The corrosion and mechanical behaviours of aluminide, FeCrAlY and CoCrAlY coatings in aggressive environments

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Abstract

The mechanical and chemical behaviours of aluminide coatings applied by pack cementation, FeCrAlY coatings applied by plasma spraying and CoCrAlY coatings applied by electrodeposition were studied. The coatings were pretreated for 0.5 h in argon at 1373 K to improve the adhesion and structural homogeneity via diffusion of the elements into the substrate to some extent. In particular, the influence of the temperature on their protective behaviours was studied. Corrosion studies have been carried out between 823 and 1123 K in oxidizing-sulphidizing environments.

In aggressive environments and under stress-free conditions the aluminide coatings showed the best results, probably owing to the presence of a protective oxide scale. Because of the tendency for crack formation, any applied stress will lead to cracking of the layer and the onset of severe corrosion attack. The FeCrAlY coatings showed the best protection.

1. Introduction

Advanced coal conversion processes such as atmospheric fluidized bed combustion and coal gasification are attractive energy production techniques for the near future. One advantage of these processes is the reduction of SO_2 and NO_x emissions to acceptable levels, which is of great importance because of increasing environmental problems.

In the combustor the coal is burnt at high temperatures, which limits the use of materials for high temperature applications: corrosion, erosion, erosion-corrosion and mechanical stress may occur as a result of the operating conditions.

Metallic components to be used in these systems are thus subjected to severe conditions. Although the present generation of high temperature alloys show generally sufficient mechanical properties, their corrosion resistance in these applications is a significant limitation. Owing to the low oxygen and high sulphur activities of the environments, the formation of a protective oxide layer may be difficult and rapid sulphidation can

be expected. Even at temperatures as low as 823 K, most construction metals and alloys cannot be used in practice, where useful lifetimes of at least one or more years are usually required.

This means that for applications at or above this temperature, where considerable sulphur partial pressures are encountered, metallic or ceramic protective layers have to be used for obtaining an acceptable resistance.

In general, two types of coating processes can be identified: one type changes the composition of the surface of an alloy by diffusion, the other is based on the deposition of a metallic or ceramic overlay. A review discussing the present state of the art of coating technology is given by Saunders and Nichols [1].

Metallic coatings are applied by diffusion-coating processes such as pack cementation (chromizing and aluminizing), slurry cementation and metallizing and by overlay-coating processes. Overlay-coating processes involve the deposition of an alloy of the MCrAlY series. Techniques suitable for applying these overlay coatings are physical vapour deposition and thermal spraying.

In this paper a study is reported on the mechanical and corrosion properties of heat-

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treated aluminide, FeCrAlY and CoCrAlY coatings in aggressive environments. The aluminide coatings were applied on Incoloy 800H by pack cementation, the FeCrAlY coatings on HP40Nb by plasma spraying and the CoCrAlY coatings on Incoloy 800H by electrodeposition. The corrosion resistance to aggressive gas mixtures was determined by thermogravimetric measurements. The deformation and cracking behaviours of aluminide coatings in oxidizing and of FeCrAlY coatings in oxidizing and oxidizing–sulphidizing environments have been studied by constant-extension-rate (CER) tests. This method permits an evaluation of the susceptibility of metals and protective coatings to stress corrosion cracking (SCC) and is a rapid laboratory method to evaluate SCC susceptibility in aggressive environments [2, 3]. The present paper also concentrates on the influence of test parameters such as temperature, time of exposure and partial pressures of oxygen and sulphur on the different coating types.

2. Experimental details

2.1. Materials

The chemical compositions of the investigated materials are given in Table 1.

2.2. Preparation of the specimens

The substrate materials were annealed for 1 h at 1350 K, water quenched, heated for 1 h at 1230 K and water quenched again. The heat-treated bars were machined to cylindrical samples (20 mm length by 5 mm diameter) which were used to study the sulphidation resistance. The CER test specimens had an effective gauge length of 30 mm with a corresponding reduced diameter of 2.5 mm.

The final surface finish of the substrate prior to coating was grinding with 180-grit carborundum paper. Additionally, the specimens were ultrasonically cleaned with hexane and ethanol prior to coating and/or oxidation–sulphidation.

