Stress corrosion cracking study of austenitic stainless steels by the drop evaporation test

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***ABSTRACT**: The drop evaporation test (DET) is useful for study of stainless steels and related alloys resistance to stress corrosion cracking (SCC) in the chloride containing water environments at elevated temperature. This standardised test simulates the initiation of cracking under severe evaporating conditions with possibility of local chloride content increasing and precipitation (deposition) of salts and the test can be also modified. In the contribution the austenitic stainless steels (X9CrNi 19-9, X1CrNiCr 18-14-4, X2CrNiMoN 20-18-6, annealed) were compared and evaluated by the DET. The small specimens were resistively heated (≈250°C) in the exposed section under dropping of diluted NaCl water solution. The initiation and short cracks growth as well as pits were observed during test. The sequence of material resistance to SCC was determined according to relations time to fracture - tensile stress and conventional threshold stresses. The subcritical transcrystalline corrosion cracks and ductile shearing transcrystalline mechanism of unstable final fracture were confirmed by a light and scanning electron microscopy.*

INTRODUCTION

The stainless steels with sufficient resistance to a general corrosion can be susceptible to a localized corrosion in certain environment under specific conditions [1]. Stress corrosion cracking (SCC) is not well predictable and can cause a dangerous failure of pressure vessels, pipes, apparatus, etc. For testing of the material resistance to SCC at higher temperatures (100-400°C) in water environments were proposed several methods [2].

The drop evaporation test (DET) is useful for comparison and evaluation of resistance of stainless steels and related materials to SCC in water environments containing chlorides [3-5]. This test follows the results of failure analysis in cases, when evaporation of solution (steam generators, boilers) can increase the content of chlorides in solution and/or it can form of salts (incrust) on material surface.

The relatively new DET can replace older SCC tests in boiling solution of $MgCl_2$ (which gives controversial results in comparison with a resistance in some cases in practice) and DET can partially replace expensive and

complicated tests in autoclaves at higher temperature (200 – 400˚C) and pressures. During DET is good possibility to observe a sample surface, initiation and propagation of cracking as well as pitting.

According to review [2] the DET using a 0,1 mol/l NaCl solution is approximately severe as test in boiling 35% $MgCl_2$ water solution or in autoclave at 230°C (100 ppm $Cl^- + O_2$) for austenitic stainless steels. More severe is SCC test in saturated boiling 42% $MgCl_2$ (154°C) solution. DET test can be used at temperature in the range 100~500°C and with a lower Cl^- water content (0-100 ppm).

The cyclic changes of temperature and dynamic thermal stresses during dropping are complicated and this deficiency can lower the reproducibility of DET. The process of thermal and corrosion fatigue is superposed on SCC mainly in the stage of initiation and propagation of short cracks especially in case of a higher difference of temperature between drops and heated sample. The DET simulates also the influence of heat transfer from material to environment on localized corrosion under evaporating conditions.

MATERIALS AND SPECIMENS

The SCC tests have been performed according to standard [3] with high alloy austenitic stainless steels after dissolution annealing. The chemical composition is described in Table 1.

TABLE 1: Chemical composition (% wt.)

Material	C	S	P	Si	Mn	Ni	Cr	Mo	N
X1CrNiSi 18-14-4	0,007	0,009	0,008	4,13	1,7	14,1	17,6	0,01	0,027
X2CrNiMo 20-18-6	0,017	0,009	0,011	0,403	0,71	17,9	19,7	6,0	0,195
X9CrNi 19-9	0.085	0,021	0,02	0,24	1,12	9,2	19,4	-	0,034

The specimens in the form of small rods (overall length 100 mm, cross section min. 2x2 mm, central circular section ϕ1,8 x 10 mm for corrosion exposition) were made from rolled plates by water jet cutting with addition of erosive particles, followed by shaving, precision turning and finish grinding of circular section in order to minimize a surface roughness ($R_a \approx 0,1$ μm) and residual stress. Before testing the specimens diameters were precisely measured by micrometer and circular section were cleaned.

