CORROSION OF X2CrNiMoSi18-5-3 DUPLEX STAINLESS STEEL

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Abstract. Duplex stainless steels offer economical properties of strength and corrosion resistance. There are ferritic-austenitic stainless steels popular as construction materials used in industrial applications. The fraction of each phase is approximately 50 %. These steels present excellent corrosion resistance of austenite steel, and high mechanical behaviour of ferrite steel. General important corrosion problems in duplex stainless steels at 475 ºC have already been detected. Although the worst temperature is 475 ºC, corrosion can still form at temperatures lower or higher. The corrosion resistance depends on increasing the chromium content and morphology of the microstructure, the percentage of each phase, so the properties depend on the composition, technological processes and heat treatments. However, the performance presented by duplex stainless steels can be drastically reduced if undesirable phases, such as the sigma phase, chi phase, secondary austenite and a lot of rich chromium and carbides precipitates. The purpose of this work was to ascertain how 30-minutes isothermal heat treatments at 530 ºC and corrosion time effect the relative mass loss and profile roughness parameters of X2CrNiMoSi18-5-3 duplex stainless steel. The influence of boiling nitric acid on the steel corrosion resistance was investigated using weight loss and profile roughness parameters.

Keywords: stainless steel, duplex steel, corrosion, corrosion rate, profile roughness.

Introduction

The first stainless steels were developed almost hundred years ago. Mainly grades of these steels are ferritic, austenitic and martensitic steel microstructure. In 1930's from a mistake in the melt shop in adding too much chromium to austenitic steel two-phase (ferritic-austenitic) duplex steel was melted. High chromium and molybdenum contents provide excellent resistance to pitting and crevice corrosion. For the most part, the corrosion resistance of a welded joint is slightly lower than the parent material [1-7].

Duplex stainless steels are among the most popular construction materials. They are used in a wide range of industrial applications, but their properties are continuously studied to improve the quality of the properties. Low maintenance costs and very high material circulation, good environmental reasons for using will be further important arguments to enhance the selection of these steels. It is of great importance to have duplex steels readily available to fabricators and end users. Because of this skilled technical support, well known properties in different temperatures are required to widen the application areas of duplex steels [8-13].

Duplex and superduplex stainless steel has equal amounts of two phases: ferrite and austenite. The microstructure and utility properties of steels are determined by phase transformation during thermal processing [14-15]. While the phase relationships during the manufacturing process are user-independent, then the range of stability or volume fraction of each with phases depends on individual maintenance (mainly thermal conditions). The percentage of each phase depends on the composition, technological processes, heat treatments and critical cooling rate obtained with the manufacturing method applied [16-24].

General important corrosion problems in duplex stainless steels at 475 ºC have been already detected. Although the worst temperature is 475 ºC, corrosion can still form at temperatures lower or higher. There steels are more prone than austenitic steels to precipitation of phases causing embrittlement and reduced corrosion resistance. The formation of intermetallic phases such as the sigma phase occurs in the temperature range 600-950 ºC and reformation of ferrite occurs in the range 350-525 ºC (530 ºC embrittlement). However, the performance presented by duplex stainless steels can be drastically reduced if undesirable phases, such as the sigma phase, chi phase, secondary austenite and a lot of rich chromium and carbides precipitates. Sigma phase is rich in chromium and molybdenum is formed by ferrite decomposition, in the temperature over 500 ºC. In normal alloying, heat-treatment or welding processes the risk of embrittlement is not to high [8; 12; 25]. However a risk exists, for example, in the failure that can arise during operation causing overheating, especially if cooling is slow. Generally, the higher the superheating temperature, the higher the ferrite content. However, steel must be heated to a very high temperature to become completely ferritic. Then heat

treatment processes, for both solution annealing and stress relieving, are advisable at certain temperatures with subsequent rapid cooling in water [2; 7; 26]. A lot of authors report that corrosion resistance of stainless steels depends on rich chromium precipitates in microstructure [2; 3; 20; 26].

The purpose of this work was to ascertain how 30-minutes isothermal heat treatments at 530 ºC and corrosion time effect the relative mass loss and profile roughness parameters of X2CrNiMoSi18-5-3 duplex stainless steel.

Materials and methods

The experiment was performed with duplex stainless X2CrNiMoSi18-5-3steel. The chemical composition of the X2CrNiMoSi18-5-3steel is presented in Table 1.

