

## Behaviour of coated and uncoated ferritic steels under isothermal and cyclic steam oxidation conditions

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### Abstract

Next generation steam turbines are expected to operate at 600–650°C and at these temperatures, currently available high strength ferritic-martensitic steels need to be coated to prevent oxidation. Slurry deposited aluminide coatings have shown excellent performance up to 650°C under isothermal conditions. The behaviour of these coatings as well as that of uncoated P92 under thermal cycling conditions has been studied both in steam and in air at 650°C. The tested specimens were characterized by field emission scanning electron microscopy. A comparison with isothermal steam oxidation has been established. In cyclic oxidation, evidence of scale spallation from uncoated substrates was observed at shorter exposure times than for specimens tested under isothermal conditions. In the coated specimens, cracks originally present in the “as deposited” coating did not propagate or become sites of preferential oxidation during isothermal steam testing. However, the cracks widened and propagated causing substrate oxidation when the specimens were tested by thermal cycling in steam or in air.

### 1. Introduction

New generation steam turbines are expected to operate at 600–650°C and at these temperatures 8–10 wt. % Cr steels are attacked by steam, forming very thick scales in relatively short times [1, 2]. In recent studies carried out within the framework of COST actions 522 and 536, as well as in the European Project “Coatings for Supercritical Steam Cycles” (SUPERCOAT) the use of oxidation resistant coatings on these steels has been considered as an alternative to employing higher Cr alloys. Among the tested coatings, diffusion aluminides are very protective. These coatings are deposited by applying an Al slurry followed by a diffusion heat treatment at 700°C with thickness ranging from 40 to 100 µm [3–5]. Electron microprobe analysis as well as electron diffraction carried out in a Transmission Electron Microscope, confirmed the presence of an outer Fe<sub>2</sub>Al<sub>5</sub> zone with Cr rich precipitates, and an inner and thinner FeAl layer on top of a zone containing acicular precipitates of AlN. The same zone shown in Fig. 1.

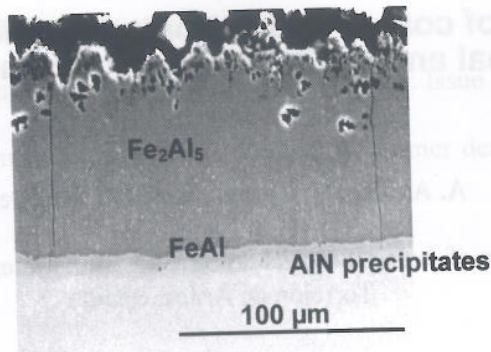


Figure 1. Microstructure of a slurry aluminide coating on P92.

The coating microstructure exhibit stress relieving cracks formed during cooling after the diffusion heat treatment. The behaviour of these coatings as well as that of uncoated P92 under thermal cycling conditions has been studied both under steam and under air at 650°C. The tested specimens were characterized by metallography, FESEM and XRD. A comparison with isothermal steam oxidation has been established.

## 2. Experiments

### 2.1 Materials

Ferritic steel P92 (C: 0.1, Mn: 0.5, Si: 0.03, Cr: 8.8, Ni: 0.06, Mo: 0.4, W: 1.8, V: 0.20 w%, Fe: bal) was obtained from Nippon Steel Corporation. The commercial Al slurry was obtained from Indestructible Paints Ltd.

### 2.2 Coating deposition

The coatings were deposited by applying the Al slurry by brush or spray gun. The commercial Al slurry required a "curing heat treatment" at 350°C for 30 minutes under air. The diffusion heat treatments were performed on a tubular furnace under flowing Ar.

### 2.3 Microstructural characterisation

The coated specimens were characterized by optical and field emission electron microscopy (JEOL JSM-6400 equipped with an Oxford EDS microanalyzer) of metallographic polished cross sections before and after exposure.

## 2.4 Steam oxidation laboratory testing

**Isothermal Testing.** The schematics of the closed loop laboratory rig employed at INTA is shown elsewhere [3]. Prior to testing, air is displaced from the chamber by means of  $N_2$  which is kept flowing while heating up to  $650^\circ\text{C}$  (approximately at  $600^\circ\text{C/h}$ ). Once the test temperature is achieved, the  $N_2$  flow is cut and pure steam is introduced at a linear velocity of 8 cm/s. The steam temperature is measured and controlled by a thermocouple located inside the test chamber. To carry out weight measurements or to remove samples, they are furnace cooled to about  $300^\circ\text{C}$  under  $N_2$  and subsequently removed. The reheat cycle is also carried out under  $N_2$ . Samples were removed at different time intervals for metallographic analysis.

