STRESS CORROSION BEHAVIOUR OF HIGHLY ALLOYED STAINLESS STEELS UNDER SEVERE EVAPORATIVE CONDITIONS

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ABSTRACT

Using the Drop Evaporation Test (DET), the stress corrosion resistance of highly alloyed stainless steels under severe evaporative conditions have been compared. The Drop Evaporation Test involves electrical heating of a tensile specimen under constant load and at the same time slowly dripping a dilute (0.1M) sodium chloride solution onto the specimen. The paper presents the performance of the newly developed high nitrogen superaustenitic stainless steel Avesta 654 SMO™ as well as Avesta 254 SMO® and 904L in the Drop Evaporation Test and compares these results with the performance of the duplex stainless steels Avesta SAF 2507®, Avesta 2205 and Avesta SAF 2304®. All the steels perform far better than ordinary stainless steels type 304 and 316. The highly alloyed, fully austenitic stainless steels rank higher than the duplex stainless steels in their SCC resistance under the severe evaporative conditions established in the test.

INTRODUCTION

The inherent possibility that a dilute and thereby harmless solution of chlorides can turn into a concentrated solution, if enough water evaporates, is a returning concern, when evaluating possible stainless steels for a specific application.

In so far that "near to dryness" evaporation leads to a very small volume of electrolyte, the risk for severe localised corrosion in the form of perforating pits and crevice corrosion is likely to be small in most practical situations. Some staining and superficial pits may be observed, but not with any significant depth in the corrosion attack.

However Stress Corrosion Cracking (SCC) of stainless steels under evaporative conditions has for long been recognised as a factor that needed special attention, since the crack propagation rate of a SCC crack can be many times the propagation rate of a pit. This means that failure of a component due to SCC can occur within very short periods of time, that is within a few days or even hours in the most extreme cases. At the same time it should also be noted that SCC is observed to occur in situations where pitting does not.

The development of the Wick test (Dana test) by Dana and Delong [1] is one early example, where a SCC test was proposed that specificly tried to simulate evaporative conditions. In this case evaporation occurs from an insulation material wetted with a dilute chloride solution in contact with a hot stainless steel surface. This initial test regarding SCC under wet thermal insulation was standardized in 1971 in ASTM C692 [2], which has beeen updated in 1977 and 1990.

In the beginning of the 70'ies a new concept towards SCC testing under simulated evaporative conditions, the Drop Evaoporation Test (DET), was proposed by "Studsvik Energiteknik", Sweden. The development of this test was supported by the Swedish Ironmasters Association and done in cooperation with a number of swedish stainless steel producers.

The main aim of the Drop Evaporation Test was to be able to give a more realistic *ranking* of stainless steels with regard to SCC under evaporative conditions.

The resulting test method, the Drop Evaporation Test [3], was soon implemented in MTI Manual No. 3 [4] as a supplementary method for ranking stainless steels with regard to SCC resistance. The more conventional technique proposed in the MTI Manual was U-bend specimens immersed in a $MgCl_2$ solution, but this test has for long been recognised as giving results that were difficult to correlate to actual service experiences.

The developmental work on the DET-method was followed in the beginning of the 80'ies by a round-robin test [5], which led to slight alterations in the test procedure compared to what was published earlier.

In the present investigation a follow up on DET-results already published by Wallén et. al. [6], is presented, whereby the performance with regard to the Drop Evaporation Test of the full spectrum of the highly corrosion resistant stainless steels produced by Avesta Sheffield AB today is illustrated. The investigation covers both duplex as well as fully austenitic stainless steels.

EXPERIMENTAL

Test Material

The test material was taken from cold rolled plate, 2-7,5mm thick, direct from current production, except 654 SMO, which was taken from a 11 mm thick hot rolled plate. The chemical composition of the tested steel grades are shown in table 1.

Table 1 Chemical composition of test materials.

