

Chromium Diffusion Coatings on Low-Alloyed Steels for Corrosion Protection Under Sulphidizing Conditions

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Introduction

To be able to comply with the strict environmental requirements for emission of substances such as sulphur and nitrogen oxides, electricity producers are looking for cleaner combustion methods. New combustion methods include: coal gasification and low-NO_x techniques. These methods share the characteristic that their fuel gases are more or less reducing [1] (pO₂ approximately 10⁻²⁸, pS₂ approximately 10⁻⁹).

Under these conditions, boiler steels that are traditionally used for evaporator walls cannot build a protective oxide layer. Consequently, the corrosion rate is high. Therefore, under such circumstances it is necessary to use materials of higher corrosion resistance. To be considered are materials with a Cr content of at least 20 %. In principle, two kinds of material appear to qualify:

- *co-extruded pipe material;*
 - a high-alloyed steel which has been coextruded on a low-alloyed steel
- *chromium diffusion coating on a low-alloyed steel.*

An important asset of the diffusion coating is the fact that it is less expensive than co-extruded materials. A drawback is the fact that there is as yet too little information available on mechanical properties, structural stability and corrosion resistance.

KEMA has conducted research into the properties and composition of Cr diffusion coatings in general. By means of strictly monitored laboratory simulations of operating conditions as applicable for the evaporator walls, it is possible to gain a proper insight into the behaviour of the diffusion coatings.

As the preparation method and the composition of the steels greatly influence the structure of the Cr diffusion coatings, and hence their corrosion resistance, a great deal of attention has been paid to these aspects.

Application of Diffusion Coatings

Chemical Background

The pack cementation process for the application of high-Cr coatings is over fifty years old [2, 3]. The process was used mostly to apply thin, wear-resistant chromium-carbide layers to steels with over 0.35 % C. For evaporators, steels are used with lower C contents (i.e. 0.10 - 0.15 % C). The diffusion coatings applied to these steels consist of a Cr carbide top layer with the corrosion-resistant metallic high-Cr layer underneath.

The pack cementation process is carried out on an industrial scale by placing the entire objects to be coated in a fine powder mixture (i.e. the pack). This powder consists of an inert filler (Al₂O₃), an activator (usually NH₄Cl) and chromium. Heating in a hydrogen atmosphere at about 1100 °C for 24 hours will create a coating of some 150 - 300 μm thickness on a suitable kind of steel.

Figure 1a gives a diagram of the assembly, while Figure 1b shows a cross-section through a coating.

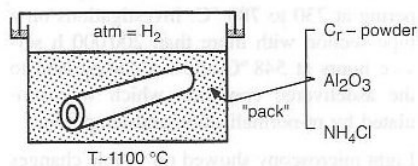
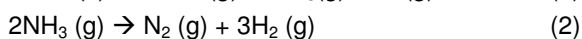
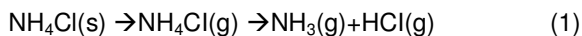


Fig. 1a. Pack cementation assembly for the preparation of Cr diffusion coatings.

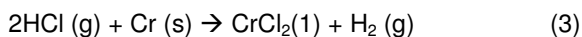


Fig. 1b. Cross-section (light microscope) through a Cr diffusion coating on 10CrMo910 (etched with Nital). The coating is located at the top, with a decarburized zone underneath and at the bottom the normal steel structure of ferrite with perlite islands in it.

During heating of the pack, the activator is cracked according to reaction [4].



The hydrochloric acid formed reacts with chromium, mainly along the lines of the following reaction (see Figure 2 a):



Besides, a small amount of CrCl₃ is formed as well. The partial pressures of the chromium chlorides (CrCl_x) are sufficiently high to transfer a part via the gas phase to the steel surface at the application temperature (approximately 1100 °C). At the steel surface the CrCl_x are converted in the reducing environment into metallic Cr and gaseous hydrochloric acid, according to the following reaction:



The gaseous hydrochloric acid is subsequently transferred to the Cr powder, where it reacts again and is converted into CrCl_x (reaction 3).

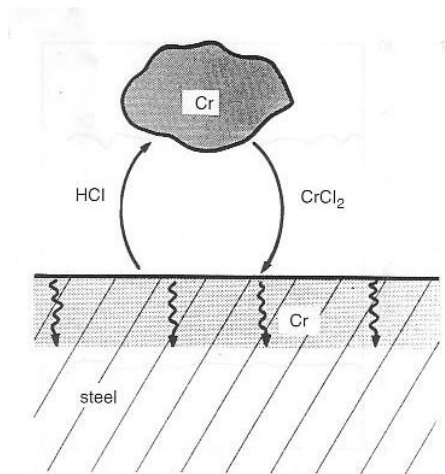


Fig. 2a. Schematic diagram of the pack cementation process for the preparation of Cr diffusion coatings.

