

STAINLESS STEEL FOR DESALINATION PLANTS

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Summary

The first part (three sections) contains general information about stainless steel in terms of basic metallurgy, how stainless steels are composed and how properties are governed. The second part reflects the use of stainless steels for different types and different parts of desalination plants.

Properties of stainless steel are partly depending on the crystal structure of the material and partly on the content of alloying elements. Different structures, e.g. austenite, ferrite, and martensite, are described and also how the content of alloying elements affects the structure. Chemical compositions, mechanical and physical properties of mainly austenitic and ferritic-austenitic grades, the two most important types, are described.

One important aspect is the number of propriety alloys proposed and also used for

certain applications in desalination plants and these grades are thoroughly described. A major portion of the first part contains information about the most important types of corrosion on stainless steel when used in desalination plants, i.e. pitting, crevice corrosion, and stress corrosion cracking. Causes and preventive measures are discussed.

The second and more conclusive part of this contribution describes experience reported from the use of stainless steel. The history of materials selection for multi stage flash distillation vessel shells include plain carbon steel, stainless steel lining, stainless steel clad material, and the latest option, highly alloyed 6Mo solid stainless steel. A similar history is reported for multiple effect desalination plants though also other alternatives are proposed as more cost efficient. The discussion also includes a variety of internal components and materials for ventilation systems. High pressure piping for seawater reverse osmosis plants are covered as well as filter materials, membrane housings included.

1. Introduction

Stainless steel is no doubt a relatively young construction material compared to ordinary carbon steel but its particular suitability for a number of industrial processes is beyond question. The modern industrial revolution which took place during the mid-20th century has brought with it large-scale pulp and paper production, chemical and petrochemical industries, food processing, microchip production for the electronic industry, and last but not least, desalination of brackish water and sea water.

None of these developments would have been possible without suitable metallic construction materials, of which stainless steel is undoubtedly one of the most important.

The merits of stainless steel include formability and weldability, which enable the fabrication of complicated items, and also a level of corrosion resistance, which is adequate for a number of environments. "Stainless steels are quite close to ideal materials for desalination plant construction" according to Malik et al. (1993), spokesmen for Saline Water Conversion Corporation (SWCC) in Saudi Arabia, the biggest producer of desalted water in world.

One drawback of stainless steel in the past has been its relatively low strength in comparison with construction steel but this has since been overcome by the introduction of improved variants of conventional grades and also by introduction of new grades. Another drawback has been the susceptibility to localized, chloride induced corrosion in the form of pitting, crevice corrosion and stress corrosion cracking (SCC), the latter often referred to as the Achilles heel of stainless steel. Modern steel processing techniques have enabled the development of grades, which can also cope with chloride containing environments, in particular, seawater.

The purpose of this paper is to describe different types and grades of stainless steels, which are already being used in the desalination industry. It will also discuss stronger and more corrosion-resistant steels which enable slimmer design and less maintenance of different components, resulting in lower life cycle costs (LCC) and lower cost of the

water produced.

The discussion will also cover the corrosivity of the process flows, i.e. aerated and deaerated brackish water, seawater and brine, and also the resultant product, fresh water. Furthermore it will report on the experience gained from the use of different steel grades for different components in the three main processes, multistage flash (MSF), low temperature multiple effect desalination (LT-MED), and reverse osmosis (RO).

2. Stainless Steel

2.1. General

Stainless steel is by definition a group of iron-based alloys with chromium as the most important alloying element. The addition of chromium results in the formation of a thin, protective layer on the steel surface - a "passive layer" - which, prevents or at least diminishes corrosion of the steel surface. The protective capacity of this passive layer will be improved by increasing the chromium content, and at a level of approximately 12 per cent chromium, the passive layer is so protective that the steel will not corrode in a humid atmosphere; it has become stainless. Other alloying elements can also be added to strengthen this passive layer, both metallic and non-metallic, molybdenum and nitrogen being two such examples.

The passivity of stainless steel will be discussed in more detail in the section on corrosion resistance.