Table 1

Chemical composition of the X2CrNiMoSi18-5-3steel

Mean chemical compositions, wt. %								
C	Si	Mn	P	S	Cr	Mo	Ni	N
0.02	1.6	1.53	0.02	0.001	18.46	2.82	4.92	0.07

Before the experiments, the specimens with an area of 13 cm^2 (4 x 1 x 0.5 cm) were successively polished with 400 grades of emery paper, next mechanically cleaned with 95 % alcohol.

The samples were held at a temperature of 530 ºC by 30 minutes and cooling down on air. Accordance with the standard PN EN ISO 3651-1, Determination of resistance to intergranular corrosion of stainless steels. Part 1: Austenitic and ferritic-austenitic (duplex) stainless steels. Corrosion test in nitric acid medium by measurement of loss in mass (Huey test), corrosive media were represented by boiling nitric acid V 65 %.

The samples of X2CrNiMoSi18-5-3steel (about 10 mg) were analyzed using Dynamic Scanning Calorymetry measurement by NEITSH DSC204 F1 Phoenix and DSC/dt in nitrogen atmosphere (with a constant flow of 20 ml·min^{-1}) using Neitsch-Proteus 5.1 software. DSC measurements were carried out in a temperature range (20-610 ºC) with a heating rate of 10 ºC·min^{-1}.

The corrosion rate of the X2CrNiMoSi18-5-3steel measured in mm·year^{-1} was calculated with the use of the below formula (1), but measured in g·m^{-2} were calculated with the use of the below formula (2):

$$r_{corm} = \frac{8760 \cdot m}{S \cdot t \cdot \rho},$$ (1)

$$r_{corg} = \frac{10000 \cdot m}{S \cdot t},$$ (2)

where t – time of treatment in a corrosive solution of boiling nitric acid, hours;
S – surface area of the sample, cm^2;
m – average mass loss in the boiling solution, g;
ρ – sample density, g·cm^{-3}.

The influence of boiling nitric acid on the X2CrNiMoSi18-5-3steel corrosion resistance was investigated using the weight loss. The mass of the samples was measured by Kern ALT 3104AM general laboratory precision balance with accuracy of measurement 0.0001 g.

Profile roughness parameters were analyzed according to the PN-EN 10049:2014-03 standard (Measurement of roughness average Ra and peak count RPc on metallic flat products) by the Diavite DH5 profilometer.

Results and discussion

The microstructure of raw X2CrNiMoSi18-5-3steel is presented in Fig. 1. The effect of hot rolling on the phase orientation presents the elongated austenite phase (white area) at the background of the ferrite (gray area). Dynamic Scanning Calorimetry curves of heating measurement from 400 to 600 ºC

(according to literature – embrittlement temperature of 530 ℃) of duplex steel for heating rate 10 ℃·min^{-1} as an example is presented in Fig. 2.

Fig. 1. **Microstructure of raw X2CrNiMoSi18-5-3 rolled duplex steel: light etched austenite and dark etched ferrite**
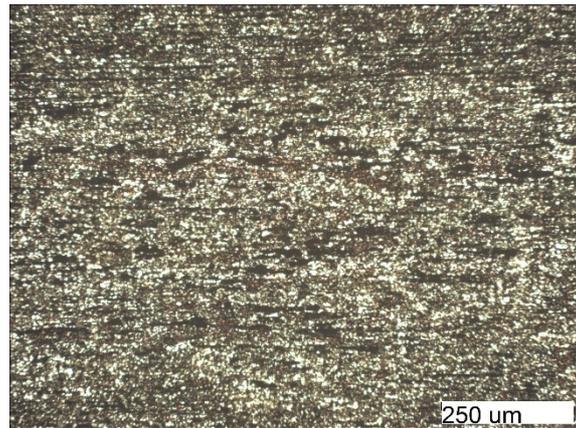

Fig. 2. **Surface of X2CrNiMoSi18-5-3 steel annealed at 530 ℃ by 30 minutes and cooling down on air after corrosion tests in boiling HNO₃ for boiling time 288 hours**