This concludes the cycle of Cl in the gas phase. The metallic Cr deposited at the steel surface diffuses into the metal. In this way the high-Cr metallic diffusion layer builds up gradually. For industrial application of the pack cementation process it is a great asset that it can be easily scaled up.

Diffusion of Chromium

Figure 2 b shows the trend of Cr concentration over a diffusion coating on a low-alloyed steel. It is clear that the high Cr content from the surface of the diffusion coating is steadily falling. It is typical of Cr diffusion coatings on iron and low-alloyed steels that the coating ends rather abruptly at a (Cr percentage of about 12 weight %. The cause of the abrupt transition can be explained by means of the phase diagram of FeCr (Figure 3a) and the diffusion coefficient of Cr in Fe-Cr alloys (Figure 3b).

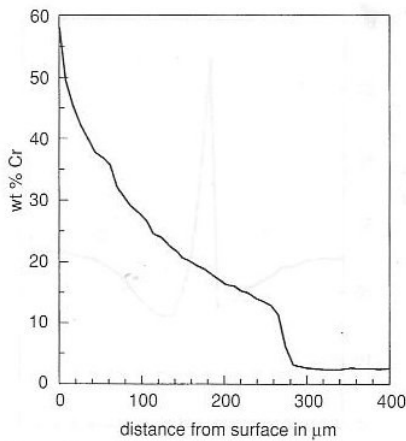


Fig. 2b. Concentration gradient of chromium in a diffusion coating on 10 CrMo 9 10 (EDS technique).

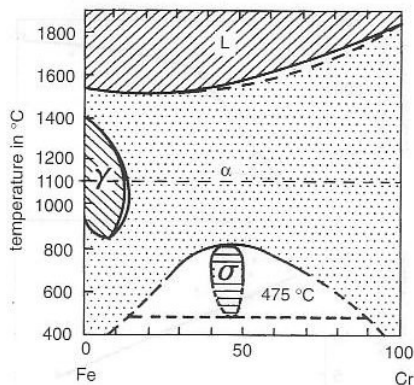


Fig 3a. Phase diagram of iron-chromium (according to [5]).

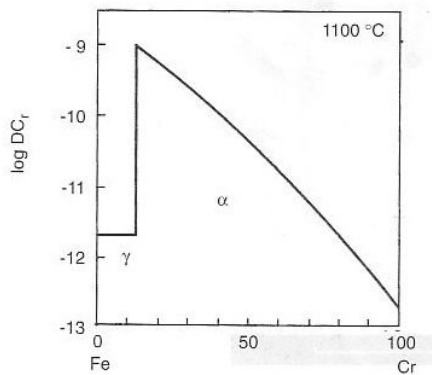


Fig. 3b. Diffusion coefficient of chromium in iron-chromium alloys (according to (6)).

The Fe-Cr phase diagram shows that at 1100 °C at the surface the high-Cr ferritic α phase is stable. Deeper into the coating the chromium percentage drops to 12%. The Fe-Cr phase diagram shows that from that point onwards the austenitic (γ) phase is stable. The diffusion coefficient of Cr in the ferrite phase (Figure 3b) is far higher than that in the austenite phase. This means in practice that only very little Cr diffusion takes place in austenite, which causes a rather abrupt fall in the Cr concentration profile at 12%.

Based on the phase transitions and diffusion coefficients it is possible to calculate the diffusion of Cr in Fe at various temperatures by means of a computer programme. As an example the formation of a Cr coating has been calculated in Figure 4.

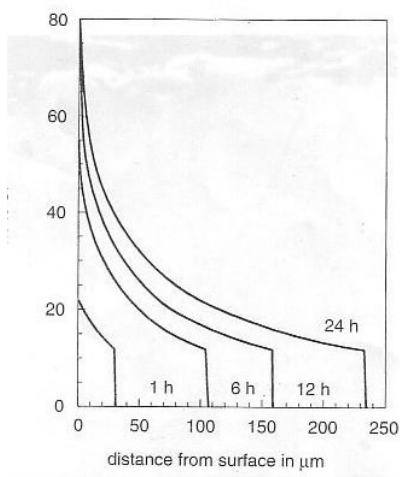


Fig. 4. Formation of a chromium diffusion coating on iron after varying time intervals at 1120 °C, as calculated by means of a simulation programme.

Influence of Steel Composition

It appears that especially carbon (C) in the steel has a great influence on the structure of the diffusion coating. At the high temperature of 1100 °C at which the coatings are applied, C is able to move relatively freely through the metal lattice. This enables it to diffuse from the steel towards the Cr coating. At the surface Cr carbides (CrC_x) are then formed. These carbides form a diffusion barrier through which less Cr can penetrate into the metal. The result is that the formation of a thick metallic Cr layer is seriously hampered so that a thinner metallic chromium coating develops. Underneath the coating a decarburized zone will be formed.

