

PITTING STABILITY OF AISI 321 STEEL IN CHLORIDE CONTAINING MEDIA

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ABSTRACT

The influence of δ -ferrite amount ferrite in AISI 321 steel on its general corrosion, critical pitting temperature and potential in simulated circulating waters. The samples were made in the form of rectangular 3x3x1 mm parallelepipeds by cold mechanical method. Surface of the samples was subjected to electro-polishing. The amount of ferrite phase was determined by empirical formula. It was established, that after electromagnetic saturation of the samples, δ -ferrite content in five heats of AISI 321 steel was calculated. Research has shown, that δ -ferrite content varied from 0.099 smelting 4 to 0.36% by melting 2 and 3. It is established that the content of δ -ferrite in AISI 321 steel affects its pitting resistance in low-mineralized chloride-containing media. It is shown that in a chloride-containing solution with a pH of 4 and a chloride concentration of 600 mg / l, a parabolic dependence takes place between the ATP steel of AISI 321 steel and its δ -ferrite content. With an increase in the δ -ferrite content from 0.099 to 0.24% by volume, the critical pitting temperature of steel increases to 50.5 °C, and with a subsequent increase in the volume of δ -ferrite to 0.36% by volume, the critical pitting temperature of steel decreases to 44 °C.

Keywords: corrosion resistance, critical pitting temperature, chloride containing media, protective properties, AISI 321 steel.

INTRODUCTION

The corrosion-resistant steel AISI 321 is referred to austenitic class and has been alloyed on type 18-10, has a high corrosion resistant in many aggressive media, therefore it is often used for making capacitive and heat-exchange equipment. However, the circulating chloride-containing waters used in their work are often the cause of pitting, and subsequently their ulcerous corrosion [1-4]. Therefore a prediction of pitting-resistant steel AISI 321 in these media is the actual problem. In works [5-8] it was proposed to estimate a pitting-resistance of the corrosion-resistant steels and alloys

in chloride-containing media using critical values of their electrochemical potentials or $\Delta\phi$ -criteria. However, such approach to estimation of their pitting-resistance in practice was not effective because the parameters of chloride-containing medium used for electrochemical tests at times are differed from those, which are present in work of heat exchanger. The estimation of pitting-resistance of steel AISI 321 on critical temperatures of pitting-formation gave a possibility to predict its behaviour in model circulating waters, which on content of chlorides and pH are close to the conditions of exploitation of this equipment. In this case, the operating instructions of the heat exchangers provided information on the critical temperatures of pitting-formation (CTP) of steel in the model circulating waters with pH4...8 and concentration of chlorides from 350 to 600 mg/dm³. They were calculated using the established empirical dependences between CTP of steel and its chemical composition and structural heterogeneity in this model circulating waters [9-10]. However, this methodology of estimation of pitting-resistance of steel also has its defects connected with identification of metastable and stable pittings. Since these pittings were identified by geometrical features that are not stable and depend on parameters of medium and steel [11].

In works [12-15] it has been substantiated and proposed for the first time the identification of pittings, using the coefficients of selective dissolution of Cr. Later on, this criterion was universal and independent of mark of steel or alloy and parameters of chloride-containing medium. However, the influence of alloying elements and structure of steel AISI 321 on selective dissolution of metals in pittings, forming on its surface has not been investigated. Therefore, the work has been devoted to the solution of this problem, because the mechanisms of influence of steel parameters on corrosion losses in pittings will allow to optimize its composition and structure.

