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Effect of fluoride contamination on the growth of ZrO_2 films

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Abstract

The mechanism by which fluoride ion degrades the oxide film on zircaloy-2 has been investigated by deliberately contaminating specimens. Delaying the washing of specimens for 0, 60 and 1800 s after pickling gave sets of, respectively, well-pickled, poorly-pickled and pickle-stained specimens. These were oxidised initially in dry steam (300°C, 3.5 MPa) and were then transferred to water (300°C) for short periods (1, 2 or 7 days). The oxides produced were examined by weight gain, interferometry, impedance spectroscopy and optical, SEM and TEM microscopy. The initial oxidation rates in steam were little different for the three groups of specimens (1 or 2 days), although the interference coloured oxides showed a very different distribution of oxide thicknesses between the well-picked specimens and the other groups. Transfer to water rapidly resulted in thick, friable, porous oxides on the pickle-stained, but not the other specimens, that could not be examined by many techniques because of ready loss of oxide. The techniques that could be applied to these specimens showed that they consisted of apparently large oxide crystallites in multiple layers nearly normal to the oxide metal interface. The original surface topography was still visible in areas where this surface had not spalled, showing that the degradation occurred within the oxide. The severity of this attack was determined by the extent to which the original preparation technique had left oxyfluoride layers on the initial surfaces. It was deduced that these oxyfluoride layers developed porosity in which concentrated fluoride solutions could form during high temperature exposures in water. These solutions attacked the ZrO_2 film by hydrothermal dissolution and recrystallisation to give the large layered platelets in the degraded films. The oxyfluorides appear to be sufficiently hygroscopic that the same degradation process occurred generally in 300°C, 3.5 MPa steam, only locally in 0.1 MPa steam and not in moist air. © 1997 Elsevier Science B.V.

1. Introduction

The chemical polishing (pickling) of zirconium alloys in a mixed nitric/hydrofluoric acid bath was one of the first techniques developed for ensuring the reproducibly good corrosion resistance of the alloy surfaces during corrosion testing in laboratory autoclaves [1]. It was recognised at the same time that rapid transfer of specimens to a wash or stop-bath was important in preventing poor corrosion resistance from gross fluoride contamination (pickle staining), which occurred if any dry-out of the pickle occurred because of slow transfer to the wash bath. Depletion of the hydrofluoric acid content of the bath, while affecting the dissolution rate, did not cause pickle staining even if the bath became saturated in zirconyl fluoride. The nitric acid content of the bath was found to be essential for the prevention of smut formation in both hydrofluoric acid and ammonium fluoride baths [1] and this black smut has been identified as zirconium hydride [2].

Nevertheless, it was found that even well pickled zirconium alloy surfaces carried some fluoride contamination [3–7], and that this fluoride apparently diffused into the oxide and sometimes apparently concentrated at the oxide/metal interface of pretransition ($\leq 2\ \mu m$) oxide films formed on pickled surfaces [4]. It was also shown that poor pickling was associated with both poor corrosion resis-

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tance and with higher fluoride contamination levels than for well pickled surfaces [8–10], although some other investigators did not see such a difference [3,6]. When tested in 290–360°C (563–643 K) water, poorly pickled specimens showed severe oxide spallation after only a few days exposure [8,9], whereas in 400°C (673 K) steam much smaller initial weight losses were observed for poorly pickled specimens and subsequent weight gain rates were less than a factor of two greater than those observed for well pickled specimens [8,9]. Tests in high temperature water containing small amounts of fluoride showed that levels of 10 ppm F^- or less were capable of causing a small amount of localised attack on the zircaloy surface; this took the form of small oxide nodules associated with some intergranular penetration for stressed U-bend specimens [11]. Very severe pitting ensued at fluoride concentrations above about 100 ppm, especially in the presence of crevices [8,9,12,13].

The observations that even the best pickled surfaces carried significant quantities ($\sim 0.5\ \mu g/cm^2$) of adsorbed fluoride ion [6] led to the argument that even this amount of fluoride was responsible for the somewhat higher initial oxidation rates in 500°C (773 K), 1 atm steam of pickled surfaces when compared with electropolished surfaces [14]. These effects reversed after the transition in the oxidation kinetics, however, with the electropolished specimens showing the higher oxidation rates. A quick dip of an electropolished surface in a dilute (0.1%) hydrofluoric acid in methanol solution was sufficient to contaminate the surface with fluoride, but did not affect the oxidation rate. Removal of the surface material by repickling of the surfaces was necessary to cause increases in the initial oxidation rate and the size of the increase was a function of the exposure time during repickling [14]. These effects were complicated by the apparent involvement of absorbed Ca^{2+} ions, from the water used to make up the solutions, and by the more severe effects observed with pickling solutions not containing nitric acid, which resulted in a black smut on the surfaces [14]. Somewhat similar differences between electropolished and pickled surfaces were reported during oxidation in oxygen at 360°C (633 K) [15], however, no similar study has been reported in ~ 300°C (573 K) water, a condition more relevant to reactor operation.

When similar experiments were done with pickled and electropolished specimens in air and fused nitrate/nitrite salts [16,17] similar differences in oxidation rate were observed to those reported above, and contaminating the electropolished surfaces by a quick dip in nitric/hydrofluoric acid pickling solution also failed to affect the oxidation rates. Examination of the specimen surfaces in a scanning electron microscope showed that electropolishing removed all the second phase particles from zircaloy-2 surfaces, whereas pickling only removed the $Zr_2(Fe/Ni)$ type of intermetallic and left the $Zr(Fe/Cr)_2$ type. The number of electrically conducting sites in the thin oxide films formed on these surfaces was, therefore, very different and this effect appeared to be capable of explaining the differences in oxidation rates for the different surface preparations. Obviously, contaminating an electropolished surface with fluoride cannot put back electrically conducting intermetallic sites in the thin oxide film, only repickling can expose further intermetallics and change the conducting properties of the thin films and the initial oxidation rates [14].

These experiments seemed to explain many of the observations on oxidation rate differences during early oxidation. However, they cannot explain the reversal of the oxidation rates of pickled and electropolished specimens in 500°C (773 K), 1 atm steam after the transition in the oxidation kinetics [14]. Since the rate transition only occurs after intermetallics that were subsurface at the start of oxidation have become incorporated in the oxide film [18,19], the initial intermetallic density in the surface should not have any significant effect on the rate transition. In order to affect the rate transition it would appear to be necessary to affect the morphology of the pretransition oxide, and hence possibly the manner in which porosity develops in this at transition. No previous hypotheses have been developed to explain this phenomenon.

This work was carried out to shed light on the unresolved question of precisely what effect the fluoride contamination has on the morphology of zirconium oxide films and how does this lead to gross weight losses in ~ 300°C water in such short times? Incorporation of F^- in substitutional sites in ZrO_2 should reduce the anion vacancy concentration and hence reduce pretransition oxidation rates if anion vacancy diffusion is rate controlling (see discussion section of Ref. [12]). However, gross contamination with fluoride apparently leads to very different oxide growth rates, although it may be only the oxide mechanical properties that are changed because large weight losses are observed on all such specimens corroded in high temperature water [8,9]. This is a rapid process as half the total weight loss was observed in the first 3 days of ~ 300 day tests.

Although the initial pickling of zirconium alloy fuel cladding has been long abandoned by nuclear fuel vendors, both because of doubts about its possible effect on corrosion and for environmental reasons associated with the disposal of the spent pickle, knowledge of the long term corrosion resistance of the different surface preparations and an understanding of the precise effects of fluoride contamination on the oxide morphology and properties have important practical aspects. ^{19}F is produced in small quantities in a typical 1000 MW PWR in the reactor core by nuclear reactions with ^{18}O and fluoride contamination of the oxide films on non-pickled zirconium alloy pressure tubes has been observed after prolonged exposures in CANDU reactors [20]. This suggests that such reactor produced fluoride may be strongly adsorbed on oxidised zirconium surfaces.