**Thermal cycling in air.** The test is carried out in a tubular furnace under laboratory air. Each cycle consists of heating in 5 min to  $650^\circ\text{C}$ , hold for 1 h followed by forced cooling in 5 minutes to  $100^\circ\text{C}$  (Fig. 2a). Samples are extracted a different intervals always at the end of a cycle to record the mass variation.

**Thermal cycling in steam.** The test is carried out under a 50% steam/Ar atmosphere in a tubular furnace. Each cycle consists of heating to  $650^\circ\text{C}$  at a rate of  $6^\circ\text{C/min}$ , hold for 5.5 h and cooling to  $100^\circ\text{C}$  at a rate of  $2^\circ\text{C/min}$  (Fig. 2b). Samples are extracted a different intervals always at the end of a cycle to record the mass variation.

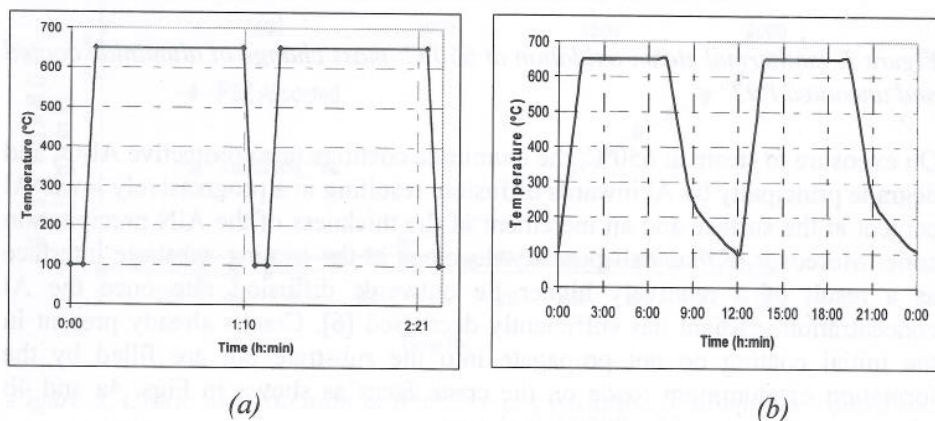


Figure 2. Thermal cycling: (a) in air, (b) in steam.

### 3. Results

#### 3.1 Isothermal steam oxidation testing

The diffusive slurry aluminide coating protects P92 from steam oxidation for a period of up to 45 000 h at 650°C (test still ongoing) as shown in Fig. 3, where the weight variation of both coated and uncoated P92 is plotted as a function of time. The initial weight loss of the coated specimen is due to spalling of residual undiffused slurry. P92 experiences a large increase in weight as shown in Fig. 3, due to formation of a thick oxide scale composed of an outer  $Fe_3O_4$  layer and inner Fe, Cr spinel.

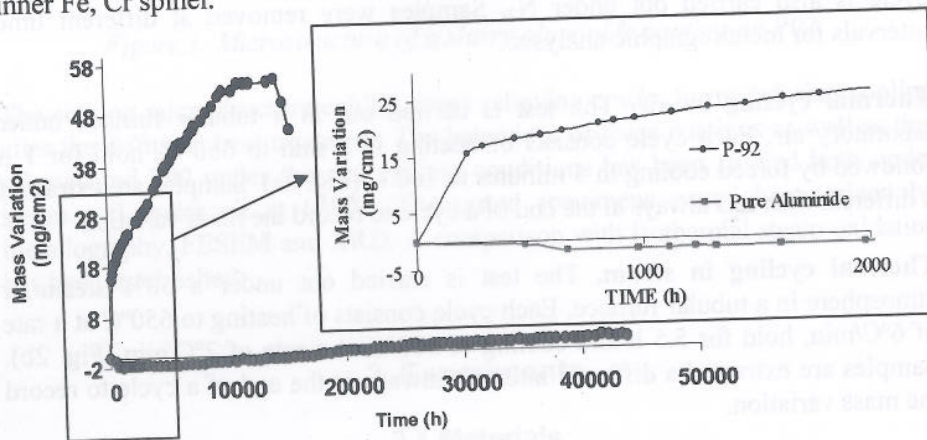


Figure 3. Isothermal steam oxidation at 650°C: mass change of aluminide coated and uncoated P92.

