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Modern Stainless Steels to Combat Chloride-induced Localized Corrosion

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From many aspects, stainless steels are excellent construction materials, but they also have drawbacks, one being their susceptibility to chloride-induced localized corrosion. However, modern stainless steels, both austenitic and ferritic–austenitic grades, have been developed to combat these types of corrosion.

This paper gives a short description of some such steels, ranging from a duplex steel with 23 per cent chromium, developed as a cost-effective alternative to conventional austenitic grades like AISI 304/304L and AISI 316/316L, to highly alloyed austenitic grades with up to 7 per cent molybdenum, which can sometimes be used instead of titanium- and nickel-based alloys.

Some corrosion data are presented ranking these modern steels in relation to well-established grades, and a short discussion of their cost-effectiveness is included. Some practical experiences from different fields of application are mentioned to demonstrate the benefits from the use of these modern steels.

Introduction

From many aspects, stainless steels are excellent construction materials: they resist corrosion in many environments, they are tough and strong, and they can easily be fabricated into various complicated forms. However, they have one serious drawback: they are susceptible to chloride-induced localized corrosion, i.e. pitting, crevice corrosion, and stress–corrosion cracking. The last-named has even sometimes been called the Achilles' heel of stainless steel.

This paper describes a series of modern stainless steels that were developed to cope with chloride-containing environments, some being cost-effective alternatives to conventional grades like AISI 316L/317L (which is intended for less aggressive environments), and some being developed to resist more severe environments (e.g. those involved in seawater handling and flue-gas desulphurization).

Modern Stainless Steels

The most important factor in increasing a steel's resistance to pitting and crevice corrosion is its chemical composition, the most important alloying elements being chromium, molybdenum, and nitrogen.

Attempts have been made to establish a measure of the resistance to pitting and crevice corrosion by calculation of the sum of these alloying elements in a weighed form. This sum is called the pitting resistance equivalent (PRE) or pitting index (PI). Different expressions have been proposed by different researchers, and one commonly used formula[1] is shown below:

$$PRE = \% Cr + 3,3 \times \% Mo + 30 \times \% N.$$

Since chloride-induced transgranular stress–corrosion cracking (SCC) in most cases starts as pitting corrosion, the same alloying elements as mentioned above also retard the initiation of SCC. The propagation of SCC is, however, also influenced by other factors. In austenitic stainless steels, a high nickel content is advantageous, but a rebalancing of the composition to give a ferritic–austenitic or duplex structure has a strong positive effect. Consequently, steels intended to resist pitting and crevice corrosion should have high contents of chromium, molybdenum, and nitrogen and, if they are intended for elevated temperatures where SCC is also a hazard, they should, in addition to this, be either austenitic with a high nickel content or ferritic–austenitic.

Modern stainless steels that were developed for these purposes are listed in Table I, which also gives some more conventional grades for comparison.

TABLE I
LEVEL OF RELEVANT ALLOYING ELEMENTS AND PRE-NUMBERS FOR SOME MODERN STAINLESS STEELS AND ONE NICKEL-BASED ALLOY

Avesta	ASTM	Cr	Ni	Mo	N	PRE*	Structure†
18-10L	304 L	18	10	—	—	20	A
17-11-2L	316 L	17	11,5	2,2	—	26	A
SAF2304‡	S32304	23	4,5	—	0,1	26	FA
17-14-4LN	S31726	17	13	4,2	0,14	35	A
904 L	N08904	20	25	4,5	—	36	A
2205	S31803	22	5,5	3,0	0,17	37	FA
254 SMO	S31254	20	18	6,1	0,20	46	A
SAF 2507‡	S32750	25	7	4,0	0,30	47	FA
654 SMO	—	24	22	7,3	0,50	63	A
Alloy 625	N06625	22	63	9	—	53	A

* Nitrogen estimated to 0,05% in non N-alloyed grades
† A = austenitic, FA = ferritic–austenitic
‡ Produced on licence from Sandvik Steel, Sweden

Corrosion Resistance

Pitting and Crevice Corrosion

One way of ranking the resistance of a steel to pitting and crevice corrosion is to use the PRE numbers given in Table I. However, more confidence is provided if the resistance is measured by means of tests in chloride-containing solutions.

