Prediction of steel resistance to stress corrosion cracking in seawater based on accelerated tests and structural studies

Svetlana Mushnikova*, Oleg Kharkov

NRC "Kurchatov Institute" - CRISM "Prometey", 191015 St. Petersburg, 49 Shpalernaya str., Russia

Abstract. The paper presents the tests results of resistance of various structural steel classes to SCC in chloride solutions. The experiments were performed using cantilever bending tests developed by NRC "Kurchatov Institute" – CRISM "Prometey" with stepwise increasing load of Charpy-type precracking specimens. The criterion estimation of resistance to SCC when $\beta = \sigma_{SCC}/\sigma_C > 0.85$ was confirmed by the laboratory test results compared with the case studies of corrosion-mechanical fracture of shipbuilding structures in real life service conditions. A new approach of SCC susceptibility of austenitic stainless steels in marine conditions is proposed. It is based on estimation of the critical temperature of SCC when testing for SSRT in a concentrated solution of calcium chloride at temperatures from 20°C to 100°C. Specific features of the structural-phase composition of steels that detrimentally affect the resistance to SCC were discovered during the complex testing.

1 Introduction

In recent years, austenitic stainless steels, hardened through the use of various methods of thermal and thermo-deformational treatments, are beginning to be used in shipbuilding together with low- and medium-alloyed steels. Common methods of hardening stainless steels are: solid-solution hardening (the elements that form the interstitial and substitutional solid solutions); dislocation hardening due to cold plastic deformation; dispersion hardening during the formation of particles of carbide, nitride or intermetallic phases from a supersaturated γ -solid solution (during isothermal aging); grain boundary hardening; substructural hardening during high-temperature thermomechanical processing (HTMP) [1-4]. Among high-strength austenitic steels, nitrogen-containing steels have the greatest potential due to the unique ability of nitrogen not only to participate, but also to play a leading role in all hardening mechanisms [5-9].

At the same time, in order to successfully introduce high-strength steels of any structural classes for the manufacture of high-loaded marine structures, it is necessary to determine their resistance to stress corrosion cracking (SCC). Stress corrosion cracking remains one of the most dangerous fracture types of medium and high alloy steels in seawater, despite significant achievements in identifying and explaining the nature of SCC [10-13]. An adequate evaluation of susceptibility to SCC depends on development of effective test methods that simulate critical maintenance conditions and include various types of loading schemes.

At present, dynamic test methods are widely used to estimate the resistance to SCC, in which samples are

continuously or discretely loaded in an aggressive environment. In this work, the results of comparative studies of resistance to SCC of low- and medium-alloyed steels and austenitic stainless steels, which were prepared with application of various strengthening mechanisms, are given.

2 Materials and methods of investigations

The object of the study was low- and medium-alloyed shipbuilding steels of different classes with yield strength of 370-1200 MPa with ferritic-bainite, bainite-martensitic and martensitic structure.

The second group of materials under study was 0.04%C-20%Cr-6%Ni-11%Mn-1.5%Mo-0.47%N-V-Nb austenitic stainless steel produced by various methods of hardening and differing in structural phase composition:

- steel with yield strength $\sigma_{0.2}$ =400-600 MPa, having a recrystallized γ -structure after austenitization, as well as from 30% to 0% δ -ferrite due to the variation of nitrogen concentration from 0.01 to 0.50% (mass.);
- sensitized steel during aging at 700°C for 2 and 10 hours having yield strength $\sigma_{0.2}$ =550-780 MPa; steel has a high density of grain boundary carbides and nitrides due to double carbon content (0.09%) compared to the required;
- steel resulting from HTMP and having yield strength $\sigma_{0.2}$ =600-980 MPa;
- cold hardening steel with a deformation structure and $\sigma_{0.2}$ =1000-1330 MPa, obtained during cold rolling with degree of plastic deformation 15-47%.

The structure, phase composition of steels was

* Corresponding author: npk3@crism.ru

studied by the following methods:

- metallographic analysis was performed using an AxioObserver (Zeiss) light inverted metallographic microscope,
- electron microstructural studies were performed on a Tecnai G2 30 S-TWIN transmission microscope with an accelerating voltage of 200 kV,
- fractographic studies were performed on Quanta 200 scanning electron microscopes with the PEGASUS, Philips SEM-535 and Stereoscan-150 systems at an accelerating voltage of 15 kV.

Steel resistance to SCC was determined by slow strain rate tests (SSRT) and by cantilever bending of pre-cracking specimens. SSRT is designed to detect the initiation of stress corrosion cracks. Already existing crack can be propagated by using the method of cantilever bending, based on the application of principles of linear elastic fracture mechanics.

SSRT were carried out according to standards ISO 7539-7 and ASTM G129 [14,15] under some conditions:

- the rate of deformation was $2 \cdot 10^{-7} \text{ s}^{-1}$ (for stainless steels) and $2 \cdot 10^{-6} \text{ s}^{-1}$ (low- and medium-alloyed steels);
- used smooth cylindrical specimens;
- tested in air to characterize the material and to use it as reference;
- tested in 3.5% NaCl at a free corrosion potential and at room temperature;
- tested in 25% CaCl₂ at temperatures 20-100°C.

