

Use of Duplex Stainless Steels in the Oil Refining Industry

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Contents

	Page
1	Scope..... 1
2	Normative References 6
3	Terms, Definitions, Acronyms, and Abbreviations 7
3.1	Terms and Definitions 7
3.2	Acronyms 7
4	Metallurgy of Duplex Stainless Steels (DSSs)..... 9
4.1	Background..... 9
4.2	Solidification..... 10
4.3	Problems to be Avoided During Welding 11
4.4	Low- and High-temperature Properties..... 13
4.5	Hardness Conversions 16
5	Potential Environment-related Failure Mechanisms 17
5.1	Chloride Pitting and Crevice Corrosion..... 17
5.2	Corrosion in Seawater and Microbiological Induced Corrosion (MIC) 20
5.3	Chloride Stress Corrosion Cracking (CSCC)..... 21
5.4	Hydrogen Assisted Cracking (HAC)/Sulfide Stress Cracking (SSC) 23
5.5	Ammonium Bisulfide Corrosion 25
5.6	Naphthenic Acid Corrosion 25
5.7	475 °C (885 °F) Embrittlement..... 27
5.8	Corrosion Under Insulation (CUI) 28
6	Material Specifications 29
6.1	Typical Specification Requirements for Wrought Materials..... 29
6.2	Welded vs Seamless Tubing and Piping..... 31
6.3	Use of Integrally Finned Tubing 31
6.4	Use of Twisted Tubes..... 33
6.6	Duplex SS Castings and HIP Components..... 33
6.7	Duplex SS Used as a Cladding Material..... 33
7	Special Considerations during Fabrication of DSSs 34
7.1	Welding Procedure Qualification (WPS/PQR) 34
7.2	Welding 34
7.3	Tube-to-tubesheet Joints 35
7.4	NDE Methods 35
7.5	Typical Welding Processes and Filler Metals..... 35
7.6	Dissimilar Metal Welding..... 36
7.7	Ferrite Measurements vs Austenite Spacing 36
7.8	Cold Working and Cold Bending..... 36
7.9	Hot Bending 40
7.10	Post-fabrication Cleaning..... 41
7.11	Hydrostatic Testing..... 41
7.12	Coating Requirements and Risk of CUI..... 41
8	Examples of DSS Applications within Refineries 41
	Annex A (informative) Example of Special Material Requirements for DSSs..... 56

Contents

	Page
Annex B (informative) Example of Special Welding Procedure Qualification Requirements for DSSs	59
Annex C (informative) Example of Special Welding and Fabrication Requirements for DSSs	60
Annex D (informative) Example of a Duplex SS Casting Specification	61
Annex E (informative) Example of Hot Isostatically Pressed (HIP) Duplex SS Material Specification	65
Bibliography.....	68

Figures

1	Comparison of the Proof Stress and Pitting Resistance (Based on PREN of the Bulk Chemistry) of Duplex and Austenitic SS	ix
2	Schematic Diagram Showing the Conditions Under Which σ -Phase and Chromium Nitrides Are Formed in a Space Defined by Temperature and Cooling Rate.	10
3	Solidification and Phase Development of Duplex Stainless Steels	10
4	Possible Precipitation Phases in DSSs	12
5	Embrittlement by Precipitation of Harmful Phases of UNS S32304, S32205, and S32507 after Long-time Annealing	13
6	Effect of Weld Metal Oxygen Concentration on the Toughness of the Weld.....	15
7	Compilation of Hardness Data for a Range of Duplex Parent Materials and Weldments Showing the Best-fit Line and ASTM E140 Conversion for Ferritic Steel	17
8	CPT for 22 % Cr, Super and Hyper DSS Alloys Compared with Austenitic SS Alloys in 6 % FeCl ₃ , ASTM G48 Test Method A	18
9	CPTs at Various Concentrations of Sodium Chloride (at +300 mV vs SCE, Neutral pH)	19
10	CPTs and CCTs for 22 % Cr and Super DSS Compared with Austenitic SS Alloys in ASTM G48 Tests	20
11	CSCC Resistance of DSS Alloys Compared with Austenitic SS Alloys in Oxygen-bearing Neutral Chloride Solutions	22
12	Results of SCC Tests of 22 % Cr and 25 % Cr DSS Alloys Compared with Austenitic SS Alloys in Constant Load Tests in 40 % CaCl ₂ , 1.5 pH at 100 °C with Aerated Test Solution	22
13a	Impact Energy Curves for Quench-annealed S32750 Alloy, Aged at 300 °C or 325 °C [$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$].....	28
13b	Impact Energy Curves for 45 % Cold-worked S31803 Alloy, Aged at 300 °C or 325 °C [$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$].....	28
14	Average Hardness (HV) on Super Duplex (UNS-S32750) Tubes after Bending to Different Bending Radius from 1.5OD to 5OD (Tubes Were 0.75 in. [19.05 mm] OD x 0.065 in. AW [1.65 mm]).....	38
15	Average Hardness (HV) on Super Duplex (UNS-S32750) Tubes after Bending to Different Bending Radius from 1.5OD to 5OD (Tubes Were 0.75 in. [19.05 mm] OD x 0.095 in. AW [2.14 mm]).....	38
16	Work-hardening Effect on Standard 22 % Cr DSS Tubes by Bend Radius.....	40

