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The Effect of Si and Mn on Microstructure and Selected Properties of Cr-Ni Stainless Steels

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Abstract

Cast stainless steel of the Cr-Ni duplex type is used, among others, for the cast parts of pumps and valves handling various chemically aggressive media. Therefore, the main problem discussed in this article is the problem of abrasion wear resistance in a mixture of SiC and water and resistance to electrochemical corrosion in a 3% NaCl- H_2O solution of selected cast steel grades, i.e. typical duplex cast steel, high silicon and manganese duplex cast steel, and Cr-Ni austenitic cast steel (type AISI 316L). The study shows that the best abrasion wear resistance comparable to Ni-Hart cast iron was obtained in the cast duplex steel, where Ni was partially replaced with Mn and N. This cast steel was also characterized by the highest hardness and matrix microhardness among all the tested cast steel grades. The best resistance to electrochemical corrosion in 3% NaCl- H_2O solution showed the cast duplex steel with high content of Cr, Mo and N. The addition of Ni plays rather insignificant role in the improvement of corrosion resistance of the materials tested.

Keywords: Cr-Ni cast stainless steels, Alloy composition, Hardness, Electrochemical corrosion, Miller slurry test machine

1. Introduction

The development of Cr-Ni austenitic stainless steels dates back to the 30s of the last century [1]. The observed growing interest of the maritime industry and the extraction industry of oil and natural gas in Cr-Ni duplex steels (DSS, SDSS) and cast steels was mainly due to their good, compared to austenitic steels (AISI 304, 316), mechanical, corrosion [2-5] and erosion-corrosion properties [6÷8]. This is particularly important in the case of storage tanks for gas and oil, which during use are exposed not only to the effect of corrosive media, but also to the high pressure (69÷207 MPa) and temperature (149÷260⍰C) [9].

The content of ferrite in the microstructure of materials included in this group is controlled by appropriately chosen ratio between the ferrite and austenite stabilizing agents, while low carbon content protects the alloy against intergranular corrosion. Recently, with the development of duplex stainless steels and cast steels, changes were introduced to the content of alloying elements added in order to maintain satisfactory mechanical properties at a comparable or better corrosion resistance in aggressive environments expressed with high PREN index values [10÷13]. Actions of this type are also dictated by the need for partial substitution of expensive elements with cheaper additives. A good example is partial substitution of Ni with increasing content of Mn and N (1% Mn corresponding to 0.4% Ni, [11])

[12]. The addition of Mn raises the solubility of N in DSS steels, thus increasing their local corrosion resistance and strength [13]. Additionally, in DSS steels, N strengthens the austenite and its effect is more intense than the effect of C at the same content of the two elements [14].

The addition of Si to the DSS steels containing 6% Mo improves the corrosion resistance especially in oxidizing environments [15].

Thinking of the use of duplex steels for cast parts of pumps and valves operating in the extraction industry as an equipment for, among others, pumping of sludge, the aim of this study was to present the results of abrasion tests carried out in a mixture of SiC and water and of corrosion tests carried out in a 3% NaCl solution on selected grades of the cast Cr-Ni stainless steel.

2. Materials and methods

Samples were taken from the three test grades of cast Cr-Ni stainless steel melted under laboratory conditions in an electric induction furnace and solution treated at a temperature of 1060C (marc A-C – Table 1). The fourth grade was supplied by one of the domestic foundries (marc D – Table 1). The chemical composition of the tested materials is given in Table 1.

Hardness of the tested cast steels was measured with Brinell hardness tester.

Metallographic examinations were carried out by light microscopy and scanning electron microscopy.

Studies of corrosion resistance of selected cast steel grades were based on polarization tests performed in a 3% NaCl-H_2O solution at a polarization rate of 1V/min (AutoLab PGStat30 station). Polarization was carried out in a three-electrode system (tested cast steel - Ag/AgCl electrode - platinum electrode).

Abrasion wear resistance was tested in a mixture of SiC and water at pH = 9.86 using Miller machine (by ASTM G75).

3. Results and discussion

3.1. Microstructures

The Cr-Ni cast steel supplied for tests by a domestic industrial plant was cast commercial 19Cr-11Ni-2Mo steel grade (corresponding to AISI 316L), characterized by austenitic microstructure with scarce precipitates of ferrite (Table 1, designation D). The other two tested grades were cast 24Cr-5Ni-3Mo and 23Cr-5Mn-2Ni-3Mo duplex steels containing 54÷60% of ferrite, where Ni has been partially replaced with increasing additions of Mn and N [12]. The fourth tested steel grade was 20Cr-21Ni cast steel with the addition of 5% Si, which improved the corrosion resistance under oxidizing conditions. The matrix of this cast steel was austenitic with the Si- and Mn-rich precipitates present in an amount not exceeding 11% [16].

