IMPROVEMENT OF CARBON STEEL SCALE RESISTANCE BY COMBINED TITANIZING AND ALUMINIZING FROM MULTILAYER COATINGS

A. M. Gur'ev,¹ K. A. Krasnikov,² S. A. Zemlyakov,³ M. A. Gur'ev,⁴ and S. G. Ivanov⁵

UDC 621.785

Results are presented for research on the problem of increasing the stability and durability of a diffusion aluminized coating on carbon steel 45 when held in an oxidizing atmosphere at 1100°C. A method is proposed for aluminizing from a three-layer impregnation mixture in which resorption of the aluminized layer is excluded and good oxidation resistance of the protected steel is provided. Experimental tests of an aluminized specimen made of steel 45 at a temperature of 1100°C for 200 hours showed that under the specified conditions there is 10% better oxidation resistance than for steel 12X18H10T and 1140% better than for unaluminized steel 45.

Keywords: aluminizing, steel, oxidation resistance, corrosion resistance.

Carbon steels are the main structural material for preparing machine components and structures. Intensive use of these steels is due to low cost and a good set of operating properties. However, carbon steel does not exhibit good heat and corrosion resistance properties that limits its use under high-temperature and corrosive media conditions. One method for improving heat and corrosion resistance and also to resistance to high-temperature corrosion is chemical heat treatment, in particular aluminizing and siliciding. Preparation of pore-free silicide diffusion layers with a high silicon content on carbon steels is connected with significant difficulties [1-4]. Aluminized diffusion coatings are free from this problem although during prolonged high-temperature exposure an aluminized diffusion layer is inclined towards "resorption" that reduces a protected surface heat resistance. It should be noted that high temperature resorption and also formation of intermetallic interlayers concerns aluminized coatings on iron-carbon alloys independent of the application method [5-9]. In this case various barrier composites, for example an underlayer of nichrome, makes it possible to reduce aluminized layer resorption rate. Research on the theme of preparing complex titanium-aluminized and also silicon-titanium-aluminized coatings is relatively sparse in publications, although good prospects are noted for the use of such coatings within the plan for improving steel corrosion and scaling resistance [10-12].

A possible method for reducing the effect of aluminized layer resorption is application of barrier intermediate layer exhibiting low diffusion permeability for aluminum (for example nichrome) or bonding aluminum into chemical compounds resistant to high temperature and exhibiting reduced diffusion permeability with respect to aluminum and in addition weak solubility in iron. One of these elements is titanium, i.e., its solubility in iron

0026-0894/21/0304-0433 © 2021 Springer Science+Business Media, LLC

¹ I. I. Polzunov Altai State technical University, Barnaul, Russia; e-mail: gurievam@mail.ru.

² OOO RosMasterStroi Barnaul, Russia; e-mail: zakazrms@bk.ru.

³ OOO UK Altai Precision Component Plant, Barnaul, Russia; e-mail: kobalt_20@mail.ru.

⁴ I. I. Polzunov Altai State technical University, Barnaul, Russia; e-mail: gurievma@mail.ru.

⁵ I. I. Polzunov Altai State technical University, Barnaul, Russia; e-mail: serg225582@mail.ru.

Translated from Metallurg, Vol. 65, No. 4, pp. 58–62, March, 2021. Russian DOI: 10.52351/00260827_2021_04_58. Original article submitted December 1, 2020.



Fig. 1. Steel 45 aluminized coating microstructure.

does not exceed 2.7 wt.%. In addition, it may bonded with both iron and aluminum forming corresponding chemical compounds with a covalent bond, stable at high temperature, so-called intermetallics.

Studies have been conducted in the present work for determining the possibility of preparing multilayer diffusion aluminum coatings resistance to the effect of resorption at temperatures up to 1200°C. Impregnation was performed in a SNOL chamber furnace fitted with a program controller on specimens of steel 45 with a size of 30X30X40 mm. A multilayer impregnation medium was used whose first layer was a mixture of ferrotitanium FTi75 and aluminum PA-3 powders in the ratio 80:20 wt.% diluted in ethyl silicate. The first coating layer thickness was 70–100 μ m. After drying the first coating layer a second coating layer was applied to the surface represented by a mixture of ferrosilicon FS25 and aluminum PA-3 powders in the ratio 15:85 wt.% diluted in ethyl silicate. The coating layer thickness was 400–500 μ m. After drying the second layer a third layer was applied represented by aluminum PA-3 powder diluted in ethyl silicate. The third coating layer thickness was not more than 100 μ m. After drying specimen with the applied coating they were place in a furnace previously heated to 900°C and held at this temperature for 1 h. At the end of exposure specimens were extracted from the furnace and stood on a metal plate. Cooled specimens were washed in warm (30–40°C) soap and soda solution and metallographic templates were cut from them.