The complications that may result from the formation of a CrC_x diffusion barrier can be reduced by binding the carbon. Stabler FeMo-carbides make the more creep-resistant material 15Mo3 better suited to be provided with a Cr diffusion coating than a carbon steel (St 35). Figure 5 clearly demonstrates the favourable effect of an increasing Mo/C ratio: i.e. an increase in coating thickness.

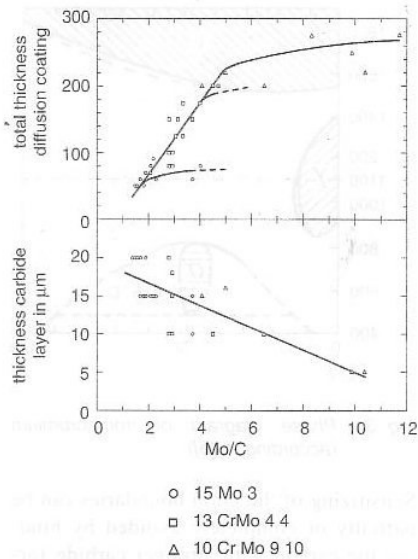


Fig. 5 As the Mo / C ratio in several batches of 15Mo3, 13 CrMo4.4 and 10CrMo9.10 increases carbon is bound progressively better as well. This reduces the thickness of the carbide diffusion barrier formed, so that a thicker coating can be applied. (All coatings are applied under identical circumstances).

In practice, however, it appears that when such a simple steel is selected, Cr carbides also deposit on grain boundaries in the Cr coating. The chromium required for this is extracted from the immediate environment, or in other words: from the coating itself. This causes the coatings to become sensitized. Figure 6 represents a line scan over a sensitized grain boundary in a Cr diffusion coating.

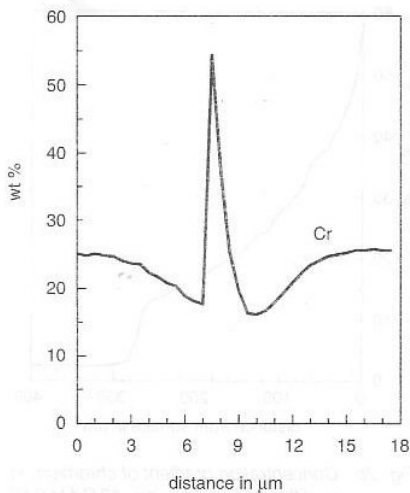


Fig. 6a. EDS linescan over a sensitized grain boundary in a Cr coating on 10 CrMo 910 shows a strong reduction in chromium percentage around the CrC_x on the grain boundary.

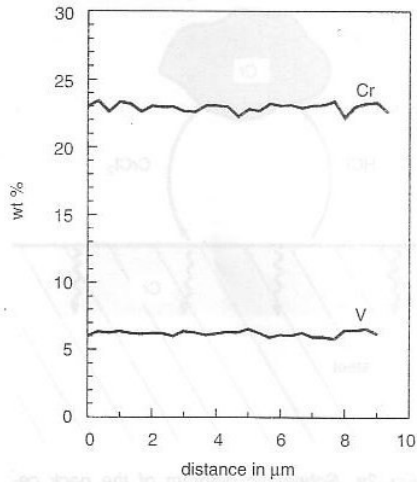


Fig. 6b. Linescan over a Cr/V coating on 10 CrMo 910. No carbides have been deposited at the grain boundaries, so that they are not sensitized.

Sensitizing of the grain boundaries can be partially or completely avoided by binding the carbon with stronger carbide formers such as vanadium (V) or niobium (Nb). In practice, V is applied together with Cr in a co-diffusion pack cementation process. This generally results in slightly thicker coatings with somewhat lower Cr contents. Figure 6b represents a line scan over a grain boundary in a Cr/V coating.

Niobium cannot be applied by pack cementation. However, there are certain special alloys with small quantities of Nb added (c.g. niobium-stabilized 10CrMo910).

During the pack cementation process the mass of the coated objects increases and the surface expands about 30-50 μm outward. As a result, part of the pack is incorporated into the top layer of the coating. Consequently, the upper 30-50 μm of the coating has a rather complicated structure. It contains carbides, Al_2O_3 from the pack, and usually pores are formed as well. Figure 7 gives a detailed representation of what the top layer of a Cr diffusion coating might look like in practice as a result of all these effects.