3.2. Abrasive wear resistance in a mixture of SiC+ H_2O

The abrasion resistance of alloys depends on many factors, which include, among others, hardness of the material (directly dependent on microstructure), temperature, abrasion conditions and properties of the abrasive agent.

Hardness tests showed that two cast steel grades were characterized by the hardness of 151 ÷ 157 HB, while hardness of the remaining grades was comprised in the range of 229 ÷ 235 HB. This difference in hardness of the alloys is one of the factors responsible for the increased abrasion wear resistance. Microhardness of the steel matrix was also measured to detect the presence of the precipitates of the second phase in the matrix of the tested Cr-Ni cast steel.

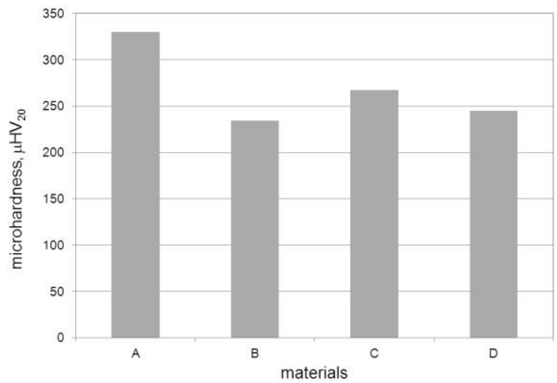


Fig. 1. Microhardness of the matrix of the investigated stainless cast steels (Table 1).

The results of abrasion tests disclosed in Figures 2 and 3 have confirmed that the abraded material characterized by higher hardness suffers lower loss in weight. The best results in the abrasion tests were obtained on the cast steel designated by symbol A, for which the total loss in weight was over two times lower than the loss in weight observed for the cast steels designated by symbols B and D.

Table 1.
Chemical composition of the investigated stainless cast steel

Samples	C	Si	Mn	Cr	Ni	Mo	Cu	P, S	other
	wt. %								
A	0.08	0.67	4.96	23.3	2.2	2.95	-	<0.01	0.27% N
B	0.03	4.8	1.27	20.03	21.5	0.21	-	<0.02	0.046% N, 0.25% V
C	0.06	0.4	1.1	24.2	5.2	2.53	2.8	<0.02	0.048% N
D	0.14	0.98	0.7	18.9	10.6	2.05	0.15	<0.01	0.046% N, 0.13% Nb

Altogether, the tested alloys of the ferritic-austenitic duplex-type structure designated by symbols A and C exhibited superior abrasion resistance compared to austenitic alloys designated by symbols B and D. Despite high hardness values, the cast steel designated by symbol C had the abrasion resistance inferior to the cast steel designated by symbol A. One of the reasons was relatively low microhardness of the matrix compared to the cast steel designated by symbol A. Altogether, the tested alloys of the ferritic-austenitic duplex-type structure designated by symbols A and C exhibited superior abrasion resistance compared to austenitic alloys designated by symbols B and D.

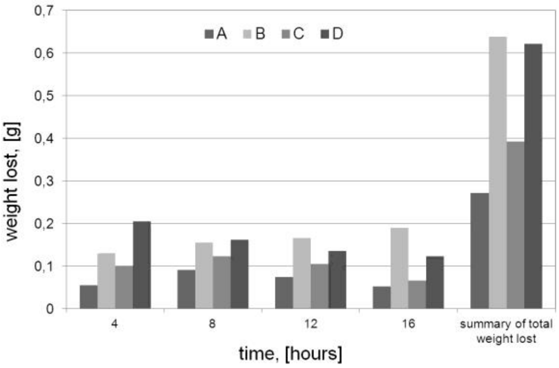


Fig. 2. Changes of weight lost of stainless cast steels during the 16-hours wear test

