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Super and hyper duplex stainless steels: structures, properties and applications

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Abstract

In oil-gas industry, the exploration and development are now targeted to the deep reservoirs with high pressures, high temperatures and extreme corrosive environments. This requires that the materials used should have a good combination of extra high strength and excellent corrosion resistance. In order to meet these challenges, hyper duplex stainless steels have recently been developed. These materials have nitrogen contents up to about 0.5% and PRE-values close to 50, and show both highest corrosion pitting resistance and highest strength among the existing duplex stainless steels.

The purpose of this paper is to provide an overview on hyper duplex stainless steels. It will mainly focus on the material development, microstructures, corrosion properties such as critical pitting corrosion temperature and crevice corrosion resistance, heterogeneous deformation behaviour of duplex stainless steel, and mechanical properties such as tensile properties and fatigue properties. These properties and the ratios of strength/weight will then be compared with those of other type of duplex stainless steels. The potential applications for hyper duplex stainless steels are also discussed.

Keywords: Oil and gas industry, material challenges, duplex stainless steels, corrosion properties, mechanical properties.

1. Introduction

The global demand for energy will continue to increase over the next few decades. The world's energy consumption is anticipated to increase by as much as 35% in the next 20 years, IEA (2011). Although the exploitation and use of renewable energy and other energy sources will increase in the coming years, the use of hydrocarbons will still play the important role at least for the next two decades. This will become a real challenge in

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the oil and gas industry since they have to search for the reservoirs with both geologically challenging and operationally complexities such as ultra-deep formations or deep water. In these deep wells, high-pressure, high-temperature and extreme corrosive environments will cause extreme corrosion and weight issues as the trends of oil-gas industry continues towards deep well drilling, DeBruijn (2008) and Akersolution (2008). The new and better materials are on the rise.

Duplex stainless steels, DSS, are a group of stainless steels with a microstructure of almost equal amount of austenite and ferrite. These materials show an attractive combination of excellent corrosion resistance and high mechanical properties comparing with either austenitic stainless steels or ferritic stainless steels, especially super duplex stainless steels, Charles (1991) and Nilsson and Chai (2011). They have been widely used oil-gas industry, Kangas and Chai (2016). Due to its high ratio of property to cost, super duplex stainless steels have become an alternative to other higher performance materials such as super austenitic stainless steels and Ni-based alloys, and have had a about 20 years' very successful applications or experiences in the oil-gas industry, Kangas and Chai (2016). With the exploration of the deeper wells, the wall thickness of tube material used may need to increase and the material may also need coating for added corrosion protection. The problem is that the increase in wall thickness will also increases the stress in the material due to its own weight. Once it reaches its allowable stress, no more length can be increased. Another problem is that increase in wall thickness can also increase the costs for the installation. This clearly shows the desires for new alloys with even higher high strength than those of the existing super-duplex stainless steels. In the other areas, new high alloyed duplex stainless steels with a combination of excellent corrosion resistance and higher high strength are needed. For these challenges, two new high alloyed duplex stainless steels, Sandvik SAF 2707HD and Sandvik SAF 3207HD, have recently been developed. The nitrogen contents in these alloys is now up to about 0.5%. They have PRE-values close to 50 without sacrificing the fabricability, and are now designated as hyper duplex stainless steel, HDSS. These new alloys show both highest corrosion pitting resistance or highest CPT and highest strength among the existing modern DSS, Chai and Kangas (2011). These new materials has a yield strength 20% higher than that of the super duplex stainless steel and a service temperature up to 90°C. The benefits when it comes to building umbilicals and control flowlines are considerable. Thinner walls and lighter installations make it possible to reach and operate ultra-deep wells that were previously too costly or too complex to exploit. At the same time, the temperature and pressure window widens. This paper will provide an overview on super and hyper duplex stainless steels, microstructure, properties and applications.

2. Super and hyper duplex stainless steel and microstructure

Duplex stainless steels belong to Fe-Ni-Cr system. Table 1 shows the nominal composition of one super and two hyper duplex stainless steels. Addition of Mo is mainly to improve corrosion resistance, but also increase the strength. Addition of N is mainly to increase strength but also improve structure stability and corrosion resistance. PRE is the pitting corrosion resistance equivalent value of an alloy. This value is believed to be proportional to the pitting corrosion resistance of a duplex stainless steel. The material with a higher PRE value may show a better corrosion resistance. PRE value is defined to be calculated as Equation 1.

