ASN, Vol 3, No 1, Pages 39-43, 2016

DE GRUYTER OPEN

Acta Scientifica Naturalis

Former Annual of Konstantin Preslavsky University – Chemistry, Physics, Biology, Geography
Journal homepage: http://www.shu.bg

Received: 30.10.2015
Accepted: 11.03.2016

Diffusion Coatings as Corrosion Inhibitors

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Abstract: ***Corrosion is the cause of irretrievable loss of huge amounts of metals and alloys. The harmful effects of corrosion can be reduced significantly by applying appropriate methods of corrosion protection. One method to protect metals against corrosion is the formation of diffusion coatings on them. High corrosion resistance is typical for the boride diffusion layers. Aluminothermy is one of the main methods for diffusion saturation of the surface of metal products with various elements, including boron, and under certain conditions with aluminum, too. Samples of steel 45 were put to aluminothermic diffusion saturation with boron in a pressurized steel container at a temperature of 1100K, for 6 hours in powdered aluminothermic mixtures. The content of B_2O_3 in the starting mixtures decreased from the optimum - 20% to 0%, and the content of Al and the activator - $(NH_4)_2.4BF_3$ is constant, respectively 7% and 0.5%. Al_2O_3 was used as filler. The borided samples were tested for corrosion resistance in 10% HCl for 72 hours. The results show that their corrosion resistance depends on the composition of the starting saturating mixture (mainly on the content of B_2O_3), and respectively on the composition, structure, thickness and degree of adhesion of the layer to the metal base.***

Keywords*: boriding, diffusion saturation, corrosion, inhibitors*

Introduction

Corrosion is the process of destruction of the materials because of the physico-chemical effects of the surrounding environment. It represents a willfully going chemical, electrochemical or biochemical process on the surface of metal products, leading to their destruction [3, 10]. Corrosion is the cause of irretrievable loss of huge amounts of metals and alloys. At the same time, the analyses made show that the harmful effects of corrosion can be reduced significantly through application of appropriate methods of corrosion protection. They are not universally applicable and their choice depends on both the characteristics of the material and the ambient conditions (i.e. the conditions of use of the facilities), and in many cases on

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DOI: 10.1515/asn-2016-0006

environmental and economic reasons as well. The methods for protection of metals against corrosion are [10]:

- Alloying of metals;
- Use of protective decorative coatings: metal (diffusion coatings, etc.); organic; inorganic;
- Electrochemical protection: cathodic and tread protection;
- Processing of the corrosion environment – it is performed by: reducing the content of the depolarizer; adding inhibitors - depending on the mechanism of action, inhibitors are: anode; cathode; mixed inhibitors.

The chemical heat treatment of steel products is a method in which their surface is saturated with a specific element (C, N, B, etc.), and as a result a diffusion layer is formed enriched in the respective element and having specific properties. When steel products are borided, a two-phase or single-phase diffusion boride layer is formed, depending on the method and conditions, that has high corrosion resistance, microhardness and wear resistance [4-7, 11]. These are parameters that depend on the composition, structure, density and degree of adhesion of the layer to the metal base.

Aluminothermy is one of the main methods for diffusion saturation of the surface of metal products with various elements, including boron, and under certain conditions with aluminum, too. The boriding aims at increasing the corrosion resistance, the hardness and the wear resistance of the processed products [1,2, 8]. In the aluminothermic boriding B_2O_3 is the major supplier of boron. The flowing of the process is guaranteed by the value of ΔG of the reaction of metalothermic reduction:

$$2/3B_2O_3+4/3Al=2/3Al_2O_3+4/3B; \qquad \Delta G=-1134kJ/mol.$$

Depending on the content of the boron-containing substance (B_2O_3) and the reducer (Al), their ratio, and the type and amount of the activator in the starting aluminothermic mixture, during the saturation process there may go a boriding process alone or bicomponent saturation with boron and aluminum with the formation of boride and aluminide phases in different proportions and location in the diffusion layer [1,8]. The purpose of this article is to summarize the results of our research on the corrosion resistance of steel samples processed in aluminothermic saturating mixtures with different content of boron-containing substance (B_2O_3).

Methods and appliances

Samples of steel 45 were put to aluminothermic diffusion saturation with boron after being ground, weighed and sized in advance. The saturation was conducted in a pressurized steel container at a temperature of 1100K, for 6 hours in powdered aluminothermic mixtures with a composition presented in Table 1. The content of B_2O_3 decreases from the optimum - 20% to 0% by a rate of 5%, and the content of Al and the activator - $(NH_4)_2.4BF_3$ is constant, respectively 7% and 0.5% [4-6]. The boriding of the steel samples is performed by active atoms of B released in the reduction of B_2O_3 from Al directly in the reaction container.