The above-mentioned definition of stainless steel does not define the upper limit for the content of alloying elements. The American Society for Testing and Materials (ASTM) has in the past used an upper limit of no more than 50 per cent, for its definition of stainless steel. The consequence has been that some highly alloyed stainless steels such as N08904 and N08367 have instead been defined as nickel alloys, indicated by the "N" in their designation. However, that limit is no longer applied and the modern version is based on the major constituents of the material. If iron, it is a steel grade, if nickel, it is a nickel alloy, sometimes also referred to as a nickel-base alloy. Consequently, the above mentioned grades are today included in the stainless steel product standards of ASTM, e.g. A 240 and others.

2.2. Metallurgy

Iron and carbon steel are magnetic, whereas a number of common stainless steels, e.g. those in the ASTM 300-series are non-magnetic. This is a consequence of their crystal structures. Iron and carbon steel has a ferritic structure, whereas many stainless steels have an austenitic structure. Stainless steels can also have a ferritic structure, i.e. when they are alloyed with high contents of ferrite stabilizing elements, of which chromium is the most important.

Ferrite is a body centered cubic structure in which the atoms are closely packed together, giving a lattice with few interspaces. One consequence of this packing is that the solubility of small atoms, interstitials, seeking space between the bigger atoms in the

lattice is limited. Carbon and nitrogen are examples of small atoms with very limited solubility in the ferrite. This is the main reason why ferritic steels are prone to precipitate carbides, nitrides and carbonitrides when these elements are present in excessive amounts. Whilst ferritic steels typically contain 13-17 per cent chromium and rather lower contents of carbon, there are some grades with a chromium content of 25-30 per cent.

If the content of carbon is very high and if the material is heat treated in a special way, heating at around 1000°C followed by rapid cooling, hardening, the carbon can be forced to dissolve in the ferritic structure. This creates very high stresses inside the lattice and results in another structure, known as martensite. Martensite, which is closely related to ferrite, is a hard and strong structure type. The carbon content mainly governs its properties. The properties can be modified by heat treatment at a lower temperature, normally in the range of 400-600°C, tempering, resulting in a partial transformation of the martensite into carbides and ferrite. Martensitic stainless steels generally contain around 12-13 per cent chromium and a carbon content of up to 1 per cent, sometimes more.

Austenite is a face centered cubic structure with a lattice that has a far greater number of interstitial sites, resulting in a higher solubility of interstitials. The most important alloying element for achieving an austenitic structure is nickel and the amount required will depend on the content of ferrite forming elements. If the chromium content is around 18 per cent, around 9 per cent nickel is required and the result will be the well-known 18/9 steel.

The most important alloying element in a stainless steel is chromium, which, as mentioned above, is a ferrite stabilizer. Consequently, stainless steels in which chromium is the only addition will develop a ferritic structure. Other strong ferrite stabilizers are molybdenum and silicon, which are also used to improve the corrosion resistance of stainless steel in certain environments.

Austenitic steels generally have a nickel content of at least 9 per cent, but increased levels of chromium and other ferrite stabilizing elements must be balanced by higher levels of austenite stabilizers. Another important austenite forming addition, besides nickel, is nitrogen. Nitrogen is a relatively cheap alloying element, which is taken directly from air and injected into the molten steel. It can not, however, be added in too high amounts since its solubility is limited.

Despite the higher solubility of austenite for nitrogen, such an addition increases the internal stresses of the lattice thereby increasing the strength of the steel. Nitrogen has a solution hardening effect. Another positive effect of nitrogen is increased corrosion resistance in certain environments and a third is that it retards the formation of secondary phases. Secondary phases, of which the sigma phase is the most well known, can be precipitated in highly alloyed stainless steel when exposed to temperatures around 700-850°C, e.g. during welding or when the cooling rate from heat treatment at higher temperatures becomes too low. If these precipitates are present in too high amounts, they can have an adverse effect on the toughness and corrosion resistance of the steel.

Some austenitic grades are alloyed with manganese. Manganese can sometimes be added instead of nickel as an austenite stabilizing element, e.g. if there is a shortage of nickel in the market. However, adding manganese can also have the effect of increasing the solubility of nitrogen, thereby improving the strength and the resistance to pitting and crevice corrosion. One drawback of a very high manganese content, as in the ASTM 200-series, is the increase in slag inclusions, which can have an adverse effect on the surface finish.