Table 1. Nominal chemical compositions and PRE values of three duplex stainless steels (wt %)

Grade	UNS	$C_{\_max}$	Cr	Ni	Mo	N	PRE*
Sandvik SAF 2507	S32750	0.03	25	7	4	0.3	42.5
Sandvik SAF 2707HD	S32707	0.03	27	7	5	0.4	48
Sandvik SAF 3207HD	S33207	0.03	32	7	3.5	0.5	50

*minimum PRE value for tube materials

$$PRE = \%Cr + 3.3\%Mo + 16\%N \text{ (\% by weight)} \quad (1)$$

The pitting corrosion resistance equivalent values, PRE, of these three alloys are also shown in Table 1. Sandvik SAF 2707HD has a minimum PRE value of 50 and Sandvik SAF 3207HD has a minimum PRE value of 48, comparing with 42.5 on Sandvik SAF 2507. A duplex stainless steel with a PRE value above 48 is nowadays designated as hyper duplex stainless steel, HDSS, Göransson (2006), Chai (2009) and (2011). Duplex stainless steels Sandvik SAF 2707HD and Sandvik SAF 3207HD are therefore hyper duplex stainless steels.

The challenge to develop highly alloyed duplex stainless steels is to control the risk for formation of intermetallic phase by increasing content of elements such as Cr and Mo or N. With modern thermodynamic simulation and calculation, however, some unexpected positive synergistic effects of addition of the elements Cr, Mo and N to high levels have been observed. Actually, Sandvik SAF 2507 is the first duplex stainless steel developed by the thermodynamic simulation, Nilsson (1992). Fig. 1 shows the phase diagrams of super and duplex stainless steels.

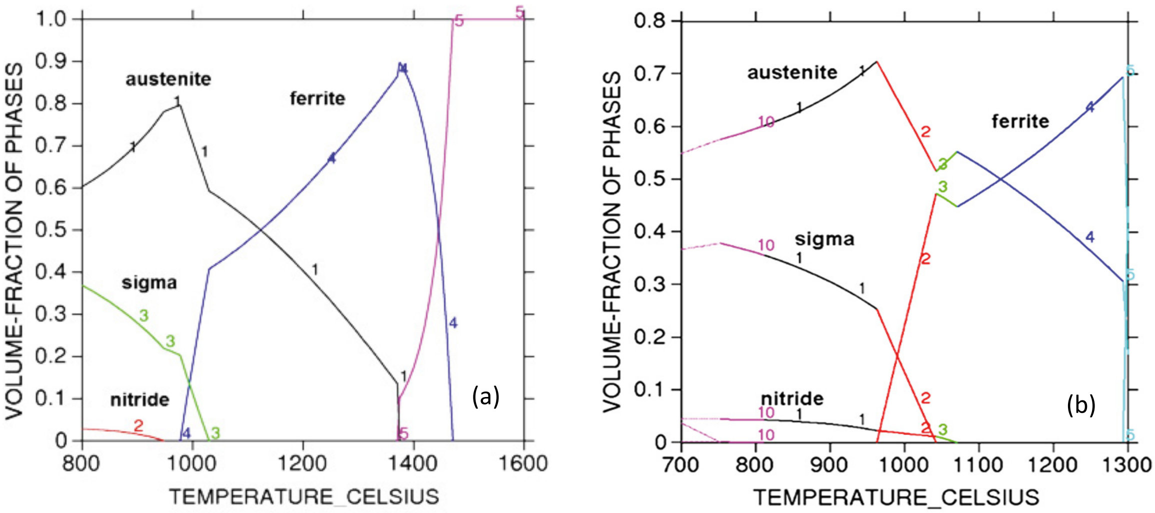

Fig. 1. (a) Phase diagram of a super duplex stainless steel; (b) Phase diagram of a hyper duplex stainless steel.

As shown in Fig. 1, besides the austenitic and ferritic phases, the other main precipitates are sigma phase and chromium nitrides from 800 to 1300°C. The crystallographic structures of these two precipitates are shown in Table 2. They are actually mostly observed experimentally in some improperly treated material as shown in Fig. 2. Chromium nitride can be observed in both isothermal treated and fast cooled material. Other precipitates can sometime be observed in some other cases. They are well described in the reference, Nilsson and Chai (2011).

