Enigmatic Moisture Effects on Al_2O_3 Scale and TBC Adhesion

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Keywords: superalloys, alumina scales, TBC, oxidation, moisture, spallation, hydrogen

Abstract. Alumina scale adhesion to high temperature alloys is known to be affected primarily by sulfur segregation and reactive element additions. However adherent scales can become partially compromised by excessive strain energy and cyclic cracking. With time, exposure of such scales to moisture can lead to spontaneous interfacial decohesion, occurring while the samples are maintained at ambient conditions. Examples of this Moisture-Induced Delayed Spallation (MIDS) are presented for NiCrAl and single crystal superalloys, becoming more severe with sulfur level and cyclic exposure conditions. Similarly, delayed failure or Desk Top Spallation (DTS) results are reviewed for TBC's, culminating in the water drop failure test. Both phenomena are discussed in terms of moisture effects on bulk alumina and bulk aluminides. A mechanism is proposed based on hydrogen embrittlement and is supported by a cathodic hydrogen charging experiment. Hydroxylation of aluminum from the alloy interface appears to be the relevant basic reaction.

Introduction

High temperature turbine alloys often rely on slow growing adherent scales of α-Al_2O_3 for protection from environmental degradation. This is true for bare single crystal superalloy blades, where tip rub repeatedly exposes unprotected material, and for TBC coated airfoil surfaces that typically rely on various alumina-forming Ni-Pt-Al or NiCrAlY bond coats. Scale, and thus TBC adherence, are currently discussed in terms of various thermomechanical, morphological, and chemical effects. Among the latter, sulfur content and its deleterious interfacial segregation occupy a prominent position. It is controlled by desulfurization, gettering by Y, Zr, Hf, etc. reactive elements, or its effects are diminished in the presence of Pt and other precious metals.

However evidence has been accumulating suggesting that an additional chemical effect is prevalent. Delayed failure of alumina scales and TBC's at ambient conditions have often been observed in the laboratory. It was surmised that moisture played a critical role. Experiments have indeed shown that water immersion or applied droplets can produce rapid decohesion. Since these somewhat dramatic effects occur at ambient temperature, a chemical role of H_2O is not self-evident. It is the purpose of this paper to characterize the common factors of some of these observations, coupled with critical experiments, in order to propose an underlying chemical mechanism. Additional supporting information is present in [1].

Experimental

Cyclic oxidation coupons were prepared by EDM of various button melted alloys or commercially cast superalloys, typically 1 cm x 1cm or larger, with thicknesses ranging from 0.5 to 5 mm. Desulfurization was produced by cyclic oxidation/polishing, hydrogen annealing, or fluxing in the melt. Some samples were coated with TBC's, both by plasma spraying or EB-PVD. A commercial Ni(Pt)Al bond coat was used for EB-PVD. Bare samples were typically prepared to 600 grit finish, whereas the PS-TBC required a grit blast for mechanical bonding. Moisture effects were recorded by weight change, optical/video imaging, or acoustic emission. Further details are given below.

Results and Discussion

Initial manifestations during sulfur purging. A dramatic moisture effect was observed over two decades ago during the first demonstration of alumina scale adhesion due to desulfurization of undoped alloys [2,3]. In this experiment, samples of undoped Ni-15Cr-13Al (wt.%), containing 10 ppm S, were repeatedly oxidized at 1120^{o}C in 1-hr cycles. After determining the weight change for each cycle, any remaining scale was lightly polished off to remove any sulfur segregation at the interface and a new cycle was begun. For the first 10 cycles, considerable Al_2O_3 scale spallation occurred as expected. However after 13 cycles, the scale remained intact after cooldown, only to 'peel off' upon contacting the water used in the subsequent wet polishing step. The amount of additional interfacial spallation was then tracked along with the sulfur content, as measured by GDMS (glow discharge mass spectroscopy), shown in fig. 1. The assessment, then, is that considerable spallation occurred on cooldown for the first 8 cycles while the sulfur content was above 5 ppmw. Observable water immersion effects increased to 0.2 mg/cm^2 after fully retained scales first became apparent, (i.e., at 13 cycles and ~ 4 ppmw S). Finally, after further cycling and desulfurization, (25 cycles and 2 ppmw S) the scales remained adherent after both cooling and water immersion, but later spalled by water immersion after being stored 1 year at ambient conditions. The generalization taken here, and persisting in many studies to follow, is that partially adherent scales obtained at intermediate sulfur contents, are subject to deleterious and sometimes time-dependent, moisture effects. Conversely, more adherent scales enabled by low sulfur contents, become resistant to moisture effects.