2.3. Application of the coatings
2.3.1. FeCrAlY coatings by plasma spraying

The FeCrAlY coatings were applied at Eindhoven on HP40Nb by atmospheric pressure $(Ar-H_2)$ plasma spraying. Figure 1 shows an illustration of plasma spraying. The maximum substrate temperature of HP40Nb was kept below 423 K. Below the FeCrAlY coating an intermediate layer of Ni-5Al (Metco 450) with a thickness of about 50 μm was applied. The top coating of FeCrAlY, type Amdry 970, consisted of Fe-24Cr-8Al-0.2Y. Its thickness was about 200 μm. The final heat treatment was done in an argon atmosphere for 0.5 h at 1373 K in order to improve the adhesion and structural homogeneity via diffusion of the elements into the substrate to some extent.

2.3.2. Aluminide coatings by pack cementation

The Incoloy 800H specimens were coated at Interturbines with an aluminide coating of 40–50 μm in a pack cementation process. The structure of the coating consists of an inner and an outer zone. The outer coating zone was identified as a $(Ni,Fe)Al$ β phase. After production a thin Al_2O_3 scale was present. Figure 2 shows a schematic view of the pack cementation equipment. The following temperature programme was adopted for the cementation process: heating from room temperature to 1173 K in 6 h; this temperature was maintained for 6 h, followed by cooling in 18 h. The final heat treatment in argon was again performed at Eindhoven [4]. This whole run of heating to 1373 K followed by equilibration and cooling to room temperature took 1.5 h.
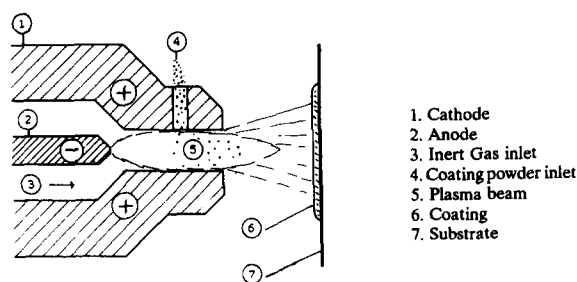

1. Cathode
2. Anode
3. Inert Gas inlet
4. Coating powder inlet
5. Plasma beam
6. Coating
7. Substrate

Fig. 1. Schematic illustration of plasma spraying.

1. Sealing
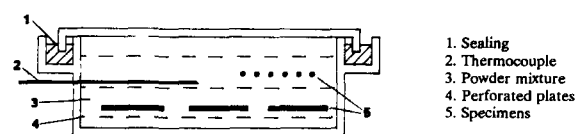2. Thermocouple
3. Powder mixture
4. Perforated plates
5. Specimens

Fig. 2. Schematic view of pack cementation equipment.

TABLE 1

Chemical compositions of alloys used (weight per cent)

Alloy	Cr	Ni	C	Mn	Si	Ti	Nb	Fe
Incoloy 800H	19.9	31.7	0.08	0.7	0.5	0.4	—	Balance
HP40Nb	23.7	33.3	0.4	1.3	1.3	—	0.9	Balance

2.3.3. CoCrAlY coatings by electrodeposition

The CoCrAlY coatings on Incoloy 800H have been produced by electrodeposition from a galvanic bath. The process parameters were: pH 5.0, temperature 328 K, cathodic current density 3 A dm^{-3}, time 5 h. The composition of the coating was Co-20Cr-4.5Al-0.5Y. The resulting layers had a thickness of about 200 μm. This coating was treated for 3 h at 573 K, 48 h at 1273 K and 0.5 h at 1373 K.

2.4. Sulphidation tests

The composition of the oxidizing–sulphidizing gas atmosphere resembled the gaseous environments of coal conversion processes, although the composition of the gas consisted of a small number of components. Thermogravimetric measurements were performed by means of a stainless steel spring balance. The test pieces were suspended in the balance, which was flushed with argon for 16 h (180 ml min^{-1}). The argon was saturated with water at 288 K. Next a flow of 50 ml min^{-1} of 5% H_2S in H_2 was introduced. After flushing the system for 2 h, the temperature was increased to the desired value. The whole system was flushed for another 5 h and then closed.

