DETERMINING SENSITIVITY TO INTERGRANULAR CORROSION OF AUSTENITIC STAINLESS STEEL 316L

Aurora Anca POINESCU [1)], Rodica Mariana ION [2,3)] Rares STAN[4)] Cristiana Zizi RIZESCU[5)]
1) Valahia University of Targoviste, E-mail: poinescua@yahoo.com,
2) Valahia University of Targoviste, E-mail: rodica_ion2000@yahoo.c.uk
3) ICECHIM, Bucharest, Analytical Department, Bucharest 4) OTELINOX S.A. TARGOVISTE,
5) Valahia University of Targoviste, E-mail:rizescu_c@yahoo.com

Abstract: *Corrosion awareness is linked both intrinsic properties of steel and especially the operations of formal work and structural imperfections caused by the design and operating conditions. Exposure to a temperature in a range of 500 to 800^{0}C, leads to the precipitation of chromium rich carbides at the grain boundaries and the formation of chromium depletion areas adjacent to these carbides. Following the precipitation phenomena, the chemical changes at the grain boundary region were determined by metallographic evaluation.*
Keywords: *corrosion, stainless steel, metallographic method*

1. INTRODUCTION

Austenitic stainless steel type 316L undergoes, in most cases, the water-cooled reactors phenomena of intergranular cracking under stress, either directly by corrosion cracking as such, either by intergranular corrosion accelerated by voltage.
The resistance of austenitic stainless steel to intergranular corrosion varies during the process of aging at temperatures between 500 and 700. This follows the well-know phenomena of precipitating of $M_{23}C6$ chromium carbides and intermetallic phases. This leads to significant Cr depletion zones at grain boundaries responsible for material sensitization to IGC. Measurement of sensitivity to intergranular corrosion of austenitic stainless steel can be determined by normalized classical tests: Huey, Strauss, Streicher and Electrokemical Potentiokinetic Reactivation non destructive test. The assessment of the sensitivity to IGC from the Strauss or equivalent tests requires cutting a sample off the material, which can be harmful to the integrity of the structure in service.
Because this phenomenon is mainly partial Cr depletion in austenite grains. It appears that the frequency stabilized austenitic stainless steel corrosion cracking is reduced, generally occurring phenomenon, in the steam generator, the secondary circuit.
Corrosion cracking this case called "dentting" and is determined mainly by water treatment technology for secondary cooling circuit.
Corrosion awareness is linked both intrinsic properties of steel and especially the operations of formal work and structural imperfections caused by the design and operating conditions.
In this respect corrosion experiments performed on austenitic stainless steel 316L produced were oriented in two directions:
a) Determination of susceptibility to corrosion of steel in heat treatment conditions for final status by checking its reaction to the phenomenon of intergranular corrosion in environments representative;
b) Behavior of 316L steel for simulating the conditions of operation of nuclear power plants cooled by presurized water.
Determination awareness of austenitic stainless steel 316L in Cr depletion phenomenon due to precipitation of intergranular carbides is by the method described in Table. 1.

Table 1. Methods for determining sensitization steels

Method	Testing condition	Evaluation
ASTM A-262 Method E	Sulfo cupric solution + copper splinter,24h	metallographic
ASTM A- 262 Method B	HNO3 65% Solution, 240h	Weight lost metallographic
Electrochemikal potentiokinetic reactivation	0,5 M H_2SO_4 – 0,01 M KSCN, temp. 30^{0}C Scanning Speed 100mV/min, Passivation at 200mV, 2 min.	Total charge Qa, C/cm^2

2. EXPERIMENTAL METHODS

Materials used for corrosion studies are:

- Steel 347 mark (or 316Nb) mark Y 29;
- Mark steel 316L marked with Y 25.

Experiments were performed chemically (sulfo cupric test solution and concentrated nitric acid) samples in the following states of heat treatment:

✓ Quenching for the solution to 1050^{0}C, 1 h, cooling water;
✓ Quenching for the solution to 1050^{0}C, 1 h in water plus 30h at 650^{0}C awareness (for Y 25) that the 650^{0}C (for Y 29);
✓ Quenching for the solution to 1050^{0}C, 1 h, water awareness addition to 100 h at 600^{0}C and 650^{0}C respectively.

The chemical composition of materials used for corrosion research are presented in table 1.