The borided samples were put to micro-structural and X-ray structural (PCA) analyses to determine the structure and composition of the formed diffusion layer. The microstructure analysis of black and white (in a 5% solution of HNO_3 in ethyl alcohol) and color developed (in a 5% solution of picric acid) microgrinds and the measurement of the thickness (δ) of the diffusion layer were held with a Neophot - 2 microscope. The degree of adhesion (S) of the layer to the metal base is defined as the positive square root of the deviations of the measured values of the layer thickness from its average values [9]. In order for the corrosion resistance to be tracked, boron steel samples were used that were previously weighed on an analytical balance with an allowance of 0.0001 g and dimensioned with a micrometer. The samples were placed in a 10% solution of HCl at 18-20˚C for 72 h.

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DOI: 10.1515/asn-2016-0006

Table 1. Composition of aluminothermic mixtures for boriding

№	B_2O_3, mass %	B_2O_3/Al_2O_3	Content of Al_2O_3
1	20	2,0:0,7	72,5
2	15	2,0:0,93	77,5
3	10	2,0:1,4	82,5
4	5	2.0:2.8	87,5
5	0,0	0,0 : 7,0	92,5

A checking sample was placed as well. At the end of the experiment the samples were washed in running water, cleaned, dried and re-weighed on an analytical balance. Based on the data for the change in the mass of the samples due to corrosion (ΔG) and their full surface (F), the corrosion rate (K), the degree of protection (Z) and the coefficient of protection (γ) were calculated [10]. The speed of the corrosion process is determined by the loss in weight of the samples as a result of corrosion related to a unit area per unit time according to the formula: **$K = \Delta G/ F.\tau$, $g/cm^2.h$;** where: K is the speed of corrosion; ΔG – the loss of mass due to corrosion, g; F- full surface of the sample, cm2; τ- duration of the corrosion, h. In order for the inhibitory properties of the tested diffusion layers to be tracked, the degree of protection (Z) and the coefficient of protection (γ) were calculated with the following formulas: **$Z = (K_0 – K\ i) / K_0 \times 100$,%; $\gamma = K_0/Ki$;** where: K_0 is the corrosion rate of the control samples; K_i - the corrosion rate of the corresponding borided sample. All measurements were performed with three replications.

Results and discussion

The results of the tests on the samples put to chemical heat treatment were processed and presented in Table 2.

The data in Tables 1 and 2 show that for high (20% and 15%) content of B_2O_3 the proportion B_2O_3 : Al is 2.0 : 0.7 to 0.93, which according to [8] guarantees the formation of a diffusion layer consisting only of iron borides with prevalence of FeB. The layers have the typical prickly structure and high adhesion to the metal base, which is also a guarantee for high corrosion resistance (low value of K, and high values for Z and γ).

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Table 2. Parameters of the formed diffusion layers

№	Composition of layers	structure	δ, μm	S, μm	K, mg/cm².h	Z, %	γ
1	FeB,Fe_2B,α-solid solution	Inglés	167±35	24,65	0,061	60,38	2,52
2	FeB,Fe_2B, α-solid solution	Inglés	182±28	18,22	0,085	44,8	1,81
3	FeB,Fe_2B, α-solid solution	Inglés	236±10	17,31	0,115	25,32	1,34
4	Fe_2Al_5 + (FeAl+Fe_3Al) + α- phase	homogeneous	138±21	11,42	0,054	60,97	2,85
5	aluminide phases	homogeneous	127±9	8,46	0,116	24,67	1,33
control	-	-	-	-	0,154	-	-

For a 10% content of B_2O_3 in the starting mixture the proportion B_2O_3 : Al is already 2 : 1.4, which according to [8] leads to the formation of a boron alitized diffusion layer with a predominance of boride phases (mainly Fe_2B and α-solid solution of boron in the iron). The diffusion layer obtained in the saturation has the prickly structure typical for the borides, uniform front of growth, and maximum thickness. According to the classification given in [1], this layer may be referred to the first type of boron alitized layers, slightly differing from the boride layer. The minimum amounts of Al, dissolved in the borides, are a probable reason for the reduction of the degree of adhesion and the decrease in the corrosion resistance (K increases to relatively high values, and Z and γ are substantially reduced).