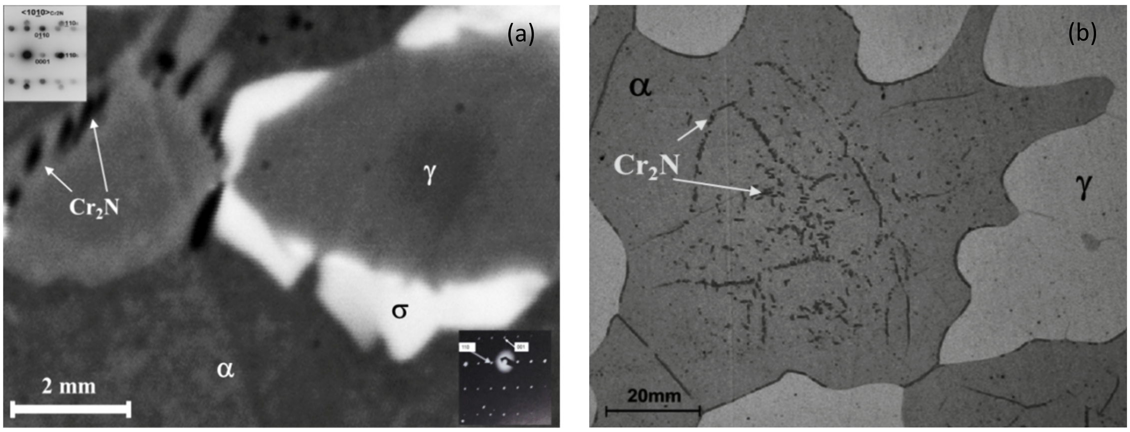

Fig. 2. (a) Typical precipitates of sigma, σ, phase and chromium nitride, Cr_2N, in isothermal treatment or slow cooling; (b) chromium nitride, Cr_2N, in fast cooling.

Table 2 Main precipitates observed experimentally in super and hyper duplex stainless steels

Type of precipitate	Chemical formula	Temperature range (°C)	Space group	Lattice parameter, nm	Reference
Sigma, σ, phase	Fe-Cr-Mo	600-1000	$P4_2/mnm$	a=0.879, c=0.454	Hall (1966)
Chromium nitride	Cr_2N	700-900	*P31m*	a=0.480, c=0.447	Karlsson (1934)

Fig. 3 shows the normal microstructures in the longitudinal (rolling) and transversal directions of a Sandvik SAF 3207 tube material. They are heterogeneous in different directions. In the longitudinal direction, the austenitic phase is elongated (Fig. 3a). In the transversal direction, the austenitic phase is isolated by the matrix: ferritic phase (Fig. 3b). These type of microstructures are normally used to describe the grain structure of duplex stainless steels. Actually, it is not true. Fig. 3c and d show the grain structures of the austenitic and ferritic phases in this material. The grain sizes of both phases are very small. The austentic grains are generally randomly distributed (Fig. 3c). The ferritic grain are however rather oriented, mainly toward [111]. It was also found that austenitic phase contains large amount of twins with mainly Σ3 twin boundaries. Actually, the twin boundary in this material is so high that it is of up to 65% of total boundaries in the austenitic phase. As expected, no or very few twin boundary could be found in the ferritic phase.