Under these conditions Al_2O_3, Cr_2O_3, Ni_3S, Co_8S_9 and FeS are thermodynamically stable at 823 and 973 K.

The CER experimental conditions were the same as for the thermogravimetric analysis (TGA) circumstances. The thermodynamic equilibrium partial pressures of O_2 and sulphur at different temperatures and the final gas composition are given in Table 2.

2.5. Constant-extension-rate tests

The CER equipment consisted of a fixed frame, a carriage, a drive mechanism, a load cell and a recorder. The constant-strain-rate values were 1×10^{-6} and 1×10^{-7} s^{-1}. The strain-to-cracking value was determined by scanning

electron microscopy (SEM) after applying the strain.

2.6. Analysis

The specimens were examined after exposure using conventional optical microscopy and SEM together with an energy-dispersive X-ray system (KEVEX).

3. Results

3.1. Constant-extension-rate tests

3.1.1. Pack-cemented aluminide coatings

In Table 3 the CER results are shown for SCC of the pack-cemented aluminide coatings. The pack-cemented aluminide coatings have been tested by the CER method in air at temperatures of 923 and 973 K. As can be seen from Fig. 3, the unloaded (as-received) specimens already showed cracks, possibly initiating SCC during the CER experiments. These cracks only reach the inner coating zone. The specimens extended in air showed an increase in the amount of cracks with reducing strain rate and/or increasing temperature (see Fig. 4). Cross-sections of the extended specimens showed cracks only reaching the underlying diffusion layer (see Fig. 5).

3.1.2. Plasma-sprayed FeCrAlY coatings

Figure 6 indicates that the as-received coatings are characterized by a very rough surface struc-

TABLE 3

Stress corrosion cracking of aluminide coatings in air

Temperature (K)	Strain rate (s^{-1})	Strain (%)	Number of cracks per specimen
—	—	—	3
923	1×10^{-6}	1.0	40
923	1×10^{-7}	1.0	99
973	1×10^{-7}	0.5	65
973	1×10^{-7}	0.4	24

TABLE 2

Equilibrium partial pressures of O_2 and sulphur as a function of temperature (1 vol.% H_2S, 1% H_2O, 79% Ar, 19% H_2)

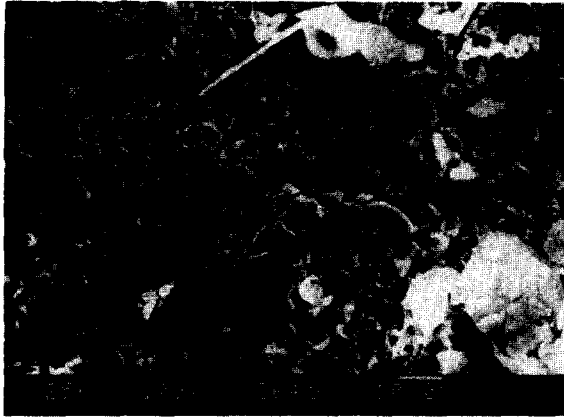|	Temperature (K)				
	823	873	923	973	1123
P_{O_2} (atm)	9.3×10^{-29}	5.8×10^{-27}	2.4×10^{-25}	6.6×10^{-24}	1.2×10^{-20}
P_{S_2} (atm)	1.2×10^{-9}	5.2×10^{-9}	2.0×10^{-8}	6.7×10^{-8}	1.5×10^{-6}

Fig. 3. Cracks in "as-received" aluminide-coated material.

Fig. 4. Cracks in aluminide coating after 1% extension; strain rate $1 \times 10^{-7}\,\mathrm{s}^{-1}$, $T = 923$ K.

Fig. 5. Cross-section of aluminide-coated Incoloy 800H extended in air at 923 K. Cracks ended at the coating–diffusion layer interface.

Fig. 6. HP40Nb (as received) coated with FeCrAlY. Note the cracks in the surface area.

Fig. 7. Cracking of plasma-sprayed FeCrAlY coating after CER test; strain rate $1 \times 10^{-7}\,\mathrm{s}^{-1}$, $T = 973$ K, elongation 1.4%.

ture. SEM examinations revealed that as-received material contained cracks but, owing to the thickness of the coating (200 μm), these do not reach the underlying substrate, though it is possible that these cracks initiate SCC during the CER tests.