2. Experimental

Specimens for the examination of the effects of fluoride contamination on oxide morphology were 2 × 3 cm pieces cut from an approximately 2 mm thick zircaloy-2 sheet (batch Ac), whose analysis has been given previously [21]. They were pickled in a 50% HNO_3, 5% HF (48%) and 45% water solution. Some specimens were immediately transferred to the wash water (good pickle), some were removed from the pickling bath and allowed to hang for 60 s before washing (poor pickle), while the remainder were removed from the pickling bath and allowed to dry for 30 min before washing (pickle-stained). Specimens were first oxidised in steam for either 1, 2 or 7 days at 300°C (573 K) and 500 psi (3.5 MPa) pressure, because previous results [7] led to the expectation that rapid appearance of effects of gross contamination might be less severe in ‘dry’ steam than in water [8,9]. A ‘dry’ start was used for the autoclave tests so that the specimens were never immersed in water. Duplicate specimens of each surface preparation were oxidised. After non-destructive examination of the oxides the 1 and 2 day steam specimens were subsequently

Table 1
Oxide thickness measured by various methods

Oxidation conditions (total)	Measurement technique	Oxide thickness (μm)		
		well pickled	poorly pickled	pickle stained
1 day 300°C, 3.5 MPa steam	$\Delta w/15$	0.34	0.34	0.34
	UV/VIS interfer.	0.45	0.51	0.47
	A/C initial	0.36	0.36	0.36
	A/C final	0.20	0.21	—
	imp. spectrum	0.12	0.11	0.15
2 days 300°C, 3.5 MPa steam	$\Delta w/15$	0.45	0.48	0.55
	UV/VIS interfer.	0.55	0.56	0.57
	A/C initial	0.48	0.51	0.59
	A/C final	0.26	0.28	0.29
	imp. spectrum	0.14	0.15	0.15
7 days 300°C, 3.5 MPa steam	$\Delta w/15$	0.33	—	3.8
7 days 300°C, 0.1 MPa steam	$\Delta w/15$	0.29	—	1.67
	UV/VIS interfer.	0.38	—	NF
1 day 300°C water	$\Delta w/15$	0.45	—	0.76
	UV/VIS interfer.	—	—	0.61
	A/C final	—	—	0.05
	imp. spectrum	—	—	0.02
7 days 300°C water	$\Delta w/15$	0.75	—	1.80
8 days 300°C water	$\Delta w/15$	—	—	1.72
1 day steam + 1 day water, 300°C	$\Delta w/15$	0.56	0.51	0.79
	UV/VIS interfer.	0.67	0.68	0.80
	A/C initial	0.60	0.54	0.85
	A/C final	0.31	0.33	0.27
	imp. spectrum	0.14	0.18	0.13
2 days steam + 1 day water, 300°C	$\Delta w/15$	0.60	0.59	0.88
	UV/VIS interfer.	0.74	0.77	0.96
	A/C initial	0.64	0.63	0.94
	A/C final	0.38	0.33	0.36
	imp. spectrum	0.18	0.17	0.18
1 day steam + 7 days water	$\Delta w/15$	—	0.70	—
1 day steam + 8 days water	$\Delta w/15$	0.79	0.72	1.14
2 days steam + 7 days water	$\Delta w/15$	0.83	0.85	1.04
2 days steam + 8 days water	$\Delta w/15$	0.74	0.80	1.21
7 days 300°C moist air	$\Delta w/15$	0.24	—	0.29
	UV/VIS interfer.	0.34	—	0.37

NF: no interference fringes obtained.

exposed in 300°C water for periods of 1 and 7 days in order to see whether or not rapid spalling ensued.

Specimens were weighed before and after each exposure and their surfaces were examined by scanning electron microscopy (SEM) and replica electron microscopy. The specimens were photographed in colour in an optical microscope after oxidation, since the oxide thicknesses on those specimens oxidised in 300°C, 3.5 MPa steam for only 1–2 days were still in the interference colour range. They were also studied by impedance spectroscopy and the oxide thicknesses were measured by interferometry using either an ultraviolet/visible (Perkin–Elmer Lambda 3B) or a Fourier Transform Infrared (Analect RFX-30) spectrometer. The heavily contaminated specimens that showed a severely cracked surface deposit in the SEM after short (1–2 day) exposures (see later) were glued to an SEM specimen stub and the two pulled apart in an attempt to remove portions of this deposit. These attempts were unsuccessful; however, after 7 day exposure in either steam or water, oxides were so brittle that much of the surface could be removed with sticky tape. Oxides grown in short exposures were stripped by dissolving the metal in 10% Br_2 in dried, deoxygenated ethyl acetate solution at 70°C (343 K) achieved by refluxing with CaH_2. Pieces of oxide so separated were examined in transmission in an Hitachi H800 transmission electron microscope (TEM) at 200 keV, with ion-milling from the oxide/environment interface, if necessary to achieve transparency. Two stage Formvar-carbon replicas of the oxide surfaces were examined in the same TEM. Small flakes of the oxide surface film were extracted on some of these replicas and were large enough and thin enough for diffraction and dark-field analysis, even though the removal of larger areas of the film by gluing on SEM stubs had been unsuccessful. These flakes appeared to have been extracted from large elliptical surface pits in the original surface.

After long (≥ 7 days) exposures in either 300°C, 3.5 MPa steam or water the oxides were very thick and porous. Large amounts of oxide were extracted by applying sticky tape to small areas of the surface. The material

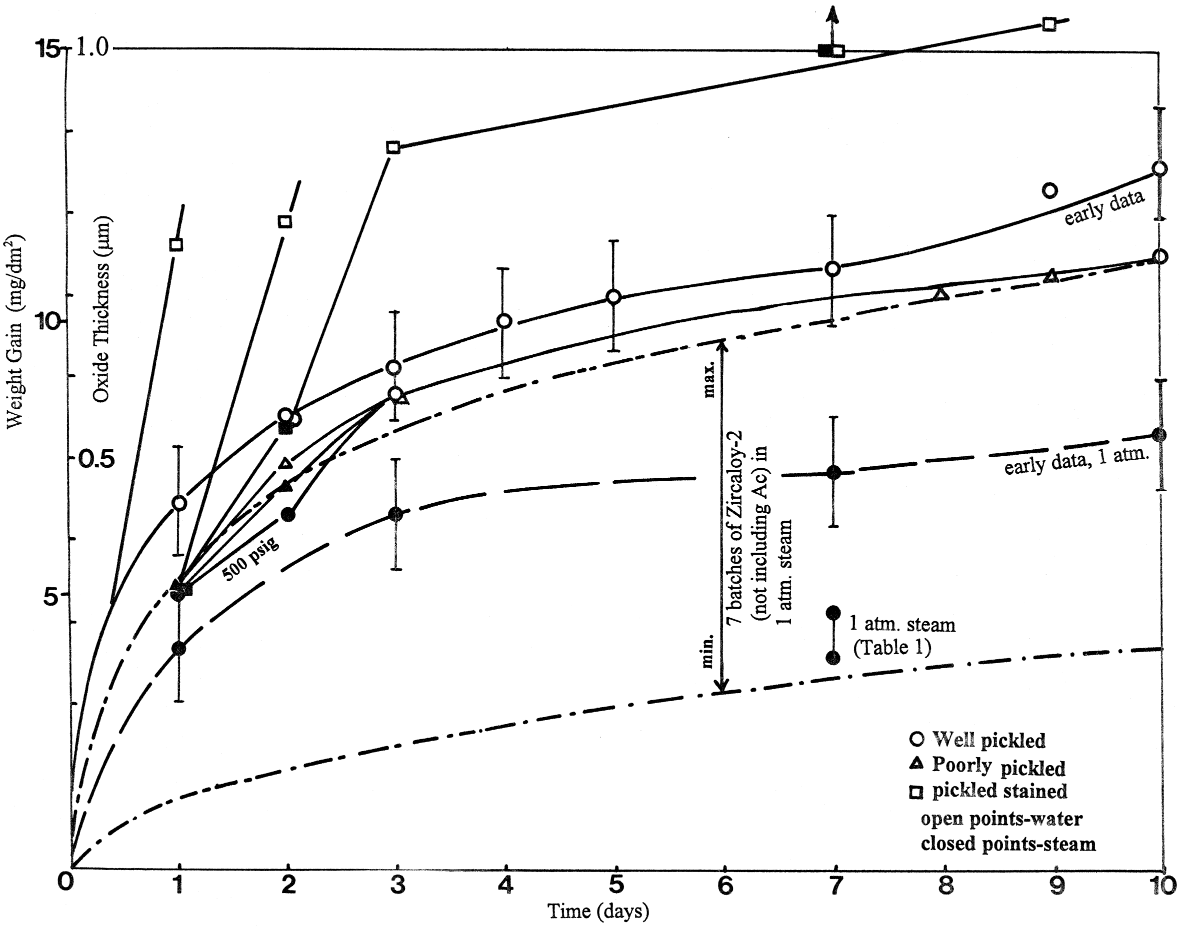

Fig. 1. Comparison of oxidation data in water and steam at 300°C with previous results on the same batch of zircaloy-2 [22].

removed was often in the form of a fine powder. However, sometimes more sizeable pieces were removed, but these were very fragile and investigative techniques other than weight gain and optical and SEM microscopy were difficult to apply. FTIR, impedance spectroscopy, oxide stripping by metal dissolution, ion milling and surface replication were all attempted but generally did not produce useful results. FTIR gave no good interference fringes; the electrolyte soaked in rapidly during impedance measurements and spread laterally from the holes in the sticky tape used to delineate the measured area; oxides disintegrated during attempts to strip and thin them and TEM replicas were covered with extracted oxide powder that was difficult to remove.

