

Corrosion Science, Vol. 35, Nos 5-8, pp. 1235-1242, 1993
 Printed in Great Britain.

0010-938X/93 \$6.00 + 0.00
 © 1993 Pergamon Press Ltd

CHROMIUM DIFFUSION COATINGS FOR THE PROTECTION OF LOW-ALLOY STEEL IN A SULPHIDIZING ATMOSPHERE

R. G. I. LEFERINK and W. M. M. HUIJBREGTS

Department of Chemical Technology and Material Research, N. V. Kema, P.O. Box 9035, 6800 ET Arnhem, The Netherlands

Abstract

The chromium diffusion process was investigated for carbon-, low-alloy and austenitic type steels. The quality of the diffusion coatings on low-alloy steels was tested using four criteria that reflect in-service reliability of heat exchangers in coal gasifiers: thermal stability, ductility, resistance to down-time corrosion and weldability. These tests have shown that good quality diffusion coatings can be made on 10 CrMo 910. The corrosion resistance of the chromium diffusion coatings can be greatly enhanced by the presence of small amounts of carbide formers like vanadium and niobium.

INTRODUCTION

In new combustion techniques such as low-NO_x combustion and coal gasification, the firing atmosphere will be relatively reducing¹ (pO₂ approx. 10⁻²³ Pa and pS₂ approx. 10⁻⁴ Pa). In these circumstances, a protective oxide layer may not be formed and the evaporator tubes have to be protected against the aggressive environment by other means. Chromium (Cr) diffusion coatings can be used to prevent corrosion in such a reducing atmosphere.²

The Cr diffusion coatings are applied with the pack cementation process (chromizing). In this process the objects to be coated are placed in a fine powder mixture (i.e. the pack). This powder consists of an inert filler (Al₂O₃), an activator (usually NH₄Cl) and chromium. During heating of the pack, the activator is cracked into hydrogen chloride (HCl), N₂ and H₂.³ The HCl formed reacts with chromium according to:



Besides, a small amount of CrCl₃ is formed as well. During the pack cementation the partial pressures of the chromium chlorides (CrCl_x) are sufficiently high to transfer them via the gas phase to the steel surface. There the CrCl_x dissociates into metallic Cr and HCl, according to:



The metallic Cr deposited at the steel surface diffuses into the metal⁴ and the HCl is subsequently transferred back to the Cr powder in the pack where it reacts to form CrCl_x (reaction 1). This concludes the cycle of Cl in the gas phase.

At approximately 1100 °C the strong interaction between the chromium and the free carbon (C) present in the steel results in the formation of chromium carbides (CrC_x) at the metal surface. These carbides act as a diffusion barrier and limit the growth of a metallic Cr-rich top layer necessary for corrosion protection. Under the coating a decarburized zone will develop. With the use of strong carbide formers the formation of the chromium carbides can be prevented. These carbide formers should either be present in the steel (e.g. small quantities of niobium) or can be added to the pack (e.g. vanadium). The large number of parameters in both the pack cementation conditions and the steel composition makes a prediction of the coating quality virtually impossible.

In this work the coating process was investigated for diffusion coatings on carbon, low-alloy and austenitic type steels. The best diffusion coatings were tested using four criteria that reflect in-service reliability:

- A. Thermal stability: evaluation of the long term stability of the coating/steel system at operating temperatures (approx. 400 °C).

- B. Ductility: the temperature fluctuations that occur during start-up and shut-down procedures will result in the formation of high tensile stresses and deformation in the material. Low strain-rate deformation in a sulfidizing atmosphere can lead to a specific form of stress-corrosion in evaporator tubes known as Alligator Skin Cracking (ASC) as noticed by Cialone.⁵ The coating should also be resistant against high strain-rate deformation.
- C. Resistance against down-time corrosion (DTC): during a shut-down period the relative humidity can exceed the dew point causing hygroscopic salts to create a very corrosive liquid on the metal surface.
- D. Weldability: the weldability of coated steel and the coatability of a weld must be evaluated.