Austenite can sometimes be transformed into martensite if the material is heavily cold worked and if the content of alloying elements is low, giving an austenitic structure bordering on martensite. Such steels are typically of the 18/9 type, but contain low percentages of nickel or nickel and chromium. The tendency for an austenitic material to induce martensite is greater at low temperatures and there are empirical formulas giving the relationship between the composition of the steel and this tendency. A typical 17/7 grade gets 50 per cent martensite at +30°C and 30 per cent cold deformation, whereas a more stable grade such as 316L has to be cooled to -100°C to induce 50 per cent martensite at 30 per cent cold deformation.

If the content of austenite stabilizers is lower than that required to achieve a fully austenitic structure, and if the content of ferrite stabilizers is high enough to avoid martensite, a dual phase material, or ferritic-austenitic stainless steel will result, often referred to as a duplex stainless steel. Modern duplex stainless steels are balanced to achieve a structure with slightly more austenite than ferrite, typical 55-60 per cent austenite and 45-40 per cent ferrite.

The compositions can also be balanced in order to develop other multi-phase structures, such as steels with ferritic-martensitic and ferritic-martensitic-austenitic structures. There are also steels where the composition has been balanced so a controlled amount of precipitates is achieved after heat treatment. These are known as precipitation hardened (PH) steels.

2.3. Steel Grades

The most common stainless steels are austenitic steels and the wide range of grades available reflects the numerous variations in corrosion resistance and mechanical properties. The physical properties are more closely related to the structure but can also vary between the different grades. The most well known grades are those included in the ASTM 300-series, i.e. AISI 304, 304L, 321, 347, 316, 316L etc.

These are basically of the 18/9 type with slight modifications to improve the resistance to intergranular corrosion, e.g. a low carbon content in 304L, stabilizing the carbon with additions of titanium and niobium in 321 and 347 respectively. There are also grades to which molybdenum has been added in order to increase the resistance to corrosion in more general terms, examples being 316/316L and 317/317L. These grades are also standardized in a number of other industrialized countries but the upper and lower limits for the content of alloying elements can vary. They are produced by most leading steel companies, ensuring availability in different product forms.

The 300-series also contains a few austenitic heat resistant grades, type 309S and 310S, intended for service at temperatures ranging from 800 to 1100°C.

There are also a number of highly alloyed austenitic grades available where the content of alloying elements has been increased to improve corrosion resistance. One interesting development concerns the so called 6Mo grades (AL 6XN[®], Cronifer 1925 hMo[®] and 254 SMO[®]) which offer far better resistance to pitting, crevice corrosion, and stress corrosion cracking (SCC) than the conventional grades included in the 300-series. They have a chromium content of 20 per cent, just over 6 per cent molybdenum and 0.2 per cent of nitrogen, but also contain between 18 and 25 per cent nickel, in order to achieve an austenitic structure. This type of stainless steel has since been developed further resulting in even more corrosion resistant grades such as S32654 (654SMO[®]) and N08031 (Nicrofer 3127hMo[®]), which are probably able to withstand the most demanding saline environments found in desalination plants.

Other types of highly alloyed austenitic grades include "Alloy 20", 904L (N08904) and similar grades. This particular steel is not generally designed to resist chloride containing water or brine as it contains neither nitrogen nor a sufficiently high molybdenum content. It was originally developed to withstand dilute sulfuric acid.

There are few manganese alloyed austenitic grades available. They typically contain 18 per cent of chromium, 5 per cent of nickel, 6 to 8 per cent of manganese and 0.2 to 0.3 per cent of nitrogen. Some contain no molybdenum, e.g. AISI 201 and 202, whilst others, e.g. S21600 and S21603, do, in view of the increased resistance to pitting and crevice corrosion that molybdenum-alloyed grades offer. The main merits of these grades are their high strength and the high surface hardness.

The first duplex stainless steels were introduced onto the market as early as the early 1930s and contained typically 25 per cent chromium, 5 per cent nickel, and sometimes also 1.5 per cent molybdenum (Olsson and Liljas 1994). The balance between austenite and ferrite forming elements resulted in a structure with a high content of ferrite, 60-70 per cent, which produced an almost 100 per cent ferritic heat affected zone (HAZ) after welding. One consequence of this was poor impact toughness of the HAZ. The corrosion resistance was also reduced due to carbide precipitates, since these steels also had a rather high content of carbon, typically 0.05 to 0.08 per cent. This type of duplex steel was mainly used for cast products and forgings rather than for sheet and plate. One such grade is still included in the ASTM 300-series, AISI 329.