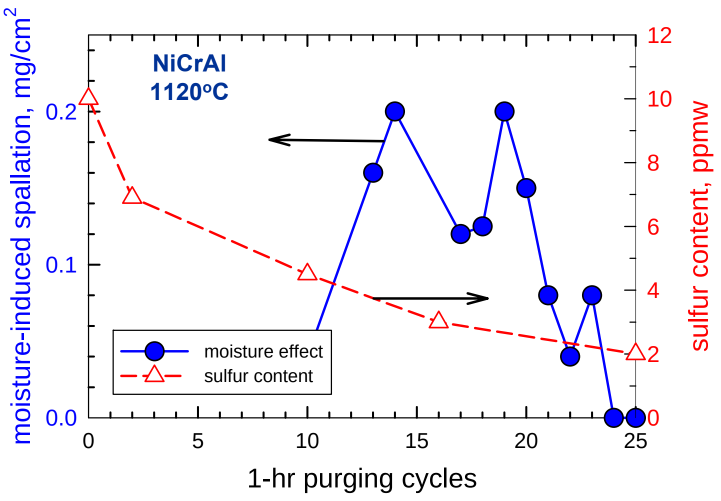

Fig 1. Onset, then decrease of moisture-induced spallation as sulfur is removed (NiCrAl, 1120^{o}C) [2].

Ni-base superalloys. Subsequent studies on desulfurizing alumina-forming superalloys employed a protocol where the samples were often exposed to moist breath or water immersion to reveal any similar moisture sensitivity. The alloys studied were PWA 1480, PWA 1484, Rene′142, and Rene′N5, all containing greater than 5% Al and Cr. Full compositions and supporting information are presented in [1]. Initially, 1-hr sulfur purging cycles were ineffective for PWA 1480 [4]. However, subsequent studies on PWA 1484 were effective with a 24 hr purging cycle, to account for the long transient oxidation period before a continuous Al_2O_3 layer developed [5]. Furthermore, this and related studies demonstrated the moisture effect also by cycling in controlled $p(H_2O)$ environments [6,7]. Given the labor intensity of the purging procedure, desulfurization annealing in 100% H_2, first demonstrated by Lees for improved Cr_2O_3 adhesion [8,9], was then used in for PWA 1480. Moisture induced spallation was frequently observed during the weighing and inspection sequence for samples produced at intermediate sulfur contents.

Subsequent studies of the same materials employed 5%H_2-Ar anneals and provided a much more effective and convenient process for removing sulfur and improving scale adhesion [10]. In this study, the desulfurization process was characterized by the diffusion product, $4D_St/x^2$, where D_S is the diffusion coefficient of sulfur at a given temperature, t is time, and x is sample thickness. Scale adhesion in 1100°C cyclic oxidation tests was mapped as a function of annealing condition, sample thickness and sulfur content. These results indicated that adhesion was maximized when the bulk sulfur content was reduced below that corresponding to the bulk equivalent of 1 monolayer of segregated sulfur.

Commensurate with this trend, the resistance to additional moisture-induced delayed spallation (MIDS) was also improved. Sample weights were recorded before and after exposure to moist breath or water immersion at 40, 200, and 500 cycles for the samples discussed above in [10]. It is seen in fig. 2 that greater amounts of MIDS (up to 0.6 mg/cm^2) correlate with higher sulfur contents (5-7 ppmw S), and spallation decreases to almost the noise level below about 0.4 ppmw S. This is the critical sulfur content predicted for 1 monolayer equivalent for 0.5 mm samples from the adhesion map [10]. It is also noted that the increased scale thickness in progressing from 40 to 200 hours results in an overall increase in the mass of spallation. However this trend reverses for the 500 hr data. Here, presumably, the scales on the high sulfur samples have transitioned to less protective oxides that apparently do not exhibit the same sulfur and moisture sensitivity as Al_2O_3 scales.