On exposure to steam at 650°C, the aluminide coatings form protective  $Al_2O_3$  and degrade principally by Al inwards diffusion, resulting in a progressively lower Al content at the surface and an increment of the thickness of the AlN precipitation zone. Moreover, Kirkendall porosity develops at the coating-substrate interface as a result of a relatively higher Fe outwards diffusion rate once the Al concentration gradient has sufficiently decreased [6]. Cracks already present in the initial coating do not propagate into the substrate but are filled by the formation of aluminum oxide on the crack faces as shown in Figs. 4a and 4b where coating exposed for 8000 h is shown.

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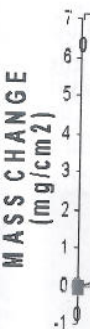


Figure 5.  
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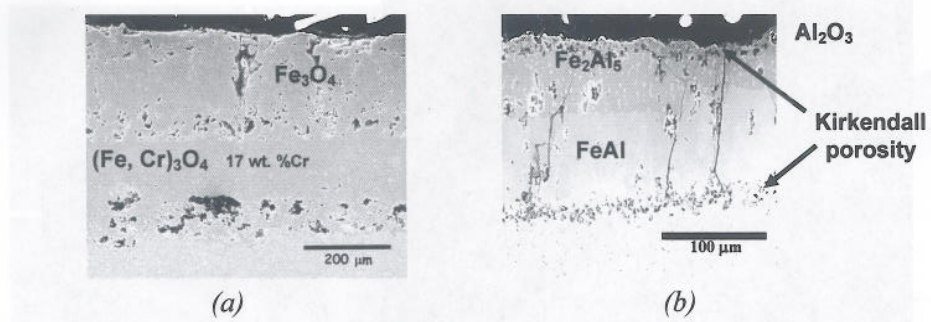


Figure 4. P92 exposed to steam at 650°C for 8000 h: (a) uncoated, (b) protected with a slurry aluminide coating.

### 3.2 Cyclic oxidation testing in air

The thermal cycling behavior of slurry aluminides has also been studied in air. Fig. 5 shows the weight variation of both coated and uncoated P92 as a function of time. The chosen cycle (see paragraph 2.4) is far too harsh for this application as a similar situation could only occur in a steam plant if boiler catastrophic failure would cause flooding of water into the turbine.

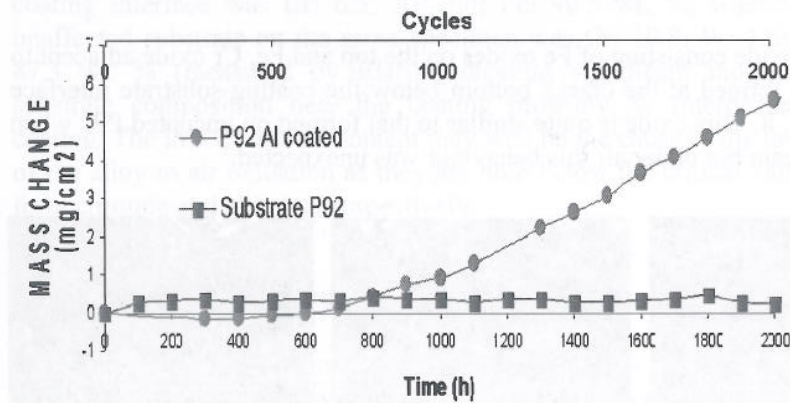


Figure 5. Cyclic air oxidation at 650°C: mass variation of aluminide coated and uncoated P92.

After 2000 h, uncoated P92 exposed to cyclic oxidation in air developed a very thin oxide layer rich in Cr and Mn as seen in Fig. 6. Other investigators have shown that uncoated P92 is quite resistant to oxidation at ambient air at 650°C, in agreement with the present results [7–10].