Table II contains results from two types of pitting-corrosion tests: one is an electrochemical test performed in 1 M sodium chloride solution; and the other is an immersion test in 6 per cent ferric chloride according to ASTM G48 practice A. The electrochemical method used is partly based on the standard method ASTM G61, but the test is carried out by means of a special cell developed by Avesta (the Avesta Pitting Cell[2]). With this cell, the pitting resistance can be measured eliminating the uncertainty caused by the simultaneously occurring crevice corrosion at the specimen holder. The recorded result is the critical pitting temperature (CPT), i.e. the temperature above which pitting is initiated. Some results from a comprehensive study by Garner are also included for comparison[3]. Garner's results, based on ASTM G48-A, are presented as the average CPT values for several commercial grades covered by the steel standard designation in question.

TABLE II
CRITICAL PITTING TEMPERATURES, CPT, FOR STAINLESS STEELS IN CHLORIDE-CONTAINING SOLUTIONS

Grade	PRE	CPT, °C		
		NaCl	$FeCl_3$	$FeCl_3$*
316L	26	12	5	14
S32304	26	16	20	—
S31726	35	54	45	44
N08904	36	61	44	42
S31803	37	52	38	—
S31254	46	90	81	87
S32750	47	90	82	—
654 SMO	63	>95	>103	—
Alloy 625	52	>95	98	—

* According to Garner[3]

Also, the results from Avesta are based on several heats with varying PRE numbers, giving varying CPT values. They are consequently not the exact figures achieved, but average values from a number of tests.

Based on the discussion above and the test results in Table II, the following conclusions can be drawn:

- the PRE number gives a fairly good description of the relative resistance to pitting and crevice corrosion
- the duplex-grade Avesta SAF 2304 is not inferior to AISI 316L
- the duplex-grade Avesta 2205 is not very inferior to austenitic grades with the same PRE numbers
- Avesta SAF 2507 and Avesta 254 SMO have the same resistance to pitting and crevice corrosion
- Avesta 654 SMO is superior to the other grades discussed.

Stress–Corrosion Cracking

The ranking of stainless steels according to their resistance against SCC is based mainly upon different types of tests in chloride-containing environments. One such test is the drop-evaporation test (DET), in which a uniaxially loaded and electrically heated sample is exposed to a dilute sodium chloride solution that is dripped onto the sample[4]. The dripping rate is adjusted to allow one drop to evaporate before the sample is hit by the next drop. The initial temperature of the sample is 200 °C, but the temperature is reduced to approximately 100 °C when the sample is exposed to the test solution.

It is obvious from the DET results presented in Table III that

- the duplex-grades Avesta SAF 2304 and Avesta 2205 are far superior to a conventional austenitic grade like AISI 316
- the highly alloyed austenitic grade Avesta 254 SMO and the duplex grade Avesta SAF 2507 are superior to Avesta 904L, which is normally considered to be very resistant to SCC thanks to its high nickel content.

TABLE III
SCC IN SODIUM CHLORIDE AS DETERMINED BY THE DROP-EVAPORATION TEST AT APPROXIMATELY 100 °C

Grade	Minimum stress for SCC		TTF* h
	R/Rp 0,2†	MPa	
AISI 316	<0,1	<21	155 158
SAF 2304	0,5	181	467 470
2205	0,5	229	360 >500
904 L	0,9	194	230 348
SAF 2507	0,9	374	415 >500
254 SMO	>0,9	>221	>500 >500

* TTF = time to failure, two samples per grade
† Applied stress related to the yield strength, *Rp 0,2* at 200 °C

Design and Economy

Mechanical Properties

All the modern stainless steels described have higher-strength than conventional austenitic grades, e.g. Avesta 17-11-2L (AISI 316L) and 904L (Table IV).