Test Material	UNS No.	Chemical composition, %(w/w)									
Heat no.		C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu
SAF2304	S32304										
376401		0,019	0,50	1,48	0,025	0,002	22,52	4,77	0,34	0,097	0,30
2205	S31803										
181716		0,022	0,37	1,40	0,027	0,001	21,53	5,58	3,01	0,151	0,26
383547		0,023	0,38	1,39	0,022	0,001	21,89	5,46	3,03	0,123	0,21
SAF2507	S32750										
462854		0,022	0,16	0,35	0,015	0,001	24,29	6,62	3,74	0,284	0,06
904L	N08904										
182970		0,011	0,59	1,58	0,022	0,001	19,78	24,71	4,34	0,067	1,44
174836		0,011	0,62	1,72	0,021	0,003	19,81	24,69	4,61	0,035	1,56
254SMO	S31254										
183277		0,018	0,35	0,42	0,023	0,001	19,92	18,05	6,18	0,204	0,67
177718		0,019	0,38	0,50	0,022	0,001	19,64	17,90	6,12	0,202	0,67
654SMO	S32654										
376985		0,017	0,29	2,01	0,021	0,001	24,27	22,00	7,30	0,452	0,43

Mechanical properties for the steels are shown in table 2. Please note, that two values are given for SAF 2304 since two different plates with different thickness was used.

Table 2 Mechanical properties for test materials at 200°C.

Test Material *Heat no.*	UNS No.	$Rp_{0.2}$ N/mm²	$Rp_{1.0}$ N/mm²	Rm N/mm²	A_5 %
SAF2304	S32304				
376401	7.5mm	327	374	559	29
376401	3.0mm	380	426	569	33
2205	S31803				
181716		448	499	682	29
383547		457	509	684	30
SAF2507	S32750				
462854		433	488	720	37
904L	N08904				
182970		228	262	532	46
174836		215	253	502	45
254SMO	S31254				
183277		246	292	597	53
177718		270	298	608	49
654SMO	S32654				
376985		333	363	693	50

Test Procedure

Specimen preparation
Test specimens, 100x2x2 mm, were cut from the plate longitudinal to the rolling direction as close to the surface of the plate as possible. A 10 mm long and 1,8 mm diameter gauge section was turned in the midle of the specimen.

After machining the specimens were degreased and electropolished in a solution consisting of 150g citric acid, 600 ml conc. H_3PO_4, 400 ml conc. H_2SO_4 and 300 ml H_2O. Electropolishing was performed at 1A/cm² for 3 minutes. The temperature of the solution is initially at room temperature, but it is raised to around 60°C (<70°C) after 3 minutes due to the current passing in the solution.

After electropolishing the specimen is rinsed with destilled water, passivated in 20% HNO_3 for 20 minutes and then again rinsed with destilled water.

Testing
The specimen is attached horizontally to two specimenholders and the load is applied vertically by weights connected to the holders by steel wires over rollers. The weights are matched to give the desired uniaxial load.

Immediately after loading, the specimen is resistance heated to approximately 300°C in the gauge section corresponding to 20-21A and approximately 0.3V across the specimen.

Air saturated 0.1M NaCl is dripped onto the specimen gauge at a rate of 6 drops per minute (0.1Hz) by a peristaltic micropump through a vertical glass tube (D_i = 0.5 mm, D_o = 4.5 mm). The distance from the glass tube orifice to the specimen is 10 mm. The current is manually adjusted, so that one drop just completely evaporates before the next drop comes in contact with the specimen.

The test is continued until complete fracture of the specimen or up to 500h. The time to fracture is recorded by a timer connected to the load train.

In figure 1, a typical temperature profile versus time for the gauge section surface being wetted and dried continuously is shown.

It should be recognised that the desired evaporative conditions is an unstable stationary situation. Very small changes in the current, the room temperature or the surface state of the specimen will affect the stationary condition. Nevertheless the desired evaporative condition can be maintained with minor adjustments, because the part of the specimen not in contact with the drops and the specimen holders act as a heat sink for the gauge section, which leads to buffering of the temperature in the gauge section.