The CER experiments performed in air at 973 K showed that no cracking occurred for extensions up to 1.5% (CER 1×10^{-6} and 1×10^{-7} s^{-1}). Extensions of more than 1.8% showed cracking of the coating. When air was replaced by the H_2–H_2S–H_2O–Ar mixture, SCC occurred at extensions above 1%. Surface examination also showed that the cracks were more pronounced above 1% extension. This is probably due to the penetration of sulphur into the crack, whereafter SCC will play a role. Figure 7 shows the spalled plasma-sprayed FeCrAlY coating after the CER test.

From the results it is clear that above the critical strain for cracking an enormous increase in
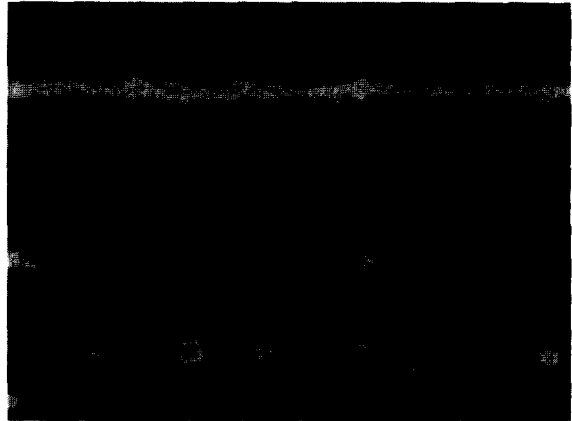
the total number of cracks per unit surface area has been detected. Moreover, these cracks are sometimes so long that they reach the substrate, indicating complete coating failure (see Fig. 7).

The attack by sulphidation after fracture of the FeCrAlY coating (gas mixture $H_2S-H_2O-H_2-Ar$, $\varepsilon = 1 \times 10^{-7}$ s^{-1}, $T = 973$ K, elongation 1.4%) is shown in Fig. 8. In this figure also the distribution of iron, chromium, nickel and sulphur is presented by X-ray maps. In this sulphidizing gas atmosphere no protective oxide scale has been formed and it is of course well known [5-7] that sulphides do not have sufficient protective properties. During the CER tests sulphidation occurred not only at the outer part of the coating but also in the created surface area inside the crack and even beneath the coating just along the interface between the outer FeCrAlY coating and the inner intermediate layer of Ni-5Al (thickness about 50 μm) (see also Fig. 8(e)). The sulphide phases formed consist mainly of iron sulphides. Owing to

the penetration of sulphur, resulting in internal corrosion involving debonding and spalling, non-coherence between the FeCrAlY coating and the intermediate layer can be caused, which may eventually lead to breakaway of the outer layer.

3.2. Sulphidation tests without applying strain

3.2.1. Pack-cemented aluminide coatings

Specimens tested in oxidizing–sulphidizing environments at 823 K for times as long as 1500 h did not show any attack. Specimens tested at 1123 K showed severe attack after 100 h. Exposure times up to 300 h at this temperature in oxidizing–sulphidizing environments resulted in breakaway of the coating (see Fig. 9).

3.2.2. Plasma-sprayed FeCrAlY coatings

In Fig. 10 the thermogravimetric results are shown for HP40Nb coated with FeCrAlY. The specimens suspended in the oxidizing–sulphidizing environment described showed corrosion attack at 823, 873 and 923 K.

Exposure of the FeCrAlY coupons to oxidizing–sulphidizing environments at 823 K revealed a relatively rapid initial weight increase followed by a very slow attack of the coating. Owing to the low mass loss (millimetres per year) of the specimen and since the coating thickness is about 250 μm, protection for at least 1 or 2 years is ensured. The sulphidation rate at 873 K is much higher, which means that the protective behaviour of the coating is less pronounced. However, this coating–substrate combination fails at temperatures of 923 K and above. The coating showed breakaway at this temperature.

Fig. 8. (a) SEM image (cross-section) of spalled FeCrAlY coating after CER test in sulphidizing gas atmosphere and X-ray maps showing distributions of (b) iron, (c) chromium, (d) nickel and (e) sulphur; strain rate 1×10^{-7} s^{-1}, $T = 973$ K, elongation 1.4%.