For a 5% content of B_2O_3 in the aluminothermic mixture the proportion B_2O_3 : Al is 2.0 : 2.8, which according to [8] suggests the formation of a boron alitized layer dominated by the alitizing. The diffusion layer formed with this saturation has a significantly smaller thickness and is dense, homogeneous, with no prickly structure, with a white line on the part of the metal base. According to the classification given in [1], the main part of this layer consists of aluminide phases - Fe_2Al_5 + superstructures (FeAl+Fe_3Al)+α-phase. The white strip lying between the aluminide phases and the main metal is probably the boride phase represented by Fe_2B, with Al dissolved in it. Despite the smaller thickness and degree of adhesion, this layer is characterized by the highest corrosion resistance (lowest value of K and respectively, highest of Z and γ), thanks to its very good density and dual structure.

In the last case of diffusion saturation the mixture contains no B_2O_3, the saturation is with aluminum only, and the resulting layer is alitized layer. It is with the smallest thickness, smooth, lacking the prickly structure of the boride phases, and there is no white stripe to the metal base. The layer has a homogenous structure and uniform growth front, but also the smallest corrosion resistance. The reasons for this are probably the small thickness of the layer and the low degree of adhesion to the metal base.

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The results of the tests for corrosion resistance of the treated samples in 10% HCl show that after a 72-hour stay in the acid, the most resistant samples are those treated in mixtures №4 and №1, and the ones that corrode most quickly are those processed in mixtures №3 and № 5. Although the borided samples have high corrosion resistance, in case the samples remain in the corroding agent for a longer period of time the results are likely to be different. The reason is the different coefficient of expansion of the steel core and the boride layer. When cooled after the chemical heat treatment, the layer is put to tension, which may lead to its cracking. This layer is no longer a barrier to the corroding agent. The acid attacks the base metal rather than the boride layer. This is confirmed by the fact that the thickness of the boride layers separated from the main metal because of the corrosion, measured with a micrometer, is very close to the thickness of the layers determined by optical means on metallographic grinds of borided samples.

Conclusions

1. An aluminothermic diffusion saturation of samples of steel 45 was implemented in powdered mixtures containing minor amounts (below 20%) of B_2O_3 and variable ratios of B_2O_3 : Al, and the corrosion resistance of the resulting diffusion layers was studied.

2. It was found out that the best corrosion resistance in 10% HCl was shown by samples processed in a mixture with 20% of B_2O_3 (the layer is only composed of iron borides with prevailing FeB) and in a mixture with 5% of B_2O_3 (the layer consists of aluminide phases - Fe_2Al_5 + superstructures ($FeAl+Fe_3Al$)+α-phase).

References

[1]. Borisenok, G., Chemical-heat processing of metals and alloys, Directory, M., *Metallurgy*, **1981**, 296-312.

[2]. Chchłowski, M.; K. Przybyłowicz, M.; Chochlowska, Aluminotermiczne borowanie stali w proszkach, *Metaloznawstwo i obrobka cieplna*, **1986**, 79, 12-17.

[3]. Dimitrov, R., Inorganic Chemical Technology, Pigmalion, Plovdiv, **1995**.

[4]. Ivanov, R., Aluminothermic Diffusive Saturation of Steel 45 with Boron, *"Amtech`07"*, **2007**, 97-101.

[5]. Ivanov, R., Aluminothermic Diffusive Saturation of Steel with Boron and Aluminium, *Annual of Shumen University, XVIII B2, Faculty of Natural Sciences*, **2008**, 156-165.

[6]. Ivanov, R., Influence of the Mode and the Quantity of Alloyng Additions in Aluminothermic Boriding Mixtures on Indexes of the Obtainedd Boriding Layers, *"Unitech`08"*, **2008**, 2, 104-107.

[7]. Ivanov, R., Two-Component Diffusive Steel Saturation, *Materials and Manufacturing Processes*, 24 (7), **2009**, 894-897.

[8]. Ljahovich, L., et al., Multicomponent Diffusion Coating, *Naukovaja dumka*, *Minsk,* **1974**, 99-118.

[9]. Matuschka, A.; G. Kunzel, *Metall*, **1985**, 30(4), 336-338.

[10]. Raychev, R.; L. Fachikov; V. Zaprjanova, Corrosion and protection of the materials – *Handbook for laboratorial exercises, Sofia,* **2002**.

[11]. Uzunov, N.; R. Ivanov, Aluminothermic powder boriding of steel, *Applied Surface Science*, **2004**, 225, 72-77.

Acknowledgements

We would like to express our gratitude for the support of this work by research grant of FSI RD-08-266/10.03.2015 of Shumen University.

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DOI: 10.1515/asn-2016-0006