The tensile tests were also performed on the small specimens for comparison purposes and for determination of relative stresses (σ/R_m, $\sigma/R_p0,2$, where σ is external tensile stress). The main mechanical properties (R_m - tensile strength, $R_p0,2$ - yield strength, A – elongation, HV – Vickers hardness (at 10kp = 98,1N)) of tested steels are given in Table 2.

TABLE 2: Mechanical properties (at room temperature)

Material	R_m [MPa]	$R_p0,2$ [MPa]	A [%]	HV10
X1CrNiSi 18-14-4	675	353	57	197
X2CrNiMo 20-18-6	696	374	51	176
X9CrNi 19-9	620	261	49	165

TESTING PROCEDURE

The susceptibility to corrosion cracking for selected materials was determined according to standard of DET at a constant external load [3]. The scheme of test device is shown in Figure 1.

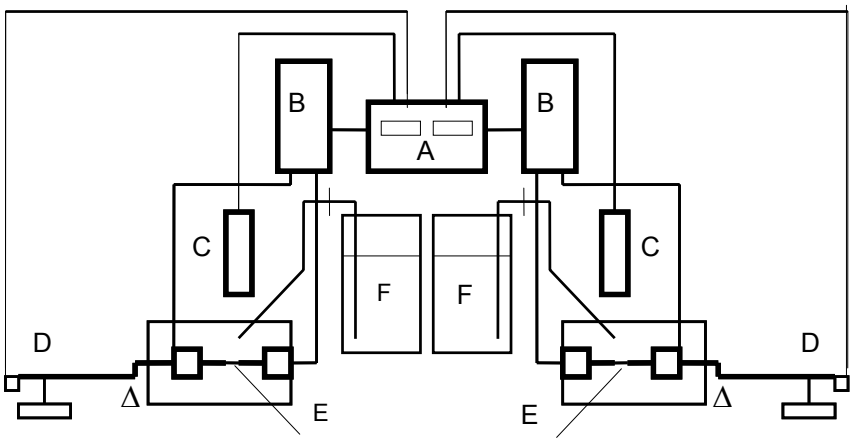

Figure 1: Scheme of device for drop evaporation test

A – control and regulating unit
B – power transformer
C – infrared probe
D – loading and button switch
E - specimen under loading
F – glass tank for solution

The specimens, fixed horizontally into grip jaws, were resistively heated by a passing current (20~30 A) up to 250˚C in the exposed section during dropping of 0,1 mol.l^{-1} NaCl water solution with frequency about 0,1 Hz on surface. The upper specimen temperature was controlled by means of non-contact optical probe, which uses an infrared radiation (pyrometer method) and a thermoregulator with suitable transformers [5,7].

At testing the specimens were observed in order to evaluate the parameters of the fracture initiation and a length of short cracks on surface.

When the specimen fractured, time to fracture was registered by electromechanical clock and number of cycles (N_f, drops) to fracture was also calculated. If the specimen had not broken within 1500 hours, the test was interrupted and the specimen was taken out. After testing the exposed sections of specimens were cut off and fracture surfaces were examined by light and scanning electron microscope. Then specimens were prepared for metallographic study of structure and cracks in cross section.

DESCRIPTION AND DISCUSSION OF RESULTS

From described experiments there were obtained the relations: time to fracture versus tensile stress (t_f - σ), see Figure 2, that can be transformed easily to other relations (t_f - σ/R_m, t_f - σ/R_p, N_f - σ). The conventional threshold stresses can also be determined from these relations.