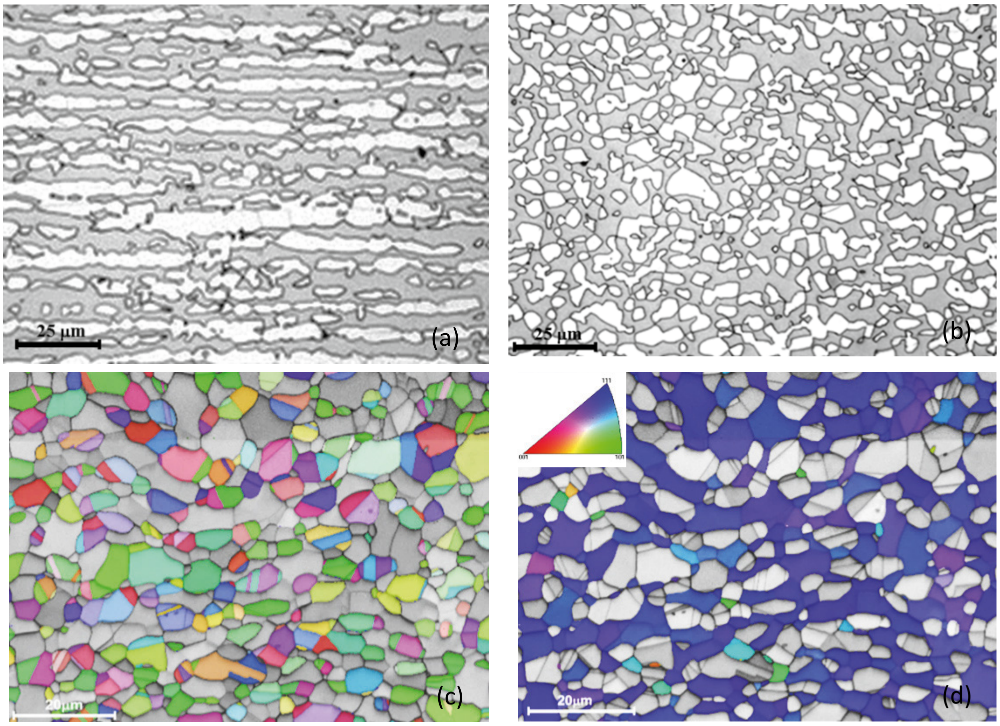

Fig. 3. Microstructure of Sandvik SAF 3207 HD tube material with a dimension of 14.7 x 1 mm (a) In longitudinal (rolling) direction from light optical microscopy (LOM), austenitic phase (white), (b). In transversal direction (LOM), ferritic phase (grey), (c). Austenitic grain structure (colored ones) in longitudinal direction from electron backscatter diffraction (EBSD), grain size is about 3.8 μm, (d). Ferritic grain structure (colored ones) in longitudinal direction from (EBSD), grain size is about 5.1μm.

3. Properties of super and hyper duplex stainless steels

3.1. Corrosion properties

The critical pitting temperature, CPT, was determined in 6% $FeCl_3$ according to the ASTM G48A test program. The critical crevice corrosion temperature, CCT, was determined using the MTI-2 crevice former. The testing time for both CPT and CCT tests was 24 hours, and the same specimen was used throughout each CPT/CCT measurement. Fig 4a shows a comparison of the CPT and CCT of super and hyper duplex stainless steels. As expected, hyper duplex stainless steels show much higher both CPT and CCT than super duplex stainless steel. CCT improves from about 50°C of super DSS to about 70°C of hyper DSS. These two hyper DSS show similar CCT. CPT improves from about 80°C of super DSS to about 95°C of hyper DSS. SAF 3207HD has shown a CPT from 85-93°C, Chai (2009). Fig. 4b shows a comparison CPT of austenitic stainless steels and duplex stainless steels and correlations between the PRE values and the CPT determined experimentally. Super or hyper duplex stainless steel can replace some super austenitic stainless steels. Recent G48C/G48D corrosion tests show that Alloy 625 and Alloy C-276 are susceptible to crevice corrosion at temperatures far below those of SAF 2707HD (Table 3). This indicates that SAF 2707HD can replace these alloys in some applications and is much more cost efficient (far less nickel).

