

Structure Formation and Corrosion Resistance of Austenitic Steel Treated with High-Temperature Energy Sources

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Abstract

The results obtained in investigations of stress corrosion specimens of 08Cr18Ni10Ti steel, produced by welding with electrodes with basic and rutile coatings, are discussed. We present the results of metallographic analysis of the surface of corrosion failure. Investigation of stress corrosion cracking tests performed by automatic measurement of deflection patterns, depending on the test time, using the displacement sensor. We found that two structural factors – structure homogeneity of weld metal and morphology of non-metallic inclusions – provide high corrosion resistance. The experimental results show that the metal of the welded joints in the high-alloy chromium-nickel austenitic steels produced with the electrodes with a basic coating has higher resistance to corrosion failure in the corrosive medium of chloride salts in comparison with the weld metal produced with the rutile electrodes.

Keywords: high-alloy steel, weld, joint, electrodes, structure formation, non-metallic inclusions, corrosion resistance

1. Introduction

The problem of the corrosion resistance of constructions in a production environment is a relevant and important within the implementation of many technological processes. Structure and properties of products produced of high-alloy corrosion resistant steels are strongly dependent on processing by high-temperature energy sources: plasma, laser surface treatment, arc welding, electron beam treatment (A.G. Aleksandrov, Yu. N. Savonov, 1992).

Welded joints in high-alloy steels are characterized by the highest rate of corrosion failure in comparison with the parent metal because of the high electrochemical heterogeneity, determined by the heterogeneity of the chemical composition of the weld metal, structure, properties and the stress state.

The corrosion-resisting austenitic steels have a wide range of use because of high resistance to general corrosion. However, equipment made of these steels can be damaged in service and fail as a result of the fact that the austenitic chromium–nickel steels are highly susceptible to corrosion cracking in the solutions of chlorides and alkali. In this case, failure starts without any visible traces of corrosion. Depending on the corrosive strength of the medium and the magnitude of the residual and working stresses, the rate of propagation of corrosion cracks may change in a wide range, from several hours to several years. Failure is sudden. The welded joints contain a large number of corrosion cracks (G. M. Reddy, K. S. Rao, T. Sekhar, 2008; Fadhil Sarhan Kadhimi, 2011; Triyono, Jamasri, M. N. Ilman & R. Soekrisno, 2012).

The main reason for failure of pipelines, equipment in chemical industries and heat carriers is corrosion failure formed as a result of the combined effect of residual welding stresses and chemical substances which are in most cases corrosive.

Durability to different kinds of corrosion is the main requirement submitted to weld construction of high alloyed austenitic steels. Intergranular corrosion can appear either in the weld metal or in the parent metal near the weld line and at some distance from the weld in zone of temperature influence. The mechanism of appearance of those types of corrosion is similar but the reasons of appearance of intergranular corrosion are different. Intergranular

corrosion of weld metal occurs because of precipitation of chromium carbides from austenite that leads to dechromized border volumes of grains. The main reasons of that are the high content of carbon in the weld metal and the lack of or insufficient content of titanium and niobium.

Weld resistance against intergranular corrosion decrease as a result of prolonged treatment by heat in unfavorable thermal cycle of welding or exploitation. Length of the grain boundaries increasing due to grain refinement increases the surface area, on which carbides are allocated. Emitted carbides are more dispersed and local integration of grain volume by chrome occurs at a smaller depth. Moreover the processes of diffusion in ferrite goes much faster that makes faster the process of equalization of chromium concentration in dechromized border and central parts of the grain.

Intergranular corrosion of parent metal connected with welding thermal cycle.

General corrosion, i.e. dissolving a metal in a corrosive environment, can occur in the weld metal or in the parent metal and at some distance from the weld in zone of temperature influence as well as intergranular corrosion. In some cases one can observe uniform general corrosion of parent metal and weld metal.

There is one more type of corrosion failure – corrosion cracking that occurs under the processes of tensile stresses and aggressive medium at the same time. Destruction growing both intergranular and transgranular. One of the main measures of elimination this type of corrosion is decreasing of residual welding stresses.