TABLE IV
MECHANICAL PROPERTIES OF SOME STAINLESS STEELS, MINIMUM VALUES AT 20 °C

Grade	*Rp 0,2* MPa	*Rm* MPa	A5 %
17-11-2L	210	490	45
904L	220	500	35
254 SMO	300	650	35
SAF 2304	400	600	25
654 SMO*	465	835	55
2205	480	680	25
SAF 2507	540	780	25

* Indicative values

Costs

Modern stainless steels are more expensive than AISI 316, with the exception of Avesta SAF 2304 (Table V). If, however, the strength is also considered, the cost difference becomes less and the duplex grades especially look very attractive.

One natural application for high-strength materials is in

TABLE V

RELATIVE COSTS FOR SOME STAINLESS STEELS BASED ON PRICES FOR 5 mm PLATE IN AUGUST 1991

Grade	Price per kg	Price per MPa*
17-11-2L	100	100
904L	224	214
254 SMO	300	210
SAF 2304	97	51
2205	129	56
SAF 2507	247	96

* Yield strength, *Rp 0,2* according to Table IV

pressurized items, but high strength can also be utilized in non-pressurized applications, e.g. big storage tanks in chemical factories or breweries (see also 'Applications' below).

Applications

Seawater Handling

Stainless steels of type 316L/317L are not resistant enough to handle aerated seawater at ambient or slightly elevated temperature (30 to 35 °C). Numerous failures have occurred, for example in seawater-cooling systems on board ships[5] and in desalination plants[6].

However, experience from offshore installations in the North Sea shows that highly alloyed grades like Avesta 254 SMO can be used in piping systems at temperatures[7] of up to around 40 °C. Crevice-corrosion damages have been reported[8] for 254 SMO when used in chlorinated seawater at temperatures around and above 50 °C. This is in good agreement with a comprehensive study of 254 SMO in chlorinated seawater, which found a maximum service temperature of 40 °C at a residual chlorine level of 1,5 to 2 p.p.m. when the pipes are joined by flanges[9].

Avesta 254 SMO has also been used successfully, mainly for tubes but also for sheets, in a number of power-plant condensers[10]. In most cases it has replaced copper-based alloys, aluminium, brass, and copper–nickel, but in one case also titanium. The outer layers of titanium tubes had suffered erosion from the steam side in a Swedish nuclear-power plant, and around 50 km of 254 SMO tubes were used for the replacement after tests showing the superior resistance of 254 SMO to this type of corrosion. Such damages have occurred in the condensers of several Swedish nuclear-power plants and, in another plant, shields of SAF 2507 were installed to protect the titanium tubes.

Highly alloyed stainless steels with a PRE number of 45 and above can also be used in seawater-cooled tube-and-shell heat exchangers in different process industries. One out of many such applications occurs in Abu Dhabi, where twelve heat exchangers made of 254 SMO are in service in a plant for the removal of carbon dioxide from incoming natural gas. The seawater temperature can be as high as close to 100 °C, and both titanium tubes and alloy 825 tubes failed due to hydriding from the product side and pitting from the seawater side respectively. The first 254 SMO bundle had been installed in 1985.

The most severe crevices can be found in plate heat exchangers, and experience has shown that 254 SMO and similar grades can be used in brackish waters with a chloride level of around 5000 p.p.m. at temperatures up to 40 °C, but not in full-strength seawater, i.e. at chloride levels around 20 000 p.p.m.

Coal-mine Waste Water

Waste water from coal mines contains high levels of chlorides, which often make its disposal difficult: it cannot be used for agricultural irrigation, and discharge into rivers is not allowed owing to the impact on the environment.

