# CORROSION-RESISTANT DIFFUSION COATINGS

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The aim of the present work was to study the effect of thermochemical treatment (TCT) on the corrosion resistance of carbon steels exposed to aqueous solutions of organic and inorganic acids, salts and alkalis, and to investigate the possibility of replacing stainless steels with diffusion-coated carbon and low-alloy steels.

TCT was conducted using powdered, prereduced alumothermic mixtures in containers with fusible seals, and following the schedules presented in Table 1. Corrosion resistance was assessed by the weight loss per unit surface area after the specimens had been exposed in open vessels to the aggressive environments according to the standard methods. For comparison, specimens made from the corresponding uncoated carbon steels (in the as-received condition), as well as specimens of 12Kh18N9T stainless steel, were used as standards.

TABLE 1

| Schedule number | Diffusion coating | Chemical composition of saturating medium * |
|---|---|---|
| 1 | Cr | 95% [30% $Al_2O_3$ + 70% (80% $Cr_2O_3$ + 20% Al)] + 5% $AlF_3$ |
| 2 | Ti | 93% [30% $Al_2O_3$ + 70% (70% $TiO_2$ + 30% Al)] + 5% $AlF_3$ + 2% $NH_4Cl$ |
| 3 | B ($B_4O_4$) | 60% $Na_2B_4O_7$ + 40% $B_4C$ |
| 4 | B (SiC) | 60% $Na_2B_4O_7$ + 40% SiC |
| 5 | Al | 98% (70% $Al_2O_3$ + 30% $CaAl_2$) + 2% $NH_4Cl$ |
| 6 | Si | 70% [60% (KF + NaF) + 40% $SiO_2$] + 30% SiC |
| 7 | Cr—Si | 98% {40% $Al_2O_3$ + 60% [20% Al + 80% (85% $Cr_2O_3$ + 15% $SiO_2$)]} + 2% $NH_4Cl$ |
| 8 | Ti—Si | 98% {40% $Al_2O_3$ + 60% [25% Al + 75% (85% $TiO_2$ + 15% $SiO_2$)]} + 2% $NH_4Cl$ |
| 9 | Zr—Si | 98% {40% $Al_2O_3$ + 60% [25% Al + 75% (85% $ZrO_2$ + 15% $SiO_2$)]} + 2% $NH_4Cl$ |
| 10 | Cr—Ti | 95% {40% $Al_2O_3$ + 60% [15% Al + 85% (70% $Cr_2O_3$ + 30% $TiO_2$)]} + 5% $AlF_3$ |
| 11 | Cr—Al | 95% [30 $Al_2O_3$ + 70% (70% $Cr_2O_3$ + 30 Al)] + 5% $AlF_3$ |
| 12 | Ti—Al | 93% [70% (50% $TiO_2$ + 50% Al) + 30% $Al_2O_3$] + 5% $AlF_3$ + 2% $NH_4Cl$ |
| 13 | Zr—Al | 95% [30% $Al_2O_3$ + 70% (50% $ZrO_2$ + 50% Al)] + 5% $AlF_3$ |
| 14 | Al—Si | 98% [50% $Al_2O_3$ + 50% (70% $SiO_2$ + 30% Al)] + 2% NaF |
| 15 | V—Al | 95% [60% $Al_2O_3$ + 40% (40% $V_2O_5$ + 60% Al)] + 5% $AlF_3$ |
| 16 | B—Al | 98% [70% $Al_2O_3$ + 30% (40% $B_2O_3$ + 60% Al)] + 2% NaF |
| 17 | Cr—Al—Si | 95% {30% $Al_2O_3$ + 70% [30% Al + 70% (85% $Cr_2O_3$ + 15% $SiO_2$)]} + 5% $AlF_3$ |
| 18 | Ti—Al—Si | 95% {40% $Al_2O_3$ + 60% [40% Al + 60% (85% $TiO_2$ + 15% $SiO_2$)]} + 5% $AlF_3$ |
| 19 | Zr—Al—Si | 95% {40% $Al_2O_3$ + 60% [40% Al + 60% (85% $ZrO_2$ + 15% $SiO_2$)]} + 5% $AlF_3$ |
| 20 | Cr—Ti—Al | 95% {40% $Al_2O_3$ + 60% [45% Al + 55% (70% $Cr_2O_3$ + 30% $TiO_2$)]} |

*Mass %.