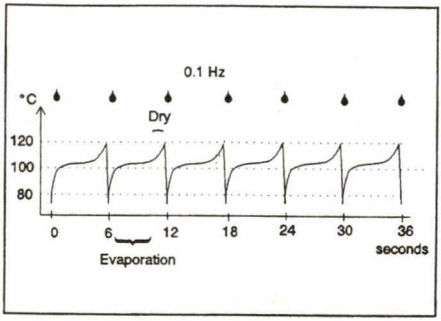

Figure 1 Typical temperature-time profile for tested surface in the DET-test

During testing the evaporative conditions are checked two times (morning and evening) every day, except at weekends. Adjustments are usually only necessary once or twice every week.

If the drop seems to evaporate too slowly to obtain complete dryness before the next drop hits, the current is raised slightly.

If the drop tends to boil on the surface, indicating that the specimen is too hot, the temperature of the specimen is lowered by either adjusting the current or in some cases cooling the specimen with a small stream of destilled water beside the specimen gauge.

RESULTS

Time to failure

Table 3 shows the obtained results from the Drop Evaporation Test. The shaded areas indicate alloy-load combinations where likelihood for failure due to SCC is minimal or non-existent.

Table 3 Results from the Drop Evaporation Test for various alloys

Material	Heat No.	Time (hours) to failure at various % of $Rp_{0.2}$(200°C) "n.c." (no cracking), indicates no failure due to SCC within 500 hours								
		20%	30%	40%	50%	60%	70%	80%	90%	100%
SAF 2304	376401	n.c. n.c.	n.c. n.c. n.c. n.c. n.c. n.c.	n.c.	454 n.c. n.c. 324 176 118	412 503	235 241 288 444 414		69 58 144 31 20	
2205	181716		n.c. n.c.	471 n.c.	462 188	384	246 178	145 206	295 159	97 119
	383547	n.c.	n.c. n.c.	89 432 133 431 407	n.c. n.c. n.c. n.c.		147		112 188	
SAF 2507	462854				n.c. n.c.		408 n.c. n.c.	n.c. n.c.	220 93 114 n.c. 75 166	
904L	182970					n.c. n.c.	n.c. 328	160 150 447		463 111
	174836	n.c.		n.c. n.c.			n.c. n.c.		230 348	
254 SMO	183277						n.c. n.c.	n.c. n.c.	n.c. n.c.	n.c. n.c.
	177718						n.c. n.c.	n.c. n.c.	n.c. 438	186 140
654 SMO	376985						n.c. n.c.	n.c.	n.c. n.c. n.c. n.c.	n.c. n.c.
		20%	30%	40%	50%	60%	70%	80%	90%	100%

In most cases the "n.c.", that is "no cracking", indicates no failure within 500 hours and no cracks visible on the surface by visual examination. In the case of SAF 2304 at 30% load relative to $Rp_{0.2}$(200°C), several of the "n.c." specimens

did fail, but the failure was caused by thinning of the gauge section due to general corrosion without any signs of SCC.

Earlier, data for 2205, 904L and 254 SMO have been published by Wallén et. al. [6].

Visual examination
All specimens have been examined visually in a stereo microscope (x30) and a representative number of failed specimens have further been evaluated through exmination of micro sections.

The general appearance after testing of all gauge sections on the specimens, whether they have failed or not, shows a rather heavy staining in reddish and brown colours - in some cases, where cracks are present, also with a bluish tint.

In most cases the staining of the surface of a non-failed specimen can be attributed to small pits or cracks, however in the case of 654 SMO no pits, cracks or any other localised corrosion was observed after a thorough investigation of the surface in a Scanning Electron Microscope.

Specimens of SAF 2304, which is the lowest alloyed of the test materials, were severely corroded in a form that has to bee termed "general corrosion" and not localised corrosion. Figure 2 shows a cross section of a failed SAF 2304 specimen without signs of stress corrosion cracking being involved.

Crack appearance
In figure 3 a typical SCC crack formed during the DET is shown.