EXPERIMENTAL METHOD

All pack cementation runs were carried out at 1120°C for 24 h in a pack containing 75 wt% Al₂O₃, 21 wt% Cr-powder, and 4 wt% NH₄C1. In "CrV" packs 5 wt% of Cr was replaced by V. The atmosphere was kept reducing by purging with 5 vol% H₂ in Ar. The following steels were chromized: carbon steel (St 35), low-alloy steels (15 Mo3, 13 CrMo4.4, 10 CrMo9.10, 10CrMoNb9.10, composition shown in Table 1) and austenitic type steel (AISI 310). The best diffusion coatings were tested using the following procedures:

- A. Thermal stability: samples were sealed in evacuated quartz ampules to prevent oxidation. The ampules were heated at 450°C for up to 8000 hours. Accelerated aging was performed at 550 and 700°C.
- B. Ductility:
 - (1) the resistance to ASC was determined by low strain-rate deformation using the Constant Extension Rate Technique (CERT) at 400°C and a strainrate of 14×10^{-10} s⁻¹. The sulphidizing atmosphere contained 19 vol% H₂, 1 vol% H₂S, 1.5 vol% H₂O and 78.5 vol% Ar.
 - (2) high speed deformation was induced by denting the coating with a hammer;
- C. Resistance against DTC: a screening test⁶ was used in which the coatings were covered with a 2 mm thick layer of a mixture consisting of 90 wt% coal ash, 3.7 wt% NaCl and 6.3 wt% FeCl₂. The samples were then exposed to water-saturated air for 24 h at 70°C.
- D. Weldability: uncoated 10CrMo9.10 with a low-alloy weld was chromized and a Cr coating on 10CrMo9.10 was welded with the high-alloy material AISI 310.

TABLE 1. THE COMPOSITIONS OF THE ALLOYS
Average composition (wt%)

Alloy	C	Si	Cr	Mn	Mo	Ni	Nb	Fe
15 Mo 3	0.17	0.23	0.0	0.71	0.29			Bal.
13 CrMo 4 4	0.13	0.2	1.25	0.7	0.5			Bal.
10 CrMo 9 10	0.10	0.26	2.25	0.42	1.04			Bal.
10 CrMoNb 9 10	0.10	0.35	2.44	0.49	1.05	0.45	1.10	Bal.

All samples were cross-sectioned and analysed for structural changes with a light microscope and an SEM equipped with EDS and WDS.

EXPERIMENTAL RESULTS AND DISCUSSION

Coatability

After examining the coatings formed, their structures were divided into different categories (Table 2). The coatings on carbon and austenitic steel easily crack during deformation due to the brittle phases they contain.

The coating types on these steels were considered unsuitable and were consequently not subjected to further examination.

In low-alloy steels (without Nb) the C is mainly bonded by molybdenum (Mo). Although Mo is a less strong carbide former than Nb and V, the favourable effect of an increasing Mo/C ratio is clearly demonstrated in Fig. 1. However, in low-alloy steels, Cr carbides also deposit on grain boundaries of

the coating. The required Cr is extracted from the coating itself which causes the Cr-coatings to become sensitized. By using a CrV pack, the grain boundary in a coating on 10CrMo9.10 was free of carbides. The CrV coatings on 15Mo3 and 13CrMo4.4, however, still contained grain boundary carbides.

TABLE 2. THE COATABILITY OF THE STEELS

Steel-coating combination	Coating characteristics
Carbon steel: St 35-Cr or CrV	30-50 μm brittle Cr(V)-carbide layer* no metallic Cr(v) coating
Austenitic steel: AISI 310-Cr or CrV	80-100 μm thick metallic Cr(V) coating coating contains brittle sigma phase all CrV coatings are cracked
Low-alloy steel: 15Mo3 -Cr or CrV 13CrMo4.4 -Cr or CrV 10 CrMo9.10 -Cr	5-20 μm Cr(V)-carbide toplayer 100-250 μm metallic Cr(V) coating grain boundaries with carbides running from top to bottom of coating
Low steel alloy: 10CrMo9.10 - CrV	5 μm CrV-carbide toplayer 275 μm metallic CrV coating no carbides on grain boundaries
Low-alloy steel with Nb: 10CrMoNb9.10 - Cr or CrV	no carbide toplayer 250-300 μm metallic Cr(V) coating no carbide on grain boundaries