Remark. Saturations following schedules No. 3 and 4 were carried out at 900°C, the rest at 1100°C; saturation time for all schedules was 4 h.
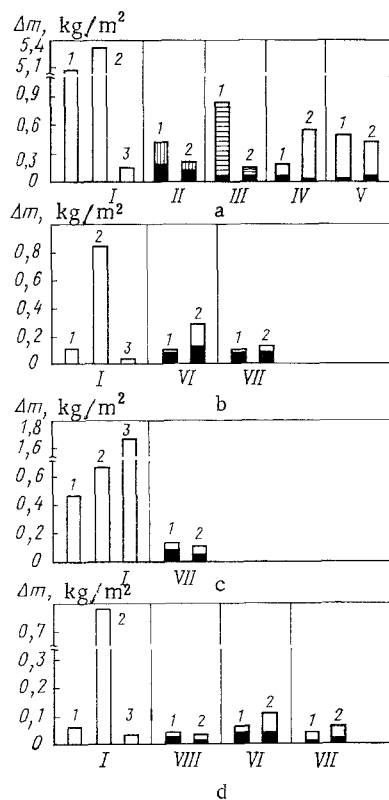
Fig. 1. Corrosion resistance of diffusion coatings before and after optimization ($\Delta m$ is specific mass loss of a specimen): a) in 10% $HNO_3$ solution; b) in 10% $HCl$ solution; c) in 30% $H_2SO_4$ solution; d) in 40% $H_3PO_4$ solution. 1) Technical iron; 2) Steel U8; 3) Steel 12Kh18N9T ; I) without coating; II, III, IV, V, VI, VII, and VIII) Cr, Cr—Al—Ti, Cr—Al, Cr—Ti, Al—V, B and Cr—Si coatings respectively. Unshaded columns, and vertically and horizontally shaded columns represent corrosion resistance before optimization, test times 5, 20, and 50 h, respectively; blackened parts of the columns represent corrosion resistance after optimization (test time 50 h).

In decreasing order of their corrosion resistance in 10% $HNO_3$ solution, the diffusion coatings studied on low-carbon steels can be presented as follows: Cr—Al, Cr—Si, Ti—Al, Cr—Si—Al, Ti—Si—Al, Zr—Al, B—Al, and Zr—Si—Al. The maximum improvement of corrosion resistance for low-carbon steels (from 20 to 150 times) was observed for the specimens with Cr—Al, Cr—Si, Ti—Al, and Cr—Ti—Al coatings.

Diffusion coatings on medium and high-carbon steels can be presented in decreasing order of corrosion resistance as follows: Cr, Cr—Si—Al, Ti—Al, Cr—Al, Cr—Ti—Al, and Ti—Si—Al. All the other diffusion coatings on medium and high-carbon steels exposed to 10% $HNO_3$ did not provide any effective corrosion protection. Chromium, chromium—aluminum—silicon, and titanium—aluminum coatings decrease the corrosion rates of medium- and high-carbon steels by 15-40 times.

Corrosion resistance of low-carbon steels in 10% $H_2SO_4$ solutions can be improved only by boron and vanadium—aluminum coatings. Corrosion resistance of high-carbon steels in that environment can be increased 7-10 times also by chromium and chromium—silicon coatings. The