The rolling of X2CrNiMoSi18-5-3duplex steel forms a fine elongated lamellar structure of light etched austenite and light etched ferrite phase (Fig. 1). The annealed of X2CrNiMoSi18-5-3 steel at 530 ℃ by 30 minutes and cooling down on air does not sharply change the microstructure (Fig. 2).
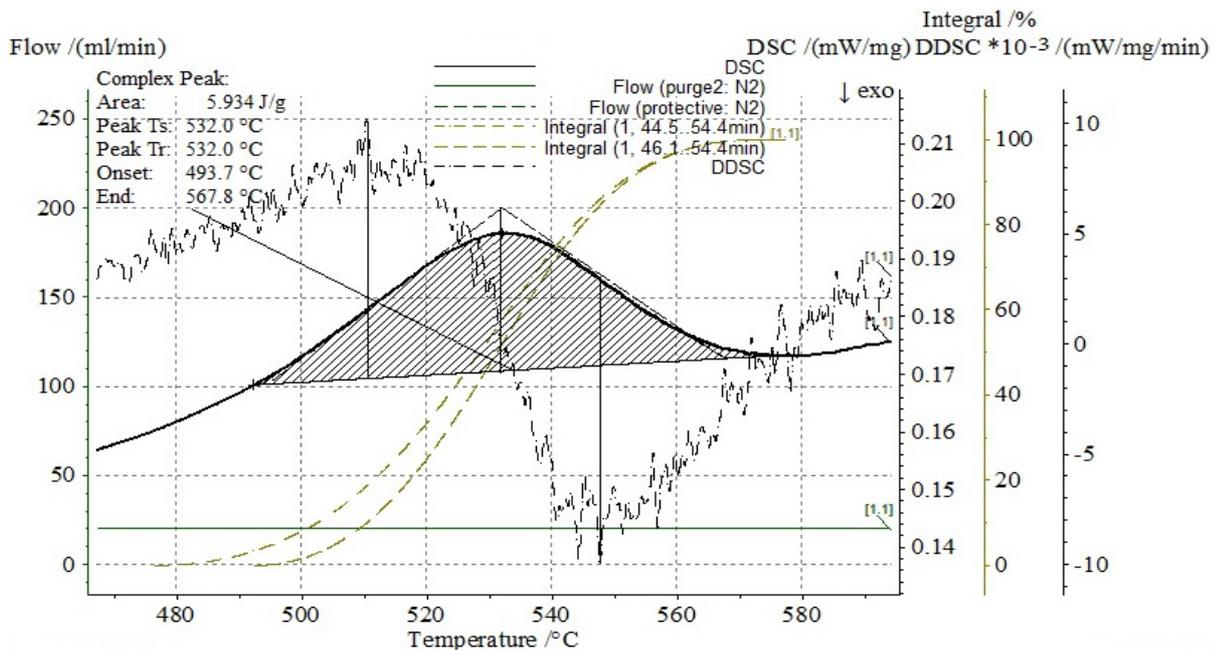

Fig. 3. **Heating curve of X2CrNiMoSi18-5-3steel, static nitrogen atmosphere, cooling rate 10 ℃·min^{-1}**

For this sample C_p is about 0.032 J·(gK)$^{-1}$. The endothermic peak (Fig. 3) involving 5.9 J·g^{-1} of reaction enthalpy with a T_{onset} at about 494 ℃, T$_{end}$ at about 568 ℃ and T_{peak} about 475 ℃ according to literature [2; 7; 11; 19] represents dissolving of chromium-rich α'-phase. The reformation of ferrite occurs in the range 350-525 ℃ determining the 475 ℃ embrittlement. But the particular temperatures depend on the heating rate of steel.

Profile roughness parameters of X2CrNiMoSi18-5-3steel are presented in Fig. 4. Profile roughness parameters of X2CrNiMoSi18-5-3steel with: R_a – arithmetic average of absolute values (µm), R_p – maximum peak height (µm), R_q – root mean squared (µm), R_t – Maximum Height of the Profile (µm) after corrosion tests in boiling HNO₃ for different boiling time are presented in Fig. 5, regression equation and correlation coefficient r at (3-6):

$$R_a = 0.0063 \cdot t + 2.4964 \text{ and } r = 0.9839, \tag{3}$$

$$R_q = 0.008 \cdot t + 3.2328 \text{ and } r = 0.9909, \tag{4}$$

$$R_t = 0.0002 \cdot t^2 - 0.023 \cdot t + 23.1 \text{ and } r = 0.9934, \tag{5}$$