Tables

1	Chemical Compositions of Commonly Used DSSs and Other Alloys.....	3
2	ASME, ASTM, and ISO Specifications for DSSs.....	6

Contents

	Page
3	Mechanical Properties of Various Duplex and 316L SSs..... 6
4	ASME Code Maximum Allowable Temperatures, °C (°F) 16
5a	Partitioning of Alloying Elements Between Phases in 25 % Cr Alloys 26
5b	Partitioning of Alloying Elements Between Phases in 22 % Cr Weld Metals (Approx. Wt. %) 26
5c	Partitioning of Alloying Elements Between Phases in 22 % Cr Base Metal and SMAW Weldments with Varying Arc Energy (Wt. %)..... 26
5d	Partitioning of Alloying Elements Between Phases in 22 % Cr Base Metal and GTAW Weldment (Wt. %)..... 27
5e	Partitioning of Alloying Elements Between Phases in 22 % Cr DSS Base Metal 27
5f	Partitioning of Alloying Elements Between Phases in 25 % Cr DSS Base Metal 27
6	Summary of Corrosion Testing of Integrally Finned DSS (S31803/32205) Completed by One Refiner 32
7	Summary of Corrosion Testing Results of Low Finned Tubes in the As-finned Condition As Well in the Annealed Condition after Finning 32
8	Average Hardness Values of Hyper DSS S32707 Twisted Tubes 33
9	Summary of Ferrite Content and Corrosion Testing Results per ASTM G48-A on Hyper DSS S32707 Twisted Tubes 33
10	Welding Consumables 35
11	Summary of Corrosion Test Results of Super Duplex Tubes in the As-bent Condition..... 39
12	Pitting Corrosion Tests Results for S32205 and S32750 U-bend Specimens 40
13	Pitting Corrosion Testing for S32205 and S32750 As-finned Tubes 40
14	Case Histories of DSS Uses Reported in NACE International Refin-Cor 42
15	Case Histories of DSSs Uses Reported by Other Sources 47
16	Summary List of DSSs Refinery Applications to Date 55
D.1	Impact Test and Corrosion Test Requirements for Castings with a Net Weight over 450 kg (1000 lb)..... 62
D.2	Welding Consumables 64

Introduction

Duplex stainless steels (DSSs) are finding increasing use in the petroleum refining industry, primarily because they often offer an economical combination of strength and corrosion resistance. These stainless steels (SSs) typically have an annealed structure that is nominally half ferrite and half austenite, although the ratios can vary from ~35/65 to 65/35. Most refinery applications where DSSs are used are corrosive, and DSSs or other higher alloys are required for adequate corrosion resistance. In some refineries, DSSs are being considered as a “baseline” material.^[1] In these facilities, DSSs are being used in applications where carbon steel may be acceptable, but DSSs have been shown to be more economical, considering their higher strength and better long-term reliability.