3. Results

The oxide thicknesses obtained by the various techniques are given in Table 1. Those obtained from the weight gains are plotted in Fig. 1 and in general results obtained from interferometry were in good agreement with them, as were many of the initial impedance readings following immersion in the 1 M NH_4NO_3 electrolyte. Interpretation of the final impedance readings, when the film was saturated with electrolyte, is difficult. A much lower apparent oxide thickness than for the initial reading indicates a porous oxide film, but obtaining a value for the minimum barrier oxide thickness from this requires a knowledge of the total area of the pores approaching the

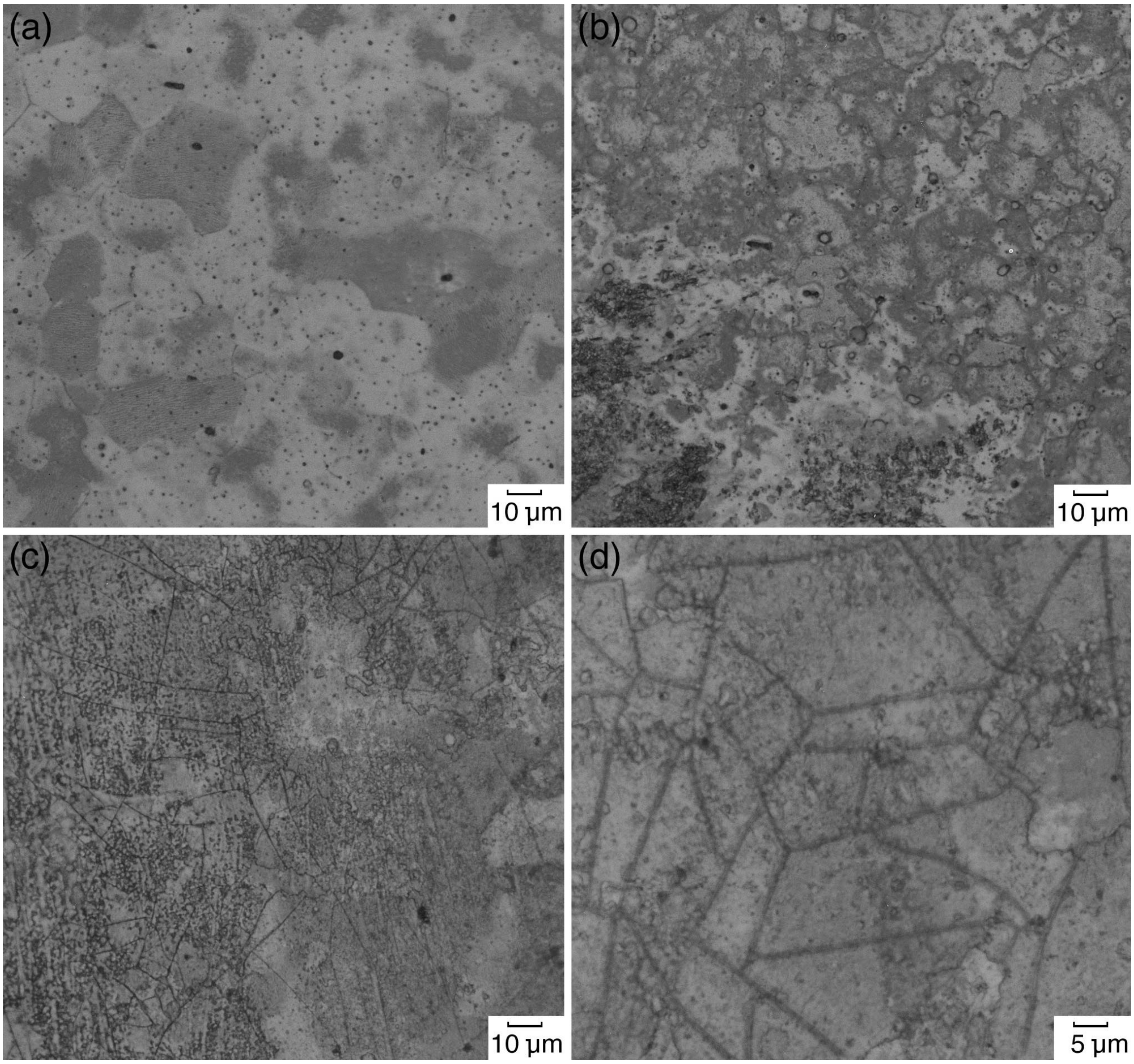

Fig. 2. Optical micrographs of well and poorly pickled specimens after 1 day in steam at 300°C (573 K), (a) good pickle, (b) poor pickle, (c, d) pickle stained specimen. Note that the oxide thickness varies from grain to grain in (a), but grain structure has disappeared in (b) except where grain boundary etching shows a few thin black lines, and (c) note that most of the area in (c) appears to show lines of heavy pits under the milky film.

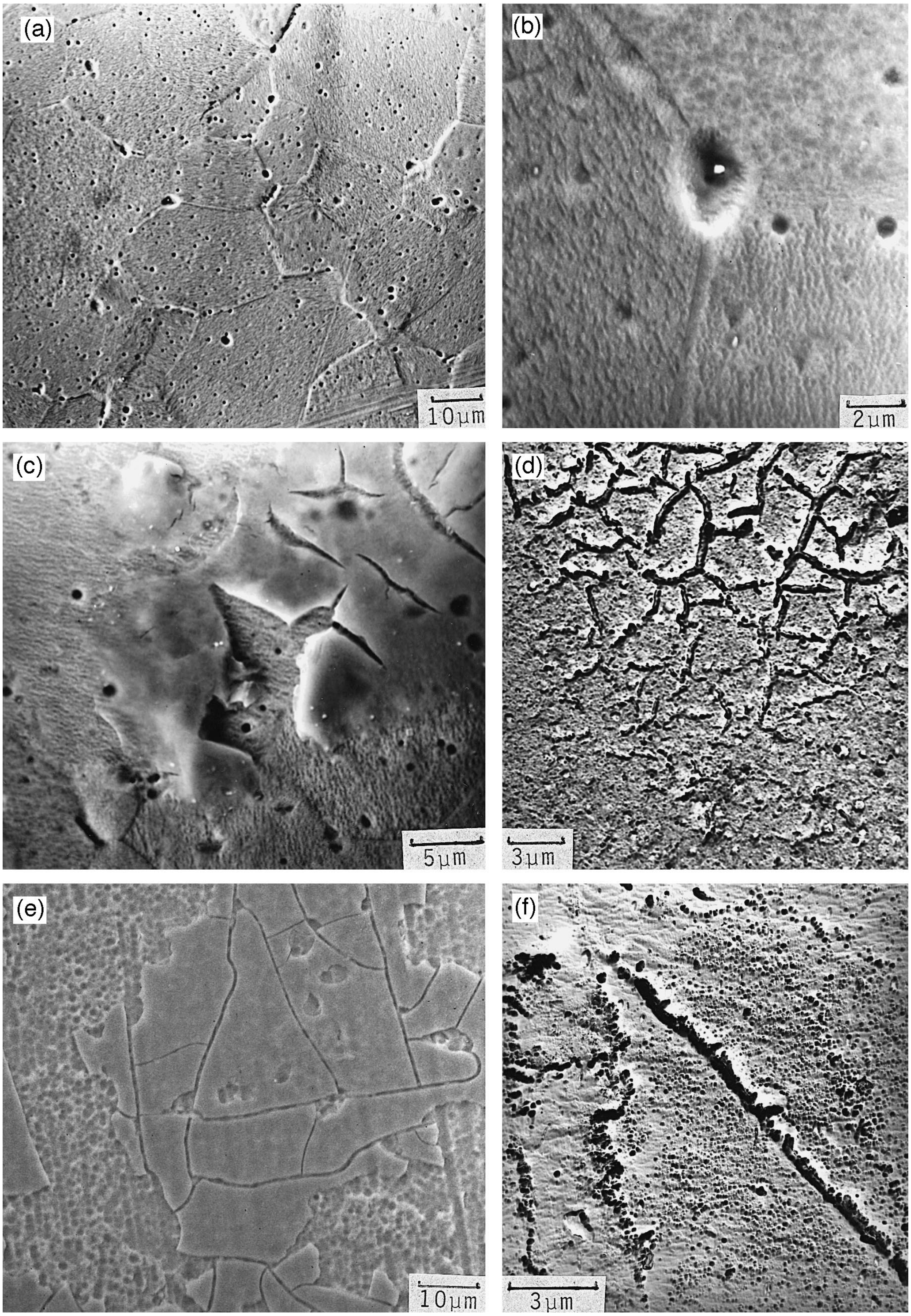

Fig. 3. SEM and replica TEM micrographs of the same unoxidised pickle-stained specimen, (a, b) SEM of areas not covered with a milky deposit, (c, d) SEM and TEM replica of an area covered with a milky deposit, and the appearance after 1 day exposure in 300°C steam (e, f).