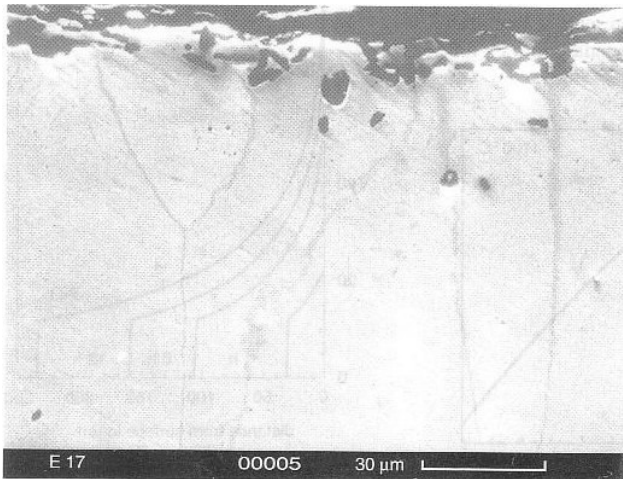


Fig. 7. A detailed photograph of a Cr coating on 15Mo3 shows the complicated structure of the layer at the surface.

Fig. 7b. Explanation of phases..

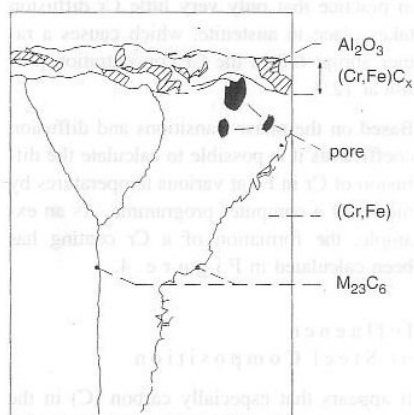


Fig. 7b. Explanation of phases..

Coatability of Steel

Owing to the large number of variables in process conditions and steel composition, it is extremely difficult to predict the coating quality. Therefore research of chromium diffusion coatings was started by establishing the coatability of a variety of steels. Table 1 gives the composition of the steels.

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Table 1. Composition of steels into which Cr and Cr/V diffusion coatings have been applied.

Steel	Average composition (weight%)							
	C	Si	Cr	Mn	Mo	Ni	Nb	Fe
St 35	0.32	0.34	0.07	0.53	0.01	—	—	bal.
15 Mo 3	0.17	0.23	0.0	0.71	0.29	—	—	bal.
13 CrMo 44	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 CrMo 9.10 Nb	0.10	0.35	2.44	0.49	1.05	0.45	1.10	bal.
AISI 310	0.08	1.8	24.3	0.7	—	19.1	—	bal.
AISI 310S	—	0.8	26.0	1.7	0.3	19.0	—	bal.

After examining the coatings formed, it appears that their structures can be divided into the following categories:

- mainly Cr(V) C_x : St 35
- Cr(V) C_x top layer on metallic Cr layer: 15 Mo 3, 13 CrMo 44, 10 CrMo 9.10
- metallic Cr(V) layer: 10 CrMo 9.10 (Nb)
- metallic Cr(V) layer with sigma phase: AISI 310, AISI 310S.

The coatings on the steels in category a) are brittle and will easily crack during plastic formation. Coatings from category d) are extremely sensitive to cracking due to hard, brittle sigma phase. (In fact the vanadium containing coatings from category d) were all cracked after the coating process). The coating types in categories a) and d) are considered unsuitable and were consequently not subjected to further examination.

Coating Behaviour Under Simulated Operating Conditions

The diffusion coatings were assessed for the following four criteria relevant to practical use under operating conditions:

- thermal stability
- mechanical deformation
- resistance to down-time corrosion
- weldability.

These four criteria were examined under specific simulated conditions. Table 2 summarizes the test results

Thermal Stability

Thermal stability is the resistance of a material to structural changes caused by diffusion processes and/or phase transitions in the coating. These effects are temperature-induced only. Samples are subjected to prolonged heating in vacuum, whereupon an examination for structural changes is conducted with a Scanning Electron Microscope (SEM). The samples, Cr and Cr/V diffusion coatings on 15 Mo 3 and 10 CrMo 9.10, were heated up to 450 °C during varying periods up to 8000 hours. Accelerated ageing is achieved by heating at 550 and 700 °C. Evidently, there are three degradation mechanisms together determining the thermal stability of a Cr diffusion coating:

Diffusion of the Cr into the Base Material

Diffusion of the coating into the base material has often been designated as a potentially dangerous degradation mechanism. In this process the chromium slowly leaks away into the steel, causing the chromium content, and hence the protective action, to reduce. At 450 °C this effect turns out to be insignificant. Even after 8000 hours at 700 °C only a small decrease in Cr content is found at the metal surface.

Formation of Sigma Phase (σ -phase)

At 550 and 700 °C the top layer of the coating is converted after some time into a hard, brittle sigma phase. The Fe-Cr phase diagram (Figure 4a) indicates that formation of the sigma phase takes place at temperatures over 475 °C only. At that point a phase separation occurs into a sigma phase with approximately 45 weight % Cr and a ferritic phase with 25-30 % Cr. Under evaporator operating condition the temperature remains below 465 °C, so that no sigma phase is formed. Figure 8 shows the sigma phase, formed in the top layer of a Cr coating on 10 CrMo 910.