DSSs are often used in lieu of other grades of SS, such as the austenitic, ferritic, and martensitic types, because of their superior properties and corrosion resistance. For example, DSSs provide improved resistance to chloride pitting and chloride stress corrosion cracking in comparison to austenitic SS. Higher alloyed DSSs like super duplex and hyper duplex are an economic alternative to more expensive alloys with similar corrosion resistance. [Figure 1](#) provides a comparison of DSS alloys with various austenitic SS showing the difference in strength and chloride corrosion resistance expressed as pitting resistance equivalent number (PREN), which is defined in [5.1](#).^[2] This chart shows the excellent combinations of higher strength and corrosion resistance available with DSSs. It also shows that there are “subfamilies” of specific grades within both the DSSs and austenitic families. This is also illustrated in [Table 1](#).

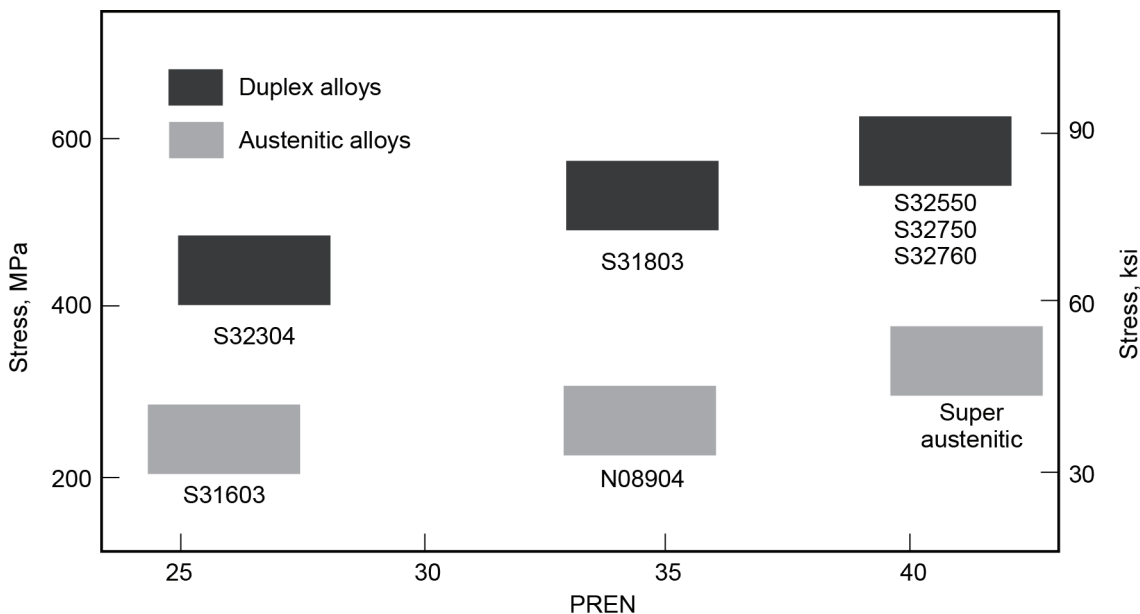


Figure 1—Comparison of the Proof Stress and Pitting Resistance (Based on PREN of the Bulk Chemistry) of Duplex and Austenitic SS^[2]

DSSs have existed since the 1930s. However, the first-generation alloys such as Type 329 (UNS S32900) had unacceptable corrosion resistance and toughness in weldments.^{[3] [4] [5]} Hence, the initial applications were almost exclusively limited to heat exchanger tubing, particularly in corrosive cooling water services and shafts or forgings. In the 1980s, second-generation DSSs that had overcome the problems with welds became commercially available. These new grades had nitrogen additions promoting better austenite/ferrite balances at welds and heat-affected zones (HAZs). Additionally, improved DSS welding practices led to improvement in weldment mechanical strength, toughness, and corrosion resistance, achieving values comparable to annealed base metal. DSSs most commonly used in refineries today include those with 22 %, 25 %, and 27 % Cr. The 22 % Cr alloy is the industry workhorse. The 25 % Cr (super duplex grades) and 27 % Cr (hyper duplex grade), containing more molybdenum and nitrogen (having higher PREN values than 22 % Cr duplex steels) are finding more applications. Lean DSS grades are beginning to be accepted in less arduous environments (e.g., cooling water exchangers).

