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CORROSION OF X2CRNIN23-4 LEAN DUPLEX STAINLESS STEEL ANNEALED AT 485°C

Key words

Stainless steel, duplex steel, corrosion, corrosion rate, profile roughness.

Abstract

Lean duplex stainless steels are ferritic-austenitic steel, and they present the excellent corrosion resistance of austenite steel and the high mechanical behaviour of ferrite steel. General important corrosion problems in duplex stainless steels at 475°C have been already detected. Although the worst temperature is 475°C, corrosion can still form at lower or higher temperatures. The purpose of this work was to ascertain how 30-minutes isothermal heat treatments at 485°C and corrosion time effect the relative mass loss and profile roughness parameters of X2CrNiN23-4 lean duplex stainless steel. The real critical temperature for researching steel was determinate by the DSC method. Corrosion tests were conducted in a nitric acid medium by the measurement of loss in mass (Huey test). The corrosive media was boiling nitric acid V 65%. The corrosion rate of the X2CrNiN23-4 steel was measured in mm/year and in g/m^2.

Introduction

The family duplex stainless steel was introduced more than 85 years ago. One with of the famous products is lean duplex steel. It is a very attractive combination of the austenitic and ferritic steels. They have high corrosion resistance (the chloride pitting and crevice corrosion), good mechanical properties and excellent low cost when compared to the other stainless steel with high performance materials, mainly Ni-based. The properties of duplex steels are functions of chemical compositions and fabrication processes. Corrosion performance of duplex steels primarily depends on alloy content. The main elements for pitting corrosion resistance are Cr, Mo, N, and W. For these elements, pitting corrosion resistance is measured with PREN (Pitting Resistance Equivalent Number). Lean duplex steel is one of the cheaper steels in the duplex family [1–6].

General and important corrosion problems in duplex stainless steels at 475°C have been already detected. Although the worst temperature is 475°C, corrosion can still form at lower or higher temperatures. 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 of 600–950°C and the reformation of ferrite occurs in the range of 350–525°C (embrittlement). However, the performance presented by duplex stainless steels can be drastically reduced if undesirable phases, such as the sigma phase, the chi phase, or secondary austenite, and a lot of rich chromium and carbides precipitates. The sigma phase is rich in chromium and molybdenum, and it is formed by ferrite decomposition, at temperatures over 500°C. In normal alloying, heat-treatment or welding processes, the risk of embrittlement is not to high [1, 3]. Generally, the higher the superheating temperature, the higher is the ferrite content. However, the steel must be heated to very high temperatures to become completely ferritic. Then heat treatment processes, for both solution annealing and stress relieving, is advisable at certain temperatures with subsequent rapid cooling in water [4, 6]. Many authors report that the corrosion resistance of stainless steels depends on rich chromium precipitates in the microstructure [1–3].

The purpose of this work was to ascertain how 30-minute isothermal heat treatments at 485°C (embrittlement temperature) and corrosion time effect the relative mass loss and profile roughness parameters of X2CrNiN23-4 lean duplex stainless steel, which is important for industrial uses.

1. Materials and methods

The experiment was performed with lean duplex stainless X2CrNiN23-4 steel. The chemical composition of the X2CrNiN23-4 steel is presented in

Tab. 1. Before the experiments, the specimens with an area of 13 cm^2 (4 × 1 × 0.5 cm) were successively polished to R_a = 0.16 μm, and then mechanically cleaned with 95% alcohol.

Table 1. Chemical composition of the X2CrNiN23-4 steel

Mean chemical compositions [wt.%]								
C	Si	Mn	P	S	Cr	Mo	Ni	N
0.02	0.45	1.42	0.02	0.001	22.05	0.47	4.20	0.10

The samples were held at a temperature of 485°C for 30 minutes and air cooled. The experiments were conducted in accordance with standard PN EN ISO 3651-1:2004 (Determination of resistance to intergranular corrosion of stainless steels. Part 1: Austenitic and ferritic-austenitic (duplex) stainless steels). Corrosion test were conducted in a nitric acid medium by measurement of loss in mass (Huey test), and the corrosive media were represented by boiling nitric acid V 65%.

The samples of X2CrNiN23-4 steel (about 10 mg) were analysed using Dynamic Scanning Calorimetry measurement by NEITSH DSC204 F1 Phoenix and DSC/dt in nitrogen atmosphere (with a constant flow of 20 ml/min) using Neitsch-Proteus 5.1 software. DSC measurements were carried out in the temperature range of 20–650°C with a heating rate of 10°C/min.