However, such waste water can be desalted, and two coal mines in Poland have installed a desalination plant with a capacity of approximately 12 000 m^3/d. The feed contains 10 000 to 20 000 p.p.m. of chlorides, and first passes two reverse-osmosis (RO) units of 3500 and 8700 m^3/d respectively. The brine from the RO units contains 72 000 p.p.m. of chlorides, and is further concentrated in a brine concentrator before it enters a crystallizer, where the end-product is sodium chloride. The brine concentrator and the crystallizer operate at a temperature of around 100 °C.

Materials discussed for this type of desalting plant often include costly nickel-based alloys or titanium, but an extensive test programme has established that Avesta 254 SMO is resistant in these environments. Steel 254 SMO was selected for the high-pressure piping in the RO units and the crystallizer, while the brine evaporator was made of 254 SMO and titanium. The equipment was installed in 1990, but no service experience has yet been reported.

Hot-water Handling

Hot tap water or well water is handled within several industries, of which breweries are one example.

The water can sometimes contain several hundred p.p.m. of chlorides, which, together with a temperature in the range 80 to 95 °C, involves the risk of SCC. One way to solve this problem is the use of a duplex stainless steel like Avesta SAF 2304. Avesta 2205 has been used in the past, but 2304 should be enough for waters containing up to 500 p.p.m. of chlorides.

Considerable cost savings should be possible from the use of duplex grades instead of austenitic grades for big storage tanks. In a Swedish fertilizer plant, Avesta 2205 was selected instead of AISI 317L for a tank to store phosphoric acid. The reason for the choice was mainly the better resistance of 2205 to uniform corrosion in wet-process phosphoric acid, but additionally the higher strength of the duplex steel could be utilized even though it was not a pressurized vessel. This tank[11] of 1590 m^3 was 11 t or 35 per cent lighter when made of 2205. The same design philosophy can be applied to large hot-water tanks made of 2304, and the consequence of such weight saving is, of course, not only lower material costs but also easier workshop handling, transportation, and erection.

Another example of weight saving is provided by domestic water heaters, which are about 15 per cent lighter[11] if made of 2304 instead of a ferritic grade of type S44400.

Production of Chlorate

The production of both sodium and potassium chlorates involves several steps at pH values of 6 to 7, where the corrosivity of the process stream is too severe for most highly-alloyed stainless steels. At the end of the processes, however, the pH value is raised to around 10 by an addition of hydroxide. The environment is still too aggressive for most stainless steels, and tests in a distribution tank resulted in severe corrosion on 904L and alloy 825, while 254 SMO, alloy 625, and alloy C-276 were completely resistant[12].

Chlorate crystallizers made of AISI 316 have suffered severe crevice corrosion, and titanium has sometimes been used. There are two potassium chlorate crystallizers made of 254 SMO in service. The first was installed in a Swedish plant in 1985, but some parts originate from an old test in a 316 crystallizer that was installed in 1978.

The corrosive component of the environment is the chloride ion, 6 to 9 per cent, which, together with a high level of oxidants (close to 50 per cent chlorate and some hypochlorite and bichromate) offer a pronounced risk of pitting and crevice corrosion despite the high pH value.

Recovery of Solvents

Air contaminated with solvents in the form of chlorinated hydrocarbons is sometimes purified in an active carbon filter with a stainless-steel housing. When the filter is saturated, it is backflushed with steam at high temperature. The steam temperature varies depending on the filter design, but it can go as high as 180 °C. At such a high temperature, the solvent can decompose under the formation of hydrochloric acid.

In a Swedish electronics factory, trichlorethylene was used as the cleaning agent, and the housing of the active carbon filter was made of AISI 316, which performed satisfactorily for many years. However, after a change of cleaning agent to methyl chloride, the corrosive conditions were aggravated and leaks due to pitting and crevice corrosion were detected after only four months.

A new filter, where the housing was made of Avesta 254 SMO, was installed in 1984, and it was still in perfect condition after five years of service, when an alkaline solution replaced the methyl chloride as cleaning agent.