TABLE 2

| Diffusion coating | Weight loss, kg/m², after testing in the solutions | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5% citric acid | | | 5% wine acid | | | 50% acetic acid* | | | |
| | steel 10 | steel 45 | cast iron SCh 18 | steel 10 | steel 45 | cast iron SCh 18 | technical iron | steel 20 | steel 45 | steel U8 |
| Cr | 0,0566 | 0,035 | 0,265 | 0,031 | 0,013 | 0,026 | 0,013 | 0,016 | 0,012 | 0,014 |
| Ti | 0,0352 | 0,617 | 1,414 | 0,054 | 0,050 | 0,155 | 0,021 | 0,034 | 0,054 | 0,053 |
| Al | 1,2657 | 0,294 | 1,286 | 0,977 | 0,201 | 0,336 | 0,052 | 0,038 | 0,031 | 0,032 |
| Si | 0,6570 | 1,507 | 4,632 | 0,495 | 0,300 | 0,331 | 0,105 | 0,110 | 0,130 | 0,110 |
| B | 0,0924 | 0,063 | 0,374 | 0,040 | 0,025 | 0,052 | 0,010 | 0,015 | 0,020 | 0,019 |
| Cr—Ti | 0,040 | 0,058 | 0,069 | 0,018 | 0,011 | 0,006 | 0,007 | 0,007 | 0,010 | 0,014 |
| Cr—Al | 1,197 | 0,274 | 2,370 | 1,059 | 0,331 | 0,493 | 0,013 | 0,013 | 0,018 | 0,021 |
| Cr—Si | 0,050 | 0,028 | 0,384 | 0,022 | 0,013 | 0,044 | 0,014 | 0,012 | 0,004 | 0,004 |
| Ti—Al | 0,037 | 0,108 | 0,760 | 0,040 | 0,082 | 0,224 | 0,008 | 0,009 | 0,095 | 0,090 |
| Ti—Si | 0,101 | 0,341 | 3,484 | 0,033 | 0,017 | 0,168 | 0,019 | 0,012 | 0,013 | 0,033 |
| Al—Si | 0,026 | 0,111 | 1,077 | 0,154 | 0,175 | 0,460 | 0,105 | 0,110 | 0,115 | 0,100 |
| Cr—Ti—Al | 0,039 | 0,09° | 0,618 | 0,016 | 0,096 | 0,168 | 0,009 | 0,014 | 0,023 | 0,015 |
| Cr—Ti—Si | 0,042 | 0,154 | 0,120 | 0,045 | 0,068 | 0,036 | — | — | — | — |
| Cr—Al—Si | 1,361 | 0,122 | 1,555 | 1,553 | 0,238 | 0,302 | 0,110 | 0,105 | 0,100 | 0,100 |
| Ti—Al—Si | 0,051 | 0,258 | 1,395 | 0,023 | 0,168 | 0,629 | 0,020 | 0,033 | 0,050 | 0,090 |
| Uncoated | 0 564 | 1,297 | 4,340 | 0,444 | 0,158 | 0,891 | 0,042 | 0,039 | 0,044 | 0,042 |

*$\tau_{test}$ = 70 h, in all other cases $\tau_{test}$ = 400 h.

Remark. Data reported in [2] is used.

TABLE 3

| Diffusion coating | Weight loss, kg/m², after testing* in | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 3% NaCl solution | | | | 30% NaOH solution | | | |
| | technical iron | steel 20 | steel 45 | steel U8 | technical iron | steel 20 | steel 45 | steel U8 |
| Cr | 0,0011 | 0,0072 | 0,0006 | 0,0009 | 0,0009 | 0,0040 | 0,0006 | 0,0004 |
| Al | 0,0041 | 0,0056 | 0,0053 | 0,0050 | 0,0090 | 0,0070 | 0,0070 | 0,0062 |
| Ti | 0,0012 | 0,0015 | 0,0009 | 0,0011 | 0,0009 | 0,0009 | 0,0004 | 0,0003 |
| B (B₄C) | 0,0056 | 0,0100 | 0,0130 | 0,0140 | 0,0040 | 0,0080 | 0,0120 | 0,0110 |
| B (SiC) | 0,0060 | 0,0040 | 0,0060 | 0,0070 | 0,0050 | 0,0005 | 0,0005 | 0,0003 |
| Si | 0,0130 | 0,0150 | 0,0120 | 0,0090 | 0,0100 | 0,0120 | 0,0130 | 0,0130 |
| Cr—Si | 0,0037 | 0,0030 | 0,0015 | 0,0006 | 0,0012 | 0,0007 | 0,0025 | 0,0007 |
| Ti—Si | 0,0110 | 0,0070 | 0,0070 | 0,0050 | 0,0013 | 0,0020 | 0,0012 | 0,0016 |
| Zr—Si | 0,0040 | 0,0050 | 0,0020 | 0,0031 | 0,0020 | 0,0030 | 0,0010 | 0,0020 |
| Cr—Ti | 0,0025 | 0,0036 | 0,0049 | 0,0059 | 0,0006 | 0,0009 | 0,0005 | 0,0020 |
| Cr—Al | 0,0031 | 0,0021 | 0,0025 | 0,0018 | 0 | 0 | 0 | 0,0005 |
| Ti—Al | 0,0010 | 0,0009 | 0,0005 | 0,0005 | 0 | 0 | 0 | 0 |
| Zr—Al | 0,0003 | 0,0003 | 0,0012 | 0,0009 | 0,0005 | 0,0005 | 0,0190 | 0,0050 |
| Si—Al | 0,0019 | 0,0032 | 0,0052 | 0,0058 | 0,0019 | 0,0029 | 0,0018 | 0,0077 |
| V—Al | 0,0020 | 0,0039 | 0,0090 | 0,0052 | 0,0020 | 0,0050 | 0,0002 | 0,0004 |
| B—Al | 0,0020 | 0,0040 | 0,0080 | 0,0090 | 0,0060 | 0,0050 | 0,0070 | 0,0080 |
| Cr—Si—Al | 0,0025 | 0,0019 | 0,0017 | 0,0015 | 0,0026 | 0,0024 | 0,0012 | 0,0017 |
| Ti—Si—Al | 0,0030 | 0,0040 | 0,0070 | 0,0060 | 0,0020 | 0,0019 | 0,0016 | 0,0018 |
| Zr—Si—Al | 0,0030 | 0,0030 | 0,0020 | 0,0020 | 0,0009 | 0,0013 | 0,0011 | 0,0012 |
| Cr—Ti—Al | 0,0090 | 0,0060 | 0,0030 | 0,0040 | 0,0020 | 0,0040 | 0,0030 | 0,0040 |
| Uncoated | 0,0100 | 0,0052 | 0,0045 | 0,0055 | 0,0008 | 0,0016 | 0,0005 | 0,0015 |