The corrosion rate of the X2CrNiN23-4 steel measured in mm/year was calculated with the use of formula (1), and when the corrosion rate was measured in g/m^2 the second formula (2) was used. They are as follows:

$$r_{corm} = \frac{8760 \cdot m}{S \cdot t \cdot \rho} \tag{1}$$

$$r_{corg} = \frac{10000 \cdot m}{S \cdot t} \tag{2}$$

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 boiling solution [g],
- ρ – sample density [g/cm^3].

The influence of boiling nitric acid on the X2CrNiN23-4 steel corrosion resistance was investigated using weight loss. The mass of samples were measured by a Kern ALT 3104AM general laboratory precision balance with an accuracy of measurement of 0.0001 g.

Profile roughness parameters were analysed 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.

2. Results

Dynamic Scanning Calorimetry curves of heating measurement from 350 to 650°C (according to literature – embrittlement temperature of 485°C) for the duplex steel for the heating rate of 10°C/min, as an example, are presented in Fig. 1.

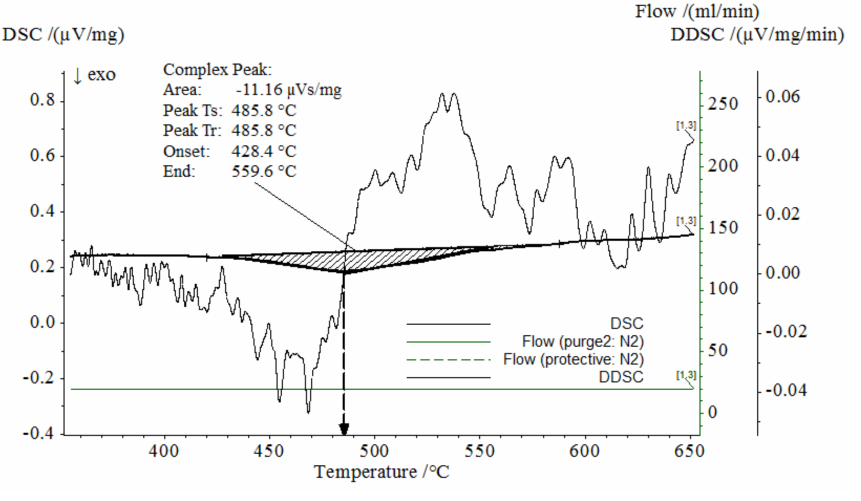

Fig. 1. Heating curve of X2CrNiN23-4 steel, static nitrogen atmosphere, cooling rate 10°C /min

The microstructure of raw X2CrNiN23-4 lean duplex steel is presented in Fig. 2. Hot rolling with the phase orientation of X2CrNiN23-4duplex steel forms a fine elongated lamellar structure of light etched austenite and a light etched ferrite phase. The surface of X2CrNiN23-4 steel annealed at 485°C for 30 minutes and air-cooled after corrosion tests in boiling HNO_3 for a boiling time of 48 hours is presented in Fig. 3.

Profile roughness parameters of X2CrNiN23-4 steel are presented in Fig. 4. Profile roughness parameters of X2CrNiN23-4 steel 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 HNO_3 for different boiling times is presented in Fig. 5. Regression equations (3–6) were used to calculate correlation coefficients, r.

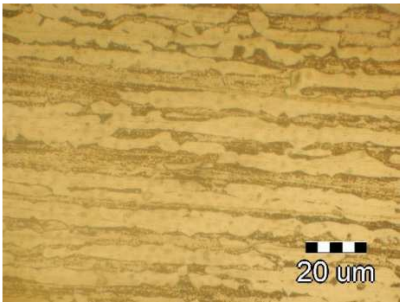

Fig. 2. Microstructure of raw X2CrNiN23-4 rolled duplex steel: light etched austenite and dark etched ferrite

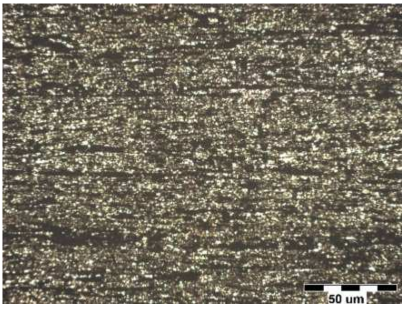

Fig. 3. Surface of X2CrNiN23-4 steel annealed at 485°C for 30 min. and cooling down on air after corrosion tests in boiling HNO_3 for time = 48 h