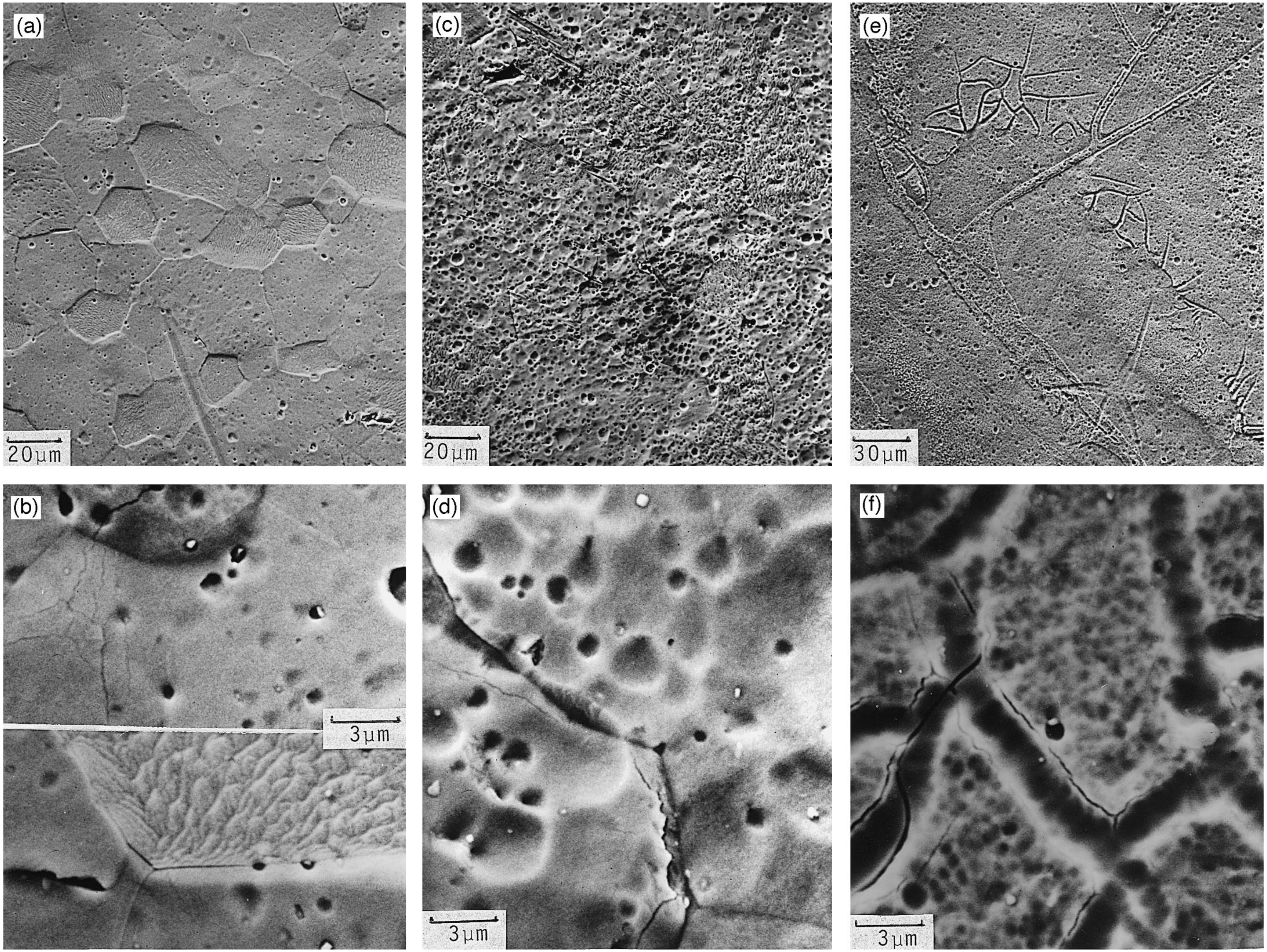

Fig. 4. Scanning electron micrographs of specimens oxidised 2 days in 300°C steam showing small cracks in all oxide films. (a, b) well pickled, (c, d) poor pickle, (e, f) pickle stained. In (f) the milky film is now very porous.

oxide/metal interface, a value that is not generally known. Oxide thicknesses estimated from the impedance spectrum of the saturated film were generally less than those obtained at 10^3 Hz during the soaking process, but again require the unknown area of the pores for a more accurate interpretation.

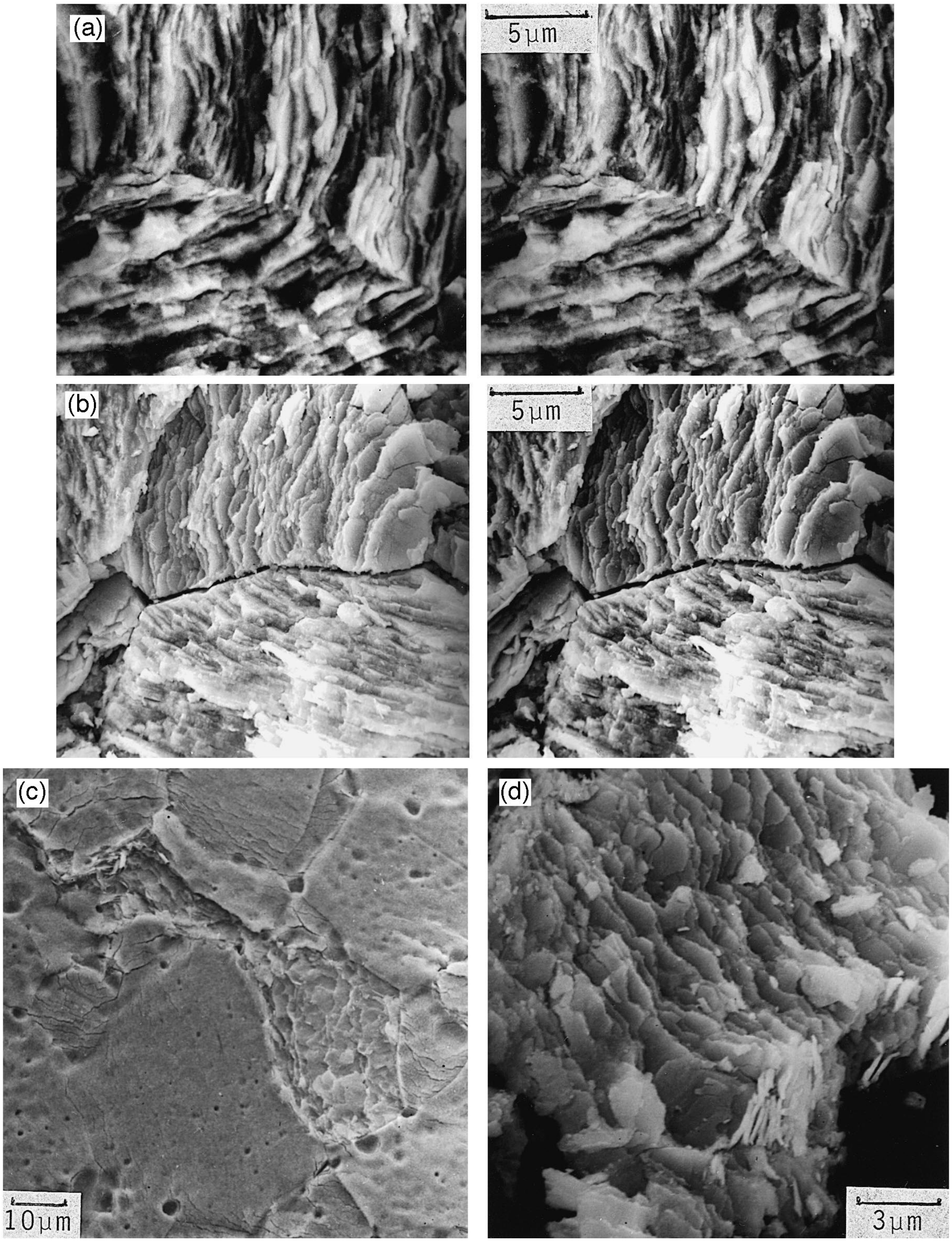

Fig. 5. Scanning electron micrographs of a pickle-stained specimen after 7 days in 300°C, 3.5 MPa steam. (a) Stereo-pair of oxide adhering to metal after extraction of surface oxide with sticky-tape, (b) stereo-pair of the same area of oxide adhering to the sticky tape, (c) micrograph of large oxide platelets, (d) surface of oxide film formed after 7 days in 0.1 MPa steam.