Another problem of welding high alloy austenitic steels is the tendency to form hot cracks during welding. They can occur as microcracking and as visible cracks. Hot cracks can appear within heat treatment as well as exploitation process at hot temperature.

Weld metal characterized by cellular-dendritic forms of crystallization that leads to formation of large columnar crystals and enrichment of interdendritic sections by low melting phase with sulfur. In austenitic welds dendritic structure is the most clear.

Applying methods of grinding crystals and removal of dendritic structure increases weld resistance against hot cracking. One of such methods is obtaining weld with some δ -ferrite in structure. Positive effect of δ -ferrite in austenitic-ferritic weld is connected with changing the mechanism of crystallization and better solubility of liquating phase with sulfur in ferrite. Contemporaneous crystallization of austenite and δ -ferrite crystals from liquid phase leads to grinding and disorientation of dendrites. The probability of hot cracks formation decreases as a result. Obtaining of austenitic-ferritic structure achieved by extra alloying of chrome, aluminum, molybdenum et al.

In this article, we examined the features of the structure of weld joints of high alloyed austenitic steels, made by electrodes with different types of coatings – rutile and basic, namely austenite homogeneity and presence of non-metallic inclusions. Heterogeneity of weld joints structural composition of high austenitic steels causes heterogeneity properties, high localization of stress state and the most intense corrosion fracture in contradistinction to the parent metal.

Establishing the structural dependence of welds properties works (E.A. Krivonosova E.A. Sinkina, 2014; E.A. Krivonosova, E.A. Sinkina, A.I.Gorchakov, 2013) were taken into account. Those works shows that two structural factors are essential – structure homogeneity of weld metal and morphology of non-metallic inclusions (softens carbonitride and dispersed intermetallic).

2. Materials and Methods of Research

The subject of research was weld metal of steel AISI 321 (08Cr18Ni10Ti) obtained by manual arc welding with different types of coatings: basic B (01Cr20Ni10Mn2Nb) and rutile R (02Cr20Ni10Mn2). One should know that for high alloy steel welding it's necessary to use electrodes to ensure minimum carbon content in the weld metal.

Influence of electrode coating on structure and fracture of the weld metal is very important, as it is shown in (E.A. Krivonosova, E.A. Sinkina & A.I.Gorchakov, 2013; E.A. Krivonosova, 2005). It is also necessary to take into account a significant difference in alloyage systems of compared electrodes: unstabilized low carbon rutile coating and niobium stabilized basic coating. The following table 1 shows a typical weld metal chemical composition of matched electrodes.

Table 1. Weld metal chemical composition

Electrodes	Chemical composition of weld metal, % mas.								Ferrite content, %
	C	Mn	Si	Ni	Cr	S	P	Nb	
Basic coating (B)	0,10	1,8	0,53	9,8	20,8	0,011	0,020	0,99	2,5-10
Rutile coating (R)	0,03	0,8	0,8	10,0	19,5	0,030		0,01Ti	5-9

2.1 Methods of Stress Corrosion Cracking Tests

Stress corrosion cracking tests was a tool in investigation of the corrosion resistance.

To investigate the corrosion resistance were carried out on stress corrosion cracking tests. We conducted tests in special four-bearing arrangement brackets to provide the desired level of tensile stresses due to the creation of permanent deformation. Loading scheme for testing samples for corrosion cracking and stress diagram is shown in Figure 1.

Devices are made of steel 12X18H10T. The specimen were isolated from the device by pads of fluoroplastic. Test of samples were carried out at a tensile stresses equal to 60% of the tensile strength of test steel. Measure the deformation of the sample is the deflection f .

Deflection (maximum deflection in the middle of the specimen) depending on the desired tensile stresses was calculated as follows:

$$f = \frac{\sigma (3l^2 - 4a^2)}{12hE}, \quad (1)$$

where f - deflection, mm;

σ - predetermined tensile stresses, MPa;

E - modulus of elasticity, MPa;

h - thickness of specimen, mm;

l, a - the distance between supports mm ($l = 0,09\text{m}$, $a = 0.03\text{ m}$).