Fig. 9. Breakaway of aluminide coating after 300 h at 1123 K in sulphidizing environment.
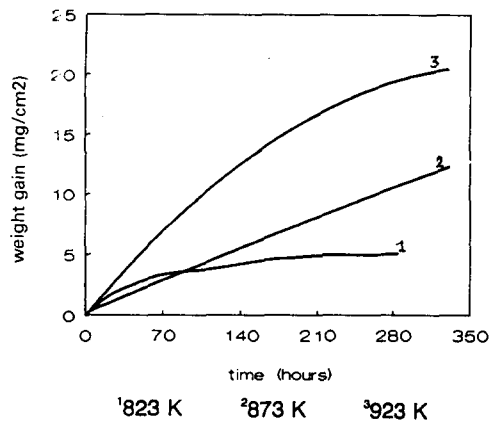
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Fig. 10. TGA results for FeCrAlY-coated specimens in sulphidizing atmosphere at different temperatures.

Figure 11 presents an SEM image (cross-section) and X-ray maps showing the distribution of the elements nickel, iron, chromium, aluminium and sulphur for an FeCrAlY-coated specimen exposed to the oxidizing–sulphidizing atmosphere for 320 h at 873 K. Examination of the sulphidized specimen after exposure to the aggressive environment indicated that a sulphide scale had formed with a thickness of more than 100 μm. Energy-dispersive X-ray (EDX) investigations revealed that this sulphide scale had formed only at the outer part of the coating, consisting of an outer iron-rich zone (mole ratio Fe:S ≈ 1) and a chromium-rich inner zone (mole ratio Cr:S ≈ 1) adhering to the coating. In this zone iron depletion has also been observed, probably due to the outward diffusion of iron. Between the sulphide scale and the coating, separation has been detected.

No internal corrosion attack has been identified along the FeCrAlY coating–intermediate Ni–Al layer interface. This is in contrast to the specimens investigated after CER tests (see Fig. 8).

3.2.3. Electrodeposited CoCrAlY coatings

Figure 12 shows the thermogravimetric results for CoCrAlY on Incoloy 800H. From this figure it can be deduced that the weight gain in an oxidizing–sulphidizing environment is higher than for FeCrAlY coatings. In an $H_2O-H_2-H_2S-Ar$ gas mixture after 150 h a weight gain of at least 20 mg cm^{-2} is observed at 823 K.

Figure 13 presents an SEM image (cross-section) and X-ray maps of the elemental distribution of sulphur, chromium, iron, cobalt and nickel for a CoCrAlY-coated specimen exposed to the
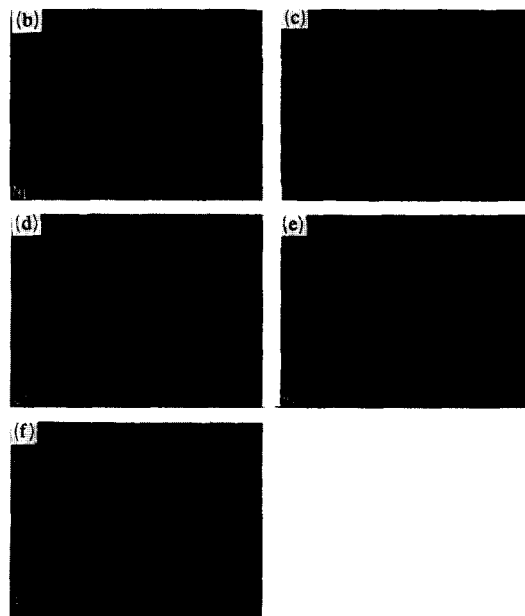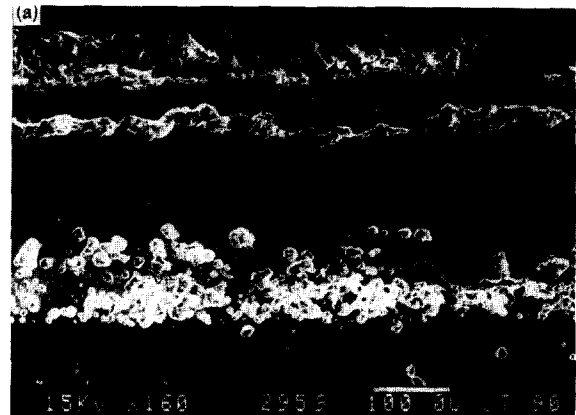