Similar studies on PWA 1484 produced even better cyclic oxidation resistance, given the presence of Hf and absence of Ti. Now adherent behavior was demonstrated for 2000 1-hour cycles at 1100°C (0.8 mg/cm^2) for melt-desulfurized or hydrogen annealed material (0.25 ppmw S or 0.01 ppmw S), in contrast to conventionally cast as-received material (@ 1.2 ppmw S resulting in -32 mg/cm^2) [11]. Water immersion spallation effects were studied after oxidation at 400, 800, and 2000 cycles. It can be seen in fig. 3 that the as-received material exhibited additional considerable spallation to bare metal (1.1 mg/cm^2) after 800 cycles. In contrast, the hydrogen annealed sample did not exhibit any additional measurable spallation.

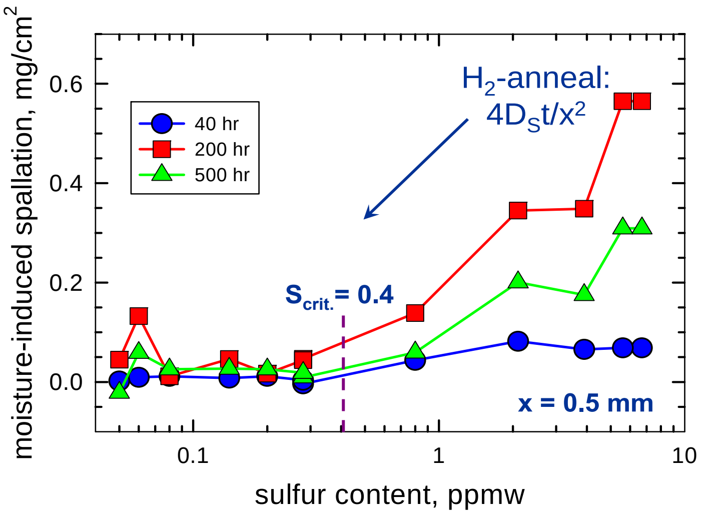

Fig. 2. Moisture-induced spallation for PWA 1480, oxidized at 1100°C, decreasing with desulfurization [10]. Arrow shows increasing effect of diffusion product, D_st/x^2 in H_2-annealing. Critical sulfur content, 0.4 ppmw, predicted for 0.5 mm thick samples.

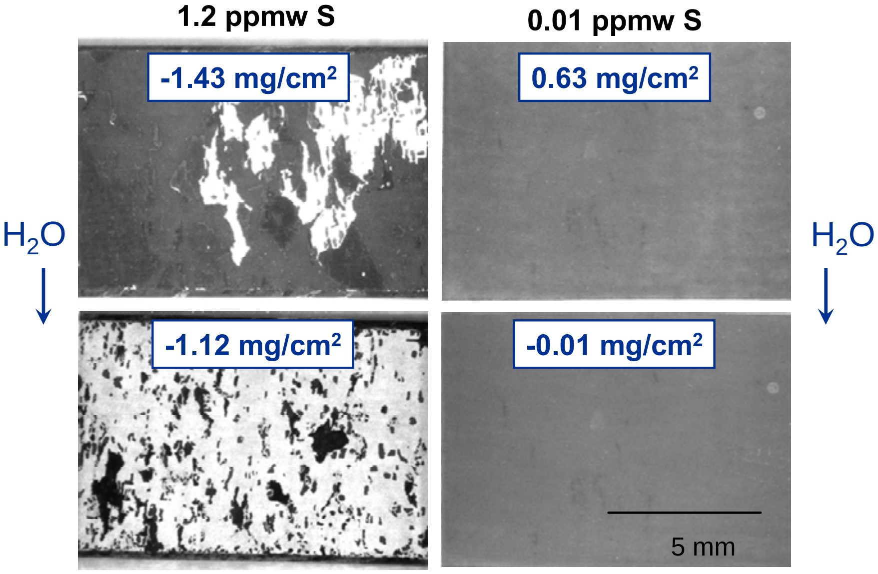

Fig. 3. Macrographs before (top) and after (bottom) immersion in water (H_2O arrows) show increased spalling to bare metal for as-received PWA 1484 (left), but no effect for H_2-desulfurized sample (right.). (Pre-oxidized for 800 1-hr cycles at 1100°C).

MIDS (i.e., intentional immersion) effects were studied on Rene′N5 samples that had been oxidized at 1150°C for 1000 1-hr cycles [12]. A number of MIDS-related phenomena came to light, as summarized in fig. 4, showing additional weight loss, increased spall area, and cumulative acoustic emission events due to immersion. First, undoped samples with 2.6 ppmw sulfur exhibited more MIDS spallation than Y-doped samples (@ nominally 50-100 ppmw Y).