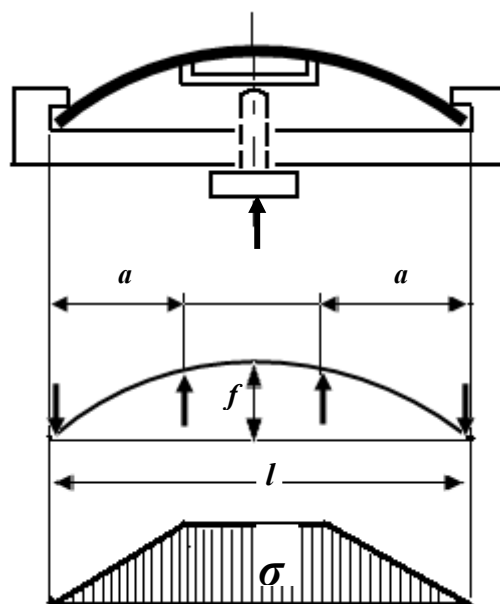


Figure 1. Scheme for testing specimen for corrosion cracking and stress diagram

Investigation of stress corrosion cracking tests performed by automatic measurement of deflection patterns depending on the test time, using the displacement sensor.

Kinetic curves of specimen destruction were constructed via MathCAD Professional in following coordinates: a change in deflection (Δf) from the time of the test (t).

2.2 Methods of Electrochemical Corrosion Tests

The electrochemical corrosion tests were carried out in a boiling solution of a mixture of salts $MgCl_2$, $NaCl$ and KCl for 600h.

We chose the option of aggressiveness level according to following condition: aggressiveness of medium has to be not less than real aggressiveness of environment in which test materials will serve.

After the tests specimen were cut in the transverse direction for metallographic evaluation of the depth and character of corrosion failure.

3. Results of Research

Chemical and phase analysis established the presence of titanium carbides in the weld made with rutile electrodes and the presence of niobium carbide in the weld made with basic electrode (Table 1).

Moreover, these researches shown that crystallization of weld metal at the same time is accompanied by softening of nonmetallic inclusions, exogenous and endogenous nature. Inclusion of an exogenous nature, mainly oxides of complex composition, appear due to incomplete oxidation-reduction reactions in the weld pool with components of coating.

Figure 2 shows the structure of weld metal cross-sections. Welds are layered, zone of temperature influence is clearly visible.

The welded joint, produced with the R electrodes with a rutile coating, has a non-uniform structure. The structure of the weld metal, produced with the B electrodes with the basic coating is more homogeneous throughout the entire welded joint. Evidently, this is explained by the modifying and stabilizing effect of niobium transferred into the welded joint from the electrode coating.