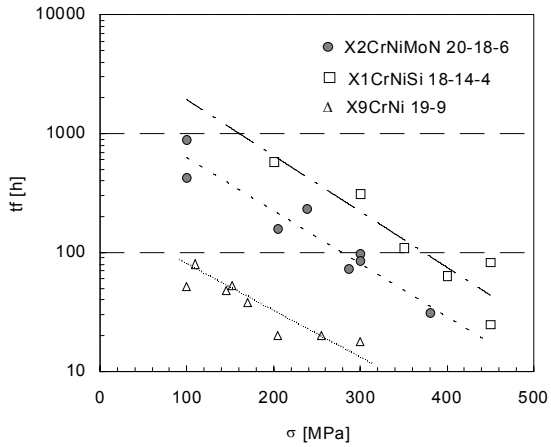

Figure 2: Dependences of time to fracture on tensile stress

The linear trends ($\log t_f = a + b.\sigma$) show that time to fracture (life-time) of steel X2CrNiMoN 20-18-6 is 8 - 10 x higher then steel X9CrNi 19-9, and steel X1CrNiSi 18-14-4 reached on the average 3 x longer life-time than X2CrNiMoN 20-18-6 as compared under the same conditions (stress). The higher scatter of time to fracture could complicate the comparison of results.

The SCC crack initiation and propagation accompanied by corrosion thermal fatigue mean that there does not exists the marked threshold stress ($\sigma \rightarrow \sigma_\infty$, $t_f \rightarrow \infty$), but the conventional threshold stress can be set up, e.g. for time 1 500 h [6] and/or for 2.10^5 cycles (drops) or according to [3, 4] for 500 hours (σ_{500}). These conventional values are approximately 320 MPa, 130 MPa and 0 MPa (or 0,90; 0,35; and 0 $R_p0{,}2$) for tested steels (Figure 2).

The threshold stress values described in [2,8] are much higher for steel X2CrNiMoN 20-18-6 (0,95 $R_p0{,}2$) in comparison with steel X9CrNi 19-9 or X2CrNiMo 17-12-2 (0,05 $R_p0{,}2$). Corrosion cracking has appeared at relatively low stresses, corresponding to the severe corrosion conditions of DET for classical stainless steels.

The initiation of small pits or short cracks was accompanied by small elliptical spots (max. ϕ 0,5 mm) of a bright color, different from the rest of an exposed area of sample with dark gray and black color after longer test time. The localized change of the surface color is the result of intensive electrochemical corrosion reactions – cyclic anodic dissolution in the pits or crack tips and a cathodic reduction in their vicinity (galvanic cells).

In accordance with dropping direction the number of cracks was higher on the upper side of sample (2 – 5 cracks per mm of length on the exposed part, X9CrNi) while on the bottom was smaller number (0 – 2 cracks/mm). The numbers of cracks on exposed surfaces are in relation with the time to fracture: for steel X2CrNiMoN 20-18-6 on the average 8 cracks and for steel X1CrNiSi 18-14-4 on the average 5,5 cracks.

The initiation of cracks was probably facilitated by thermal fatigue process, because first short cracks were observed earlier than 0,1 of time to fracture. Also higher number of shorter cracks can be explained by thermal fatigue, when crack growth rate decreases with the increasing crack length. The short crack growth rates were found out in the range 0,1-10 nm/s.

The transcrystalline corrosion cracks were observed, mostly brittle and normal to specimen axis with limited branching, see Figure 3 and 4.

The fracture surfaces were formed of 50–80 % by corrosion crack propagation and were normal to the applied tensile stress. On the other hand the final unstable fracture was angular (~ 45º) to the sample axis and can be characterized as irregular in the space with clear metal appearance and with a shear ductile transcrystalline micromechanism of cracking.