When tested by SSRT elongation and reduction of area were measured on broken specimens. Values δ and ψ obtained in a corrosive environment were compared with same characteristics obtained in air.

An original technique has been developed for testing with cantilever bending. According to the method, prismatic Charpy-type precracked specimens (with a machined notch and a fatigue crack) were periodically (stepwise) loaded on a special installation. The cantilever bending of precracking specimens were carried out at room temperature in the same corrosive media. Tests were conducted on a time base of 720 hours. After the breakdown of specimens the crack length was determined and the failure stress (σ_{SCC} or σ_C) was calculated according to the requirements of ASTM E1681 and ISO 7539-9:2003 [16, 17]. A quantitative assessment of resistance to SCC was to calculate the ratio of breaking stresses in a corrosive environment to air ($\beta = \sigma_{SCC}/\sigma_C$).

3 The results of experimental studies and their discussion

3.1 Test results of low and medium alloyed steels

Figure 1 presents the test results of low and medium alloyed steels obtained with the periodically increasing load in the form of a generalized dependence « $\sigma_{0,2} - \beta = \sigma_{SCC}/\sigma_C$ ». Comparison of accelerated laboratory tests results for steels that have shown susceptibility to SCC

(fig. 1) with incidents of steel damage because of generation corrosion cracks in real life service conditions of shipbuilding structures in natural sea water, allowed us to determine the threshold value of parameter $\beta > 0.85$.

Fig. 1 - Influence of yield strength of low and medium alloyed steels on the characteristic of resistance to SCC β when tested by the method of stepped cantilever bending in 3.5% NaCl:

- 1– ferritic-bainitic low alloy steels,
- 2– bainitic-martensitic medium-alloyed steels;
- 3, 6– martensitic alloyed steels;
- 4– low carbon martensitic steels;
- 5– medium carbon martensitic steels

In addition, the same criterion β value was obtained as a result of long (up to 10 thousand hours) tests of cantilever bending under constant load in seawater (fig. 2). The value $\beta = 0.85$ corresponded to the moment of the beginning of the decrease in the K_{QSCC} value.

Fig. 2 - Influence of yield strength of shipbuilding steels on threshold stress intensity factor (K_{QSCC}) when tested by the method of cantilever bending under constant load in sea water and relative ratio (K_{QSCC}/K_{QC}) [18]

The studied low and medium alloyed steels were conditionally divided according to the strength levels into 6 areas, each of which corresponds to a certain structural-phase composition of the steel.

It was found (fig. 1) those low- and medium-alloyed steels with ferritic-bainitic, bainitic-martensitic and martensitic structures and yield strengths from 370 to 1000 MPa are resistant to SCC in 3.5% NaCl at a free corrosion potential. In low-carbon medium-alloyed steels

with the structure of the lath martensite, SCC is observed at a value of the yield strength above 1000 MPa (Fig. 1, sector 4). A significant effect on the appearance of the SCC has a dislocation density. At density of dislocations $\rho \geq 4 \cdot 10^{14} \text{ m}^{-2}$ low-carbon medium-alloyed steels with yield strength over 1000 MPa are subjected to SCC in 3.5% NaCl. Other factors of the structural state of martensitic steels have almost no effect on SCC.

Medium carbon steels with a needle martensite structure begin to undergo SCC when $\sigma_{0.2} > 1050 \text{ MPa}$ (Fig. 1, sector 5). Fractographic studies have shown that the character of fractures of specimens undergo to SCC depends on the level of strength: at $\sigma_{0.2} = 1050\text{--}1080 \text{ MPa}$, breakdown occurs predominantly with a transcrystalline quasi-cleaved, and at $\sigma_{0.2} \sim 1200 \text{ MPa}$, brittle grain-boundary fracture with the formation of spillages.

Tests of smooth specimens under slow strain (SSRT) did not detect the sensibility of high-strength medium-alloyed steels to SCC in 3.5% NaCl at free corrosion potential unlike cantilever bending with stepwise increasing load (Fig. 3). This is obtained despite the identical time base of tests (720 hours) and the similar nature of (stepwise or continuous) deformation.

Fig. 3 - Influence of yield strength of low and medium alloyed steels on the characteristic of resistance to SCC ψ_{SCC}/ψ_C when tested by SSRT in 3.5% NaCl

3.2 Test results of nitrogen-containing austenitic stainless steel produced by various methods of hardening and differing in structural phase composition

3.2.1 Tests in 3.5% NaCl at room temperature

The resistance to SCC of samples of nitrogen-containing steel of basic composition 0.04%C-20%Cr-6%Ni-11%Mn-1.5%Mo-0.47%N-V-Nb was studied in 3.5% NaCl at room temperature using two methods. Generalized SSRT-test results for steels manufactured using various technologies are presented in fig. 4. All investigated variants of nitrogen-containing steel with the exception of sensitized steel retain resistance to SCC up to $\sigma_{0.2} = 1330 \text{ MPa}$ (fig. 4) [19-21].