Secondly, hydrogen annealing (5%H_2-Ar, 1250°C, 100 hr) reduced the sulfur content of the undoped sample to 0.01 ppmw, improved cyclic performance drastically, and reduced moisture-induced spallation. Y-doping at 15-100 ppmw Y produced a similar effect. However, hydrogen annealing also caused further improvements to the Y-doped samples, especially in regards to moisture effects at room temperature, but without removing sulfur. This has not been fully explained, but was discussed in terms of partial decarburization from ~ 500 ppmw C down to ~ 100 ppmw C.

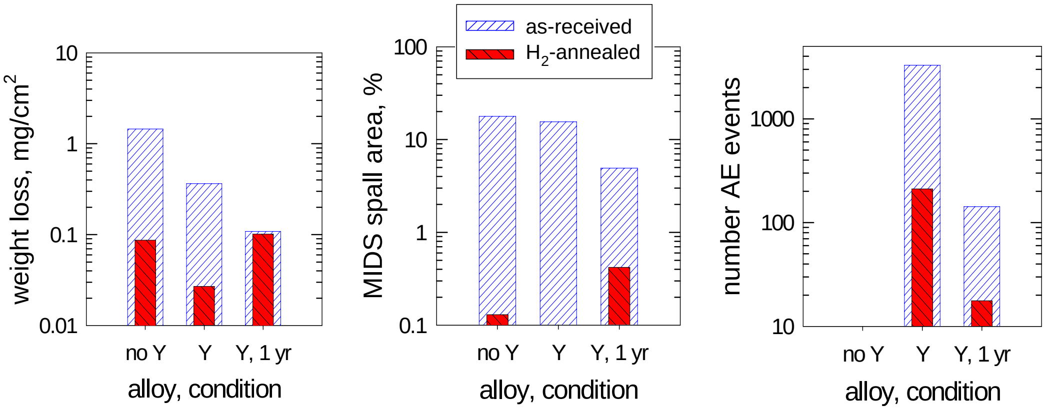

Fig. 4. Effect of aging (1 yr) and H_2-annealing on moisture-induced effects for Rene′N5±Y (oxidized for 1000 1-hr cycles at 1150^{o}C): a) weight loss, b) spall area, c) acoustic emission response [12].

Finally, an effect was noticed for Y-doped samples that were retained for 1 yr before immersion. On average, these samples appeared to show less immersion effects than those exposed directly within a day after the test ended. This may imply some form of stabilization effect from extended exposure to ambient humidity prior to immersion (in contrast to NiCrAl). The acoustic emission response was more than an order of magnitude less for such samples. Furthermore, the response was delayed over a period of hours and occurred in discreet rapid bursts, rather than the immediate and continuous response from those directly exposed to moisture [12].

Given the direct effect of alumina scale spallation on TBC life, moisture effects were also examined for plasma sprayed 250 μm 7YSZ TBC's tested in conventional cyclic oxidation [11]. Here PWA 1484 substrates were used without a bond coat to exhibit a more direct effect of substrate sulfur content on scale adhesion and TBC life. The results for complete delamination of the entire TBC as one sheet are summarized in fig. 5. The lifetime can be seen to increase from 200 to 2000 cycles by decreasing the sulfur content. Furthermore, of the 8 surfaces coated, 6 failed by delayed desk top spallation (DTS), with no intentional exposure to increased humidity conditions. One failed upon cool down, (CD) and one surface on the 0.01 ppmw S sample did not fail until immersed in water (H_2O). Corresponding oxidation ranged from about 0.5 to 1 mg/cm^2. These results are somewhat analogous to substrate oxidation effects discussed shown in fig. 3. However the uncoated low sulfur sample was quite immune to water immersion even after 2000 cycles, suggesting the additional strain energy provided by the TBC promotes cracking and failure.

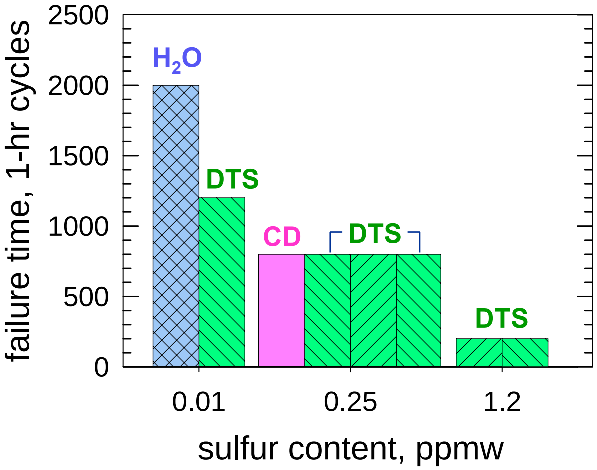

Fig. 5. Effect of sulfur content on TBC life and desk top spallation for PS-7YSZ on PWA 1484 (no bond coat) oxidized at 1100°C. One bar indicates one sample. Immersion (H_2O) caused one failure [11].