Also, a German motor-car factory has successfully used 254 SMO adsorption vessels since 1985.

Pulp and Paper Industry

Pitting, crevice corrosion, and SCC, together with uniform corrosion, are responsible for a major portion of the maintenance required within the pulp and paper industry. The use of modern stainless steel can, however, reduce both investment and maintenance costs, and a few examples are given below.

In the past, kraft digesters have been made mostly of mild steel, and later also of clad steel or cold-stretched austenitic steel of type AISI 304. The duplex stainless steels have, however, such a high strength that solid stainless steel without cold stretching is another alternative. The use of Avesta 2205 for two batch digesters installed in New Zealand in 1989 made it possible to reduce their weight by 50 per cent in comparison with the previous digesters made of mild steel. In addition to this, the new digesters are resistant to uniform corrosion. The service experience is good, and three more digesters, each having a volume of 280 m^3, were installed in another plant in 1991.

Avesta SAF 2304 should also be suitable for use in digesters, and preliminary results from tests in kraft white liquors show that 2304 performs very well in such environments[13]. Similar experiences[14] were reported in Helsinki in 1989.

Very corrosive environments are also found in bleaching plants, where the acid-stage filter washers are particularly prone to pitting and crevice corrosion. Extensive field testing and practical experience reported elsewhere show that highly alloyed austenitic grades like Avesta 254 SMO are the best grades for the most severe environments[15-17].

Flue-gas Cleaning

Although not commercially competitive for use in huge utility boiler scrubbers, where rubber-lined mild steel seems to be preferred owing to its lower price, 254 SMO has been used extensively for flue-gas cleaning. In the Swedish metallurgical industry, when copper is smelted, 254 SMO is the dominant construction material in the flue-gas cleaning systems, being used for conditioning towers, scrubbers, gas ducts, valves, expansion bellows, and also in two electrostatic precipitators.

Pulp plants always include a boiler for the combustion of cooking liquors. The flue gas is desulphurized in a scrubber, which can be of the packed-bed or spray-tower type but is sometimes a venturi type. Alloy 254 SMO has been used for all these types in Finland and Sweden, and also in central Europe, in some cases replacing alloy 825.

The incineration of municipal waste or garbage can result in very corrosive flue-gas condensates if the waste contains PVC or PTFE. Avesta 254 SMO has been used successfully for flue-gas condensers in waste-incineration plants in Sweden. In one plant, the raw flue gas is condensed directly in a 254 SMO cooler, but the condensate is recirculated in the cooler by special means, thereby reducing the corrosivity of the first-formed condensate. The condensate has a pH value of 1 to 1,5, a chloride level of 10 000 to 15 000 p.p.m., and a temperature of 50 to 55 °C. In another plant, 254 SMO was used for a condenser installed downstream of a scrubber, which involves less severe conditions.

Also, the duplex stainless steel 2205 has been used in flue-gas desulpurization (FGD) units. In New Zealand it has been used for a venturi scrubber, duct work, fans, a dewatering cyclone, and a chimney stack in a steel plant. Furthermore, a chimney stack made of 2205 has been installed on top of the FGD unit of a soda-recovery boiler in a Swedish pulp and paper mill.

Conclusions

(1) The duplex stainless steel UNS S32304 (Avesta SAF 2304) can in many cases be a cost-effective alternative to conventional austenitic grades like AISI 304L and AISI 316L, thanks to its combination of good resistance to chloride-induced localized corrosion and high mechanical strength.

(2) The duplex stainless steel UNS S31803 (Avesta 2205) can in many cases replace conventional grades of type UNS S31726 (Avesta 17-14-4LN) and UNS NO8904 (Avesta 904L) owing to its good corrosion resistance and, because of its high strength, it can be a cost-effective alternative to AISI 316L.

(3) The austenitic stainless steel UNS S31254 (Avesta 254 SMO) should be considered seriously for applications where other stainless steels have inadequate resistance to localized corrosion.

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