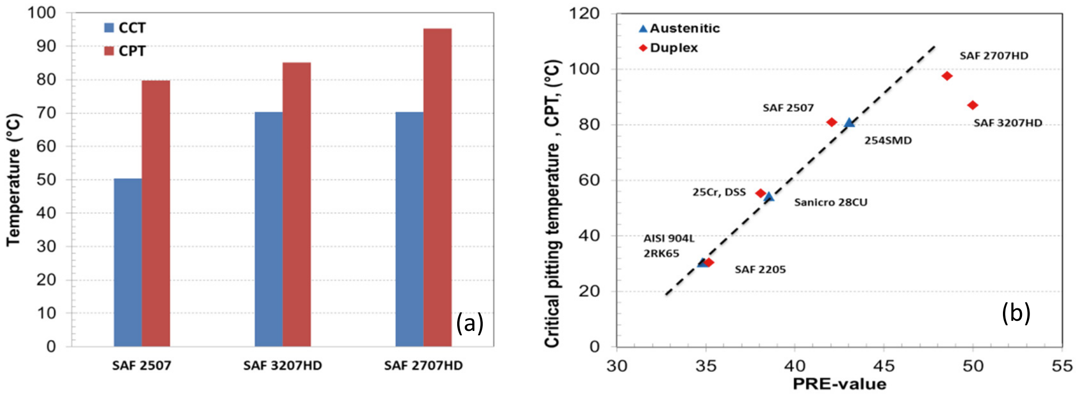

Fig. 4. (a) CCT and CPT of duplex stainless steels, (b). Correlations between CPT and PRE values.

Table 3 CPT and CCT of Ni based alloy with G48C/G48D

Grade	Test method	CPT/°C	CCT/°C
SAF 2707HD	G48C/G48D	>95	70
Alloy 625	G48C/G48D	>85	35
Alloy 276	G48C/G48D	>85	45
Alloy 22	G48C/G48D	>85	75
Alloy 686	G48C/G48D	>85	>85

Another test done recently was a comparison to titanium material of CP Ti grade 2 which will experience crevice corrosion in seawater between temperature 70–80°C. Since G48B is a worse solution than the seawater, a comparable crevice corrosion test in artificial seawater (ASTM D1141) has been done. The results show that Sandvik SAF 2707HD can resist crevice corrosion up to 90°C, which is higher than that of CP Ti grade 2. This is also a possible replacement.

3.2. Mechanical properties

Since austenitic and ferritic phases in a duplex stainless steel have different mechanical behaviors, the bulk mechanical behavior of a DSS material strongly depends on that of the individual phase. This can be expressed by equation 2

$$\sigma_{macro}=\sigma^{\alpha}V^{\alpha}+\sigma^{\gamma}V^{\gamma} \qquad (2)$$

Where σ is the stress, α is the ferritic phase, γ is the austenitic phase, V is the volume fraction of the contributing phases. Fig. 5 shows micro stress responses in a super duplex stainless steel during an in-situ tensile test in X-ray diffractometer and with a multiscale simulation. When a stress was applied the phase stresses responded differently (Fig. 5a). The stress in the ferrite increased much faster than that in the austenite. As a stress of 560 MPa was applied the stresses in the phases became almost equal. Beyond this point the stress in the ferrite began to decrease and remained at a level of approximately 500 MPa till the loading was stopped. Meanwhile the stress in austenite increased rapidly and reached its limit at around 960 MPa at a strain of 14.1%. During the whole test the austenite took a higher load. The macro stress in the material could therefore be calculated using Equation 2. The simulation shows the similar attendance, where the austenitic phase will yield earlier than the ferritic phase. However, the austenitic phase has a higher deformation hardening rate.

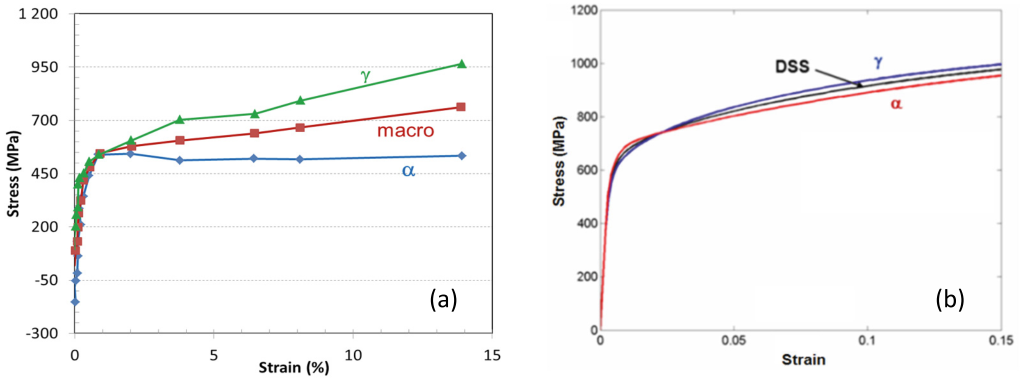

Fig. 5. (a) Stress versus strain curves in the individual phases and bulk material in a super duplex stainless steel with 0.2%N and 49% volume of ferrite measured by X-ray difffractometer, (b). Simulated stress versus strain curves in the individual phases in a super duplex stainless steel with 0.27%N and 50% volume of ferrite.