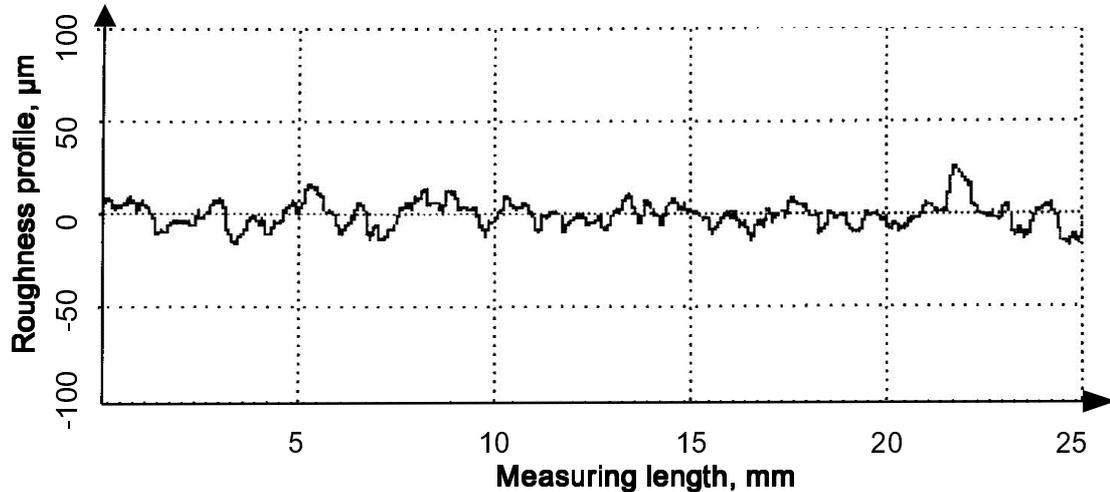$$R_p = 7 \cdot 10^{-5} \cdot t^2 - 0.0003 \cdot t + 22.4 \text{ and } r = 0.9772. \tag{6}$$

Fig. 4. **Profile roughness of X2CrNiMoSi18-5-3steelannealed at 530 ºC for 30 min and cooling down on air after corrosion tests in boiling HNO₃ for boiling time 432 hours**
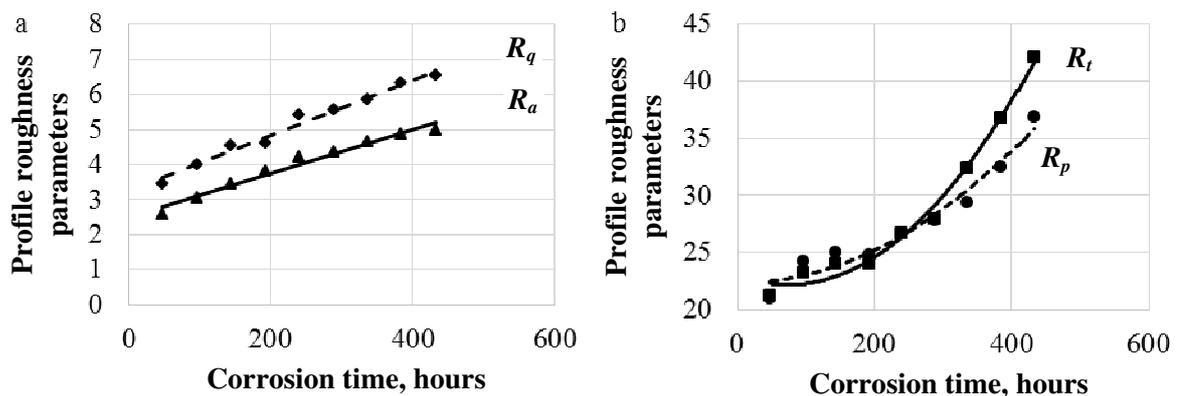

Fig. 5. **Profile roughness of X2CrNiMoSi18-5-3steel annealed at 530 ºC for 30 min and cooling down on air after corrosion tests in boiling HNO₃ for different boiling time:**
a) R_a – arithmetic average of absolute values, µm; R_q – root mean squared, µm;
b) R_p – maximum peak height, µm; R_t – maximum height of the profile, µm

Percentage effects of corrosion time on the relative mass loss (RML) of X2CrNiMoSi18-5-3steel annealed at 530 ºC by 30 minutes and cooling down on air arepresented in Fig. 6, regression equation and correlation coefficient r at (7).