3.1. Oxide appearance after 1 day in 300°C steam

Oxide thicknesses during the first exposures in 300°C 3.5 MPa steam showed little or no effect of poor surface preparation. The interference colours were in the same range (Fig. 3) but, whereas well pickled specimens showed variations in oxide thickness (interference colour) that varied with grain orientation, both the poorly pickled and pickle stained specimens showed a much wider spread in colours, and these were unrelated to grain orientation and varied in a random patchy fashion. Both thicker and thinner areas of oxide than those on well pickled specimens were visible in the interference colours of poorly pickled and pickle stained specimens. Thus, almost equal average thicknesses were obtained from weight gain and interferometry on all specimen preparations initially. Both these techniques average over areas larger than the patches visible in the interference colour micrographs. It would be possible on poorly pickled specimens, with a technique measuring very small areas of surface, to find local areas where the oxide was thinner than on well pickled surfaces. The pickle-stained surfaces were covered with a milky film which had no apparent effect on the interference colours and showed ‘dried mud’ type cracks (Fig. 2c and d), merely resulting in more muted interference colours with a similar distribution to those on the poorly-pickled surfaces.

Attempts to look for differences between the initial air-formed oxides on well pickled and pickle stained specimens were largely unsuccessful. Dissolving the metal matrix resulted in no collectible material. Occasional small amorphous pieces of what might be the milky-film were obtained from pickle-stained surfaces. However, after 1 day exposure in 300°C, 3.5 MPa steam, stripping the oxides and examining them by TEM resulted in what appeared to be duplex oxides, with the initial air-formed oxide protruding from the edges of the much thicker 1 day steam oxides. The air-formed film on the pickle-stained surfaces was nano-crystalline (∼ 1–2 nm), whereas that on the well pickled surface appeared to consist of relatively large (∼ 70 nm) crystallites, that were much bigger than expected. Dark-field images of these oxide crystallites showed sizes of equiaxed crystallites that agreed with the bright-field images. However, because of specimen drift during the long exposures necessary for the dark-field images the resultant images were distorted. None of these are presented here. These films were compared with a sol–gel ZrO_2 film stripped from a glass substrate after 15 h in 300°C air. This was also nano-crystalline, with a similar crystallite size to that obtained from the pickle-stained specimen. Prior to heating at 300°C the sol–gel film was amorphous and, thus, the question of whether the initial film on a pickle-stained surface was also amorphous must remain unanswered.

SEM and TEM replicas of the initial pickle-stained specimen surfaces (Fig. 3) showed areas with and without the milky film. Areas without the milky film were generally no more heavily pitted than the poorly pickled specimens which were more heavily pitted than well-pickled specimens but otherwise showed the same metallurgical features. Areas covered with the milky film showed the ‘dried-mud’ cracking but the state of the surface under the milky film could not be readily seen. After 1 day exposures in 300°C, 3.5 MPa steam, significant areas of this milky film had flaked off revealing that the surface beneath was completely covered with pits, aligned with residual polishing scratches. Areas such as these were also visible in the optical micrographs (Fig. 2c) because of the transparency of the milky film in the visible spectrum, but not in the SEM. TEM replicas showed that between the ‘mud-cracks’ the milky film had now developed a complete array of fine pores (Fig. 3e and f).

3.2. Oxide appearance after 2 and 7 days in 300°C steam and water vapour

After 2 days in 300°C, 3.5 MPa steam the oxides were only slightly thicker than after 1 day, yet there were already some fine cracks developing in the oxide on both well and poorly pickled specimens (Fig. 4b and d). The milky film and mud-cracking on the pickle-stained specimens were clearly visible (Fig. 4e and f), but the general porosity in the milky film was now large enough to be visible in the SEM. By contrast after 7 days in 300°C, 3.5 MPa steam the oxides on pickle-stained specimens were thick (Table 1) and heavily degraded. Surfaces were powdery and layers of oxide could be removed with sticky tape. SEM stereopairs of matching surfaces of the oxide remaining on the metal (Fig. 5a) and removed with sticky tape (Fig. 5b) show arrays of large fractured oxide (or oxyfluoride) platelets arranged nearly normal to the oxide/metal interface and oriented with relation to the underlying metal grains. Individual platelets can be matched showing that the large oxide platelets were easily fractured during removal of the outer layers with sticky tape.

The severe oxide degradation in 3.5 MPa steam was a surprise, since it was initially thought that this would be dry enough to show major differences from water exposures (see below). Reducing the steam pressure to 1 atm did not completely eliminate this oxide degradation after 7 days exposure, but caused it to be restricted to small local areas of ∼ 15 μm (Fig. 5c and d). No such anomalous features were seen on pickle-stained specimens after 7 days in 300°C moist air. Some interference colours were still visible and were related to the metal grain structure rather than being patchy.

Transmission electron microscopy was restricted to oxides given the shorter exposure, since the thick degraded oxides disintegrated during attempts to ion-mill them. In the case of poorly-pickled specimens small areas of oxide