Fig. 11. (a) SEM image (cross-section) of FeCrAlY-coated HP40Nb specimen after sulphidation for 320 h at 873 K and X-ray maps showing distributions of (b) nickel, (c) iron, (d) chromium, (e) aluminium and (f) sulphur.
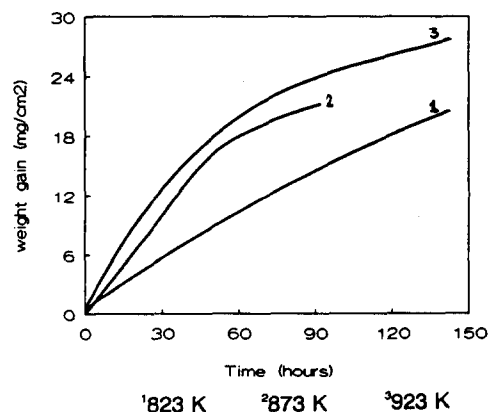

Fig. 12. TGA results for CoCrAlY-coated specimens in sulphidizing atmosphere at different temperatures.
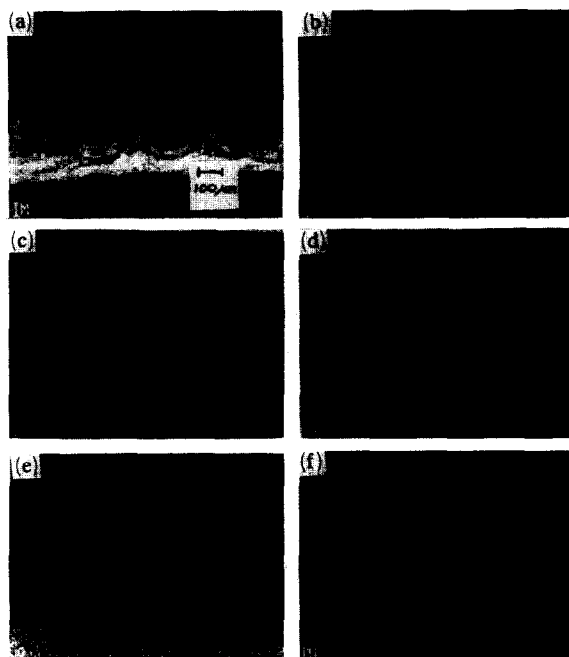
Fig. 13. (a) SEM image (cross-section) of CoCrAlY-coated Incoloy 800H after exposure in aggressive environment for 100 h at 923 K and X-ray maps showing distributions of (b) sulphur, (c) chromium, (d) iron, (e) cobalt and (f) nickel.

oxidizing–sulphidizing gas mixture for 100 h at 923 K. From this figure it is clearly seen that during the exposure in the aggressive atmosphere only external sulphidation has occurred, resulting in a scale with three separate zones. The element mapping of the cross-section of the CoCr-AlY-coated Incoloy 800H specimen revealed the formation of an outer layer containing only cobalt and sulphur (mole ratio $Co:S \approx 2$). The inner zone at the scale–coating interface also contained a high percentage of cobalt and sulphur but also small amounts of iron, nickel and chromium. The intermediate layer is characterized by a relatively low sulphur content. Cobalt was the major component, followed by chromium, iron and nickel. From Fig. 13 it is also clear that spalling has occurred within the formed sulphide scale, probably due to poor adherence.