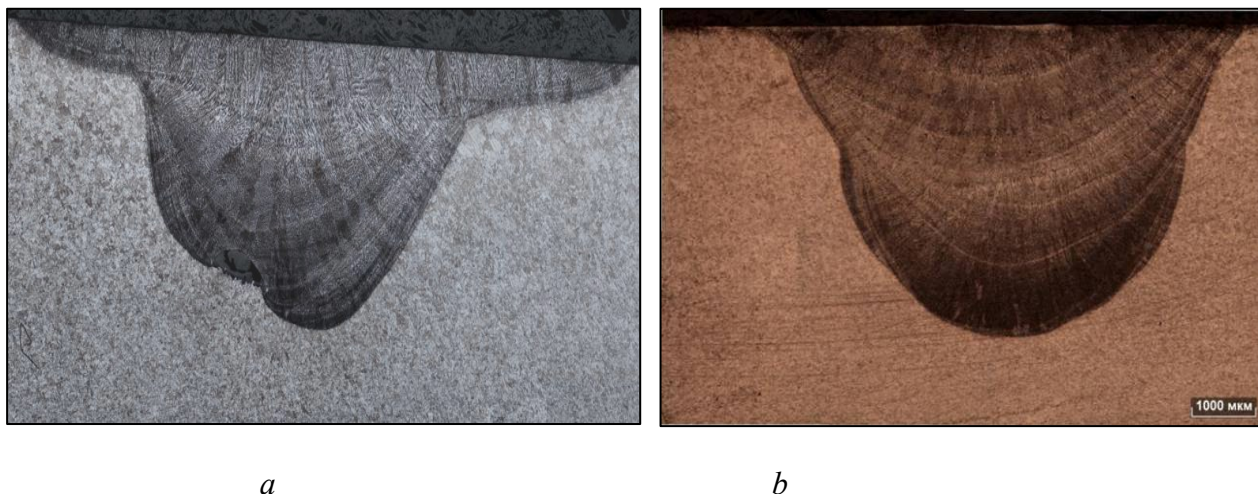


Figure 2. Cross-section of the welding joint of electrodes with rutile (a) and basic coating (b)

Figure 3 shows the microstructure of welding joints produced with rutile and basic coated electrodes. Comparison of fragments Figure 3 shows that structure of welding joint of rutile electrodes is finer (see Figure 3a) than structure of welding joint of basic electrodes (see Figure 3b). In addition, for joints with basic coated electrodes can be traced sharp structural disorientation in the direction of crystallites growth on axes, which is not observed in the weld metal rutile electrodes. While welding high-alloy steel by rutile electrodes type the main role in structure formation plays process of welded joint metal modifying by titanium. Carbonitride phase of titanium modifies the structure inhibiting crystal growth of the austenite, that leads to suppression of a larger structure formation. In the case of welding by base coating electrodes the structure in general is larger in comparison with the structure of the seam of rutile electrodes as modifying effect manifests itself in less degree.

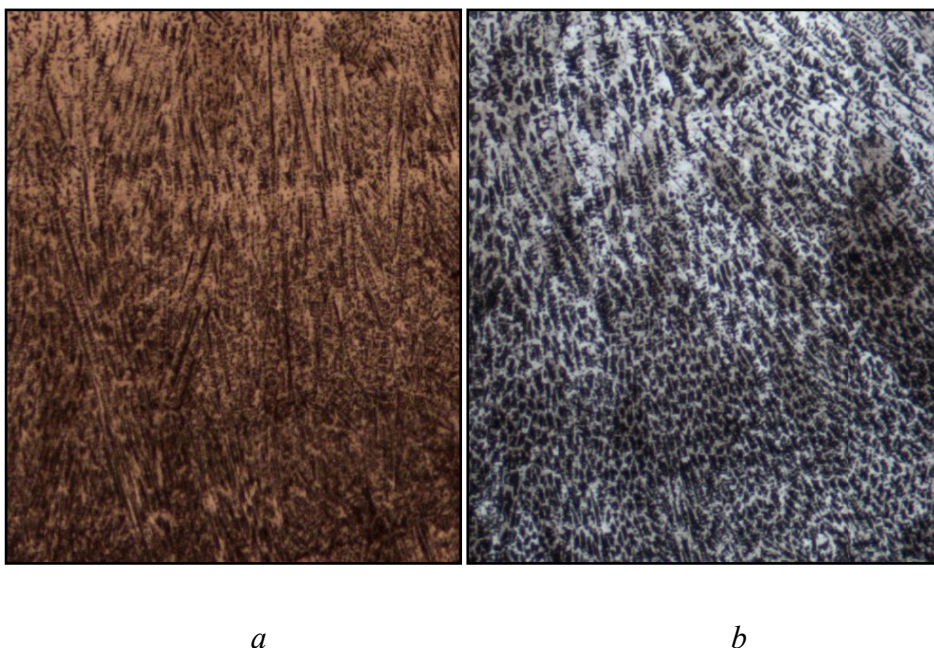


Figure 3. The structure of the weld joint of the electrode with basic type of coating (a) and rutile type coating (b), x 1000

Figure 4-5 shows compared level of contamination by nonmetallic inclusions welding metal samples with rutile and basic coating.