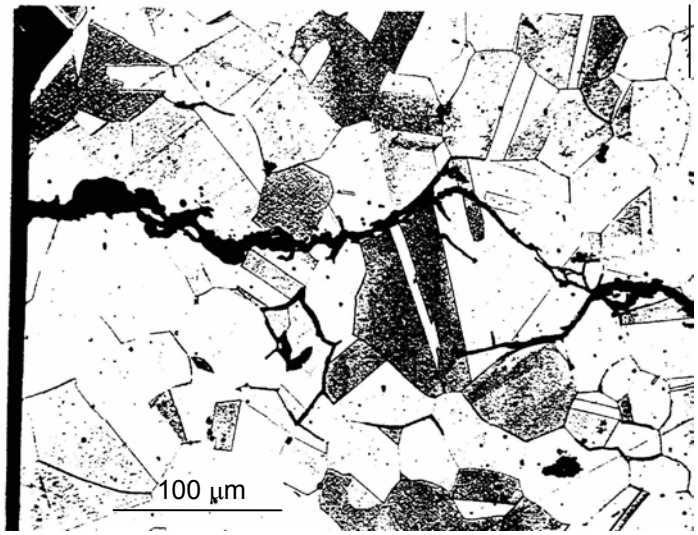

Figure 3: Cracks in steel X2CrNiMoN 20-18-6

Although on the surface of austenitic stainless steel X1CrNiSi 18-14-4 were formed pits, its resistance to SCC was a higher than that of other tested steels (Figure 2). These results are in agreement with the knowledge about positive influence of silicon on improving SCC resistance of steels. The higher susceptibility of steel X1CrNiSi 18-14-4 to pitting was also confirmed by the potentiodynamic polarization tests, e.g. depassivation potential at 100°C in 1 mol/l NaCl water solution have value –300mV (SCE), whereas steel X2CrNiMo 20-18-6 and X9CrNi 19-9 have the corresponding values 700 mV and 0 mV (SCE).

These experimental results are in agreement with distribution of thermal cyclic stresses in the sample. The sharp tensile thermal (two-axial, saw type "quick-slow") stress peaks appear on the sample surface, when the water drops cool down the hot sample. The higher is value of external constant stress, the relatively smaller influence of cyclic thermal stresses.

The fatigue striations have not been found by scanning electron microscopy, because of the anodic dissolution of material in the crack tip and formation corrosion products inside cracks. The final fracture was metallic clean and the ductile shearing fracture micromechanism was observed. The cleavage fasets and/or areas were not found out too.

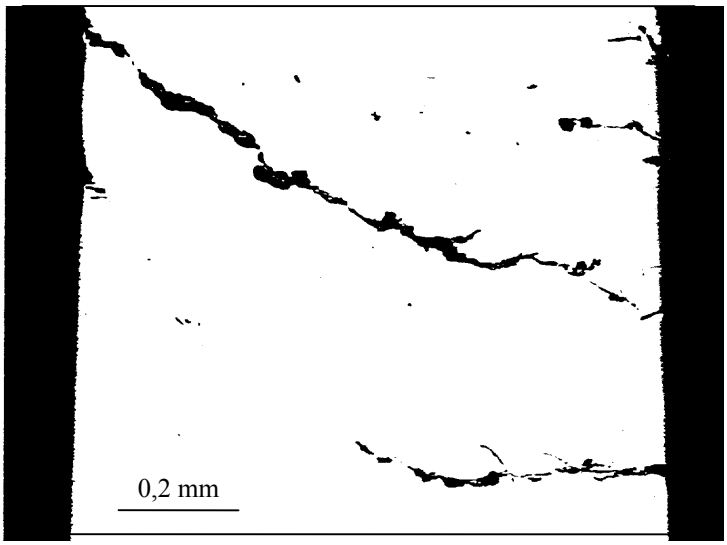

Figure 4: Typical corrosion cracks in steel X1CrNiSi 18-14-4

The initiation of cracks or a propagation of short cracks is also influenced by state of the sample surface mainly by surface roughness [6], residual stresses and surface strengthening. The value of these factors were the same and minimal for all tested samples.

Further crack propagation through the cross section of sample is influenced by the chemical composition and structure of stainless steel, including sensitization [9,10].

CONCLUSION

In the contribution is compared and evaluated the resistance of high alloy austenitic steels (X1CrNiSi 18-14-4, X2CrNiMoN 20-18-6, X9CrNi 19-9, after solution annealing) to stress corrosion cracking at elevated temperature ≈ 250°C by the drop evaporation test (DET). This method is effective for observation of short corrosion cracks growth and can be also used for experimental study of pitting or thermal fatigue corrosion.

The sequence of tested stainless steel with respect to SCC resistance under DET conditions have been found according to relations of time to fracture – tensile stress: X1CrNiSi 18-14-4, X2CrNiMo 20-18-6, X9CrNi 19-9 or according to conventional threshold values.

Metallographic and fractographic observation was aimed at a mechanism of cracking, geometry and number of short cracks. The transcrystalline crack propagation was observed in tested steels.

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