4. Discussion

It is clear (see Fig. 3) that even the unloaded aluminide-coated specimens (as received) show cracks, extending from the surface to the inner coating zone. After the final heat treatment performed in an argon atmosphere the specimens were cooled. Probably during this cooling, cracking at the surface occurred owing to the mismatch of the thermal expansion coefficients between the outer (identified as (Ni,Fe)Al β phase with low ductility) and inner coating zones and the brittle alumina. A longer heat treatment may reduce the sharp aluminium gradient and the crack propensity at the surface. It is well known [8, 9, 12] that the presence of cracks in the outer coating zone has a detrimental effect on the protective behaviour of the specimens in sulphidizing environments. Our results show that good protection can be achieved for the unloaded specimens at 823 K at a sulphur partial pressure of 1.2×10^{-9} atm. Increasing the temperature to 1123 K leads to severe attack after 100 h. After 300 h breakaway of the coating was detected. This means that owing to the higher temperature and the higher partial pressure of sulphur, the coating and the surface area inside the cracks are more susceptible to sulphidation. At 1123 K no protection of the coating can be achieved. Thus the higher the temperature and the partial pressure of sulphur, the smaller is the incubation time [9] before sulphidation will start. Majid and Lambertin [9] reported that immunity only occurs after pre-oxidation. The corrosive compounds can very easily reach the underlying substrate by penetration through pre-existing cracks, voids and defects [8, 9], resulting in breakaway of the coating due to internal sulphidation. This interfacial segregation of sulphur resulting in spalling of the coating was also found and discussed by other investigators [8, 9, 12]. This interfacial corrosion also occurs if the coating is used under conditions leading to deformation by mechanical or thermal stresses. More cracks will form, resulting in an increased penetration of the sulphur.

The results show that aluminide coatings are good protective barriers in sulphidizing environments at temperatures up to 823 K. Severe attack of the coated specimen will occur at 1123 K, probably due to the inward diffusion of sulphur through cracks, eventually leading to breakaway of the coating after 300 h. However, a number of cracks have already been detected on the as-received material. The amount of cracks increases abundantly if any stress is applied, which may mean that the protective behaviour of the coating is diminished rather rapidly.

FeCrAlY-coated specimens do not give sufficient protection against aggressive atmospheres, as seen in Fig. 10. The incubation time of these

test specimens during the sulphidation experiments is almost zero, indicating fast corrosion attack as soon as the specimens are exposed to the aggressive gas mixture at high temperatures. This means that no protective scale has formed during the initial stage of the experiments. From the calculated partial pressures of sulphur and O_2 it is found that Cr_2O_3, Al_2O_3, FeS and NiS are the most stable phases. During the initial stage of the sulphidation experiments, competition between oxidation and sulphidation might take place. Owing to the higher sulphidation rate, the formed oxides will be overgrown by the sulphides. The reason why sulphides exhibit a much higher reaction rate is that the crystal lattice is far from ideal owing to their highly defective structure. As seen in Fig. 11(a), the scale consists of a small oxygen-rich layer adjacent to the coating substrate and an outer sulphide scale consisting of a duplex layer. The outer sulphide layer is iron rich, probably mainly consisting of FeS, and the inner layer is probably CrS rich. No internal sulphidation along the coating–alloy interface is detected. As described before, no protection has been obtained because of the failure of the formation of a protective oxide layer. It is suggested that at the initial stage of sulphidation the scale is iron and chromium rich, but after some time the sulphides will become more iron rich, probably owing to the different diffusion coefficients of iron and chromium [10, 11]. Eventually an external scale of FeS and an internal chromium-rich sulphide scale are formed. The outer scale is assumed to grow only by diffusion of the metal ions and without inward diffusion of sulphur.

The results from the CER tests with FeCrAlY-coated specimens revealed that the critical strain for cracking in aggressive, i.e. sulphidizing, environments is lower than for oxidizing environments. Therefore it is reasonable to assume that the SCC susceptibility is enhanced in the presence of sulphur. When fracture of the coating occurs, the substrate is exposed to a sulphidizing gas atmosphere, preventing the formation of a protective oxide scale. Significant damage to the specimen then occurs. Severe cracking and spalling of the coating have been observed just above the intermediate Ni–Al layer. This means that, owing to the elongation and thus spalling of the coating, sulphidation will take place under the coating. Vertical cracking in plasma-sprayed coatings is not typical and would not be acceptable in a commercial situation. An extensive reduction of

the protective capability of the applied coating is observed. In spite of the fact that beneath the coating chromium oxide is thermodynamically the most stable phase, chromium sulphide has also been detected by SEM and EDX examinations.