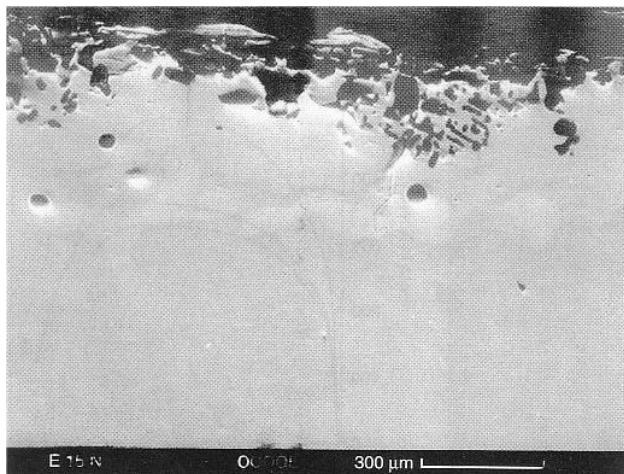


Fig. 8. During prolonged annealing at 550 and 700 °C a thin layer with sigma phase (light grey) is formed at the surface of Cr coatings on 10CrMo910. This effect does not occur under operating conditions (below 475 °C).

Precipitation of Carbides

The third and most important degradation mechanism appears to be the precipitation of carbides in the coating. The coatings on 15 Mo 3 turn out to show an entirely different behaviour from those on 10CrMo9 10.

15Mo3

With the Cr and Cr/V coatings on 15Mo3 an increase of the number of chromium carbide precipitates in the coating was already detected after a few months at 450 °C. Especially near the surface a great deal of precipitates are formed.

During prolonged heating C, which is insufficiently bound in the 15Mo3 underneath the coating, diffuses into the coating, where it forms mainly Cr(V)C_x. The Cr (and V) needed for this are extracted from the immediate surroundings. Owing to the abundant supply of C a large number of Cr(V) carbide precipitates is formed in 15Mo3, resulting in a reduction of chromium content to an unacceptably low level.

At all test temperatures it was found that carbide growth does not stop. This means that the Cr and Cr/V diffusion coatings on 15Mo3 are not thermally stable and are therefore unsuitable for high-temperature applications. Figure 9 shows the carbide precipitates formed during heating.

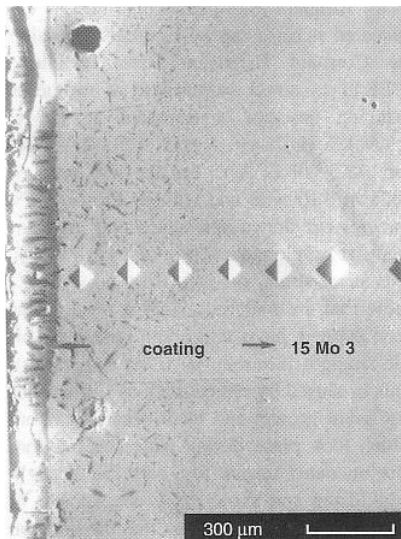


Fig. 9. By heating of the diffusion coating on 15 Mo 3, carbide precipitates (dark grey) are formed throughout the entire coating (not just at the grain boundaries). This results in serious chromium depletion in the coating, causing a decrease of its protective action. (Cr/V coating on 15Mo3), 2500 hours at 550 °C).

10CrMo9.10

No carbides are formed in the diffusion coatings on 10CrMo9.10, not even during high temperature annealing (at 700 °C) as can be seen in Figure 8.

Mechanical Deformation

Temperature fluctuations during operation and with starts and stops cause mechanical stress and sometimes even local plastic deformation. The coatings are required to be crack-resistant at both high and low deformation rates.

High Deformation Rate

To gain an impression of crack-resistance at high deformation rates, a hammer was used to dent the coatings. Analysis of the surfaces and cross-sections shows that the metallic part of the

coatings undergoes plastic deformation without any cracks occurring. The coating thickness in the dented parts decreases only slightly, as the base material deforms as well (see Figure 10).

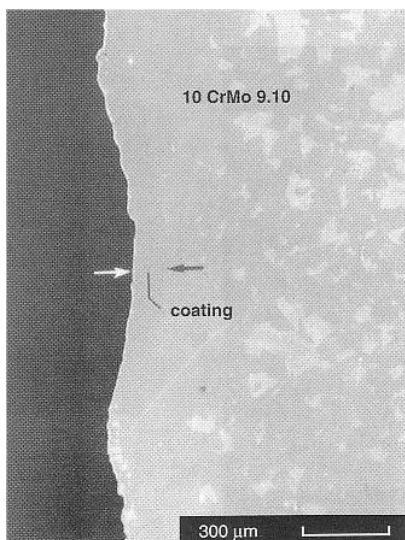


Fig. 10. Cross-section of a dent struck with a hammer in a chromium diffusion coating on 10 CrMo 9.10.