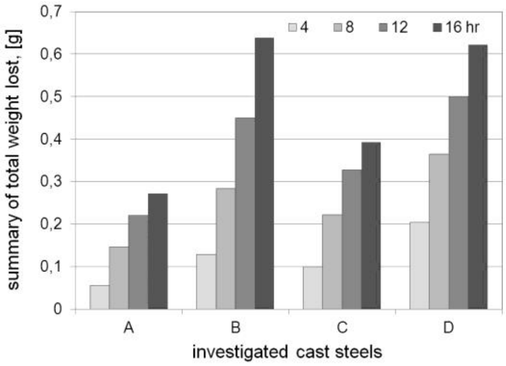


Fig. 3. The relative weight lost observed in the tested stainless cast steels

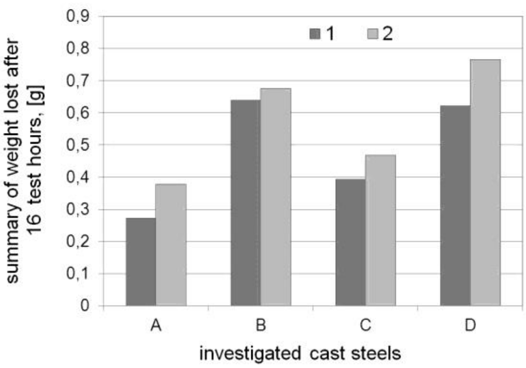
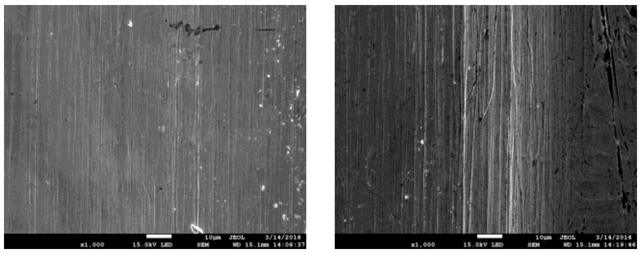


Fig. 4. The summary of the weight lost of the stainless cast steels after two 16 hours tests

Based on the results of two 16-hour abrasion tests (Fig.4) carried out on the examined materials, comparing the weight loss in samples after the first four-hour stage of the test, it was found that each of the tested materials behaved in a different way. The weight losses during the test were subjected to minor changes. In graphs plotting the weight losses in time, three trends were observed: a continuous increase in the weight loss, a continuous decrease in the weight loss, and the occurrence of a maximum during the abrasion process. Changes in the weight of samples were also due to interaction between the hard SiC particles and the tested material (including penetration of SiC particles into the soft matrix). High abrasion resistance in a mixture of SiC + water of the cast two-phase duplex steel designated by symbol A was mainly due to nitrogen content higher in this material than in the remaining tested cast steel grades. Nitrogen dissolved in austenite has raised the strength of this cast steel. The abrasion resistance of the steel designated by symbol A expressed as a total loss in weight was comparable to the resistance of Ni-Hard 4 cast iron with an austenitic matrix containing chromium carbide precipitates characterized by the hardness of 373 HV20 [17].
Visual assessment of the surface of the examined cast steel after the abrasion test showed that the cast steel with high hardness and microhardness of the matrix suffered only mild surface degradation compared to the cast steel designated by symbols B and D (Fig.5). All surfaces showed the mechanical wear of the tested material in the form of furrowing but without any signs of corrosion.



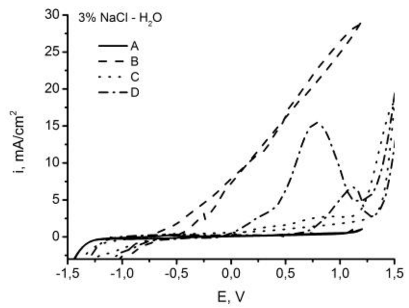
cast steel – A cast steel - B

Fig. 5. Examples of the surface after abrasion tests

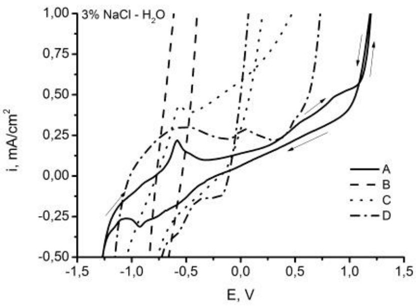
Scanning of the worn out surfaces has shown that the wear by furrowing was stronger when non-metallic inclusions were accumulated on the abraded surface.

3.3. Electrochemical corrosion tests in chloride solution

The study shows that the best corrosion resistance boasts the cast steel sample designated by symbol A, mainly due to the high value of the breakdown and re-passivation potentials (Fig.6). In this case, the potentials of both breakdown and re-passivation have nearly the same value. This cast steel is also the least sensitive to local corrosion (Fig.7,8). This behaviour can be attributed to the high content of Cr, Mo and nitrogen. Other samples are characterized by much higher anodic current densities.



a)



b)

Fig. 6. Polarisation curve of different stainless cast steels at ambient temperature: a) full current range, b) anodic current range

It was also shown that the passivation process in the tested materials is a slow process. Among the remaining materials the sample made of the cast steel designated by symbol B has the highest value of the current The system with sample B is unstable, but inhibition of the anodic process (very slight) is noticeable. To evaluate the effect of Si on the corrosion resistance of cast steel designated by symbol B, the SEM/EDX analysis is necessary. For the cast steel designated by symbol C, the active-passive transition takes place at a potential of approx. 0.7 V. The current densities are 10 times higher than for the alloy A. The stable passive state occurs below 0.1 V. The cast steel from the industrial melting process with the symbol D is characterized by two current peaks on the polarization curve. It has a large hysteresis loop and even lower re-passivation potential of approx. -0.1V. This cast steel is not resistant to local corrosion, which results, among others, from its austenitic matrix (Fig.6,9).