* Cr(V): Cr in case of a Cr coating or CrV in case of a CrV coating

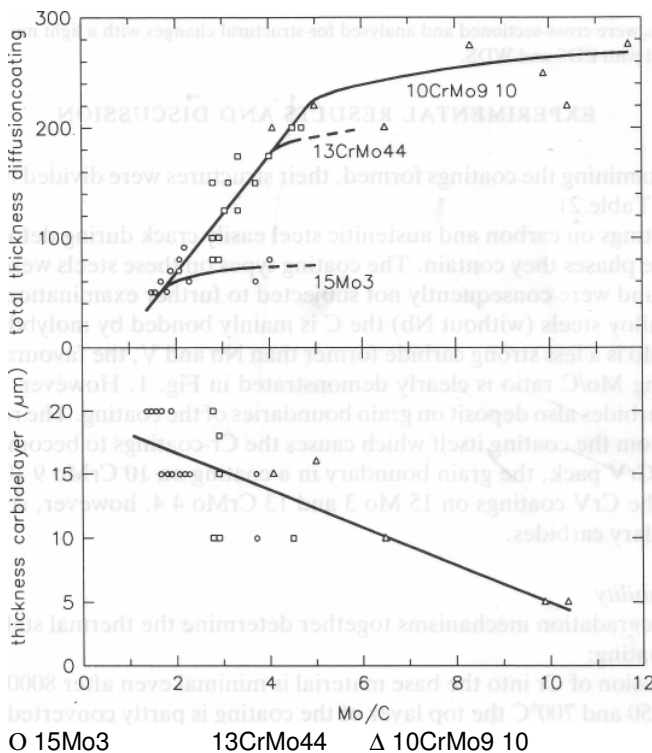


Fig 1. The influence of the Mo/C-ratio in different heats of low-alloy steels on the total coating thickness and the thickness of the carbide toplayer.

Thermal stability

Three degradation mechanisms together determine the thermal stability of a Cr diffusion coating:

- (1) Diffusion of Cr into the base material is minimal even after 8000 h at 700 °C.
- (2) At 550 and 700 °C the top layer of the coating is partly converted into a hard, brittle sigma phase that is formed above 475 °C.⁷ Under evaporator operating conditions, the temperature remains below 475 °C so that no sigma phase is formed.
- (3) The most important degradation mechanism is the precipitation of carbides in the coating. In this respect, the coatings on 15Mo3 behave entirely differently from those on 10CrMo9.10.

- 15 Mo 3.
An increase of the number of Cr (and V) carbide precipitates and a substantial decrease in the Cr(V) amount in the metallic part of the coating were detected after a few months at 450 °C (Fig. 2). This is caused by the abundant supply of carbon from the 15Mo3 underneath the coating. The Cr(V) needed for the formation of carbide precipitates was extracted from the coating, thus resulting in a reduction of chromium content to unacceptably low levels. Because the growth of the precipitates does not stop with increasing time, the Cr and CrV diffusion coatings on 15Mo3 are not thermally stable. Therefore they are unsuitable for high-temperature applications.
- 10CrMo9.10.
The structures of the Cr and the CrV coatings on 10 CrMo 9 10 do not change, not even during high-temperature heating at 700 °C.