However, the thermodynamical predictions cannot readily be used alone because of the fact that chromium sulphide was also detected. It is believed that chromium sulphide is formed owing to the fact that the O_2 and sulphur partial pressures at the metal–scale interface differ from the bulk and associated kinetic effects.

Only a few studies have been reported on the oxidation [13, 14] and sulphidation [15] properties of CoCrAlY coatings. The process parameters of these experiments differ so much from ours that a direct comparison is not possible. CoCrAlY coatings showed almost the same results as the FeCrAlY coatings: only the corrosion attack is somewhat more severe. A typical cross-section of a CoCrAlY-coated specimen (100 h, 923 K) including X-ray maps is shown in Fig. 13. The sulphide scale is duplex. The outer scale consists mainly of cobalt and sulphur, the inner scale of cobalt and sulphur with small amounts of iron, nickel and chromium. From thermodynamic data it is known that Co_8S_9, FeS, NiS and Cr_2O_3 are the most stable compounds. Compared to the FeCrAlY coatings tested under the same circumstances, in this case no oxygen-rich layer has been detected. It has been suggested that the formation of a duplex scale took place by the rapid outward diffusion of cobalt through the sulphide scale containing high defect concentrations [7].

5. Conclusions

Aluminide coatings applied by pack cementation and pretreated for 0.5 h in argon at 1373 K are in principle able to provide a good protection against sulphidation at temperatures up to 823 K, probably owing to the presence of a protective Al_2O_3 scale and the absence of sulphide-forming elements. Increasing the temperature or superficially applied stress leads to cracks, resulting in severe corrosion attack and even breakaway of the coating.

Thick FeCrAlY coatings pretreated for 0.5 h in argon at 1373 K are useful at temperatures up to 823 K. At higher temperatures the sulphidation attack increases rapidly and at 923 K the coating

shows severe breakaway. The CER tests revealed that strains up to 1% at 973 K did not induce stress corrosion cracking.

A comparison of CoCrAlY coatings pre-treated at 1373 K with the FeCrAlY coatings revealed that the CoCrAlY coatings showed a higher susceptibility for sulphidation, probably owing to the large amount of chemical and physical defects in the coating.

Acknowledgments

References

1 S. R. J. Saunders and J. R. Nichols, *Mater. Sci. Technol.*, 5 (1989) 780.
2 M. Schutze, *Oxid. Met.*, 24 (1985) 199.
3 V. A. C. Haanappel, T. Fransen, B. Geerdink and P. J. Gellings, *Oxid. Met.*, 30 (1988) 201.
4 J. M. Houben, *Technical University of Eindhoven Ann. Rep. NL-16, COST 501/1 Project*, 1983-1984.
5 S. Mrowec, *Corros. Sci.*, 6 (1966) 47.
6 S. Mrowec, *Werkstoffe Korros.*, 31 (1980) 371.
7 P. Kofstad, *High Temperature Corrosion*, Elsevier, London, 1988.
8 F. H. Stott, F. M. F. Chong and C. A. Stirling, *Proc. Ninth Int. Congr. on Metallic Corrosion*, Vol. 2, National Research Council of Canada, Toronto, 1984, p. 1.
9 Z. E. Majid and M. Lambertin, *Oxid. Met.*, 27 (1987) 333.
10 T. Narita and K. Nishida, *Oxid. Met.*, 6 (1973) 154.
11 A. Rahmel, M. Schorr, A. Velasco-Tellez and A. Pelton, *Oxid. Met.*, 27 (1987) 199.
12 Y. Ikeda, M. Tosa and K. Yoshihara, *Mater. Sci. Eng. A*, 120 (1989) 179.
13 J. A. Sprague, V. Provenzano and F. A. Smidt Jr., *Thin Solid Films*, 95 (1982) 57.
14 C. A. Liu, M. J. Humphries and R. C. Krutenat, *Thin Solid Films*, 107 (1983) 269.
15 R. H. Barkalow and G. W. Goward, *Proc. High Temperature Corrosion, San Diego, CA, March 2-6, 1981*, National Association of Corrosion Engineers, Houston, TX, 1983, p. 502.