MATERIALS AND METHODOLOGY OF INVESTIGATION

The five melts of steel AISI 321 have been investigated. The chemical composition and structural heterogeneity was previously determined [9, 10]. The samples of the studied steel were sustained in chloride-containing solutions with pH4...8 and concentration of chlorides 600 mg/dm³ at temperature 343K for 240 hours. In this case in chloride-containing solutions with pH4; 5; 7 and concentration of chlorides 600 mg/dm³ on surface of the samples the stable, and with pH6; 8 – metastable pittings were formed. The pittings were identified on geometrical parameters [11] and coefficients of selective dissolution of Cr from (Z_{Cr}). In particular, if $Z_{Cr} < 1$, the steel pittings with formation of stable ones and, if $Z_{Cr} > 1$, – metastable pittings. The corrosion losses of Fe, Cr and Ni from surface of pittings were previously determined [12-15], using the methodology [12]. The empirical dependences between corrosion losses ΔCr , ΔNi , ΔFe of steel from pittings and its chemical composition and structural heterogeneity were determined in work [14], using correlation and regression analysis of the results of the investigation [20]. The direction of influence of the chemical composition and steel structure elements on its corrosion losses ΔCr , ΔNi , ΔFe from pittings are presented in Tables (1 – 3). In this case, in Tables there are only presented the direct proportional dependences between these values with significance level 0,10, which was estimated on t – Student's test.

RESULTS AND DISCUSSION

In the model circulating water with pH4 and concentration of chlorides 600 mg/dm³, where the steel AISI 321 pittings, a surface of the stable pittings is depleted with Fe, which can favor its diffusion from its volume. Under such conditions the corrosion losses ΔFe from pittings on steel surface grow in increase of volume of titanium nitrides and average diameter of austenite grain and also a decrease of content of Ni and volume of δ -ferrite (Tab. 1).

Table 1. Scheme of influence of the chemical composition and components of structure of steel AISI 321 on its ΔFe in the model circulating waters with concentration of chlorides 600 mg/dm³

Chemical composition and components of structure	pH of circulating water				
	4	5	6	7	8
C			↓	↑	↓
Si		↓	↓	↑	↓
Mn		↓			
Cr		↑	↑	↓	↑
Ni	↓				
N		↑	↑		
P					
V _H	↑	↓	↓	↑	↓
L _H			↓	↑	↓
V _{OK}			↓	↓	
L _{OK}			↑		↑
P α	↓				
d ₃	↑		↓	↑	↓

Consequently, Ni favors enrichment of surface of stable pittings of Fe. At the same time in increase of steel volume of titanium nitrides and average diameter of austenite grain a hard-phase diffusion of Fe atoms to surface of stable pittings near titanium nitrides located on boundaries of austenite grains is reinforced. This favors growth of ΔFe steel from pittings. However, an inclusion of δ -ferrite is the source of

origination of metastable pittings, which decelerates a growth of stable and favors decrease of ΔFe from them. This is agreed with data of work [15].

In the model circulating water with pH4 and concentration of chlorides 600 mg/dm³, where the steel pittings, a surface of stable pittings is enriched with Cr, which can favor its diffusion in volume of steel. Under such conditions the corrosion losses ΔCr from pittings on steel surface grow in increase of Mn content, volume of titanium nitrides, average diameter of austenite grain and decrease of content Ni in it (Tab. 2).

Table 2. Scheme of influence of the chemical composition and components of structure of steel AISI 321 on its ΔCr in the model circulating waters with concentration of chlorides 600 mg/dm³

Chemical composition and components of structure	pH of circulating water				
	4	5	6	7	8
C					
Si					
Mn	↑	↑	↑	↑	↑
Cr				↑	
Ni	↓	↓	↓	↓	↓
N				↑	
P		↓			
V _H	↑				
L _H		↓		↓	
V _{OK}			↓		
L _{OK}					
P _α				↑	
d ₃	↑				

Consequently, Mn favors depletion, and Ni – enrichment of surface of the stable pittings of Cr. In this case, the mechanism of influence of titanium nitrides and average diameter of austenite grain on ΔCr steel from pittings is analogous to mechanism of influence on ΔFe from pittings, which was considered above.

In the model circulating water with pH4 and concentration of chlorides 600 mg/dm³, where the steel is subjected to pitting formation, a surface of the stable pittings is depleted with Ni, which can favor its diffusion from steel volume. Under such conditions the corrosion losses ΔNi from pittings on steel surface grow in increase of Mn content, volume of titanium nitrides, average diameter of austenite grain in it and also decrease of Ni content and volume of δ -ferrite (Tab. 3).