Ductility

- (1) Low strain-rate deformation: the stress-strain curves of the CERT experiments (Fig. 3) show that the coated materials achieve a lower tensile strength. This is caused by effects such as full annealing, grain growth and local decarburization, which occur during pack cementation. Uncoated test specimen are strongly sulphurized and show deep cracks at the surface, which indicates that the material is sensitive to ASC (Fig. 4a). The coated specimen did not corrode and only micro-cracks appear near the fracture zone. Cross-sections (Fig. 4b) reveal that these microcracks are shallow and stop in the area where the Cr content is still high, namely approx. 35%.
- (2) High strain-rate deformation: cross-sections reveal that the metallic part of the coatings undergoes plastic deformation without any cracks occurring. The coating thickness in the dented parts reduces only slightly (Fig. 5).

Resistance against down-time corrosion

Cr and CrV coatings on 15Mo3 and Cr coatings on 10CrMo9.10 show serious attack along the sensitized grain boundaries. When the DTC mixture reaches the base material it is severely attacked, causing cavities to form underneath the coating (Fig. 6). The CrV coatings on 10CrMo9.10 suffer only superficial attack by the DTC mixture and the Cr and CrV coatings on Nb-stabilized 10CrMo9.10 are not attacked at all. In the latter three coatings, no carbides are formed on the grain boundaries. Hence, the stabilizing action of Nb and V is demonstrated in the DTC test.

Weldability

Cross-sections through the coated weld and the welded coating show that in either situation it is possible to deliver high-quality welds (Fig. 7). In the heat affected zone, no carbides or cracks were formed.

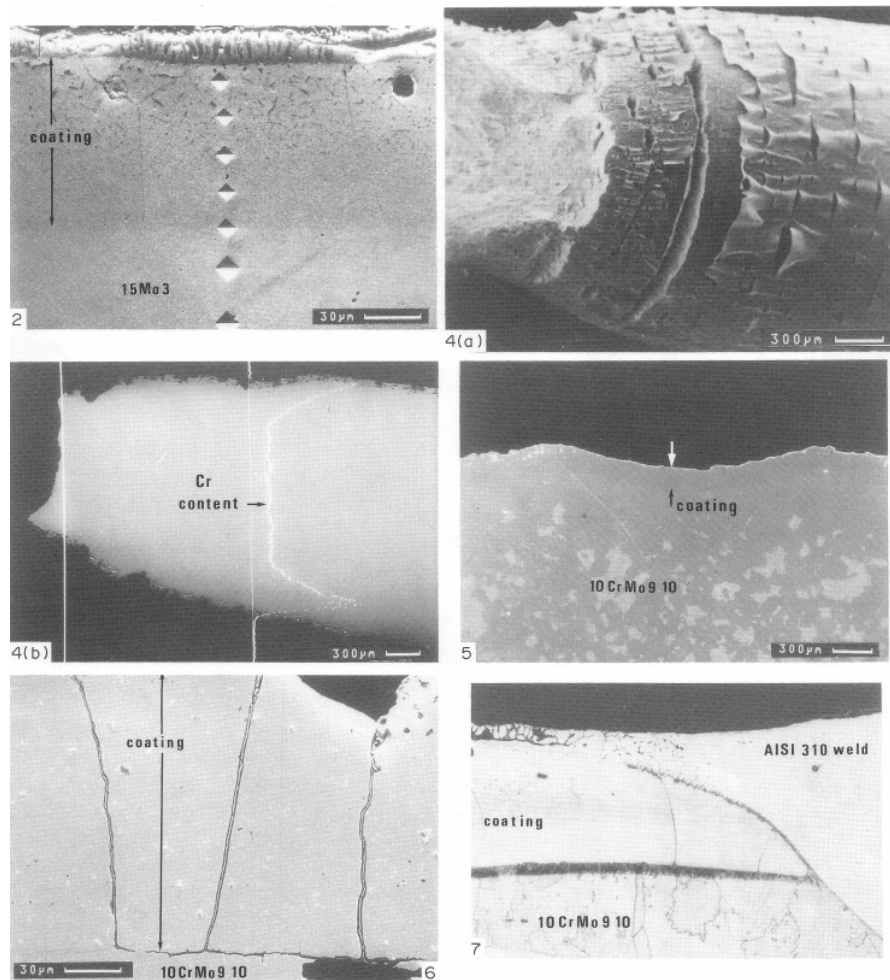


Fig. 2. During the thermal stability test carbide precipitates are formed throughout the entire coating on 15Mo3.