As Figure 4-5 shows, metal joint welded by the rutile electrodes has large inclusions of up to 30 microns.

Statistical processing of the images showed that the average number of inclusions in the field of view of the metal joint welded by the rutile electrodes on 86% more than in the samples, produced with the basic electrode (see Figure 6).

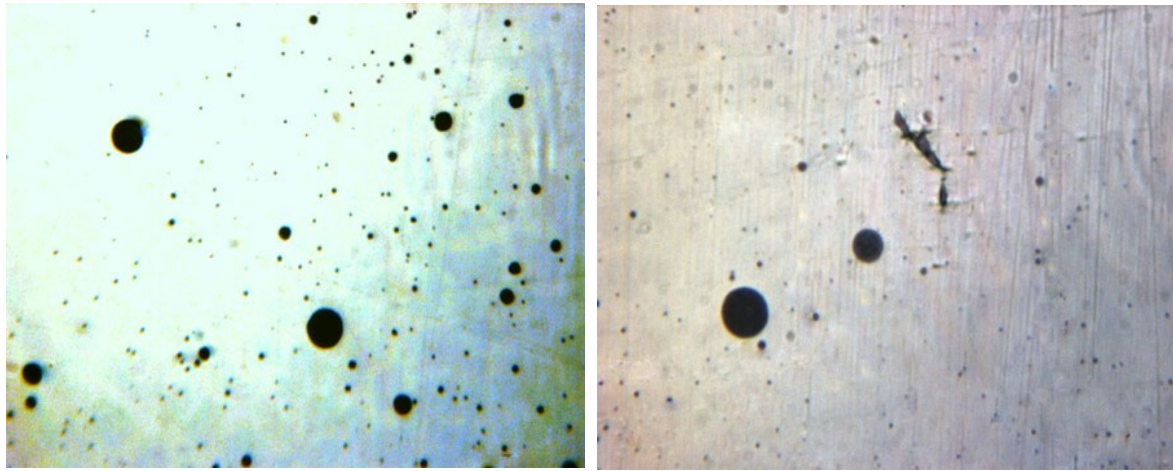


Figure 4. Non-metallic inclusions in the structure on the cross-sections of the samples, produced with rutile type electrodes, x 450

Thus, these researches confirm the predominant effect of modifying welding metal of high-alloy steel by titanium, introduced through the electrode coated welding by rutile type electrodes.

Obviously, finely dispersed parts of titanium carbonitride phase modify the structure in the solid state, inhibiting the growth of austenite crystals and suppressing formation of large-scale structure, what consents with researches of microstructure. Modification process plays leading role in the structure formation, but the level of contamination of non-metallic inclusions in these joints is high enough.

Structure formation of welding metal of basic type electrode coating accompanied by increased effect of deoxidation, so that the level of contamination by nonmetallic inclusions are significantly lower.

The obtained regularities of structure formation in high-alloy steels welding confirmed by results of researches of joints corrosion resistance, which is one of the most structure-sensitive properties (E.A. Krivonosova & E.A. Sinkina, 2014).