Table 3. Scheme of influence of the chemical composition and components of structure of steel AISI 321 on its ΔNi in the model circulating waters with concentration of chlorides 600 mg/dm³

Chemical composition and components of structure	pH of circulating water				
	4	5	6	7	8
C			↑	↓	
Si		↓	↑		
Mn	↑		↓	↑	
Cr		↑			
Ni	↓			↓	
N					
P				↑	
V _H	↑		↑		↑
L _H					
V _{OK}			↑		
L _{OK}			↓		
P _α	↓		↑	↓	
d ₃	↑				↑

Consequently, Mn favors depletion, and Ni – enrichment of surface of the stable pittings of Ni. It should be noted that the mechanism of influence of titanium nitrides, average diameter of austenite grain and volume of δ -ferrite as well as their influence on ΔFe from stable pittings about which mentioned above. Such tendencies have been connected with that the atoms of less precious Fe activate the ionization of atoms of more precious Ni, which is agreed with data of work [13]. In this case, it should be

noted that the corrosion losses ΔCr of steel from pittings on rectilinear dependence grow from $275 \cdot 10^{-6}$ (melt № 4) to $3922 \cdot 10^{-6}$ mg (melt № 1) [14] in increase of volume of titanium nitrides from 0,23 (melt № 4) to 0,47 rev.% (melt № 1) and average diameter of austenite grain from 0,196 (melt № 5) to 0,312 mm (melt № 1) in it. At the same time the corrosion losses ΔNi of steel from pittings very intensively grow from $2755 \cdot 10^{-6}$ (melt № 3) to $21756 \cdot 10^{-6}$ mg (melt № 1) in increase of average diameter of austenite grain from 0,211 (melt № 3) to 0,312 mm (melt № 1) and volume of titanium nitrides from 0,40 (melt № 2) to 0,47 rev.% (melt № 1) in it [9], and ΔFe from pittings from $127 \cdot 10^{-6}$ (melt № 3) to $47528 \cdot 10^{-6}$ mg (melt № 1) [14] in increase of average diameter of austenite grain from 0,211 (melt № 3) to 0,312 mm (melt № 1), volume of titanium nitrides 0,40 (melt № 2) to 0,47 rev.% (melt № 1) in it [9]. In this case, in accordance with data [16], Mn and Ni content equally influence on intensity of ΔNi , ΔFe and ΔCr from pittings, and a volume of δ -ferrite on ΔFe and ΔNi . Thus, generalizing the above-mentioned one, it can be noted that such elements of steel structure as an average diameter of austenite grain, titanium nitrides and δ -ferrite largely influence on growth of the stable pittings than Ni and Mn, being austenite-forming elements of structure.

CONCLUSIONS

1. It has been established as a result of investigation of the mechanisms of influence of the chemical composition of steel AISI 321 and its structural incoherence on corrosion losses of ΔCr , ΔNi and ΔFe from metastable and stable pittings that they have been closely connected with characteristic peculiarities of the selective dissolution of these metals from their surface. In particular, a surface of metastable pittings is enriched with Fe and depleted with Cr and Ni and stable ones is enriched with Cr and depleted with Fe and Ni.

2. It has been established that in the model circulating water with pH4 and concentration of chlorides 600 mg/dm^3 , where the steel AISI 321 pittings with formation of the stable pittings, Ni favors enrichment of their surface by Fe, Cr and Ni, and Mn – depletion by Cr and Ni. At the same time it has been proved that the average diameter of austenite grain, titanium nitrides being a source of origination of stable pittings and δ -ferrite largely influence on intensity of growth of the stable pittings than Ni and Mn.