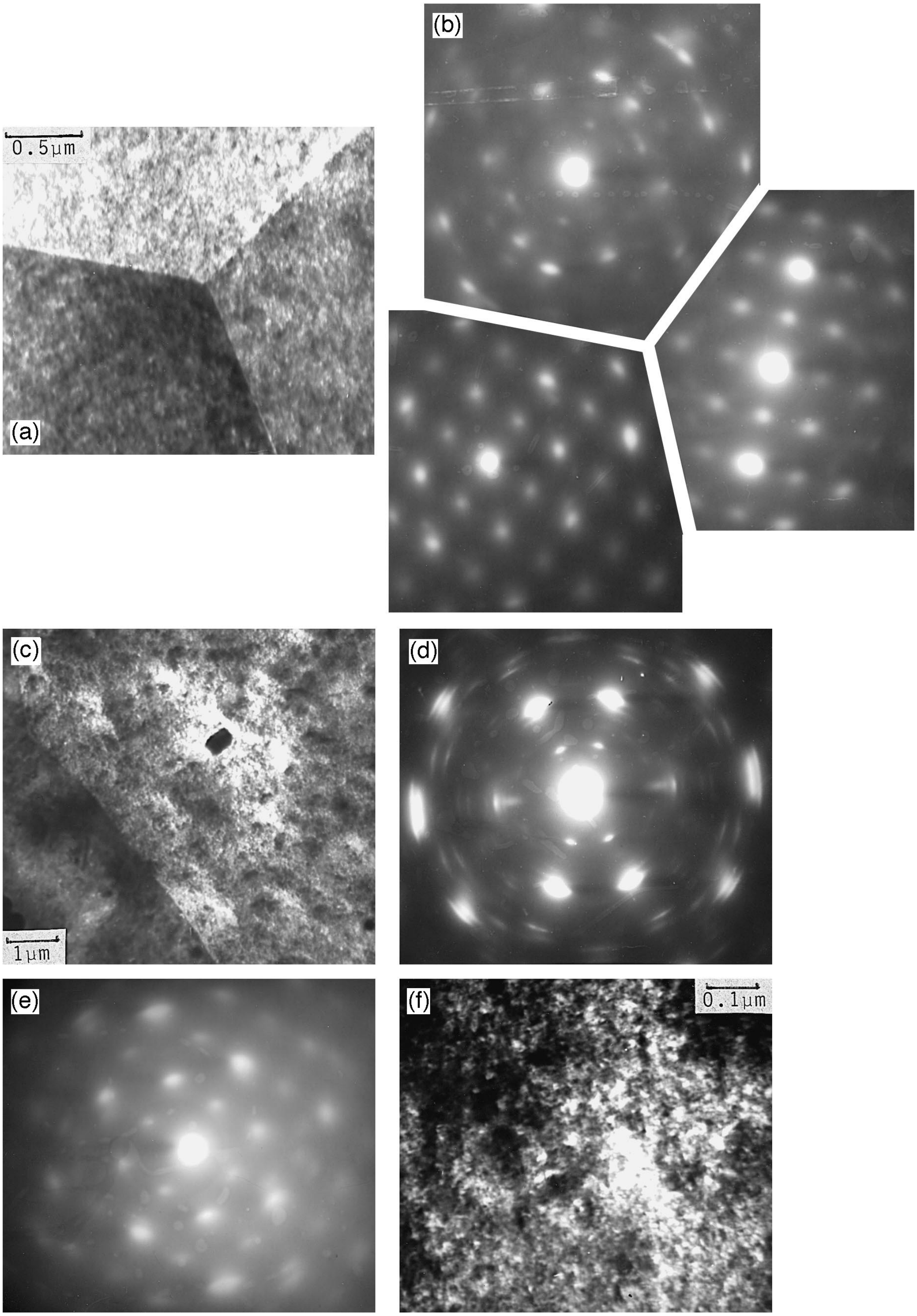

Fig. 6. TEM micrographs of stripped oxides formed on specimens after 1 day oxidation in steam. (a) Bright-field image from a well-pickled specimen showing three grains, (b) diffraction patterns from the three grains, (c) bright-field image from a pickle-stained specimen showing two prior metal grains, (d) diffraction pattern from upper right grain, (e) diffraction pattern from lower left grain, (f) higher magnification bright field image of oxide formed on a pickled stained surface.

were extracted and viewed while adhering to the replicas. They apparently came from within large elliptical pits in the original metal surface. The reasons for the ellipticity of these pits is not understood. They were not aligned with the rolling direction. They appeared to consist of isolated crystallites (10–20 nm) in a matrix that was either amorphous or of smaller crystallite size. Diffraction patterns were spotty rings that fitted an oxyfluoride structure and dark field pictures from the more spotty parts of the rings appeared to illuminate only the isolated crystallites visible in bright field. It is not known whether these flakes are typical of the whole oxide film or represent only the outer layer of the oxide, since they did not require thinning for electron transparency.

Oxides from small areas of well-pickled and pickle-stained specimens were stripped by dissolving the metal and ion-milled to transparency from the oxide/environment interface thus giving views of the oxide adjacent to the oxide/metal interface. Results for well-pickled (Fig. 6a and b) and pickle-stained (Fig. 6c–f) oxides were very similar. Crystallite sizes were small, similar in size for both oxides and consisted primarily of monoclinic-ZrO_2. It is possible that the area of oxide examined from the pickle-stained specimen had not been coated with a milky film and this may account for the similarity of these two oxides and the dissimilarity with those extracted from pits on poorly-pickled specimens by replication. The edge of the oxide stripped from the well-pickled specimen showed a ‘frayed’ appearance of bent and branched columnar grains (Fig. 7a and b), which appeared to be bent single crystals in dark-field. This suggested that there might be poor adhesion between the columnar crystallites often observed in ZrO_2 films. A similar conclusion had been reached earlier from the examination of fractures of specimens oxidised in 500°C oxygen, where much larger and straighter columnar crystallites were observed (Fig. 7c).

3.3. Oxide appearance after transfer to 300°C water

Transfer of well-pickled and poorly-pickled specimens to 300°C water, after exposure in 300°C, 3.5 MPa steam resulted in only minor increases in corrosion rate (Fig. 1) after one day exposure. Pickle-stained specimens showed much larger increases in rate, and rates were very similar whether or not the specimens had oxides previously grown in steam on their surfaces. Thus, the steam formed films offered no protection from high corrosion rates in 300°C water (Fig. 1). TEM replicas show a very highly porous oxide after 1 day in water; similar in appearance to those in Fig. 4(e) and (f). After 7 days in water the oxides were severely degraded and small areas of TEM replicas taken from them (that remained free from extracted oxide) showed evidence of similar porosity to that seen after 1 day in 300°C water. SEM pictures (Fig. 8) showed the heavily blistered nature of much of the oxide (leading to differential charging in the SEM) and the large broken

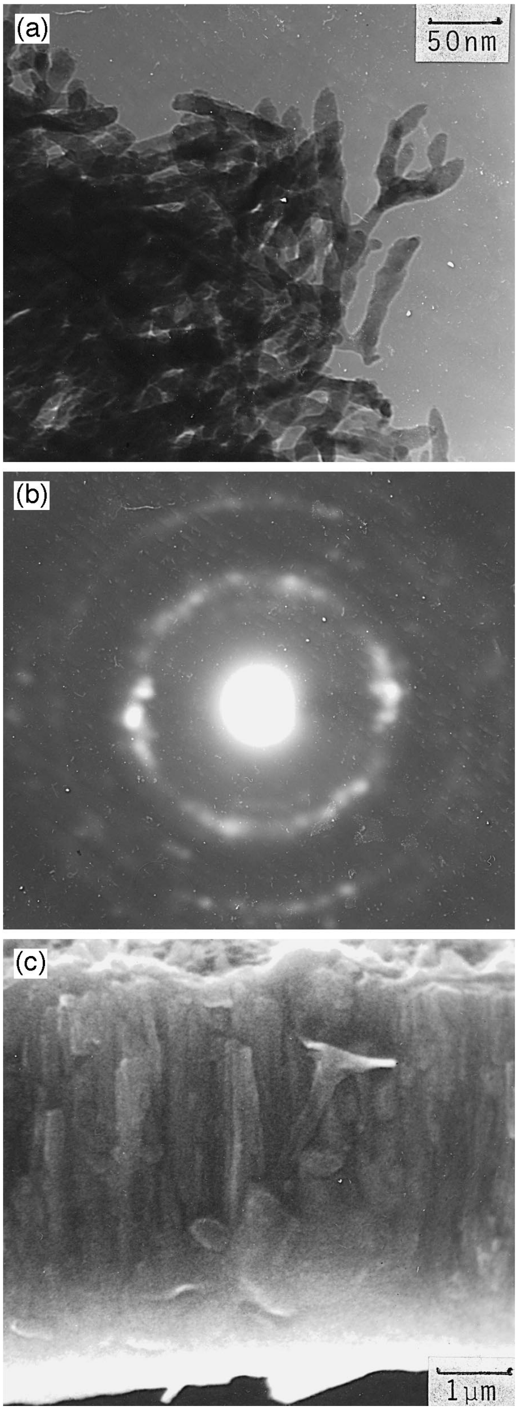

Fig. 7. TEM images of the ‘frayed’ edges of pieces of stripped oxide from a well pickled specimen, (a) bright field image, (b) diffraction pattern from frayed area, 1 day in 300°C, 3.5 MPa steam; (c) SEM of a transverse fracture of 6 μm oxide formed on van Arkel Zr in 500°C, O_2.