The cracks produced in both the fully austenitic as well as the duplex stainless steels are transgranular, but less branched than "classical" stress corrosion cracks. The walls of the cracks are significantly corroded.

The duplex stainless steels show transgranular cracks accompanied by selective dissolution of the ferrite. The surface appearance of the primary crack has a stringy appearance, which can be attributed to the selective dissolution of the ferrite phase.

The crack tip in the duplex stainless steels tends to avoid the austenite phase resulting in a kind of staircase path for the crack tip, but the final crack propagation path is still transgranular in both the ferrite and austenite phase. The staircase path is less obvious away from the crack tip due to continued corrosion of the crack sides as the crack propagates.

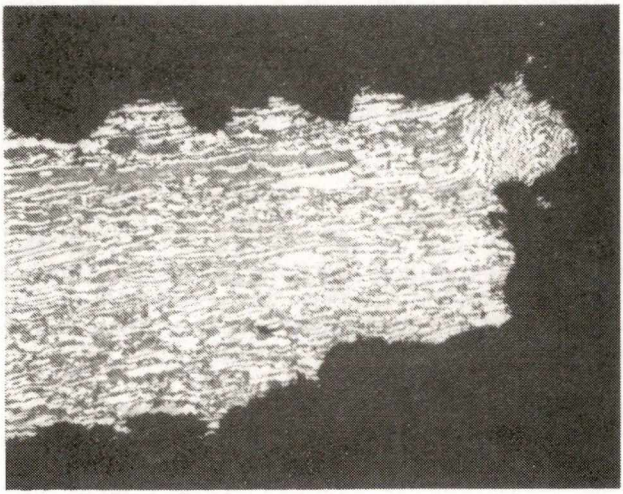

Figure 2 Failure due to general corrosion. SAF 2304 after testing at 30% $Rp_{0.2}$ for 442 hours. Etchant: Murakamis (x50). Photo No.: M39532

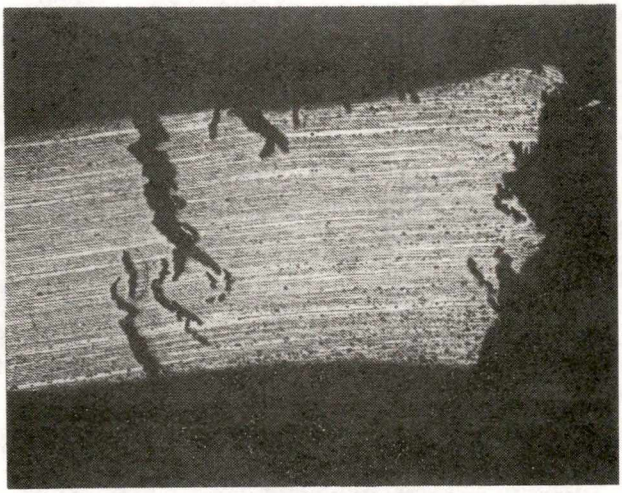

Figure 3 Typical crack appearance. SAF 2507 after testing at 90% $Rp_{0.2}$ for 114 hours. Etchant: Murakamis (x50). Photo No.: M39465

DISCUSSION

Ranking

The main aim of the Drop Evaporation Test is to establish a ranking order with regard to SCC resistance under evaporative conditions.

In table 3 all load-alloy combinations where no failure due to cracking was observed has been shaded together with load-alloy combinations that show indecisive results.

An exact relative threshold load is difficult to define, nevertheless the relative ranking seems quite obvious. A tentative list of threshold loads relative to the yield stress have been extracted from the data in table 3. These thresshold values are shown in table 4.

Table 4 Relative threshold stresses (data for type 304 and 316 have been taken from ref. [5] and [6]).

Material	% of $Rp_{0.2}$ at 200°C below which no failure due to SCC is expected
654 SMO	> 100
254 SMO	≈ 90
904L, SAF 2507	≈ 70
2205, SAF 2304	≈ 40
(316, 304)	(≤ 10)

The ranking of all the special stainless steels is clearly above the relative performance of conventional stainless steels type 304 and 316.