Table 1

%	C	Mn	Si	P	S	Cr	Ni	Mo	Co	N	Nb
Y -25	0,02	1,53	0,65	0,027	0,01	16,0	11,7	2,9	0,23	0,065	-
Y - 29	0,05	1,7	0,99	0,03	0,011	17,7	12,33	2,78	0,21	0,068	0,52
316L	max. 0,03	max. 2,0	max. 1,0	max.0,045	max. 0,030	16-18	10-14	2-3	-	max. 0,1	-

Studies regarding the choosing stainless steel with an appropriate resistance to intergranular corrosion for use in nuclear reactors showed that type 18-10 steels having equivalent resistance to intergranular corrosion in a given environment, satisfying the relationship:

$$Cr_{ech} - 100C_{ech} = k \qquad (1)$$

where: Cr_{ech} – is an equivalent carbon content correcting the influence of nickel content, this element reduces the solubility of carbon in austenitic matrix, leading to intergranular precipitation of chromium carbide.

It is used generally following calculation formula:

$$Cr_{ech} = \%Cr + \alpha\%Mo \qquad (2)$$

$$C_{ech} = \%C + 0{,}002\%Ni - 10 \qquad (3)$$

Coefficient α = 1.2 or 1.7, depends largely on tests used to determine the intergranular corrosion and other factors affecting the foundry modest intergranular dissolution process (eg. Segregation).

Equation 1 reveals that all steels have equivalent resistance to intergranular corrosion compositions located along a straight line with slope k, Cr =f(C) diagram (C) (figure 1).

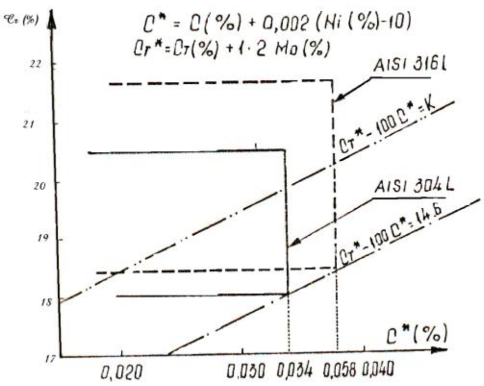

Figure 1. Diagram (Crech., Cech.) - The equal right to intergranular corrosion resistance, areas of composition for 316L and 304L steel.

Selecting a steel for a given environment, be compared kmin.*, corresponding environmental resistance to intergranular corrosion test with kmin.

Appropriate steel composition and selected compositions which satisfy the inequality:

$$Kmin. \geq kmin.* \qquad (4)$$

Strauss Test purpose:

α = 1,7 şi kmin.*= 15,7

Given the composition of Y25 and Y29 is determined that in according with Table 2

Table 2

Y 25	Cr_{ech} = 16+1,7x2,9 = 20,93 C_{ech}. = 0,02 + 0,002x2,33 = 0,0234 K_{min}. = 20,93 – 100x0,0234 = 17,59
Y 29	Cr_{ech}. = 17,7 + 1,7 x 2,78 = 22,426 C_{ech}. = 0,05 + 0,002 x 2,33 = 0,0546 K_{min}. = 22,426-100 x 0,0546 = 16,966

As shown in coefficient calculation kmin. for 29Y and 25Y, both batches must resist intergranular corrosion test in sulfo cupric solution having the value of k_{min} (17.59 for 25Y respectively 16,966 for Y 29) greater than the amount required for k_{min} 15.7.

This finding is consistent with results in intergranular corrosion test sulfo cupric solution, metallographic examination of samples subjected to this test revealed no intergranular corrosion even at times raising to 100 hours (Fig. 2 and 5).

The results obtained fall also in the corresponding resistance to intergranular corrosion established for steel 316L in demineralized water at 298^0C.

Corrosion tests on nitric acid medium, in this environment is more severe than those working in nuclear reactors cooled with water and although little is known corrosion resistance of steels with molybdenum in the environment, however, attempts were made corrosion to fit to obtain additional data.

Experiments carried out on samples from samples of Y25 and Y29 revealed the following:

• General corrosion speeds on samples of Y-25 both charge state and the state toughened sensitized as well as selective attacks intergranular corrosion (Fig. 6, 7)

• Evidence of charge to the state toughened Y29, general corrosion rate is 0.3 mm / year (below the limit allowed by the existing rules, respective 0.5 mm / year according to GOST 6032-75) and there is no selective intergranular attack is found (Fig. 8).