$$RML = 0.27 \cdot t + 17.7 \text{ and } r = 0.9948. \tag{7}$$

Effects of the corrosion time on the corrosion rate measured in mm per year of X2CrNiMoSi18-5-3 steel annealed at 530 ºC by 30 minutes and cooling down on air are presented in Fig. 7, regression equation and correlation coefficient r at (8).

$$r_{corm} = 11.8 \cdot \ln(t) - 43.03 \text{ and } r = 0.9939. \tag{8}$$

Effects of the corrosion time on the corrosion rate measured in gram per m² of X2CrNiMoSi18-5-3 steel annealed at 530 ºC by 30 minutes and cooling down on air are presented in Fig. 8, regression equation and correlation coefficient r at (9).

$$r_{corg} = 10.75 \cdot \ln(t) - 39.296 \text{ and } r = 0.9939. \tag{9}$$
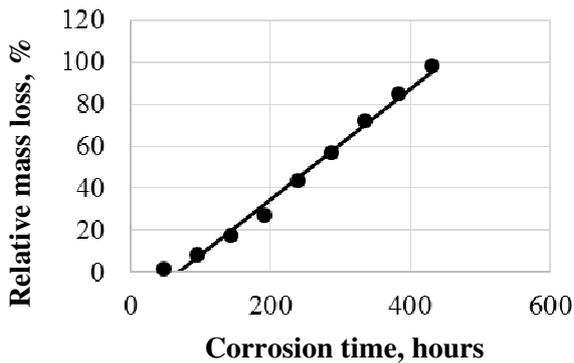
Fig. 6. **Percentage effects of the corrosion time on the relative mass loss (RML) of X2CrNiMoSi18-5-3 steel annealed at 530 ºC for 30 minutes and cooling down on air**
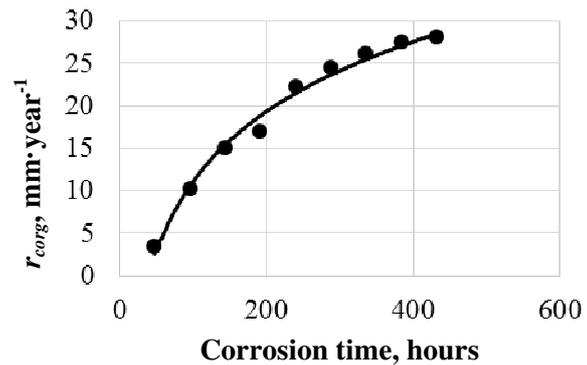
Fig. 7. **Effects of the corrosion time on the corrosion rate measured in mm per year of X2CrNiMoSi18-5-3steel annealed at 530 ºC for 30 minutes and cooling down on air**
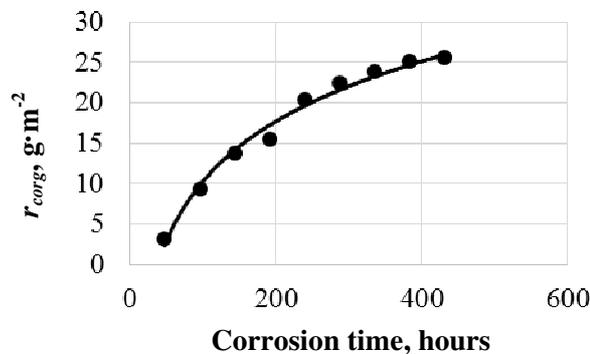

Fig. 8. **Corrosion rate measured of X2CrNiMoSi18-5-3steel annealed at 530 ºC for 30 minutes and cooling down on air**

Conclusions

1. Annealing duplex steels from temperature 494 ºC to 568 ºC probably causes dissolving of the chromium-rich α'-phase.
2. The results of the tests indicate that the loss of weight of X2CrNiMoSi18-5-3 steel annealed at 530 ºC by 30 minutes and cooling down on air is proportional to the time of corrosion.The roughness of the sample increases, but the corrosion rate decreases with time. This is because over time the pits become deeper (mainly through grain boundaries). While the corrosion rate by (1) and (2) decreases: with decreasing M and S and increasing the time which is in the denominator.
3. Profile roughness parameters such as R_a and R_q increase with increase of the time of the corrosion process. While R_t and R_p parameters in the first stage of corrosion did not change, in the second period the parameters increase by exponentially function.
4. Based on profiles of the roughness parameters for every of the research times the size of duplex steel corrosion is determined.

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