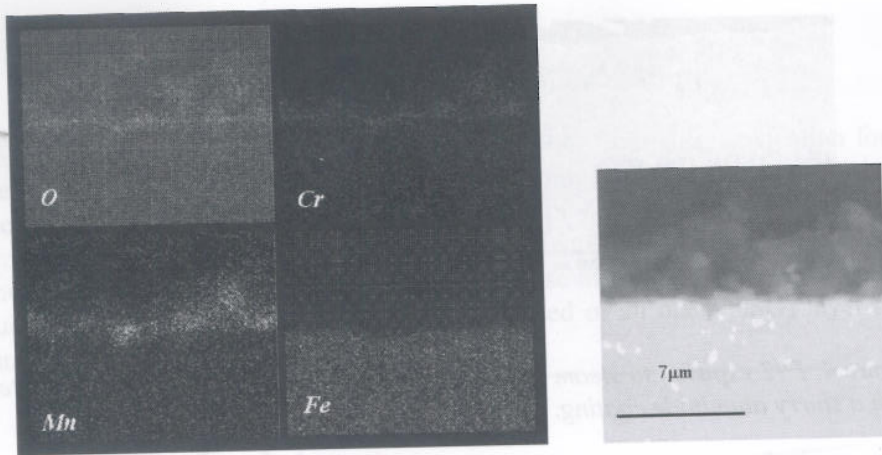


Figure 6. Uncoated P92 exposed to cyclic oxidation in air.

P92 aluminide coated samples showed no evidence of degradation or crack propagation after 100 cycles (Fig. 7). However, after 1000 cycles the cracks widened and propagated deflecting at the coating-substrate interface and the underlying substrate had started to oxidize. The cracks therefore have not healed by filling themselves with protective oxide because it grows very slowly under air at 650°C and/or because it spalls frequently, due to the thermal stresses originated by the fast heating and cooling rates.

A dual layer oxide consisting of Fe oxides on the top and Fe, Cr oxide adjacent to the substrate, formed at the cracks bottom below the coating-substrate interface as seen in Fig. 8. This oxide is quite similar to that formed on uncoated P92 when exposed to steam but under air this behaviour was unexpected.

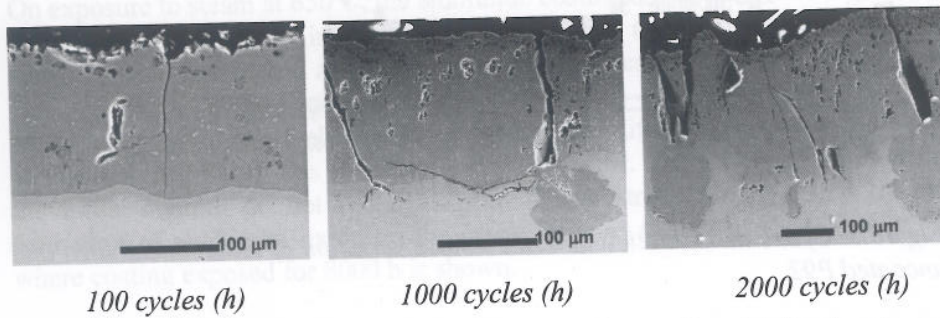


Figure 7. Slurry aluminide coated P92 exposed to cyclic oxidation in air.

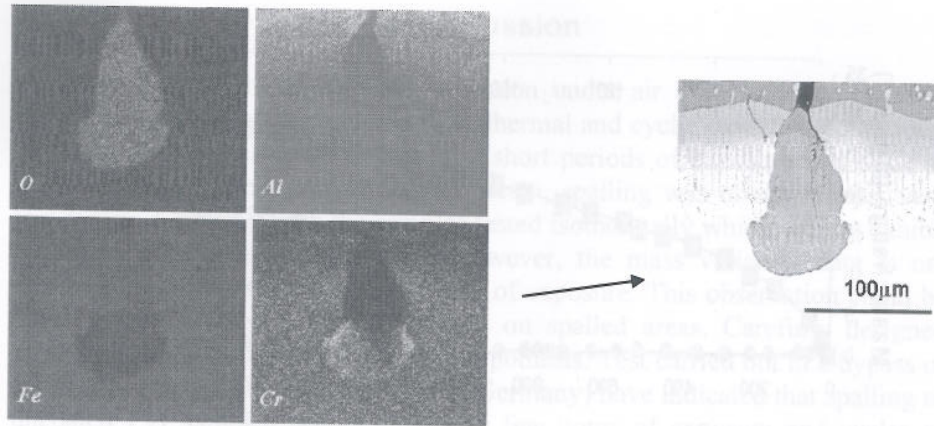


Figure 8. FESEM-EDS concentration mapping of the oxide developed at the coating-substrate interface after 1000 thermal cycles in air at 650°C.