Similar tests were performed for commercially applied EB-PVD YSZ coatings, with a Pt-aluminide bond coat, on Rene′N5 substrates [13]. Thermal cycling inevitably resulted in DTS for all 6 coatings tested at both 1135°C with 45 minute cycles and at 1150°C with 60 minute cycles. That is, no failures occurred while the samples remained warm (~150°C) and dry at the top of the vertical cyclic furnace tubes. In some cases, as the coatings approached the average coating life, they could be made to fail at room temperature simply by the application of a water drop. The sequence of fig. 6 shows a TBC beginning to dimple locally upon cooldown (A) after 260 1-hr cycles to 1150°C. This becomes the site of excessive buckling after the first application of a water drop (B). Finally, the entire coating failed after a second application (C). The whole process took place over the course of just a few minutes. A video recording has been made of another sample that remained intact after cool down, but then failed completely within 10 seconds of applying two water droplets [13]. Furthermore, the phenomenon has been independently verified by Rudolphi, Renusch, and Schütze at KWI-DECHEMA for a 150 μm vacuum plasma sprayed NiCoCrAlY bond coat followed by 250 μm of an EB-PVD YSZ TBC, preoxidized at 1050°C for 310 hr [14]. The results show acoustic emission triggered by water drop application and complete failure within 5 seconds. This is in contrast with the absence of AE or spallation for as-coated samples treated identically.

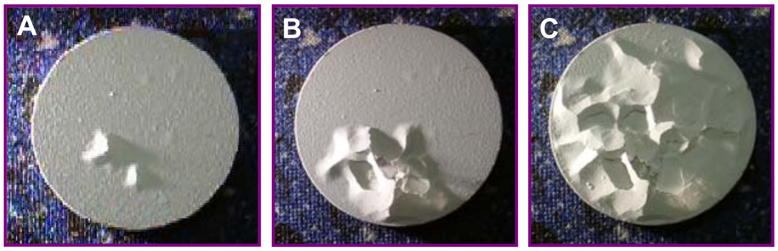

Fig. 6. Water drop failure of an EB-PVD TBC. RE-doped YSZ, Ni(Pt)Al bond coat, Rene′N5 substrate after 260 1-hr cycles at 1150°C. A) as-cooled, B) after one drop, C) after 3 drops. (2.5 cm dia.)

The widespread aspect of moisture-induced delayed failure is indicated by the previous results for NiCrAl, PWA 1480, PWA 1484, Rene′142, Rene′N5, plasma sprayed TBC's, PVD TBC's, LPPS NiCoCrAlY bond coats, Ni(Pt)Al aluminide bond coats, and no bond coat systems. The question arises concerning the underlying cause of failure. This had been discussed in prior works [5, 12, 15, 16] where there is general agreement that moisture causes a decrease in interfacial toughness between the scale and metal. The mechanism accounting for the decrease is under investigation, and one proposition is hydrogen embrittlement at the interface [17]. The rationale stems from the close analogy to moisture-induced hydrogen embrittlement features for intermetallic compounds.

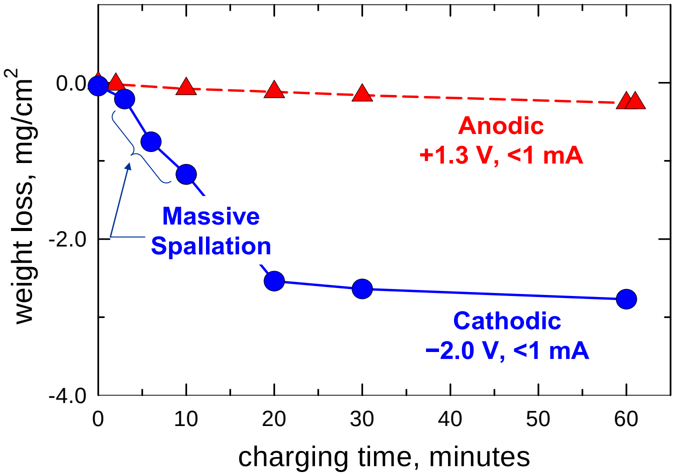

Fig. 7. Discontinuous weight loss due to cathodic de-scaling of Rene′N5+Y in 1 N H_2SO_4 (pre-oxidized for 1000 1-hr cycles at 1150°C) [17]