*$\tau_{test}$ = 70 h.

Remark. Data presented in [1] is used.

remaining thermochemical treatments cause deterioration of carbon steel corrosion resistance in 10% $H_2SO_4$ solution, or in some cases an insignificant improvement.

Corrosion resistance of low-carbon steels in 40% $H_3PO_4$ solution can be improved only by boron coatings.

For medium- and high-carbon steels the maximum corrosion resistance is provided by chromium, boron, and chromium—silicon coatings (100-300, 35-60, and 15-20 times, respectively), Cr—Al and V—Al coatings produce a 10 times increase in corrosion resistance, while Al, Ti, Si, and Cr—Ti coatings produce 2-5 times increase. All other coatings decreased the corrosion resistance of medium- and high-carbon steels in 40% $H_3PO_4$ solution.

Boron coating provides the best corrosion resistance for all steels in 30% HCl solution.

Chromium and chromium—aluminium coatings also increase the corrosion resistance of medium and high-carbon steels in that environment by 5-15 times.

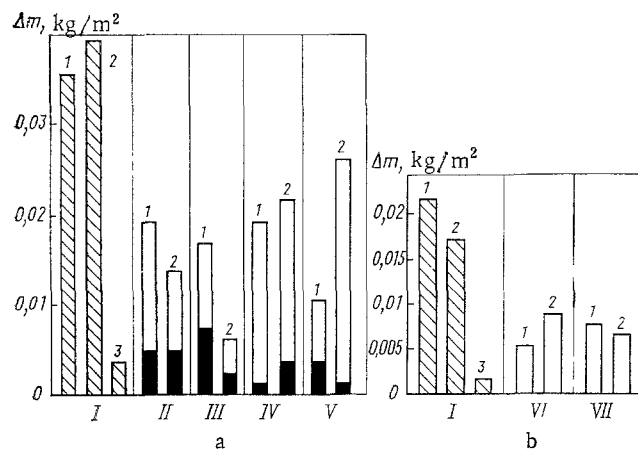The technology for the most beneficial coatings was optimized [1, 2] using mathematical

Fig. 2. Corrosion resistance of diffusion coatings in 50% acetic acid aqueous solution (a) and in 30% NaCl aqueous solution (b); 1, 2, 3) the same as in Fig. 1; I) not coated; II, III, IV, V, VI, and VII) Ti—Cr, Cr—Si, Cr—Al, Cr, Ti—Al, and Zr—Al coatings, respectively. Unshaded and partly shaded columns represent corrosion resistance before optimization; blackened parts of the columns represent corrosion resistance after optimization. Test time before and after optimization is 200 h.

experiment planning with reference to the Box—Wilson method (Figs. 1 and 2).

