Use of Duplex Stainless Steels in the Oil Refining Industry

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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.

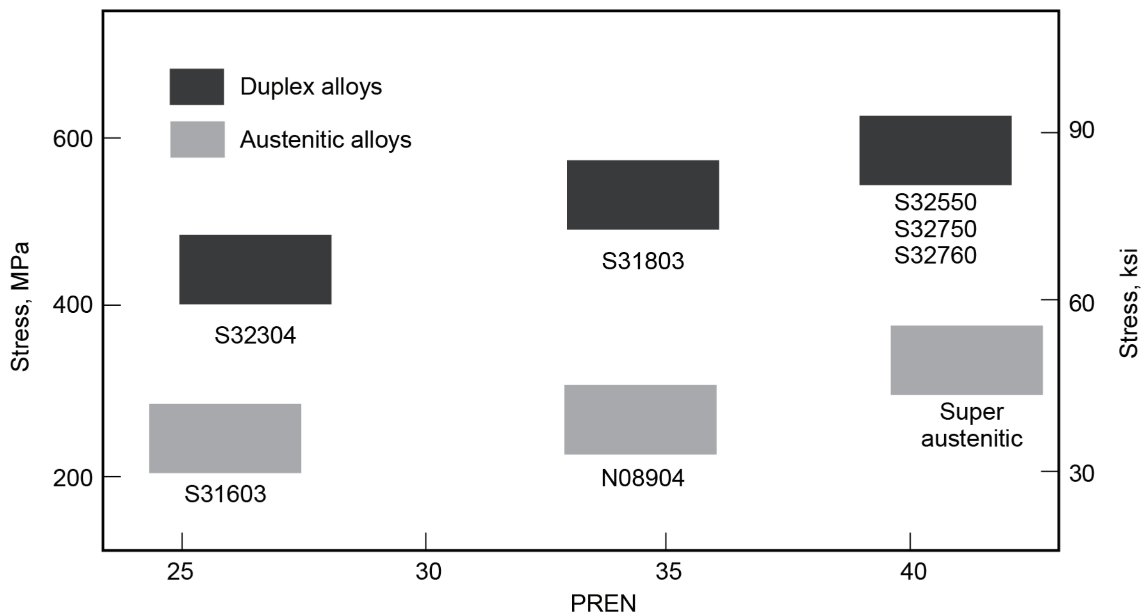

Figure 1—Comparison of the Proof Stress and Pitting Resistance (Based on PREN of the Bulk Chemistry) of Duplex and Austenitic SS [2]

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.

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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 (H_2S) 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