The relative ranking between 2205 and SAF 2304 is somewhat difficult to assess due to the severe general corrosion observed on SAF 2304 at lower stresses. However, if this is disregarded, the relative ranking with regard to SCC seems to be in favor of SAF 2304, which is in agreement with SCC results obtained in magnesium chloride environment by Gustafsson and Erikson [7].

An alternative to the ranking above based on threshold stresses relative to the yield stress of the material, would be to rank the alloys in order of the absolute thresshold stress. Using the absolute threshold stresses would change the ranking order due to the superior strength of the duplex stainless steels.

In many practical situations use of the materials actual strength is attempted, which means that stronger materials are also stessed more than less strong materials.

Furthermore, most constructions are welded, and the stresses associated with the welds are always related to the actual materials stress-strain characteristics.

In those cases where constructions do not take advantage of the actual strength of the material, the constructions tend to be over dimensioned, which only leaves bendings and weld zones as critical stress areas.

It follows from the above arguments that ranking relative to the materials actual strength is the most relevant method.

Environmental considerations

The fact that highly alloyed stainless steels like 904L and 254 SMO crack in this test, where the temperature of the test surface in wetted condition is below 120°C illustrates the severity of the test. In actual service life these alloys have shown excellent SCC resistance for many years.

The observations regarding the general corrosion of SAF 2304 and the widening of the cracks due to corrosion at the sides of the cracks even in the highly alloyed steels like SAF 2507 and 254 SMO is further evidence of the severe aggressive environment that is being established on the surface of the specimens during testing.

Several factors are likely to be involved in establishing this aggressive environment.

Firstly the extremely high chloride concentration corresponding to a saturated chloride solution due to the complete evaporation, before the next drop falls onto the specimen.

Secondly the variation of the temperature in the gauge section - as shown in figure 1 - introduces variations in the loading relative to the actual yield stress, because the actual yield stress depends on the temperature. The stress situation is further complicated by the thermal elongations and contractions that inherently follows the variation in temperature.

In the Wick test, [2], evaporative conditions at a constant or very slowly varying temperature at approximately 100°C is established. The chloride concentrations at the specimen surface are similar to those established in the Drop Evaporation Test. Never the less, results [8] based on the Wick test [2] have shown that 2205 does not crack in this test, which once again emphasises the severity of the Drop Evaporation Test. It should be noted that the Drop Evaporation Test uses constant load, whereas the Wick test involves U-bend specimens.

The relative importance of the chloride concentration, compared to the cycling of the temperature in establishing the highly aggressive environment in the Drop Evaporation Test, is uncertain at present. It is clear, however, that the cycling of the temperature during the wet and dry periods can not be disregarded without further studies.

It follows from the above discussion that it is necessary to distinguish between evaporative conditions involving, 1) cycling of the temperature due to complete evaporation in between wetting and conditions where 2) evaporation occurs, but without periods of complete dryness. The former situation is likely to be more aggressive than the latter.

As a final comment it should be remembered that the above results are based on a pure NaCl solution. The influence of other salts in the solution may in some cases promote and other cases inhibit stress corrosion cracking.

CONCLUSIONS

Ranking with regard to stress corrosion cracking resistance of highly alloyed stainless steels under evaporative conditions has been established based on results from the Drop Evaporation Test.

The following ranking was obtained

654 SMO	Most resistant
↓	
254 SMO	
↓	
904L, SAF 2507	↓
↓	
2205, SAF 2304	
↓	
304, 316	Least resistant

It has been shown that the environment that is established during the Drop Evaporation Test is highly agressive, and therefore not necessarily fully representative for all evaporative conditions.

Cracks formed during the Drop Evaporation Test are transgranular in both fully austenitic and duplex stainless steels, though the crack tip tends to avoid the austenite phase in the duplex stainless steels.

The crack appearance is generally less branched than classical stress corrosion cracks. The walls of the cracks are significantly corroded.

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