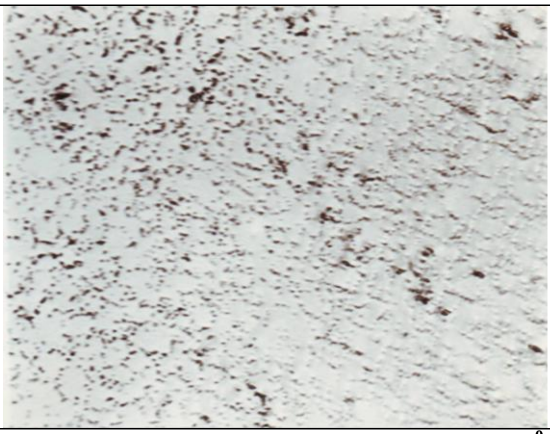

Figure 2. Microstructure of a Y 25 sample (1050^{0}C hardening heat treatment, 1h, water and sensitize 600^{0}C, 30h, after testing with sulfo cupric solution) Chromic anhydride attack, magnification x250

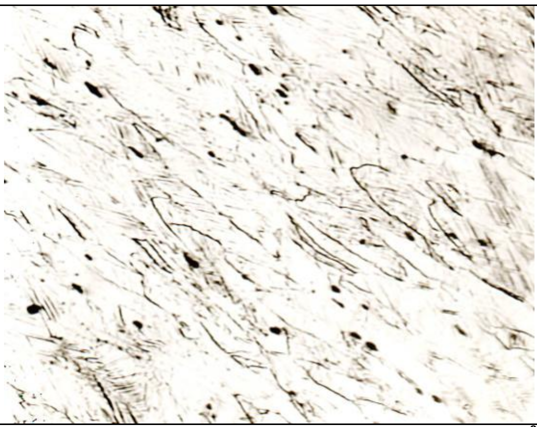

Figure 3. Microstructure of a Y 25 sample (1050^{0}C hardening heat treatment, 1h, water and sensitize 600^{0}C, 100h, after testing with sulfo cupric solution) Chromic anhydride attack, magnification x250

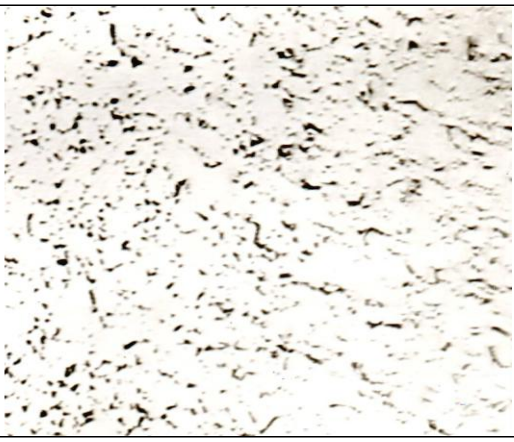

Figure 4. Microstructure of a Y 29 sample (1058^{0}C hardening heat treatment, 1h, water and sensitize 650^{0}C, 30h, after testing with sulfo cupric solution) Chromic anhydride attack, magnification x250

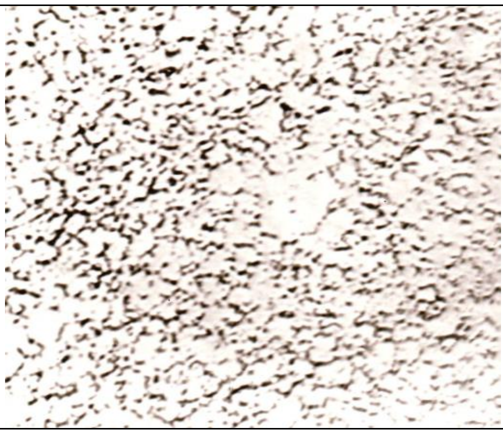

Figure 5. Microstructure of a Y 29 sample (1058^{0}C hardening heat treatment, 1h, water and sensitize 650^{0}C, 100h, after testing with sulfo cupric solution) Chromic anhydride attack, magnification x250

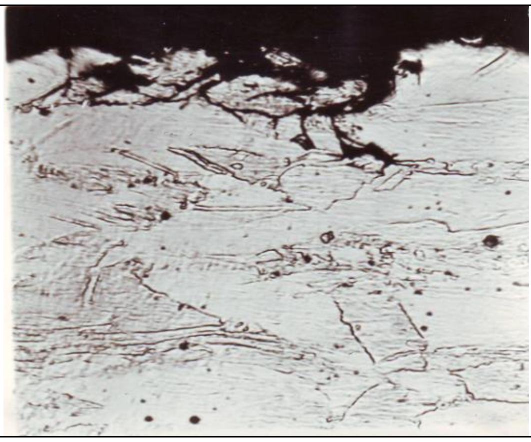

Figure 6. Microstructure of a sample of Y25 after test batch nitric acid solution, 240 hours. Heat treatment tempering 1050^{0}C, 1 h, water, Chromic anhydride attack, magnification x250