Specimens were cut in a MICROCUT-201 precision cutting machine and pressed in a METAPRESS metallographic press into BAKELIT compound. Grinding and polishing was performed in an automatic DIGIPREP grinding and polishing unit. Metallographic etching was performed successively in two stages: in the first stage the overall microstructure of the steel substrate was revealed by means "Nital" etchant (4% alcoholic HNO₃ solution), and in the next stage the coating structure was revealed by means of modified Keller etchant (2 mliter HF, 3 mliter HCl, 20 mliter HNO₃, 120 mliter glycerol) [13]. Analysis of the microstructure, determination of diffusion layer thickness and its components was accomplished by means of Thixomet PRO software and a Carl Zeiss Axio Observer Z1m metallographic microscope by procedures provided in [14-18].

The microstructure of a coating obtained is provided in Fig. 1. It is seen that at the steel surface there was formation of a diffusion layer with an average thickness of 80 μ m. The boundary of the layer is smooth, and the layer itself columnar crystals. There is no transition zone beneath the diffusion layer and the structure of basic material is troostite-sorbite, and structurally free ferrite is also present in the form of acicular precipitates of the Widmanstätten type.

The diffusion coating microstructure at high microscope resolution is shown in Fig. 2 where it is seen that at the diffusion layer boundary there is another layer differing morphologically from the main diffusion layer (see Fig. 2b). This underlayer is a thin barrier layer of titanium intermetallic formed from the first coating layer. The barrier layer thickness is $0.8-1.2 \,\mu\text{m}$.



(a)

(b)

Fig. 2. Aluminized layer microstructure: (a) general microstructure; (b) boundary of diffusion coating and basic metal: recording area separated by square (a), titanium intermetallic layer indicated by arrows (b).



Fig. 3. Diffusion aluminized layer microstructure after heat resistance testing.

The aluminized layer was tested for scaling resistance at 1100°C for 200 h. Tests were conducted by a gravimetric method in accordance with GOST 6130–71 "Metals. Methods for determining heat resistance (with change N1)". The comparison specimens used were made from steel 12Kh18N10T and unalloyed steel 45. Weight increase in this case was 18.72 g/cm² for steel 12Kh18N10T, 16.44 g/cm² for aluminized steel 45, and 187.81 g/cm² for unaluminized steel 45.

Therefore, compared with unaluminized material the resistance of aluminized steel 45 increased by 1140% and appeared to be 10% better than the resistance of steel 12Kh18N10T. At the surface of an aluminized specimen in this case there was formation of a clearly visible oxide layer. After testing for heat resistance an aluminized specimen of steel 45 was also subjected to metallographic analysis (Fig. 3). It is seen that during heat resistance testing the aluminized diffusion layer thickness decreased to a value of the order of 30 μ m. However, resorption of an aluminized layer and formation of a transition zone did not occur. A thin barrier layer of titanium



Fig. 4. Titanium-aluminized coating on steel 45 chemical composition with observation from the coating surface (aluminum peaks not separated).

intermetallic remains almost in unchanged form, i.e., the weight increase during testing occurred as a result of oxidation of an aluminized coating and formation of an aluminum oxide film at its surface.

According to the composition diagram for iron with titanium there may be formation of intermetallics Fe_2Ti and FeTi, and in turn titanium with aluminum stable compounds Ti_3Al , TiAl, $TiAl_2$, $TiAl_3$ [19]. Layerby-layer X-ray diffraction analysis established within a diffusion coating compounds Fe_2Ti , FeTi, TiAl, $TiAl_2$, $TiAl_3$. In order to implement layer-by-layer X-ray diffraction analysis by means of a polishing machine and diamond wheel with a grain size of 3 µm a coating layer 70 µm thick was removed from a specimen with an interval of 3 µm, and then a surface was analyzed. Results of diffraction pattern studies are provided in Figs. 4 and 5.

A record of diffraction patterns conducted in a Bruker D8 ADVANCE diffractometer with CuK_{α} -radiation ($\lambda = 1.5418$ Å). Synthesis and treatment of diffraction patterns was accomplished by means of JADE 6 software. Diffraction patterns showed that at a depth of 70 µm from surface of a diffusion coating the aluminum content, and also intermetallic titanium-aluminum phases are at a minimum, and in this case titanium-iron intermetallic phase predominates in this part of a diffusion coating. Titanium is not revealed in a free condition within a coating. From the surface a diffusion coating is represented by chemically pure aluminum in view of which aluminum peaks were excluded from identification (see Fig. 4) as they "obstructed" a useful signal.

CONCLUSION

The method developed for combined diffusion of titanium and aluminum of a three-layer coating makes it possible to improve significantly carbon steel scaling resistance. This is achieved due to the fact that at the boundary of an aluminized layer and the basic material there is formation of a thin layer titanium intermetallics, in particular Fe₂Ti and FeTi from the direction of a steel base, and TiAl, TiAl₂, TiAl₃ from the direction of a naluminized layer. Titanium intermetallics with iron and aluminum have a higher decomposition temperature



Fig. 5. Titanium-aluminized coating on steel 45 chemical composition with recording for a value of coating 70 μ m.

than iron and aluminum intermetallics. As a result of this fixing aluminum atoms within an aluminized layer is achieved and desorption of a diffusion aluminized coating is excluded with high temperature exposure.