Low Deformation Rate

Low deformation rates combined with sulphidizing conditions may lead to stress corrosion [7]. This phenomenon is also referred to as Alligator Skin Cracking (ASC). On uncoated steels it can be simulated by using the Constant Extension Rate Technique (CERT) to strain samples in a synthetic, reducing gaseous environment at 400 °C (19 vol % H₂, 1 vol % H₂S, 1.5 vol % H₂O and 78.5 vol % Ar). Tensile test bars of 10CrMo9.10 with and without Cr and CrN coatings were drawn in a sulphidizing environment, at an elongation rate of 14×10^{-5} %/s. The stress-strain curves (Figure 11) show that the materials, after a coating has been applied, have achieved a far lower tensile strength (i.e. they have become softer). This is caused by effects such as full annealing, grain growth and local decarburization, which took place during pack cementation. The uncoated tensile test bars are strongly sulphidized and show many deep cracks at the surface, which indicates that the material is sensitive to ASC (Figure 12a).

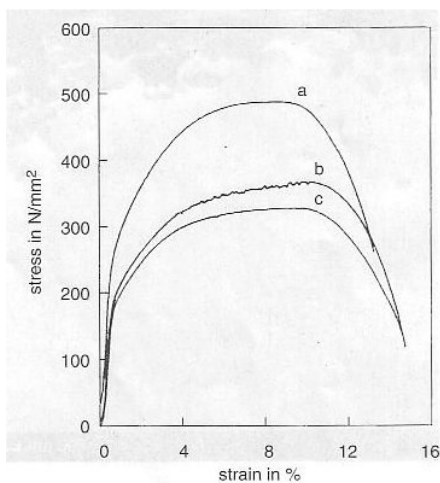


Fig. 11. Stress-strain diagram of 10 CrMo 910 without a coating (a) and with a Cr(b) or CrIV(c) diffusion coatings in H₂S containing gas.

After the tensile test of the coated test specimen it turned out that there were microcracks (Figure 12b) at the surface. Especially near the fracture zone most of the cracks are observed. The cross-sections (Figure 12c) reveal that these microcracks start in the carbide layer at the surface of the coating. Even in the area of contraction they never run much deeper than the pores just beneath the surface (Figure 12d) and stop in the area where the Cr content is still high, viz. approximately 35 %.