The same dependence, showing the absence of non-sensitized steels to SCC, was also obtained when tested by the method of stepped cantilever bending. Data obtained is in contrast to medium-alloyed steels with a well-defined dependence of susceptibility to SCC on the

strength level (fig. 1).

A comparison of susceptibility to SCC ($\beta = \sigma_{SCC}/\sigma_C$, ψ_{SCC}/ψ_C and δ_{SCC}/δ_C), obtained by aged sensitized steel testing, with the values of toughness, shows the existence of a correlation (fig. 5). In addition, it follows that SSRT method is the most effective (values ψ_{SCC}/ψ_C and δ_{SCC}/δ_C are much reduced).

Fig. 4 - Influence of yield strength of nitrogen-containing austenitic stainless steel produced by various methods of hardening on the characteristic of resistance to SCC ψ_{SCC}/ψ_C when tested by SSRT in 3.5% NaCl.

Fig. 5 - Influence of sensitized high-carbon stainless steel toughness on susceptibility to SCC in 3.5% NaCl when tested by the SSRT method (ψ_{SCC}/ψ_C and δ_{SCC}/δ_C) and stepped cantilever bend ($\beta = \sigma_{SCC}/\sigma_C$)

The lower sensitivity of cantilever bending method for austenitic stainless steels (Fig. 5) may be associated with the complicate trajectory of slow growth of the corrosion crack along the winding boundaries of austenite grains (Fig. 6) [19].

Fig. 6 - Fracture of sensitized austenitic stainless steel tested in 3.5% NaCl

3.2.2 Tests in 25% CaCl₂ at elevated temperatures

For the ranking of non-sensitized nitrogen-containing steels in order to intensify the process of SCC, tests were conducted by SSRT in 25% CaCl₂ at elevated temperatures.

It is shown that at the test temperatures of 20 and 50°C, regardless of the amount of the ferritic phase, the steel is resistant to SCC (Fig. 7). At test temperatures 70 and 90°C as the amount of δ -ferrite increases and the nitrogen content decreases, the SCC susceptibility characteristics decrease.

Fig. 7 - Influence of the content of δ -ferrite in nitrogen-containing austenitic stainless steel on the resistance to SCC when tested by SSRT in 25% CaCl₂ at elevated temperatures

Metallographic analysis shows that corrosion cracks grow from pits predominantly transcrystalline in the austenitic phase, bending around ferritic grains (Fig. 8).

Fig. 8 - The growth of corrosion cracks in nitrogen-containing steel with δ -ferrite by SSRT in 25% CaCl₂ at elevated temperatures

The nature of crack growth was explained by the repartition of alloying elements (Cr, Mo, N) between the phases of austenite and δ -ferrite. As a result, the PRE values have changed (Fig. 9).

Figure 7 shows that low-strength nitrogen-containing steel with a fully austenitic structure, obtained as a

result of high-temperature quenching in water is resistant to SCC over the entire range of temperatures studied, including 90°C.

Fig. 9 - Influence of the content of δ -ferrite in nitrogen-containing austenitic stainless steel on phase resistance to pitting corrosion ($PRE = \%Cr + 3.3 \cdot \%Mo + 16 \cdot \%N$)

High-strength steel obtained by high-temperature thermomechanical treatment (HTMP) is not yet sensitive to SCC at 70°C, but it brittle breaks down at 90°C (Fig. 10). In the aged sensitized state the steel is not resistant at room temperature. SCC resistance of nitrogen-containing austenitic stainless steel strengthened during cold rolling decreases monotonously (Fig. 10).

Fig. 10 - The dependences of the values of the relative narrowing ψ on the test temperature in 25% CaCl₂ (SSRT) with various methods of nitrogen-containing steel hardening

Analysis of the test results of the investigated variants of nitrogen-containing steel made it possible to assess the SCC resistance as a parameter of the critical temperature for corrosion cracking T_{cr}^{SCC} , as the minimum test temperature at which SCC is observed.

4 Conclusion

1. The most effective estimate of the susceptibility to SCC of low- and medium-alloyed steels in 3.5% NaCl with the potential for free corrosion is the method of cantilever bending with a stepwise increasing load of precracking specimens. The criterion estimation of resistance to SCC when $\beta = \sigma_{SCC} / \sigma_C > 0.85$ was confirmed by the laboratory test results compared with the case studies of corrosion-mechanical fracture of shipbuilding structures in real life service conditions.
2. To predict SCC resistance of austenitic steels in the marine conditions, the SSRT method is recommended as the main test method.
3. A new approach of SCC susceptibility of austenitic stainless steels in marine conditions is proposed. It is based on estimation of the critical temperature of SCC when testing for SSRT in a concentrated solution of calcium chloride at temperatures from 20°C to 100°C.
4. The presence in nitrogen-containing austenitic steel up to 30% of δ -ferrite or structure obtained at HTMP does not cause sensitivity to SCC in 25% CaCl₂ at temperature including 50°C.
5. The deformation structure (without martensitic transformation) obtained during cold plastic deformation (with a degree up to 47%) and especially the state sensitized during aging reduce the critical temperature of SCC.

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