REFERENCES

- 1. G. V. Borisenok, L. A. Vasil'ev, L. G. Voroshnin, et al., *Chemical Heat Treatment of Metals and Alloys. Handbook* [in Ruussian], Metallurgiya, Moscow (1981).
- B. P. Bimbaev, T. V. Budaev, V. A. Butukhanov, and B. D. Lygdenov, "Study of siliciding carbon steels," *Polzunov. Al'manakh*, No. 1, 21–23 (2012).
- 3. A. I. Arslanova and A. V. Rubtsov, "Features of steel siliciding," in: Proc. Mater. 69th Sci.-Tech. Conf. for Students, Aspirants, and Young Scientists of UGNTU (2018).
- A. G. Chirkova, A.V. Rubtsov, A. I. Arslanova, V. A. Gafarova, and I. R. Kuzeev, "Siliciding highly alloyed steel from a solid phase," *Neftegaz. Delo.*, 17, No. 4, 93–99 (2019).
- A. V. Golovanov, A. G. Radyuk, V. I. Slavov, V. P. Baranov, A. E. Titlyanov, and Yu. Z. Kul'mamet'eva, "Structure and phase composition of a surface layer on steel after aluminizing," *Metalloved. Term. Obrab. Metallov*, No. 6(636), 42–45 (2008.
- V. I. Murav'ev, P. V. Bakhmatov, S. Z. Lonchakov, and N. G. Chinilov, "Effect of aluminizing structural steels in molten aluminum on the structure and properties of objects made from them," *Uprochn. Tekhnol. Pokrytiya*, No. 11(107), 25–32 (2013).
- 7. V. F. Danenko, L. M. Gurevich, and G. V. Ponkratova, "Effect of aluminizing on structure and properties of steel St3," *Izv. VGTU*, No. 9(136), 30–34 (2014).
- V. G. Shmorgun, O. V. Slautin, and V. P. Kulevich, "Features of diffusion interaction n a steel-aluminum composite after explosive welding and aluminizing by charging into melt," *Metallurg*, No. 7, 84–89 (2019).
- V. G. Shmorgun, A. I. Bogdanov, A. O. Taube, and L. D. Iskhakova, "Phase composition of heat-resistant layered coatings of the Al-Cr-Ni system," *Metallurgist*, 60, No. 9–10, 1113–1119 (2017).
- 10. A. I. Kovtunov, T. V. Chermashentseva, and Yu. Yu. Khokhlov, "Study of steel aluminizing in melts alloyed with titanium," *Tr. GOSNITI*, **108**, 241–244 (2011).
- V. G. Khizhnyak, M. V. Arshuk, and O. É. Datsyuk, "Diffusion coating with participation of titanium, aluminum, and silicon on steel 12Kh," *Nauch. Vesti. Nats, Tekhn. Univ. Ukrainy, Kiev Politekh. Inst.*, No. 5(97), 84–88 (2014).
- 12. V. G. Khizhnyak, M. V. Arshuk, and O. É. Datsyuk, "Diffusion coating of titanium and aluminum with participation of a Ti barrier layer on steel 12Kh," *Izv. Vuz. Chern. Met.*, **57**, No. 9, 57–62 (2014).
- G. F. Vander Voort, et al., "Color metallography. ASM handbook," *Metallography and Microstructures*, 9, 493–512 (2004); DOI: 10.1361/asmhba0003752.

- 14. A. A. Kazakov, S. V. Ryaboshuk, D. A. Lyubochko, and L. S. Chigintsev, "Research on the origin of nonmetallic inclusions in high-strength low-alloy steel using automated feature analysis," *Microscopy and Microanalysis*, **21**, No. 3, 1755–1756 (2015).
- 15. A. Kazakov, S. Kovalev, and S. Ryaboshuk, "Metallurgical expertise as the base for determination of nature of defects in metal products," *CIS Iron and Steel Review*, No. 1–2, 7–13 (2007).
- A. Kazakov and D. Kiselev, "Industrial application of Thixomet," *Metallography, Microstructure, and Analysis*, 294–301 (2016). DOI 10.1007/s13632-016-0289-6.
- 17. G. F. Vander Voort, "Computer-aided microstructural analysis of specialty steels," *Materials Characterization*, No. 27, 241–260 (1991).
- S. G. Ivanov, A. M. Gur'ev, S. A. Zemlyakov, M. A. Gur'ev, and V. V. Romanenko, "Features of preparing specimens for automatic analysis of carbide phase for steel Kh12F1 after carburizing in a vacuum with use of Thixomet PRO software," *Polzunov. Vestnik*, No. 2, 165–168 (2020).
- 19. N. P. Lyakishev (editor), Binary Metal Ssystem Composition Diagrams [in Russian], Vol. 1 and 2, Mashniostroenie, Moscow (1996–2000).