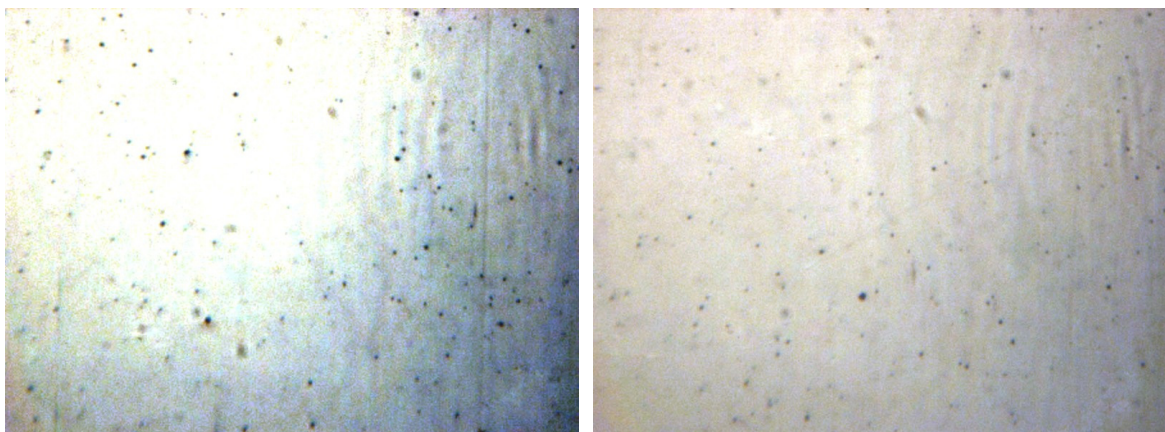


Figure 5. Non-metallic inclusions in the structure on the cross-sections of the samples, produced with basic type electrodes, x450.

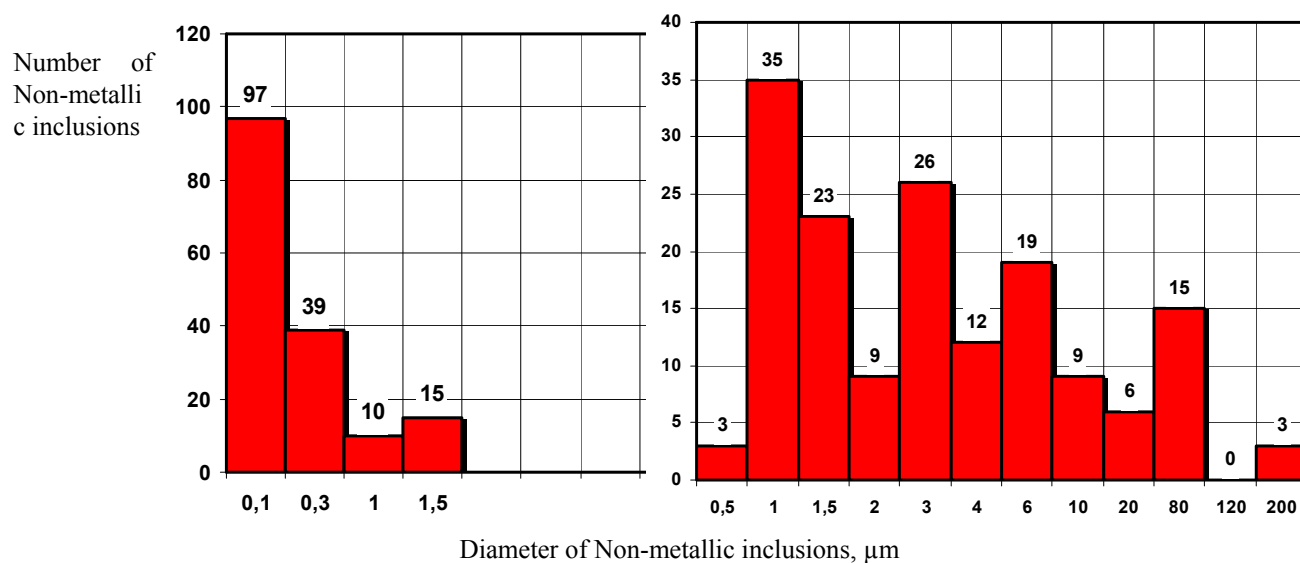


Figure 6. Statistical analysis of non-metallic inclusions contamination of the weld joint produced with the basic (a) and rutile (b) coating electrodes (thin section $0,001\text{mm}^2$ area.)

