature than that used for the LCVD process.

It was not possible to use a pre-oxidation treatment for the 21/4 Cr steel to promote adhesion of the PACVD silica coating as successfully applied to Incoloy 800H, but TiN interlayers were effective in this regard. Bull and Chalker [13] have shown that removal of impurities at the interface is an important factor in controlling adhesion of TiN layers, and it might be

expected that similar criteria are important for most other coating systems. Thus, the improved adhesion of the LCVD silica to 21/4 Cr steel with the TiN interlayer may be related to modification of the interfacial impurity levels compared with the un-oxidised or pre-oxidised steel surfaces.

4. Conclusions.

Long-term protection of metallic materials in oxidising and sulphidising atmospheres can be achieved by use of amorphous silica coatings. The interface between the substrate and the coating can degrade with long-term exposure at high temperatures but this can be controlled by the use of TiN interlayers. The interlayer structure should be optimised for the each substrate. Residual stresses derived from the differential substrate and coating thermal expansion coefficients play an important role in determining coating adhesion, and again interlayers can be developed to improve adhesion. For LCVD coatings tensile strain tolerance can be improved by altering process conditions to produce low density, low modulus coatings.

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