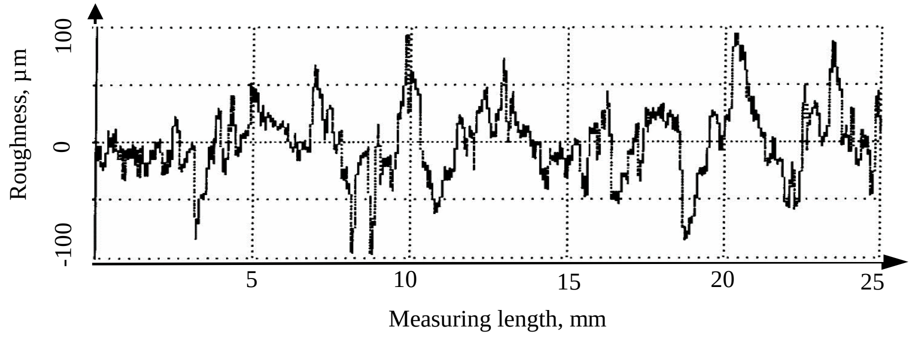

Fig. 4. Profile roughness of X2CrNiN23-4 steel annealed at 485°C for 30 min. and air-cooled after corrosion tests in boiling HNO_3 for boiling time = 48 hours

$$R_a = 0.0058 \cdot t + 2.35 \text{ and } r = 0.9763 \tag{3}$$

$$R_q = 0.0079 \cdot t + 3.18 \text{ and } r = 0.9946 \tag{4}$$

$$R_t = 0.0002 \cdot t^2 - 0.029 \cdot t + 22.3 \text{ and } r = 0.9927 \tag{5}$$

$$R_p = 5 \cdot 10^{-5} \cdot t^2 - 0.011 \cdot t + 20.61 \text{ and } r = 0.9942 \tag{6}$$

The percentage effects of corrosion time on the relative mass loss (RML) of X2CrNiN23-4 steel annealed at 485°C for 30 minutes and air-cooled are presented in Fig. 6, and regression equation (7) was used to calculate the correlation coefficient, r.

$$RML = 0.244 \cdot t - 16.35 \text{ and } r = 0.9952 \tag{7}$$

The effects of corrosion time on the corrosion rate measured in mm per year of X2CrNiN23-4 steel annealed at 485°C for 30 minutes and air-cooled are presented in Fig. 7. The regression equation (8) was used to calculate the correlation coefficient *r*. The corrosion rate measured in gram per m^2 is presented in Fig. 8, and regression equation (9) was used to calculate the correlation coefficient, *r*.

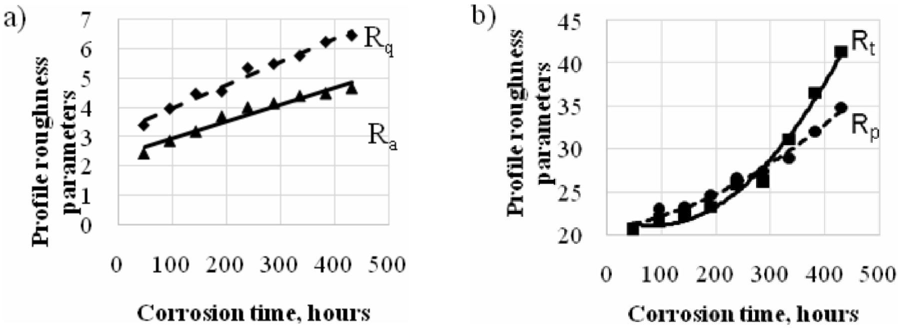

Fig. 5. Profile roughness of X2CrNiN23-4 steel annealed at 485°C for 30 min. and air-cooled after corrosion tests in boiling HNO_3 for different boiling times: a) R_a – arithmetic average of absolute values [µm], R_q – root mean squared [µm]; b) R_p – maximum peak height [µm], R_t – maximum height of the profile [µm]

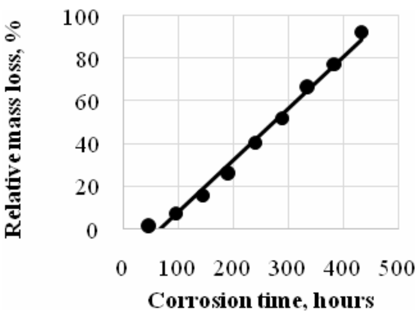

Fig. 6. Percentage effects of corrosion time on the relative mass loss (RML) of X2CrNiN23-4 steel annealed at 485°C for 30 minutes and air-cooled