The development of duplex steels in recent years has resulted in a number of grades with a better balance between austenite and ferrite and far better weldability than the old type. The corrosion resistance varies, depending on alloy content, but in general terms; duplex steels represent a span ranging from 316L to 6Mo austenitic grades. One of the lowest alloyed grades, S32304 (SAF 2304TM) has the same resistance to pitting and crevice corrosion as 316L, superior resistance to stress corrosion cracking, while the resistance to uniform corrosion depends on type of environment in which it is used. The most highly alloyed grades, so called "superduplex" grades, i.e. grades with 25 per cent chromium, 7 per cent nickel, 3 to 4 per cent molybdenum, and 0.2 to 0.4 per cent nitrogen, can sometimes be used instead of the 6Mo austenitic grades, although their main technical advantage is higher strength.

Several national standards for the duplex grade 2205, e.g. ASTM S31803, allow variations in the nitrogen content between 0.08 and 0.20 per cent. Considering nitrogen's role as an austenite stabilizer, this permissible span is too wide. With nitrogen contents in the lower range, the reformation of austenite in the heat affected zone after welding is too weak, resulting in an excessively high ferrite content, precipitates of nitrides, reduced corrosion resistance and reduced impact toughness. This has, however, been considered in the 1997 edition of the ASTM book of standards and 2205 has got a new number, S32205, where a nitrogen content of minimum 0.14 per cent is specified.

Several national standards also include ferritic grades, but these are rarely used in desalination plants due to their inferior corrosion resistance, which in turn is due to a low content of alloying elements. Superferritic grades are an exception, containing 20-30 per cent chromium, 3-4 per cent molybdenum and sometimes also 2-4 per cent nickel. These grades are mainly available as thin sheet and thin walled tubes, as weldability in heavier gauges is poor.

ASTM	Name	Cr	Ni	Mo	N	Others	PRE ¹
S21603		19	6	2.2	0.3	8Mn	31
304L		18	9				18
321		18	10			Ti	18
316L		17	11	2.2			24
317L		19	13	3.2			30
S31726	317LMN	18	14	4.5	0.15		35
N08904	904L	20	25	4.5		1.5Cu	35
	VEW A963 ^{TM2}	17	16	6.5	0.14		41
S31254	254 SMO ^{®3}	20	18	6.1	0.2	Cu	43
N08926	1925 hMo ^{®4}	20	25	6.1	0.2	Cu	43
N08367	AL 6XN ^{®5}	20	25	6.2	0.2		44
S32654	654 SMO ^{®3}	24	22	7.3	0.5	3Mn, Cu	56
N08031	3127 hMo ^{®4}	27	31	6.2	0.2	1.2Cu	51
S32304	SAF 2304 ^{TM6}	23	4.5	0.3	0.1		26
S32205 ⁷	2205	22	5.5	3	0.17		35
S32750	SAF 2507 ^{TM6}	25	7	4	0.27		43
S 32760	Zeron 100 ^{TM8}	25	7	3.5	0.25	W, Cu	41
410		13					13
S44660	Sea-Cure ^{®9}	27.5	1.9	3.4		Ti, Nb	39
S17400	17-4PH	17	4			4Cu	17

¹ PRE_N = % Cr + 3.3×%Mo + 16×%N.

² Trademark, Boehler Edelstahl GmbH.

³ Registered trademark, Avesta Sheffield AB.

⁴ Registered trademark VDM Nickel-Technologie AG.

⁵ Registered trademark, Allegheny Ludlum Corp.

⁶ Trademark, Sandvik Steel AB.

⁷ Used to be S31803.

⁸ Trademark, Weir Materials Ltd.

⁹ Registered trademark, Trent Tube.

Table 1. Chemical compositions, %, and PRE_N-numbers of some stainless steels.

Different stainless steel grades, ASTM standards and commercial names, are given

together with their chemical compositions and pitting resistance equivalents (PRE_N -numbers) in Table 1. The table only lists a few of the available grades to give examples of those discussed in the text. More information on steel grades can be found in national standards, Handbook of Stainless Steels, and product catalogues supplied by different stainless steel producers.

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