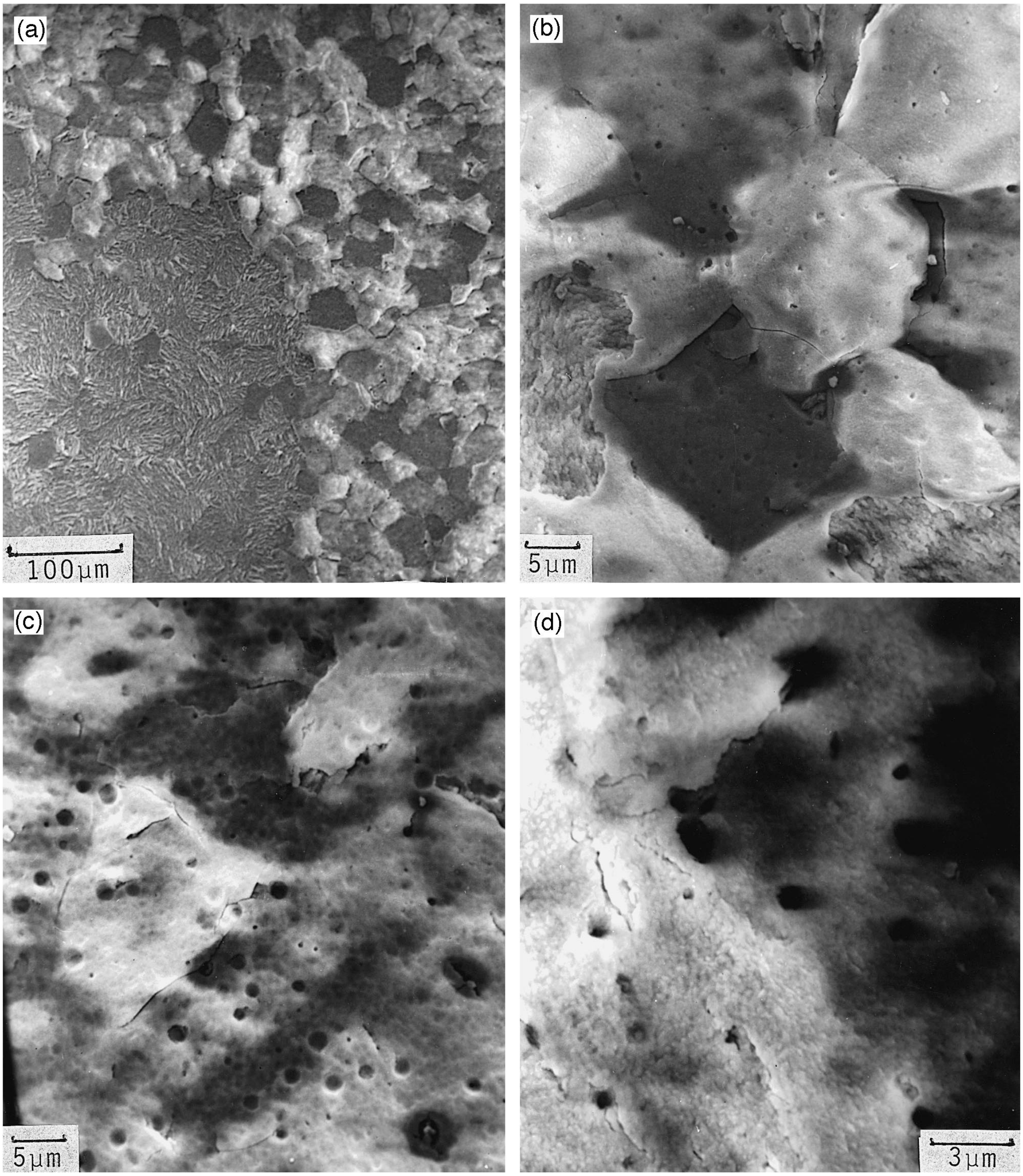

Fig. 8. Oxide surfaces of pickle-stained specimens after 7 or 8 days in 300°C water. (a) Boundary of blistered oxide and area where oxide was removed by conducting adhesive paint (7 days, water). (b) Blistered surface showing small spontaneously spalled area (8 days, water). (c) Features typical of initial oxide surface (2 days steam + 8 days water). (d) Apparently roughened surface of original oxide (7 days, water).

oxide platelets (similar to those in oxides degraded after 7 days in steam) in areas where the outer layers had spalled. The similarity of these films to those in Fig. 5 was very evident. Small areas where the surface layers were not removed by replication (and hence which may have given rise to images like those in Fig. 4f) can be seen in Fig. 8(a) and (b). The implication that the same degradation processes are occurring in both 300°C water and 3.5 MPa steam, and on a reduced scale in 0.1 MPa steam can be drawn.

4. Discussion

4.1. Films on as prepared surfaces

In the as prepared condition the well pickled specimens showed the normal surface features that have been reported before [21,22]. Thus, the metal grain structure was clearly visible, many Zr(Fe, Cr)$_2$ intermetallics remained on the surface and some shallow pits were present where precipitates had recently been removed. The poorly pickled specimen surfaces were generally similar but much more severely pitted (Fig. 6b). No oxyfluoride layers were observed after either of these surface preparations. However, small areas of a thin oxyfluoride film were extracted from the poorly pickled specimen surfaces when preparing replicas. These were about the size and shape of one of the larger pits in these surfaces and may have come from a similar location to the flakes of oxide extracted from poorly pickled specimens after 2 days in 300°C steam. This would not be unexpected as, if exhaustion of the pickling solution occurred anywhere during the 60 s delay before washing the specimens, exhaustion of the pickle and precipitation of an hydrated zirconium oxyfluoride deposit would be expected first inside large pits [12].

The pickle stained areas of surface were covered with a relatively thick hydrated oxyfluoride deposit that obscured much of the underlying surface, and had a smooth surface with major cracks ('dried mud') in some locations (Fig. 3c). Electron microscope replicas confirmed this but showed a generally rougher surface topography with little evidence of extensive porosity except for the large cracks (Fig. 3d). In areas where the oxyfluoride film was absent, a heavily pitted surface, with a rough surface topography between the pits, was seen (Fig. 3a and b). The pits were aligned with polishing scratches in the initial surface. Stripped specimens of the milky film gave only one broad, uniform diffraction ring, and dark field images obtained using a portion of this ring were uniformly illuminated. This white milky deposit on the pickle-stained specimens appears to have been initially completely amorphous and is probably a hydrated oxyfluoride film as reported by early investigators [12]. After one day exposure at 300°C in dry (3.5 MPa) steam a change in this milky film had occurred. The specimen surface now had the appearance of 'dried mud' wherever the deposit remained, and the milky deposit had flaked off completely in some areas revealing the heavily pitted surface underlying it (Fig. 3e). Electron microscope replicas not only showed the gross cracking of the 'dried-mud', but also showed that extensive porosity had developed throughout the remaining milky deposit (Fig. 3f). These changes in appearance resulted presumably from dehydration (and perhaps volatilisation) of the initial oxyfluoride deposit in 300°C steam.

Transmission electron microscopy of protruding areas of the film, resulting from 1 day's exposure to steam and examined after stripping the combined thermal and oxyfluoride films, showed a still nearly amorphous diffraction pattern. However, this now contained three prominent somewhat spotty rings that were close to the principal reflections of some reported non-stoichiometric zirconium oxyfluorides [23]. Since these oxyfluoride structures are also related to the fluorite structure on which the various ZrO$_2$ phases are based, it is difficult to establish from a few diffuse rings whether the material is an oxide, an oxyfluoride or a mixture of the two [23]. Dark-field micrographs, using portions of these rings, now showed an array of very small crystallites 3–5 nm in diameter. Unfortunately, drift in the EM stage resulted in distortion of the dark-field images during the long photographic exposures required and rendered them unsuitable for publication. The size of these crystallites is about the same as that of crystallites observed in zirconia sol–gel films [24] after drying at 300°C for 15 h and is much smaller than the size of the crystallites observed in similarly protruding pieces of the initial oxide on a well pickled specimen after 1 day in 300°C, 3.5 MPa steam. These crystallites were much larger than have been reported before [25,26] for an initial oxide on a pickled surface. It is concluded that the crystallites in the oxyfluoride film grew during the steam oxidation from an initially amorphous hydrated film that would have been morphologically similar to a sol–gel film. Some other areas of the sol–gel ZrO$_2$ film showed 'spottier' ring patterns, but dark-field micrographs still showed about the same size of crystallites. These rings from the sol–gel film were consistent with a low temperature tetragonal (or cubic) phase of ZrO$_2$ and these spacings were very similar to those reported for oxyfluoride structures [23]. This can probably be explained if the strongest reflections are determined primarily by the Zr–Zr spacings in the film. These give very similar prominent reflections for all three common phases of ZrO$_2$, which is why these are difficult to distinguish unless very sharp diffraction patterns are obtained [25]. The related structures of the zirconium oxyfluorides may also have very similar Zr–Zr distances and, hence, the most prominent diffraction spacings will also be similar.

Small flakes of the surface film extracted from the surfaces of the poorly pickled specimens after two days oxidation in 300°C, 3.5 MPa steam appeared to be similar to the 'dried-mud' films removed from the pickled-stained specimens. Nevertheless, the crystallite size is larger (10–20 nm) and the first prominent diffraction ring is split as would be expected for the mZrO$_2$ structure [25]. However, the tetragonal and orthorhombic oxyfluoride phases [23] could also give a splitting of the (111) reflections. It appears that such easily extracted films are only present locally, perhaps in some of the large surface pits formed during the delay before washing these specimens. They may not be representative of the rest of the oxide and may only be the surface layer since they did not require ion milling for electron transparency, whereas the whole oxide stripped from the specimen after 2 days in 300°C steam was opaque unless ion-milled.

The protruding areas of the original air-formed film on well-pickled specimens showed spot electron diffraction patterns typical of those reported before for thin-oxides on the zircaloys [25]. The patterns could be interpreted as fully monoclinic ZrO_2 and the dark field images showed that the films were fully crystalline with a much larger crystallite size, 50–70 nm, than the apparent thickness of the film.