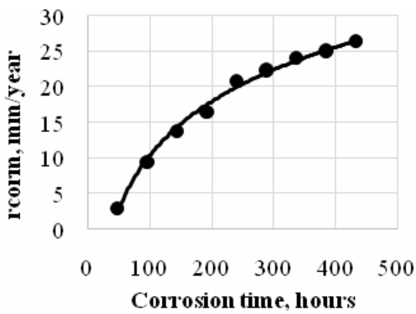

Fig. 7. Effects of corrosion time on the corrosion rate measured in mm per year of X2CrNiN23-4 steel annealed at 485°C for 30 minutes and air-cooled

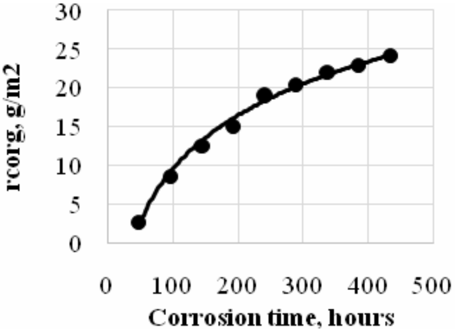

Fig. 8. Corrosion rate measured of X2CrNiN23-4 steel annealed at 485°C for 30 minutes and air-cooled

$$r_{corm} = 10.99 \cdot \ln(t) - 40.2 \text{ and } r = 0.9967 \tag{8}$$

$$r_{corg} = 10.03 \cdot \ln(t) - 36.7 \text{ and } r = 0.9967 \tag{9}$$

3. Discussion

The exothermic peak (Fig. 3) with a T_{onset} at about 428°C, T_{end} at about 560°C and T_{peak} about 486°C, according to literature [2, 7, 11, 19], represents the dissolving of chromium-rich α`-phase. The reformation of ferrite occurs in the range of 350–525°C, and embrittlement takes place at 485°C. In the studied steel, range α` phase precipitates at the cooling rate of 10°C /min from the range of 428–560°C. Most efficient precipitation takes place at 486°C. This range is very important for industries as a critical corrosion temperature range. Carrying out processes in this temperature range can lead to early damage as a result of corrosion. Figure 5 presents profile roughness parameters, and corrosion rates in Figures 6–8 indicate the effects of corrosion in relation to regression equations. These can illustrate the changes taking place on the surface of the material, and they can be used to compare the robustness in the corrosion of a product. For this purpose, two equations can be used (8) and (9). However, their application in practice requires the use of a factor that is the ratio of the aggressiveness of the acid used for the test and working medium.

Conclusions

1. Annealing the X2CrNiN23-4 lean duplex steels from temperatures of 428°C to 560°C probably causes the dissolving of chromium-rich α`-phase.

2. The arithmetic average of absolute values and root mean squarecan be described as linear functions, but the maximum peak height and maximum height of the profileare expressed as exponential functions.
3. Percentage effects of corrosion time on the relative mass loss with a very high probability are proportional with a linear nature. The corrosion rate measured in mm/year and in g/m^{2}can be described by logarithmic functions.
4. Because R_a and R_q linearly increase with the increase of the time of the corrosion process, based on the profiles of roughness parameters, every one of the research times determine the size of duplex steel corrosion.

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Korozja stali nierdzewnej lean duplex w gatunku X2CrNiN 23-4 po wyżarzaniu w temperaturze 485°C

Słowa kluczowe

Stal nierdzewna, stal duplex, korozja, szybkość korozji, profil chropowatości.

Streszczenie

Stale nierdzewne Lean duplex są stalami ferrytyczno-austenitycznymi o doskonałej odporności na korozję stali austenitycznej, a wysokich właściwościach mechanicznych stali ferrytycznej. Ważny problem korozji stali odpornej na korozję duplex w temperaturze 475°C został już stwierdzony. Chociaż najniekorzystniejszą temperaturą jest 475°C, korozja może przebiegać zarówno w temperaturze niższej, jak i wyższej. Celem niniejszej pracy było zbadanie, jak 30-minutowe izotermiczne wyżarzanie stali w temperaturze 485°C oraz czas przetrzymywania w ośrodku korozyjnym wpłynie na ubytek masowy oraz chropowatość powierzchni stali lean duplex w gatunku X2CrNiN23-4. Rzeczywista temperatura krytyczna dla badań stali została określona metodą DSC. Badanie korozyjne (ubytku masy) prowadzono w środowisku kwasu azotowego V 65% w temperaturze wrzenia (test Huey). Prędkość korozji stali X2CrNiN23-4 określono w mm/rok i w g/m^2.