Fig. 4(a). Uncoated 10CrMo9.10 will develop deep cracks (ASC) during CERT experiments in sulphidizing gas. (b) In Cr diffusion coated 10CrMo9.10 under the same conditions cracking is limited to the near-surface area where the Cr-content is high.

Fig. 5. The cross-section of a dent struck with a hammer in a diffusion coating on 10CrMo9.10.

Fig. 6. In a DTC test Cr diffusion coatings on 10CrMo9.10 are attacked along the sensitized grain boundaries.

Fig. 7. The cross-section of a Cr diffusion coating welded with AISI 310 shows that no cracking occurs.

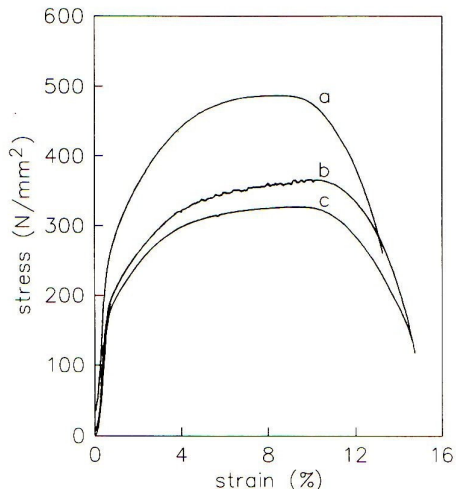


Fig. 3. Stress-strain diagrams taken in H₂S -containing gas of 10CrMo9.10 without a coating (a) and with a Cr (b) or CrV (c) diffusion coatings.

CONCLUSIONS

The main conclusions to be drawn from this study on Cr and CrV diffusion coatings for evaporators that operate in a sulphidizing atmosphere are that:

- (1) Carbon steel, austenitic steel (AISI 310) and low-alloy steel where carbon is only partly stabilized (15Mo3, 13CrMo4.4) are unsuited as base material for conventional Cr and CrV diffusion coatings.
- (2) Cr diffusion coatings on low alloy steel 10CrMo9.10 are sensitized and therefore they are sensitive to corrosion.
- (3) Cr and CrV diffusion coatings on 10CrMoNb9.10 and to a somewhat lesser extent CrV coatings on 10CrMo9.10 (without Nb) seem to be an excellent choice. These diffusion coatings will therefore be included in large scale experiments to be carried out in test installations.

Acknowledgements-This study was undertaken at the request of the Dutch Electricity Production Companies.

REFERENCES

- (1) P. L. Daniel, S. F. Chou, L. W. Rodgers and P. S. Ayres, Fireside Corrosion in Low-NO_x Combustion Systems, Report GS-6339, EPRI, Palo Alto (1989).
- (2) W. T. Bakker, C. E. Lewis and R. A. Perkins, Corrosion 86, paper no. 100, NACE, Houston (1986).
- (3) M. G. Hocking, V. Vasantasree and P. S. Sisdky, Metallic and Ceramic Coatings, p. 189 Longman Scientific & Technical, Harlow (1989).
- (4) S. K. Gupta, S. R. Adolph, L. C. Tandon and L. L. Siegle, Metall. Trans. A, 13A, 495 (1982).
- (5) H. J. Cialaone, I. G. Wright, R. A. Wood and C. M. Jackson, Circumferential cracking of supercritical boiler water-wall tubes, Report CS-4669, EPRI, Palo Alto (1986).
- (6) R. A. Perkins, D. L. Marsch, A. M. Sarosiek and W. Bakker, Downtime Corrosion in Syngas Coolers of Entrained Slagging Gasifiers, Report AP-5966, EPRI, Palo Alto (1988).
- (7) M. Hansen and K. Anderko, Constitution of Binary Alloys, 2nd Edn, p. 527. McGraw-Hill, New York (1958).