As uncoated P92 experienced very low weight variation after the same exposure than the coated specimens. These observations may be explained as a result of significant modification of the substrate composition near the coating by interdiffusion with the coating, reducing the alloy's resistance to air oxidation. The levels of both Cr and Al are below the critical value required to form chromia and alumina respectively. The composition of the substrate near the coating interface was Cr: 6.5; Al: 3.0; Fe: 90.5 wt. %, whereas that of the unaffected substrate on the same specimen was Cr: 10.8; W: 1.6; Mo: 0.3, Fe: 87.3 wt. % (measured by EDS) indicating significant modification of the substrate composition near the coating probably by interdiffusion with the coating. The low Cr and Al content may well be the cause of the lower resistance of the alloy to air oxidation as they are both below the critical value required to form chromia and alumina, respectively.

### 3.3 Cyclic oxidation testing in steam

The thermal cycling behaviour of slurry aluminides has also been studied in steam. A smoother cycle was chosen in order to better simulate the heating and cooling stages in steam turbines. Fig. 9 shows the mass variation of both coated and uncoated P92 as a function of time and the number of cycles.

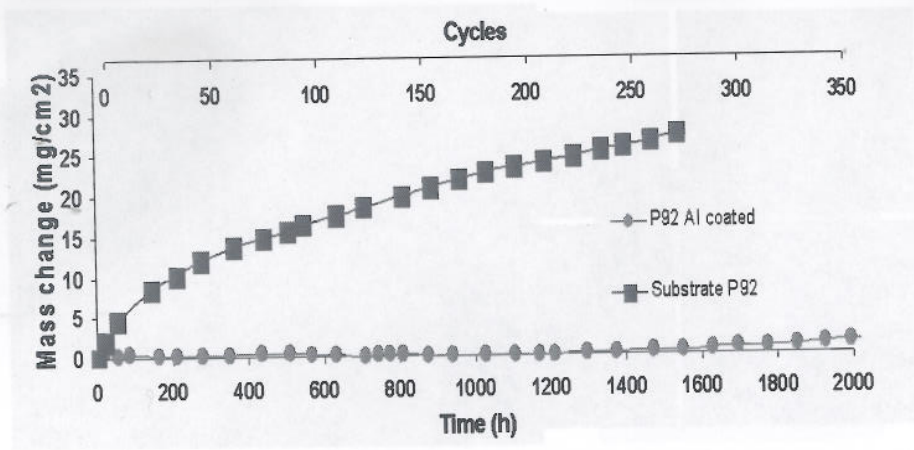


Figure 9. Cyclic steam oxidation at 650°C: mass change of aluminide coated and uncoated P92.

The uncoated specimens started to spall after first few cycles as shown in Fig. 10.

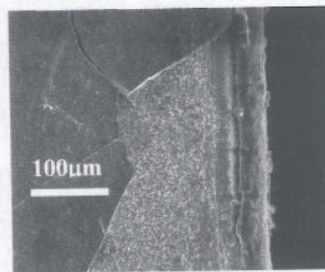
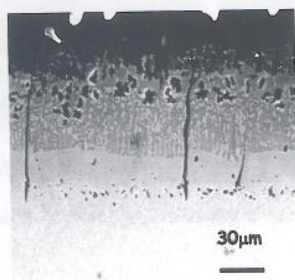
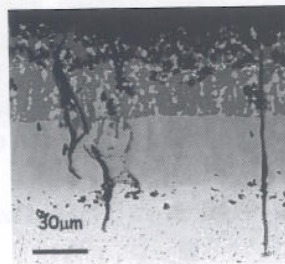


Figure 10. Uncoated P92 after 10 cycles of steam oxidation at 650°C.

Surprisingly, even at the chosen smoother cycles, the cracks originally present in the coating propagated into the substrate but after 2000 h of exposure (360 cycles) no evidence of substrate oxidation could be observed (Fig. 11).



100 cycles (550 h)



360 cycles (2000 h)

Figure 11. Slurry aluminide coated P92 exposed to cyclic steam oxidation at 650°C.