As known, a duplex stainless steel generally shows a higher strength comparing its corresponding single phase austenitic or ferritic stainless steel, Nilsson and Chai (2011). Fig. 6 shows a comparison of the yield strength of austenitic and duplex stainless steels. SAF 3207HD has a strength that is more than three times as that of AISI 316L- a very commonly used austenitic stainless steels. As discussed above, high alloying elements and fine grain size in duplex stainless can be very important factors to the high strength of duplex stainless steels. As shown in Fig. 5a, however, the yield point of the austenitic phase is actually rather low in a duplex stainless steel. A coupling yielding effect of the austenitic and ferritic phases could be another important factor. However, this is less studied, Lillbacka (2007) and Jia (2006). Fig. 6b shows the influence of temperature on the 0.2% proof strength of the super and hyper duplex stainless steel tube materials with a wall thickness of up to 4 mm. Their strengths are higher than the minimum yield strength as shown in Fig. 6a. The dimension of tube is also an important factor to the strength.

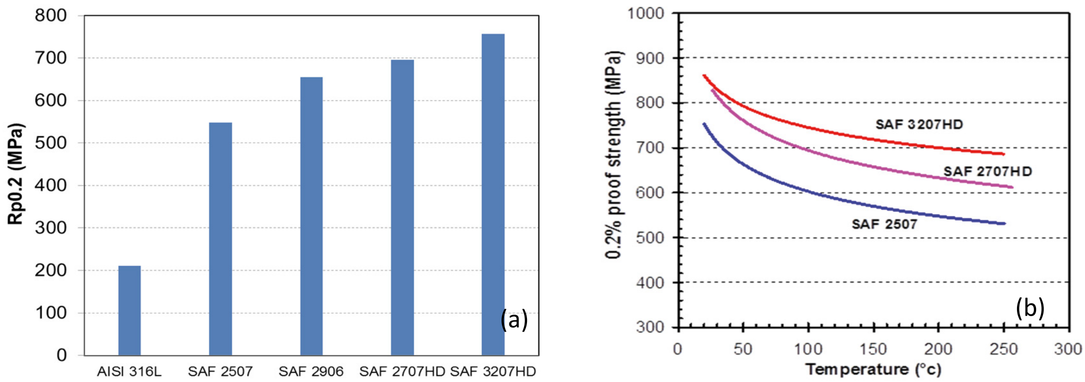

Fig. 6. (a) Yield strength of austenitic and duplex stainless steels at RT, (b). Influence of temperature on the super and hyper duplex stainless tube materials.

For some subsea applications, dynamic mechanical properties such as fatigue strength are critical to some component such as umbilicals, Chai (2009). Fig. 7 shows a comparison of both high cycle fatigue (HCF) (Fig. 7a) and low cycle fatigue (LCF) (Fig. 7b) of the super and hyper duplex stainless steels. Since SAF 3207HD has much higher strength than SAF 2507 and their elongations are similar, Sandvik SAF 3207HD has a higher HCF life as expected. The HCF properties of both super and hyper duplex stainless steels are much higher than that of DNV design curve- DNV RP C-203. For low cycle fatigue behavior, there is a transition point at about 1000 cycles. Below this number of cycle, SAF 2507 has a longer fatigue life, but Sandvik SAF 3207HD shows a higher fatigue life in the small strain range. This is due the fact that for HCF or longer fatigue life, the strength of the material is a critical factor. On the other hand or for low cycle fatigue, the fatigue life is controlled by the ductility of the material.