4.2. Oxides formed after short exposures at 300°C

The columnar crystallites that formed thermally in 300°C steam beneath this initial film appear to have nucleated independently of the crystallites in the air formed film, since they were smaller in diameter (7–10 nm) than these initial crystallites (Fig. 7). The crystallites in the air-formed film on well pickled surfaces were much larger than could be grown in a zirconia sol–gel film during the same heating time. The 'frayed' edges of the oxide stripped from a well pickled specimen after 1 day in 300°C steam (Fig. 7) suggest that the bonding at oxide crystallite boundaries may be poor even in coherent pretransition oxide films. This could be a very important observation, since it suggests that in general even good impervious oxides are held together primarily by the compressive stresses that develop in them and the interlocking nature of the columnar crystallites. When these compressive stresses are no longer present, for instance at the surface of thick oxide films, then it may be relatively easy to generate pores or cracks if the crystallite boundary adherence is poor. Although columnar crystallites are routinely found in uniform oxides grown in high temperature water or steam (30–33), no previous evidence of poor bonding at crystallite boundaries has been reported.

Considering the early reports of severe spalling of oxides from poorly pickled zircaloy specimens in 300–360°C water [8–13], the very minor differences in the thermal oxide morphology formed here during short exposures in 300°C 3.5 MPa steam on the differently prepared surfaces came as a surprise. The oxide growth on poorly pickled and pickle-stained surfaces was the same on average as on well pickled surfaces. Only the wider spread in oxide thicknesses and the loss of the clear relationship between oxide thickness and metal grain orientation distinguished the oxides on the pickle-stained specimens.

4.3. Oxide degradation after longer exposures

It was thought initially that there must be some particular effect associated with the presence of the liquid water phase, either during specimen immersion or as a liquid surface layer in wet steam. In an attempt to avoid such liquid films a steam pressure of 500 psi (3.5 MPa) that was well below the saturation pressure of 1250 psi (8.7 MPa) was chosen initially. It is possible that many of the early results in 400°C steam [8,9] could have been for autoclaves given a 'wet start'. During such an operation the specimens are immersed in water until the autoclave temperature reaches 300°C, when the excess water is 'blown-down' and the specimens are subsequently exposed only to steam. This was a common autoclave start-up mode in early studies. When the steam-oxidised specimens here were transferred to 300°C water for 1 day, weight gains were higher in the water than would be predicted from extrapolating the previous oxidation data in 3.5 MPa steam. This was especially true of the pickle-stained specimens which had shown only minor differences in weight gain in short steam exposures when compared with well-pickled specimens. Such specimens exposed to water for only 1 day (without prior steam exposure) gave almost identical oxide thicknesses (Fig. 1) to those previously exposed in steam for either 1 or 2 days, almost as though the presence of the prior steam formed film had no influence on the behaviour in water. After 1 day exposure in water the poorly pickled and pickle-stained specimens that had previously been exposed in steam still showed some evidence from the impedance measurements for a measurable barrier film thickness, whereas the fresh, pickle-stained specimens after 1 day in 300°C water showed essentially no barrier layer thickness (Table 1), when the small fraction of the total surface representing the cross-section of the pores was allowed for.

The severe degradation of the oxide that occurred after 7 days in 300°C water was thought to be indicative of the operation of hydrothermal dissolution and redeposition of the oxide because of the thick inner layer of oxide that consisted of multiple layers of apparently large ZrO_2 platelets that were generally seen to be oriented close to the normal to the oxide/metal interface (Fig. 5). Such large crystallites were not seen for well pickled zircaloy specimens and have not been observed in the past for specimens oxidised in low temperature (~ 300°C) steam or water [27–29]. However, the observation of an almost identical oxide morphology for pickle-stained specimens exposed for 7 days in 300°C, 3.5 MPa steam (that had been expected to be dry enough not to form a liquid film on the specimen surfaces) cast doubt on this interpretation.

One possible explanation of this similarity could be that the oxyfluoride deposits on pickle-stained specimens are sufficiently hygroscopic that even at a relative humidity (RH) of only 40%, a saturated solution could form on the oxide surface, or in pores in the oxide. Thus, the physical conditions seen by the pickle-stained oxide surfaces in 3.5 MPa steam could have been identical to those seen by the same type of surface in water. The question of 'wet' or 'dry' autoclave start-up techniques may then be irrelevant at 300°C, but perhaps not at 400°C which is above the critical temperature of water. In order to resolve this question, the oxidation of well pickled and pickle-stained specimens in atmospheric pressure steam at 300°C was compared. No extensive degradation and spalling of the oxide film was found after 7 days exposure. However, specimens showed some enhanced oxide growth and cracking on some metal grains, but interference colours were still visible on some other gains. This big variation in oxide thickness from grain to grain is more like the behaviour of unalloyed Zr than that of zircaloy-2 [30,31], and suggests that the intermetallics are not acting as electronic conduction paths in pickle-stained specimens [32]. Nevertheless, small pieces (10–20 μm) of oxide could still be removed with epoxy glue from the oxides formed in 0.1 MPa steam and showed signs of the presence of large oxide platelets. Thus, the formation of a liquid phase on pickle-stained surfaces in 300°C, 3.5 MPa steam appears to be the most probable explanation of the similar behaviour of specimens in steam at 40% RH and water, but it appears that even at 0.1 MPa steam pressure local areas may develop a hygroscopically induced liquid phase within the porosity. A further comparison after 7 days in 300°C moist air showed no localised oxide degradation.

4.4. Hydrothermal ZrO_2 crystal growth in fluoride solutions

It appears, therefore, that the occurrence of a hydrothermal dissolution and redeposition process is still the most probable explanation of the severe degradation of the oxide films observed when pickle-stained specimens are exposed to water or steam at $\geq 40\%$ RH for 3–7 days. These processes must be occurring at the oxide/metal interface because the oxide platelets are able to maintain an orientation relationship with the underlying metal. The very ordered layers of large oxide platelets observed after such degradation are very different in morphology from the large equiaxed oxide crystallites that seem to form when a similar degradation process occurs in lithium hydroxide solution [33]. However, differences such as this, that occur with changes in solution chemistry, are quite common when hydrothermal crystal growth experiments are conducted [34,35]. Lobachev reports [35] that ZrO_2 crystals, hydrothermally grown in NH_4F solution, changed from a platelet to a more equiaxed morphology when the temperature gradient (solubility difference) in the autoclave was increased. Fluoride solutions were found to be much more efficient than hydroxide solutions for growing ZrO_2 crystals hydrothermally [35], suggesting that small amounts of fluoride could have major synergistic effects on corrosion in LiOH, where similar hydrothermal processes are thought to be occurring [36]. These results for crystal growth in fluoride solutions also suggest that hydrothermal effects would be seen at much lower F^- concentrations than for LiOH concentrations.

5. Conclusions

These experiments suggest that hydrothermal dissolution and redeposition of ZrO_2 leading to severe oxide degradation can occur whenever sufficient residual F^- and sufficient H_2O pressures are present to hygroscopically form fluoride solutions in the porosity in oxide films. The initial surface preparations affect primarily the quantities of fluoride available and the surface topography that can determine the probability of forming fluoride solutions hygroscopically. Thus:

(i) The initial surfaces of pickle-stained specimens are largely covered with a thick, milky zirconium oxyfluoride layer in which develops an array of pores during short exposures in 300°C, 3.5 MPa steam or water. Such deposits are not present on well pickled surfaces and are present only in large pits in poorly pickled surfaces.

(ii) The initial oxide growth rates are not very different for the three types of surface in 300°C, 3.5 MPa steam. The interference colour oxides lose their well defined relationship to the grain structure on poorly pickled and pickle-stained surfaces, perhaps as a result of losing their close epitaxial relationship. This gives a much more local variation in oxide thickness on a scale smaller than the metal grain size, and a wider spread in oxide thicknesses, on both poorly pickled and pickle-stained surfaces. Thus, some small areas on such specimens have lower oxide thicknesses than on well pickled surfaces after identical oxidation exposures.

(iii) After 7 days exposure at 300°C the presence of fluoride solutions on or in the surface films leads to thick, porous, friable oxides overall in water or 3.5 MPa steam, but only locally in 0.1 MPa steam, for pickle-stained specimens. These films consist of arrays of very large oxide platelets arrayed in different directions on different metal grains, but generally roughly normal to the metal/oxide interface. In 0.1 MPa steam only very small (~ 15 μm) areas of oxide are brittle enough to be removed with epoxy glue and showed the presence of large oxide platelets. After 7 days in moist air at 300°C all such evidence had disappeared.

(iv) These large oxide platelets are thought to grow as a result of hydrothermal oxide dissolution and redeposition processes occurring primarily from concentrated fluoride solutions inside the porous oxide films, whenever the local environment is such that a concentrated fluoride solution can be generated on the specimen surface or within pores in the oxide. This occurs in water or steam at $\geq 40\%$ RH, and in small local areas even in 0.1 MPa steam, but not at much lower partial pressures of water vapour.

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