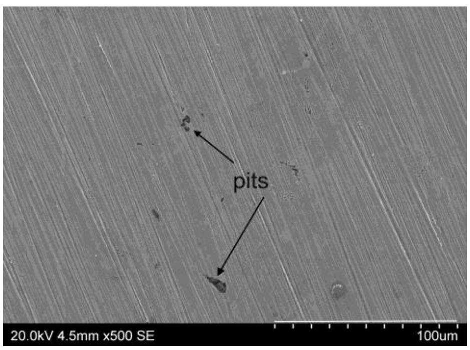
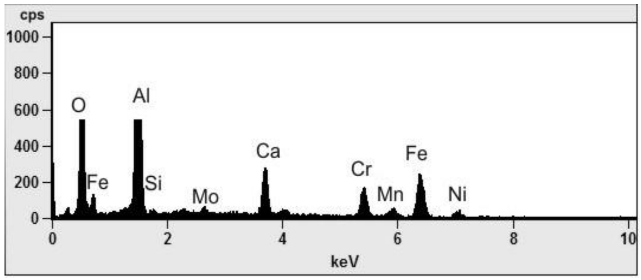
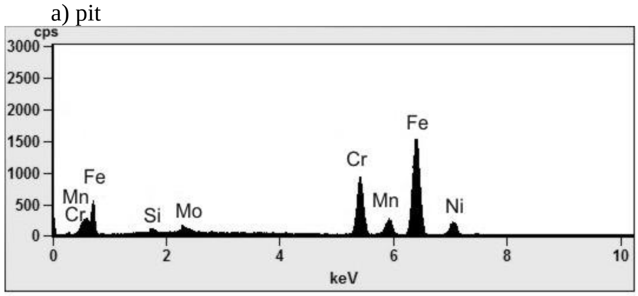


Fig. 7. SEM micrograph of the surface of stainless cast steels – A after the polarization tests in 3% NaCl solution

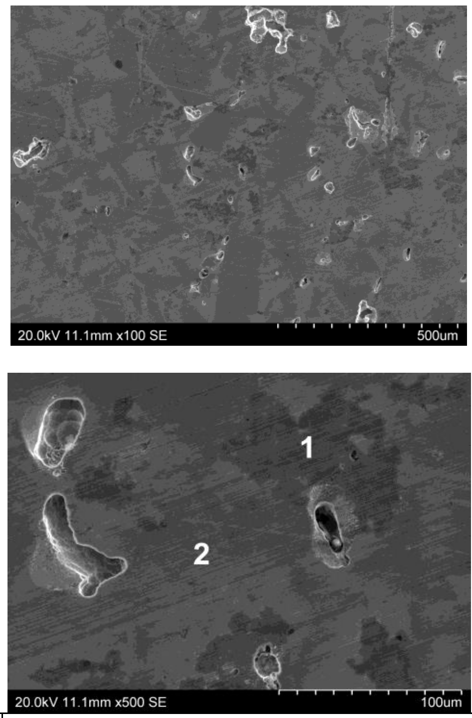


a) pit



b) matrix

Fig. 8. X-ray spectrum with energy dispersion (EDX) from the pits and matrix – Fig. 7



Area	The average of results taken from the EDX microanalysis of points, wt. %				
	O	Cr	Fe	Ni	Mo
1	13.1	15.6	58.2	9.1	1.9
2	-	17.7	68.2	10.1	2.3

Fig. 9. SEM micrograph of the surface of stainless cast steels – D after the polarization tests in 3% NaCl solution and chemical composition of area 1 and 2 examined by EDX

Non-metalic inclusion present in the investigated materials (maliny oxides, sulfides and oxy-sulfides) (Fig. 8) may support pitting corrosion and are its precursors, in particular in industrial cast. Local corrosion may also appear, which is caused by a formation of a galvanic cell between matrix and inclusions.

4. Conclusions

- Among all the tested cast steel grades, the best abrasion wear resistance in a mixture of SiC and water was obtained in the cast duplex steel with increased content of manganese (4.96%) and nitrogen.
- High hardness and microhardness of the matrix of the tested materials had some impact on the abrasion resistance. To the high hardness and ferritic – austenitic microstructure of tested materials corresponded less surface degradation observed after the test.
- The best resistance to electrochemical corrosion in 3% NaCl solution showed the cast duplex steel (designated by symbol A) with high content of Cr, Mo and N.
- The passivating components ensuring the corrosion resistance of the tested cast steel grades include Cr, Mo, N and Si.
- The addition of Ni plays rather insignificant role in the improvement of corrosion resistance of the materials tested.

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