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#### 4. Discussion

Uncoated P92 exhibits very little oxidation under air even under very harsh cycles, however, in steam under both isothermal and cyclic oxidation conditions, P92 forms very thick oxide scales after short periods of exposure at 650°C, as expected. Under cycling conditions in steam, spalling was observed after very few cycles in contrast with the samples tested isothermally which did not exhibit spallation until after 10 000 h [6]. However, the mass variation data is not significantly different for the first 2000 h of exposure. This observation could be explained by a very fast oxide growth on spalled areas. Carefully designed experiments are required to verify this hypothesis. Test carried out in a bypass of an Alstom steam turbine [3] (Westfalen-Germany) have indicated that spalling of uncoated P91 samples occurs after very few hours of exposure and cycles as shown in Fig. 12. Despite having a lower oxidation resistance than P92 [8], extensive spallation has already occur after only 3300 h of exposure.



Figure 12. Uncoated P91 samples.

The aluminide coatings are very resistant to steam under isothermal conditions and cracks originally present do not propagate and heal by producing a protective  $\text{Al}_2\text{O}_3$  scale. However, under air, substrate attack could be observed at the cracks bottom, indicating that air could reach the Cr impoverished substrate causing its oxidation. It therefore appears that under air the protective  $\text{Al}_2\text{O}_3$  scale does not grow fast enough to "seal" the cracks or spalls frequently due to thermal expansion mismatch during cycling. In contrast, in the coated samples exposed to steam cyclic oxidation there was no evidence of substrate attack although the cracks widened and propagated. Therefore, it appears that steam contributes to a faster growth of the protective  $\text{Al}_2\text{O}_3$  scale and/or that due to the lower heating and cooling rates, spalling is not significant. Aluminide coated samples tested in the Westfalen by-pass mentioned earlier did not exhibit crack propagation into the substrate after 3300 h and several cycles [3].

The expected life-time of a steam turbine is 300 000 h during which, around 3000 cycles are expected. Unless catastrophic failure occurs, these cycles are

very smooth with heating rates of around 2°C/min and cooling rates of 0.1°C/min. Results of the present experiments seem to indicate that the chosen cycles (for both air and steam thermal cycling experiments) are still too harsh and do not seem to adequately simulate the real operating conditions for coatings. Pint and collaborators found out that extending the constant temperature period of the cycle had a strong effect in reducing crack formation in aluminide coatings deposited by high temperature CVD [11]. They employed very fast cooling and heating rates but a hold time of 10 hours, almost twice that of the present experiments. On the other hand, it is clear that the on-set of spallation of uncoated substrates is accelerated by thermal cycling and in this case the results approach does obtained under real conditions.

### 5. Conclusions

P92 is quite resistant to air at 650°C and develops a protective Mn and Cr rich spinel. Under steam, a non-protective dual oxide is developed with a top Fe<sub>3</sub>O<sub>4</sub> layer and an inner layer of (Fe, Cr)<sub>3</sub>O<sub>4</sub>. Under cyclic oxidation conditions in steam, scale spallation begins after the first few cycles whereas under isothermal conditions spallation begins after 10 000 h.

Slurry aluminide diffusion coatings are very resistant to steam at 650°C. Under isothermal conditions coating degradation mostly occurs by interdiffusion with the substrate as the Al concentration becomes depleted near the protective αAl<sub>2</sub>O<sub>3</sub> scale. However when the coatings are thermally cycled (with either steep or smooth ramps), stress relieving cracks initially present in the coating widen and propagate. In air, substrate oxidation takes place through the cracks that do not appear to form protective Al<sub>2</sub>O<sub>3</sub> over their surface fast enough, for the cracks to heal and prevent air from reaching the unprotected and Cr impoverished substrate. In steam it appears that the growth of the protective scale is faster and/or the spallation slower and the resulting healing effect blocks steam from entering the crack. However, the cracks propagated into the substrate which could have very negative effects in the mechanical properties of the substrate.

Further investigations are required to determine the cycle that best simulates the operating conditions of a steam turbine for laboratory testing, as when slurry aluminide coated and uncoated specimens were tested in a steam by-pass of a power plant (Westfalen-Germany), coating crack propagation into the substrate was not observed after at least 6500 h.

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- [2] Qu Te
- [3] Ag Po
- [4] Ag 52
- [5] Ag Ma
- [6] Ag 200
- [7] Vo Ma
- [8] Enr (19)
- [9] Thi VG
- [10] Wri
- [11] Pint Mat

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