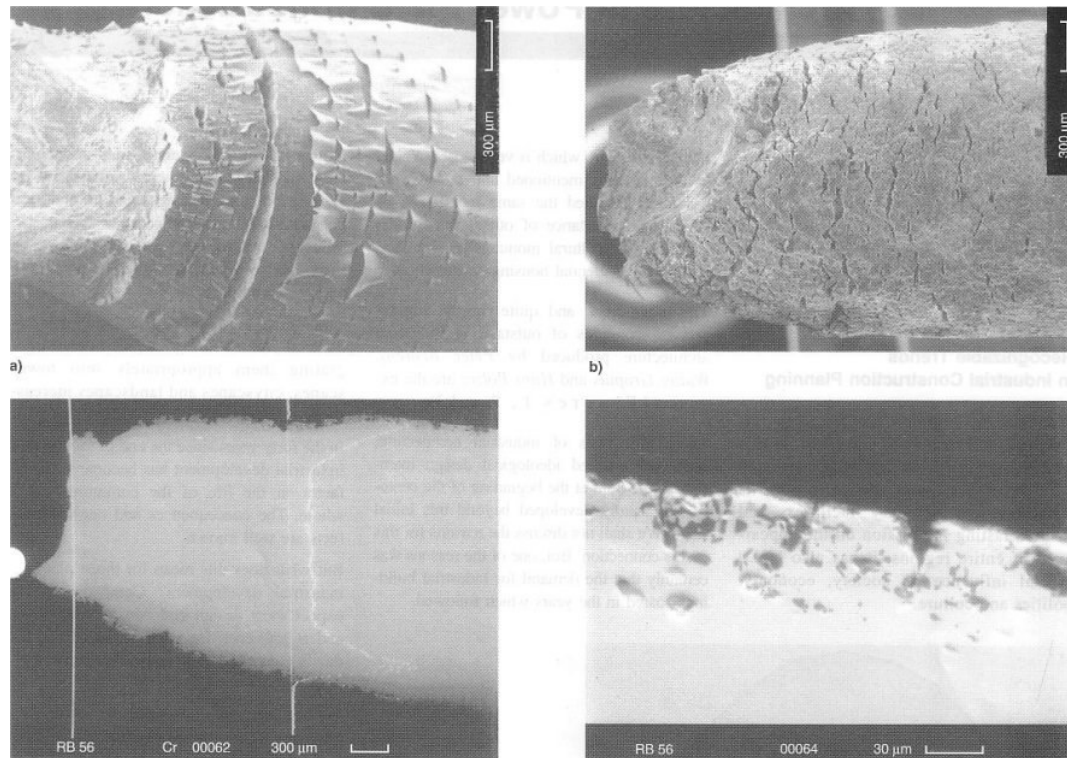


Fig. 12. Tensile tests in H_2S containing gas demonstrate the sensitivity of steels to Alligator Skin Cracking (ASC):

- a. The surface of the uncoated 10 CrMo 910 tensile test bar has a thick corrosion skin and shows deep cracks (ASC).
- b. The surface of the tensile test bar of 10 CrMo 9.10 with Cr/V diffusion coating has only shallow cracks in the part of the test bar subjected to tensile reduction of area.
- c. The cross-section of the tensile test bar in photograph 12b shows a thick coating in which cracking is limited to the surface. d) The detailed photograph of the surface shows that the cracks are shallow.

Resistance to Downtime Corrosion

The third criterion for which the coatings were assessed is their resistance to conditions as may occur during downtime (Downtime Corrosion or DTC).

During combustion, pollutants in fuels form ash and salts that can deposit on the evaporator walls. During downtime of a boiler, humidity falls below the dewpoint if no countermeasures are taken, such as blowing dry air into the boiler. The hygroscopic properties of many salts can subsequently create a highly corrosive aqueous environment on the evaporator walls. Particularly chlorides are extremely notorious in this respect.

Downtime corrosion resistance of coatings under coal gasifier conditions was tested by means of a screening test developed by EPRI [8]. In this test Cr and Cr/V coatings on 15Mo3, 10CrMo9.10 and 10CrMo9.10Nb were used. Samples are covered with a mixture consisting of 90 weight % coal ash (with unburnt coal particles), 3.7 weight % NaCl and 6.3 weight % $FeCl_2$. The samples thus covered are exposed in water saturated air at 70°C for 24 hours. Following the exposure test, sample cross-sections were analysed.

Cr and Cr/V coatings on 15Mo3 and Cr coatings on 10 CrMo 9 10 showed serious attack. These samples were invariably attacked through the the sensitized grain boundaries. When the DTX

mixture reaches the base material, this material is suffering severe attack, causing large cavities to form underneath the coating. An example of attack along the grain boundaries of a Cr coating on 10 CrMo 9 10 can be seen in Figure 13.

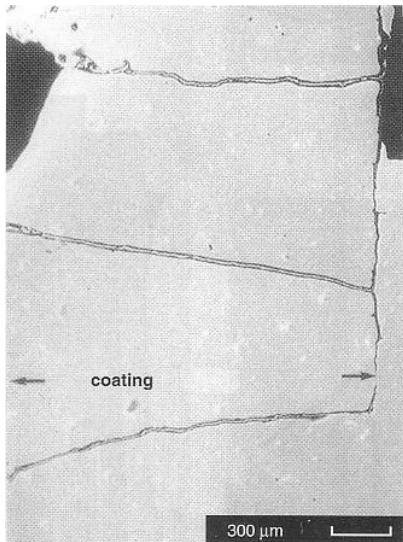


Fig. 13. The Cr coating on 10 CrMo 9 10 is seriously attacked along the sensitized grain boundaries. (See also Figure 6a) during a downtime corrosion test.

The Cr/V coatings on 10 CrMo 9 10 suffer only superficial attack and the Cr and Cr/V coatings on Nb-stabilized 10 CrMo 9 10 are not attacked by the DTC mixture at all. With the latter three coatings no carbides are formed on the grain boundaries. Hence, the stabilizing action of Nb and V is demonstrated by their high resistance in the DTC test.

Weldability

For the construction of evaporator panels a large number of welds are necessary. To gain a better insight into the coatability of a weld and the weldability of the diffusion coatings, a number of preliminary tests were conducted. Cross-sections through the welds show that in either situation it is possible to deliver high-quality welds. Figure 14 gives an example of a weld with AISI 310 in a coating. Bending tests performed on metal strips with coated welds and welded coatings demonstrate that no cracking occurs, in spite of several dozen percent elongation.

It appears, therefore, that welded joints of diffusion coatings are certainly feasible. Further research on the subject of corrosion resistance has yet to be performed.