The corrosion resistance to 10% $HNO_3$ solution of carbon steels with diffusion coatings produced by the optimized methods equals that of stainless steel 12Kh18N9T. Lowest corrosion rates are shown by specimens with Cr—Ti and Cr—Al coatings. The integrity of Cr—Ti and Ti—Al coatings was retained after the exposure times used in the present investigation; their thinning is even. Steels with Cr and Cr—Ti—Al coatings showed noticeably lower corrosion resistance in $HNO_3$ than steels with Ti—Al and Cr—Ti coatings.

Steels with optimized boron and vanadium—aluminium coatings are only slightly less corrosion resistant in 10% $H_2SO_4$ than stainless steel 12Kh18N9T. For short-term exposure (up to 100 h) boron-coated steels should be used, while for more prolonged exposure V—Al coated steels are preferable.

In 30% $H_2SO_4$ solution the best corrosion resistance was also shown by boron-coated steels. Corrosion rates of optimized boron-coated carbon steels were many times lower than their corrosion rates without coating, or than the corrosion rates of Cr—Ni steels in the as-received condition. After 100-h exposure the appearance of boron-coated specimens did not change significantly, and their weight loss was insignificant. Metallographic analysis revealed that after 100-h exposure thinning of the coating occurs evenly and the coating layer retains its integrity.

For investigation of exposure in 40% $H_3PO_3$ solution the technological processes of Cr—Si, B, and V—Al coating were optimized (Fig. 1d). The maximum corrosion resistance in that environment was shown by Cr—Si coated carbon steels, while the corrosion resistance of boron and V—Al coated steels was slightly worse. Chromium—silicon-coated carbon steels possess higher corrosion resistance to 50% $H_3PO_4$ solution than does uncoated 12Kh18N9T steel. After the 100-h exposure test the structures of Cr—Si and V—Al coated steels did not show any significant changes, while B-coated steels showed some localized disintegration of the diffusion layer.

Similar tests have been run to investigate the corrosion resistance of thermochemically treated carbon steels when exposed to aqueous organic acids (Table 2), salt and alkali solutions (Table 3).

The best corrosion resistance for low-carbon steels in 5% citric acid solution was shown by Ti—Si, Ti—Al, Ti, Cr—Ti, Cr—Ti—Al, and Cr—Ti—Si coated steels (their corrosion resistance

increased by 15-20 times), while for medium carbon steels it was achieved with Cr—Si, Cr, Cr—Ti, and B coated steels (20-45 times corrosion resistance increase) and for grey cast iron by Cr—Ti, Cr—Ti—Si and Cr coatings (15-60 times increase). It has to be mentioned that the steels and cast irons with the most-corrosion-resistance coatings (corrosion rates K = 0.065-0.094 g/m² × h) are equal in that respect to chromium and chromium—nickel stainless steels.

Similar results were obtained when studying the behavior of diffusion-coated steels and cast iron in 5% wine acid (see Table 2). The best effect on corrosion resistance in that medium is achieved through alloying of Fe—C alloys with Cr and Ti (Cr—Ti, Cr—Ti—Al, Cr—Si, and other similar coatings).

The lowest corrosion rates in 50% acetic acid were shown by steels with Cr-based diffusion coatings (Cr, Cr—Si, Cr—Al, and Cr—Ti).

The technology of Cr, Cr—Ti, Cr—Si, and Cr—Al coatings was optimized for their corrosion resistance in aqueous solutions of organic acids.

In all organic acids diffusion-coated Fe—C alloys with optimized saturation conditions show corrosion resistance as high as that of steel 12Kh18N9T.

In 3% aqueous NaCl solution the maximum corrosion resistance was shown by steels with Ti—Al and Zr—Al coatings, while in 30% NaOH solution the steels with Cr—Al and Ti—Al coatings were the best (Table 3).

The first signs of deterioration by corrosion of the steels with Ti—Al and Zr—Al coatings in 3% NaCl solution were observed after 1500 h, and even then the weight loss was insignificant. Carbon steels with Ti—Al and Cr—Al diffusion layers are many times more corrosion resistant in salt and alkali aqueous solutions than is steel 12Ch18N9T.

The kinetics and mechanisms of corrosion of diffusion coated steels were studied in [2].

As shown by the present work, it is necessary to select the best diffusion coating for each aggressive environment. The technological process for diffusion coating by thermochemical treatment has to be optimized for corrosion resistance in that particular environment. Diffusion coated carbon steels can often replace the high-alloyed Cr—Ni stainless steels.

## LITERATURE CITED

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