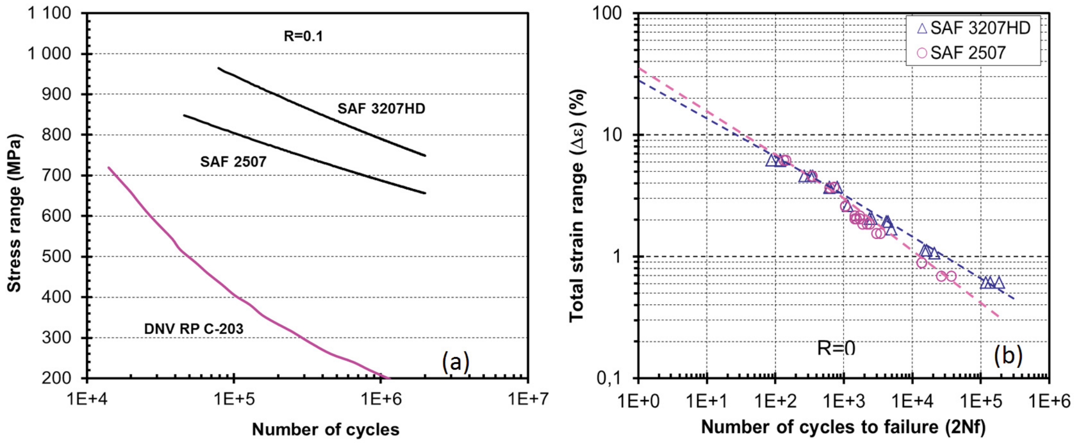

Fig. 7. (a) High cycle fatigue properties of super and hyper duplex stainless steels, and comparison with DNV design curve DNV RP C-203, (b). High cycle fatigue properties of super and hyper duplex stainless steels.

Besides the above mechanical properties, these super and hyper duplex stainless steels show also good toughness and weldability, Chai and Kangas (2011).

4. Applications

Extremely high critical pitting temperature, CPT, and critical crevice corrosion temperature, CCT, of hyper duplex stainless steels allow the materials to be used in the areas where high corrosion resistance and high service temperature are required. The good combination of extra high strength and high ductility makes it possible for hyper duplex stainless steels to allow substantial reduction in wall thickness, which leads to a reduction of weight in applications such as ultra-deep seawater, energy and refinery sectors. In all these situations the alloy's superior properties can be fully utilized to ensure reliability and safe service. One example is subsea umbilicals, which are used as a connection between a platforms control station and the wellheads on the seabed to supply necessary control signals and to inject chemicals to subsea oil and gas wells. A stainless steel umbilical has an outer plastic sheeting with stainless steel tubes and cables (electric and others) inside. The umbilical tube materials are required to have excellent corrosion resistance and high fatigue properties. Super duplex stainless steel, Sandvik SAF 2507, has been the most common choice of material since it was introduced in 1993, Kangas and Chai (2016).

Today the oil exploration strives to deeper waters, where the water depth is over 2500 meters or the pressure ratings are rising above 15000 psi. In some cases higher temperatures call for stronger and more corrosion resistant materials than existing duplex and superduplex stainless steels that can handle reliably. Sandvik SAF 3207HD is suitable for deeper wells and corrosive conditions. The proof strength of typical umbilical sizes is roughly 20% higher compared to the commonly used Sandvik SAF 2507, which means lower weight for long umbilicals and the ability to withstand higher external pressure in deep sea applications. Table 4 shows an example.

Table 4 Example for weight saving (1/2" ID (12.70 mm) 15000 psi)

Grade	ID	Wall thickness	thickness reduction	weight save
	mm	mm	%	%
Sandvik SAF 2507	12.70	2,56		
Sandvik SAF 3207HD	12.71	1.66	21	22

Another application of Sandvik SAF 3207HD is raw seawater injection where untreated seawater is injected into the well in order to replace the retrieved oil and hence increase the output from the well. The string shall support its own weight and threaded connections in combination with warm seawater which results in that very good crevice corrosion resistance in combination with high mechanical strength is of vital importance. Sandvik SAF 3207HD is an excellent solution for such application.

5. Summary

This paper gives an overview on the compositions, microstructures, properties and potential applications of the super, but mainly hyper duplex stainless steels, which can be summarized as follows.

Hyper duplex stainless steels have the highest critical pitting temperature, CPT, and critical crevice corrosion temperature, CCT, among the modern duplex stainless steels. Hyper duplex stainless steels have the highest tensile and fatigue strengths among the modern duplex stainless steels.

With a good combination of extreme high corrosion resistance and strength, hyper duplex stainless steels can be successfully used in the extreme oil and gas environments in the ultra-deep formations or deep water wells.

Acknowledgement

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