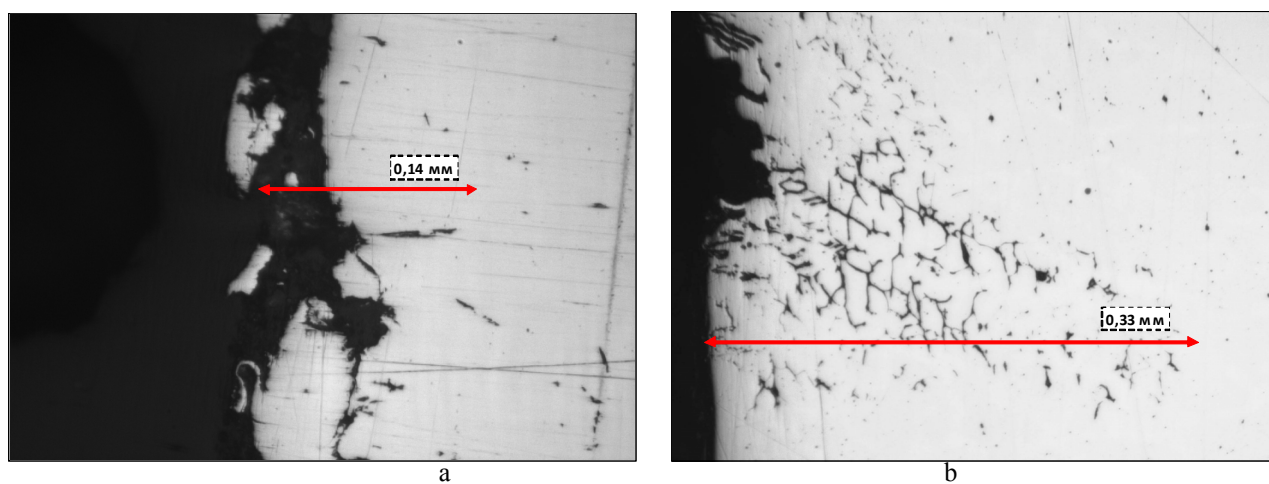


Figure 7. The depth of corrosion failure of the weld joint produced with the basic (a) and rutile (b) coating electrodes

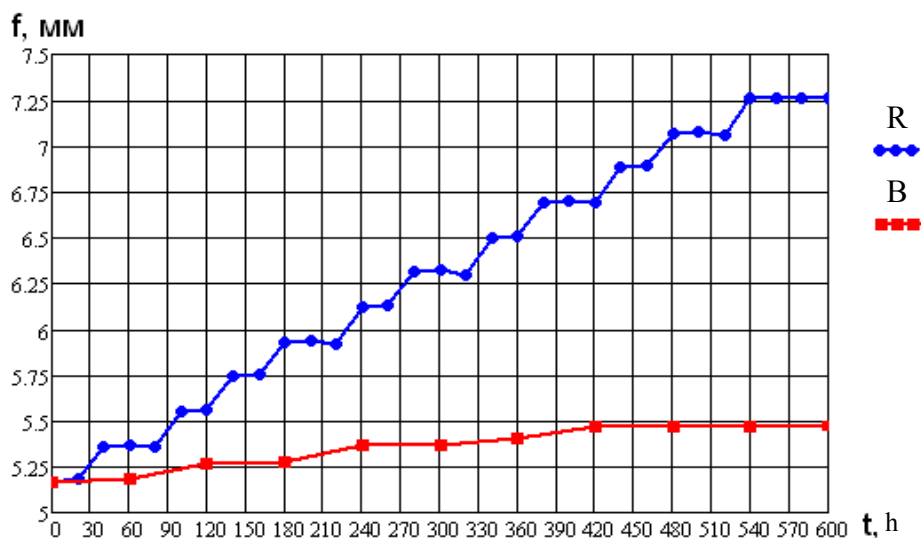


Figure 8. The dependence of the deflection (f) from the time of the test (t) on stress corrosion cracking tests of the weld produced with the basic (B) and rutile (R) coating electrodes

Analysis of the samples without etching showed that welds made by the rutile coating electrodes have a depth of corrosion failure 0.28 – 0.33mm. This is 2 times greater than the depth of corrosion cracking of the welds made by the basic coating electrodes – 0.07 – 0.14 mm (Figure7).