To test this hypothesis, very adherent pre-oxidized samples of Rene′N5+80 ppmw Y, hydrogen annealed at 1250°C for 100 hr., were subjected to an electrolytic cathodic hydrogen charging procedure [17]. The current-voltage response profile was first established, with the coupons immersed about half way in the electrolyte. A rapid decrease or knee (break) in the current occurs, showing relatively low 1 mA currents at less than -2.0 V cathodic (–) polarization or less than 1.3 V anodic (+). (This corresponded to –0.5 and +1.0 V, respectively, for bare N5 calibrated against a Ag/AgCl reference electrode). Very little response occurred at the anodic knee, either current or visual. However, at the cathodic knee, noticeable spalling to bare metal occurred after 10 minutes of polarization, along with considerable weight loss (~3 mg/cm^2), fig. 7. Examination of the exposed interface revealed highly faceted imprints of the alumina grains and no indication of chemical dissolution, fig. 8. Indeed, no change was recorded for 1 hr immersion in the electrolyte without polarization. Other features were dispersed Al_2O_3 intrusions and TaC particles.

This experiment supports the hypothesis that hydrogen embrittlement may be the operative mechanism explaining moisture-induced delayed spallation (MIDS) of alumina scales and thermal barrier coatings. The reaction often postulated for aluminum-based metals and aluminide intermetallic compounds, eqn. [1], is compared to that for bulk alumina, eqn. [2]:

$$Al_{alloy} + 3(H_2O)_{ads} = Al(OH)_3 + 3H^+ + 3e^- \qquad [1]$$
$$Al_2O_3 + 3(H_2O)_{ads} = 2Al(OH)_3 \qquad [2]$$

It can be seen that only eqn. [1], for metallic hydroxylation, produces hydrogen. Indeed, there is indication from preliminary proton induced gamma emission (PIGE) studies that some hydrogen does exist at the metal interface of oxidized alumina-formers [18].

According to many treatises on hydrogen embrittlement, a number of common aspects are in play that have parallels in the MIDS phenomenon, as discussed previously in [17]: a multi-axial tensile stress state exists which promotes hydrogen interstitial diffusion; embrittlement is maximized near room temperature, where hydrogen diffusion is sufficient to enter the material, but not so fast as to escape immediately; time delays for crack propagation are caused by this diffusion interval; and, finally, a negative synergy with interfacial sulfur exists, both experimentally and in theoretical quantum chemistry models, showing decreased M-Al_2O_3 interfacial bond strength. This is in contrast with relatively slow moisture-induced crack growth (stress corrosion, static fatigue) for bulk alumina occurring by eqn. [2].