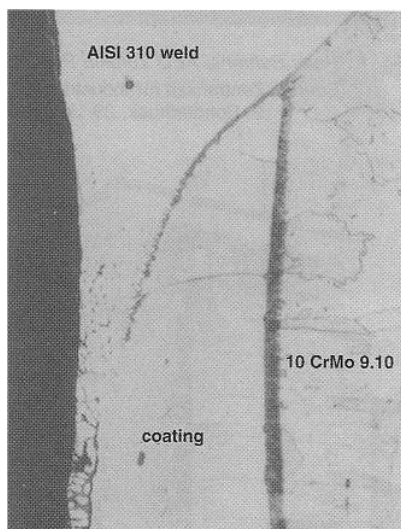


Fig. 14. Cross-section of the welded coating shows that no cracking occurs.

Conclusion

Upon the introduction of reducing firing techniques, such as low-NO_x combustion and coal gasification, measures should be taken to prevent excessive corrosion. Under these conditions chromium diffusion coatings appear to be suitable for applications on low-alloyed steels as used for instance for heat exchangers (Table 2).

Table 2. Behaviour of diffusion coatings under simulated operating conditions.

Steel/ Diffusion coating	Thermal Stability	DTC- resistance	Ductility	Weldability	Usability
15 Mo 3/Cr	—	—	—	—	—
15 Mo 3/CrV	—	—	—	—	—
10 CrMo 9.10/Cr	+	—	+	+	—
10 CrMo 9.10/CrV	+	+/-	+	(2)	X
10 CrMo 9.10 Nb/Cr	(1)	+	(1)	(2)	X
10 CrMo 9.10 Nb/CrV	(1)	+	(1)	(2)	X

— poor
+/- fair
+ good

X potential candidate for application in heat exchanger of coal gasification plant

(1) no problems are anticipated (not yet analysed)
(2) further analysis required

During the preparation of chromium diffusion coatings on low-alloyed steels there is strong interaction between unbound carbon from the steel and chromium. As a result, carbide layers are formed at the surface, obstructing further diffusion of chromium. One of the bottlenecks in production is the fact that carbon must be bound by a strong carbide former. In principle, this can be done in two different ways:

1. By means of co-diffusion pack cementation it is possible to apply, besides chromium, the carbide former vanadium in the coating,
2. a steel may be selected which already contains a strong carbide former, viz. niobium.

Research has shown that the following aspects are important in the application of chromium diffusion coatings:

1. It is not possible to apply useable coatings to the steels St 35 and 15Mo3; this is due to carbide formation at the surface.
2. In the diffusion coatings on the steel AISI 310 a hard, brittle sigma phase is formed, rendering the coating sensitive to cracking.
3. The Cr and CrN coatings on 10CrMo9.10 are thermally stable at 450 °C.
4. Cr and Cr/V coatings on 10CrMo9.10 are extremely ductile at both high and low deformation rates. Cracks originating in CERT tests are limited to the top layer of the coating.
5. Cr and Cr/V coatings on 15 Mo 3 and the Cr coating on 10CrMo9.10 appear to be sensitized by the formation of Cr(V) carbides at the grain boundaries. These coatings are sensitive to downtime corrosion.
6. With the Cr/V coating on 10CrMo9.10 and the Cr and Cr/V coatings on niobium-stabilized 10 CrMo 9 10 there is no carbide formation at the grain boundaries, so that these coatings are insensitive to downtime corrosion.
7. Welds of low-alloyed materials can be provided with a diffusion coating. Coated components can be welded with AISI 310.

References

- 1 Daniel, P.L., Chou, S.F., Rodgers, G.W., and Ayres, P.S.: Fireside Corrosion in Low-NO_x Combustion Systems. Report GS-6339, Rel search project 2154-3, EPRI (1989).
- 2 Becker, G., Hertel, E., and Kaser, C.: Z. Phys. Chem. 117A (1936), pp. 213-223.

- 3 Kelly, F.D.: Chromizing. Trans. Amer. Electrochem. Soc. Vol. 43 (1923), p. 351.
- 4 Hocking, M.G., Vasdntasree, V., and Sidky.: Metallic & Ceramic Coatings: Protection, high Temperature Properties & Applications. Longman Scientific & Technical.
- 5 Hansen, M., and Anderko, K.: Constitution of binary alloys, second edition. McGraw-Hill Book Comp. Inc. (1985).
- 6 Gupta, S.K., Adolph, S.R., Tendon, G.C., and Siegle, L.L.: Metallurgical Transactions A, Vnl. 13A, p. 495 (1982).
- 7 Cialone, H.J., Wright, L.G., Wood, R.A., and Jackson, C.N.: Circumferential cracking of supercritical boiler water-wall tubes. Report CS-46, research project 1890. December 1986, EPRI.
- 8 Perkins, R.A., Marsch, D.L., Sarosiek, A.M., and Bakker, W.: Downtime corrosion in Syngas Coolers of Entrained Slagging Gasifiers. Report AP 5966, Project 2048-1, Topical Report, EPRI (1988).

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