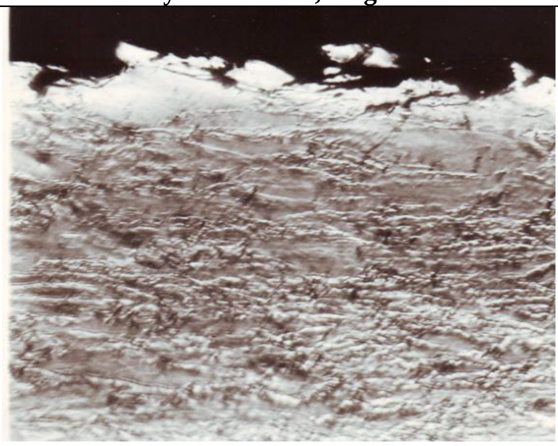

Figure 7. Microstructure of Y25 sample after testing nitric acid solution, 240 h. The heat treatment hardening 1050^{0}C, 1 h, water and sensitized the 600^{0}C, 30h. Chromic anhydride attack, magnification x250

Figure 8. Microstructure of a Y29 sample after testing nitric acid solution, 240 h heat treatment hardening 1050^{0}C, 1 h, water, Chromic anhydride attack, magnification x250

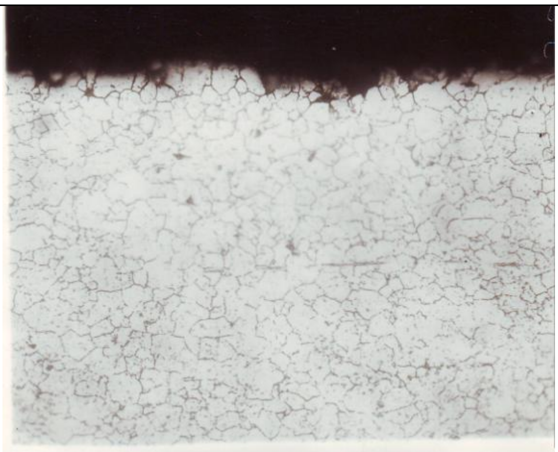

Figure 9. Microstructure of Y29 sample after testing nitric acid solution, 240 h heat treatment hardening 1050^{0}C, 1 h, water and sensitized the 650^{0}C, 30h, Chromic anhydride attack, magnification x250

3. CONCLUSION

– Short attempts to characterize the mechanical properties of tested steel types correspond to standard, so steel type 316L.
– Auxiliary type 316L steel with niobium alloy possesses the characteristics of resistance values of 190-210% above the minimum standards prescribe.
– The heat treatment performed to determine the technological parameters and conditions of the limit, showed that for this class of steels can be used to heating unlimited speeds without fissure. Optimal values of the heat treatment process parameters to be determined after completion of corrosion tests and mechanical testing.
– Weak oxidizing environments (sulfo cupric solution) similar operating conditions, produce of both batches had a proper reaction condition both qualitative and able aware journeys (100h) to maintain the awareness;
– Highly oxidizing environments (concentrated nitric acid), more severe environments than the batch operation of the two products had a poor attitude, especially in sensitized state, both in terms of general corrosion of the intergranular as well.

REFERENCES

[1] A. Kriaa, N. Hamdi, H. Sidhom, Assessment of Intergranular Corrosion of Heat Treated Austenitic Stainless Steel (AISI 316L Grade) by Electron Microscopy and Electrochemical Tests, ISSN 0033-1732, Protection of Metals, 2008, Vol. 44, No. 5, pp. 506–513. Pleiades Publishing, Ltd., 2008.

[2] L.A. Norstrom, The influence of nitrogen and grain size on yeld strength in type AISI 316L austenitic stainless steel, Metal Science, iunie 1977;

[3] N. Ohuaka, Environmental effects on the intergranular stress corrosion Craking susceptibility of sensitized type 316 stainless steel in High temperature water, BWR Split Sesion, Tokyo, mai 1978;

[4] A.S. Telelman, A.J.Mc. Evily, Fracture of Structural materials, New York, John Wiley Inc. 1967;

[5] Shigeki Kasahara, Kiyotomo Nakata, Jiro Kuniya, Effect of Ti and Nb additions on Cr depletion at grain boundaries in austenitic stainless steel irradiated with 1 MeV electrons at 523-673 K, Journal of Electron Microscopy 48(4): 431-435 (1999)

[6] N. Otsuka, Y. Nishiyama, and T. Kudo, Breakaway Oxidation of TP310S Stainless-Steel Foil Initiated by Cr Depletion of the Entire Specimen in a Simulated Flue-Gas Atmosphere, , Oxidation of Metals, Vol. 62, Nos. 1/2, August (2004);

[7] Shigeki Kasahara, Kiyotomo Nakata, Jiro Kuniya, Effect of Ti and Nb additions on Cr depletion at grain boundaries in austenitic stainless steel irradiated with 1 MeV electrons at 523-673 K, Journal of Electron Microscopy 48(4): 431-435 (1999).