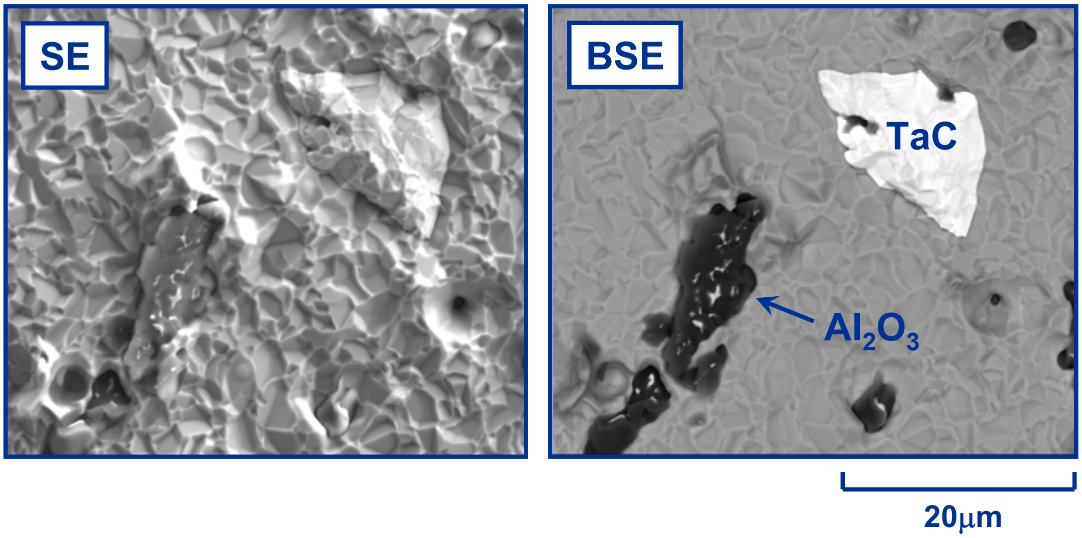

Fig. 8. Oxide imprints in Rene′N5+Y interface exposed by 1-hr of cathodic de-scaling at -2.0V. (Hydrogen annealed at 1250°C for 100 hr; oxidized at 1150°C for 1000 hr). Secondary/backscatter electron image pair.

Concluding Remarks

This paper has attempted to highlight some of the history and pertinent observations regarding moisture-induced delayed spallation of alumina scales. Some common factors promoting the phenomenon are a highly stressed, cracked, and chemically compromised scale (i.e., by S). TBC failure goes hand in hand with scale failure. Indeed, TBC's may also fail by the application of water when the above pre-requisites have been met, suggesting that natural desk top spallation is also a manifestation of MIDS. Thus, both MIDS and DTS become most apparent for thermally cycled samples that are approaching interfacial failure, but would otherwise survive the present exposure in a dry environment. Cathodic de-scaling experiments, coupled with recent PIGE evidence, strongly suggest that the root cause of these moisture effects is hydrogen embrittlement at the oxide-metal interface.

References

1. J.L. Smialek, "Moisture-Induced Delayed Spallation and Interfacial Hydrogen Embrittlement of Alumina Scales," NASA TM 2005-214030, 29 pages (Dec., 2005).
2. J. L. Smialek, *N. L. Peterson Symp. Proc. on Oxidation and Associated Mass Transport*, M.A. Dayanada, S.J. Rothman, and W.E. King, eds., TMS-AIME Oct. 6-9, (1986) 297-313.
3. J.L. Smialek, *Corrosion and Particle Erosion at High Temperatures*, V. Srinivasan, K. Vedula, eds., TMS-AIME, 1989, pp. 425-457.
4. B.K. Tubbs, J.L. Smialek, *Corrosion and Particle Erosion at High Temperatures*, V. Srinivasan, K. Vedula, eds., TMS-AIME, 1989, pp. 459-487.
5. R. Janakiraman, G.H. Meier, and F.S. Pettit, *Met. Mat. Trans*., **30A** (1999) 2905-13.
6. M.C. Maris-Sida, G.H. Meier, and F.S. Pettit, *Metall. Trans.*, **34A**, 2609-2619 (2003).
7. K. Onal Hance, "Effects of Water Vapor on the Oxidation Behavior of Alumina and Chromia Superalloys between 700^{o}C and 1000^{o}C, Ph.D., U. Pittsburgh (2005).
8. D. G. Lees, Oxid. Met., **27**, 75-81, 1987.
9. I. Melas and D.G. Lees, *Materials Science and Technology*, **4**, 455-456, 1988.
10. J.L. Smialek, "Effect of Hydrogen Annealing and Sulfur Content on the Oxidation Resistance of PWA 1480," in NASA CP 10193, Paper No. 1, May, 1997.
11. J.L. Smialek, *Ceramic Engineering and Science Proceedings*, **23**, 4, 485-495 (2002).
12. J.L. Smialek, G.N. Morscher, *Mater. Sci. Engineer. A*, **332** (1-2), 11-24, 2002.
13. J.L. Smialek, D. Zhu, and M.D. Cuy, *Scripta mat*., submitted Oct. 5, 2007.
14. M. Rudolphi, D. Renusch, M. Schütze, , *Scripta mat*., submitted Oct. 12, 2007.
15. V. Sergo and D.R. Clarke, *J. Amer. Ceram. Soc.*, **81** [12] 142-161 (1998).
16. V. Tolpygo, D.R. Clarke, *Mater. Sci. Eng*., **A278**, 142-161 (2000).
17. J.L. Smialek, *JOM*, **1**, 29-36 (Jan., 2006).
18. H. Zschau, M. Dietrich, D. Renusch, M. Schütze, J. Meijer, H. Becker, *Nucl. Instr. Met.B*, **249**, 381-383 (2005).