3. It has been revealed that in the model circulating water with pH5 and concentration of chlorides 600 mg/dm^3 , where the steel pittings with formation of the stable pittings, Si and Mn favor enrichment and Cr and N – depletion of their surface Fe. It has been shown at the same time that Ni and P favor enrichment and Mn depletion of surface of pittings of Cr. It has been established at the same time that Si favors enrichment and Mn – depletion of their surface by Ni. Thus, it has been proved that Cr and N favoring intensification of solid-phase diffusion of Fe atoms to surface of the stable pittings and Mn – Cr atoms accelerate their growth as Fe and Cr are the basic steel components. At the same time, the influence of structural heterogeneity of steel on growth of the stable pittings is less than Cr, N and Mn content in it.

ACKNOWLEDGMENTS

This work was supported by al-Farabi Kazakh National University, Institute of Experimental & Theoretical Physics by AP05130069 project “Development of nanotechnology for the synthesis of functional galvanic coatings for electrical equipment components.”

REFERENCES

- [1] Narivskiy, A., Atchibayev, R., Muradov, A., et al. Investigation of electrochemical properties in chloride-containing commercial waters // 18th Int.l Multidisc. Sc Geoconf. SGEM 2018. 18 (62).
- [2] Yar-Mukhamedova, G., Yar-Mukhamedov, E. Investigation of corrosion resistance of chrome based nano-composition coatings in the conditions of oil production // 12th Int.l Multidisc. Sc Geoconf. SGEM 2012. 12(56).
- [3] Muradov A., Korobova N. Impact of silver metallization and electron irradiation on the mechanical deformation of polyimide films /Technical Physics, 2017, Vol. 62, No. 11, pp. 1675–1678.
- [4] Darisheva A., Kasimzhanov K. Physicochemical Investigations of Scheelite Concentrate Decomposition // Eurasian Chemico-Technological Journal, № 17, p. 209–212, 2015.
- [5] Yar-Mukhamedova, G.Sh. Influence of thermal treatment on corrosion resistance of chromium and nickel composite coatings // Materials Science, 36, №6, P. 922-924, 2000.
- [6] Ved' M., Sakhnenko N., Nenastina T. et al. Electrodeposition and properties of binary and ternary cobalt alloys with molybdenum and tungsten // Appl. Surf. Sci., vol. 445, pp 298-307. 2018.
- [7] Yar-Mukhamedova, G.Sh. Investigation of corrosion resistance of metallic composite thin-film systems before and after thermal treatment by the "corrodokote" method // Materials Science. Vol.37, №1. - Pp.140-143. 2001.
- [8] Yar-Mukhamedova, G.Sh. Internal adsorption of admixtures in precipitates of metals // Materials Science. Vol.35(4), p.599-600. 1999.
- [9] Komarov Ph. , Ismailova G., Effect of thermal processing on the structure and optical properties of crystalline silicon with GaSb nanocrystals //Technical Physics. V. 60, N 9, P. 1348-1352 (2015).
- [10] Belyaev, D. V., Mussabek, G., Sagyndykov, A. et al. Modern state of composite coatings formation problem // 17th Int.l Multidisc. Sc Geoconf. SGEM 2017. 17 (61), 2017, Pp 233-240. 130800Fan
- [11] Muradov, A., Mukashev, K. et al. Mathematical model of composite materials formation // 17th Int.l Multidisc. Sc Geoconf. SGEM 2017. 17 (61), 2017, Pp 201-208. 130800
- [12] Aldabergenova, T.M., Kislitsin, S.B. et al. Effect of low-energy alpha-particles irradiation on surface structure and physical-mechanical properties

- [13] Yar-Mukhamedova, G.Sh. Investigation of the texture of composite electrodeposited chromium-carbon coatings // Materials Science. Vol. 36, №5, 2000.- Pp.752-754.
- [14] Yar-Mukhamedova, G.Sh. A mathematical model of formation of the structure of composite films by the cut-off method // Materials Science. Vol.36, No 4, p. 598-601.2000.
- [15] Muradov, A.D., Korobova, N.E., Kyrykbaeva, A.A. Influence of γ -Irradiation on the Optical Properties of the Polyimide–YBa₂Cu₃O_{6.7} System // Journal of Applied Spectroscopy. 2018.