[Table 1](#) lists the compositions and UNS numbers of various common DSSs, including some first generation DSSs for comparison. Note that UNS S32205 is a “newer version” of UNS S31803, and while it also meets the S31803 chemistry, it is produced with a higher minimum nitrogen, chromium, and molybdenum content. In many cases, the material is dual-certified as S31803/S32205 to ensure the corrosion resistance and weldability of 32205 is retained while taking advantage of the higher allowable stress values for 31803. ASME and ASTM standards for duplex SS grades are given in [Table 2](#), while [Table 3](#) provides the mechanical properties. Type 316L and other austenitic SSs are included in these tables for comparison.

This report has four primary objectives, which are to describe:

- 1) environment-related failure mechanisms associated with DSSs and the preventative measures to avoid them;
- 2) typical DSS material specification requirements used by refiners;
- 3) typical DSS fabrication specification requirements used by refiners;
- 4) examples of applications of DSSs within refineries.

Use of Duplex Stainless Steels in the Oil Refining Industry

1 Scope

This report covers many of the “lean,” “standard,” “super,” and “hyper” grades of duplex stainless steels (DSSs) most commonly used within refineries. These terms have not been firmly established by the industry, and their use may vary between literature references and suppliers. The ISO document ISO 17781 *Petroleum, Petrochemical and Natural Gas Industries—Test Methods for Quality Control of Microstructure of Ferritic/Austenitic (Duplex) Stainless Steels* provides a fairly consistent and inclusive classification of these materials based on their chemical composition and corrosion resistance.

In an attempt to facilitate future cross reference, this document adopted materials classifications consistent with ISO 17781. The following list summarizes the classification group (refer to [Table 1](#) for a complete list of grades):

- Type 20 Cr Duplex, Group A (Lean DSSs): S32001, S32101, S32202, S82011, S82031, and S82441;
- Type 20 Cr Duplex, Group B (Lean DSSs): S32003, S32304, S31500, S81921;
- Type 22 Cr Duplex (Standard DSSs): J92205, S31803, S32205;
- Type 25 Cr Duplex (Super DSSs): S32520, S32550, S32750, S32760, and S32906;
- Type 27 Cr Duplex (Hyper DSSs): S32707, S33207.

Grades that are labeled as “lean” (including grades sometimes called “semi-lean”) have lower Cr, Ni, or Mo than the standard grades and thus a lower PREN, and they are used in some process services that are less aggressive (primarily in corrosive environments to replace 304L SS). These lean DSSs have been used for heat exchanger tubing, storage tanks, and structural applications primarily for their higher strength compared with carbon steel (CS).

Formable duplex stainless steel is a new kind of DSS with improved formability due to the transformation-induced plasticity (TRIP) effect, enabling the manufacture of heavily cold-worked components like tray internals, plate and frame heat exchangers, and twisted tubes, among others. The corrosion resistance of the material in the cold-worked condition is similar to the annealed form.^[42]

Product forms within the scope of this report are: tubing, plate, sheet, forgings, castings, hot isostatically pressed (HIP) components, pipe, and fittings for piping, vessel, exchanger, and tank applications. The use of DSSs for tanks is also addressed by API Standard 650. The limited use of DSSs as a cladding is also briefly covered within this document.

The majority of refinery services in which DSSs are currently being used or being considered for use in the petroleum refining industry include:

- a) wet sour (H₂S) environments that may also contain hydrogen, ammonia, carbon dioxide, chlorides, and/or hydrocarbons, which typically have a pH greater than 7;
- b) water containing chlorides, with or without hydrocarbons—this includes many freshwater cooling water systems and some saltwater systems with higher alloy grades;
- c) hydrocarbons with naphthenic acids at temperatures higher than 200 °C (400 °F) but below the maximum up temperatures in the ASME Pressure Vessel Code Section II for DSSs (260 °C to 343 °C [500 °F to 650 °F], depending on the grade);
- d) amines, such as:
 - 1) MEA, MDEA, DEA, etc., or