The failure of the welded joints, produced with the rutile electrodes, takes place strictly along the grain boundaries, i.e. intergranular failure takes place. Centers of corrosion damage are zones of heterogeneous structure of the weld. In heterogeneous metals corrosion is local covering separate anode areas of the surface with the lower value of the electrode potential. phases and grain boundaries can appear as the anode section, while the grains themselves are cathodes. In this case the most dangerous type of corrosion takes place - intergranular corrosion. It is almost invisible from the surface and extends into the metal at the grain boundaries. Potential difference of the individual components of the microstructure contributes to galvanic corrosion. Intergranular corrosion of high-chromium steel is caused by release of carbides in the grain boundary at high temperatures. These carbides are formed due to the diffusion of carbon from the total volume of grain and chrome - only from the border areas. Carbon moves interstitial with diffusion mechanism (mechanism for implementation), which is characterized by a high mobility in comparison with the movement of atoms with the mechanism of substitution. This leads to decrease of chromium content in the border areas below its critical concentration of 12-14% and an abrupt drop in the electrode potential from +0.2 to -0.6 V. Grain boundaries becomes anode relatively to the metal within the grains.

In failure of the welded joints, produced with the basic electrodes, two mechanisms of damaging takes place: continuous surface corrosion and subsurface failure (like pitting). One can see that continuous surface corrosion is uneven, so that the rate of corrosion varies on the surface of certain areas. Subsurface corrosion is characterized by defects on the surface and further can spread under the surface to a depth of 0,07- 0,14mm (subsurface rupture). Subsurface corrosion often causes swelling and delamination of the metal. It's possible to define it only with the help of microscope.

Investigation of stress corrosion cracking tests performed by automatic measurement of deflection patterns depending on the test time, using the displacement sensor. Kinetic curves of specimen destruction were constructed via MathCAD Professional in following coordinates: a change in deflection (f) from the time of the test (t). (Figure 8)

One can see that the kinetic curves of failure of the specimens, produced with the electrodes with different types of coating, differ quite considerably. This fact matches the results of the previously described qualitative analysis of corrosion failure. The welded joint produced with the electrodes with a rutile coating is characterized by a higher corrosion rate, and the nature of failure and increase in the deflection has discrete stepped form. In the welded joint produced with the electrodes with the basic coating, the deflection increases smoothly at a lower rate.

4. Conclusions

1. While welding high-alloy steel AISI 321 (08Cr18Ni10Ti) by rutile electrodes type the main role in structure formation plays process of welded joint metal modifying by titanium. Obviously carbonitride phase of titanium modifies the structure inhibiting crystal growth of the austenite, that leads to suppression of a larger structure formation.
2. However, in joints made with rutile type electrodes there is a fairly high level of contamination of non-metallic inclusions, that is connected with insufficient amount of manganese in the weld as the main element of refining.
3. The formation of the weld metal made of basic electrodes accompanied by increased effect of reducing and refining, so that the level of contamination of non-metallic inclusions are significantly lower. However, in this case, the structure in general is larger in comparison with the structure of the seam of rutile electrodes as modifying effect manifests itself in less degree.
4. Size of non-metallic inclusions in welds produced with the rutile type electrode varies over a wider range in comparison to joints produced with the basic type electrodes, while the total number of inclusions in joints made with rutile coating is greater than about 80%.
5. The failure of the welded joints, produced with the rutile electrodes, takes place strictly along the grain boundaries, i.e. intergranular failure takes place. The failure of the welded joints, produced with the basic electrodes takes place by two mechanisms: continuous surface corrosion and subsurface failure.
6. Welds produced with the rutile electrodes have a depth of corrosion destruction 0.28 – 0.33mm. This is 2 times greater than the depth of corrosion cracking of the welds produced with the basic coating electrodes – 0.07 – 0.14 mm. The rate of corrosion damage are 0.9 for basic and 3.65mm / year for electrodes with rutile.

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