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 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 generally half ferrite and half austenite, although the ratios can vary from approximately 35/65 to 55/45. Most refinery applications where DSSs are used are corrosive, and DSSs or other higher alloys are required for adequate corrosion resistance. However, some plants are also starting to consider DSS as a “baseline” material [1]. These plants are using DSS 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 austenitic SS in services where the common austenitics would have problems with chloride pitting or chloride stress corrosion cracking (CSCC). Higher alloyed DSSs like super duplex and hyper duplex are an economic alternative to higher alloys with similar corrosion resistance. Figure 1 (in Section 1) shows a comparison of DSSs with various austenitic SSs, 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 indicates that there are “subfamilies” of specific grades within both the DSSs and austenitic families. This is also illustrated in Table 1 (in Section 1).

DSSs have existed since the 1930s. However, the first generation steels, such as Type 329 (UNS S32900) had unacceptable corrosion resistance and toughness at weldments [3], [4], [5]. Hence, the initial applications were almost exclusively for heat exchanger tubing, particularly in corrosive cooling water services, and shafting or forgings. In the 1980s, second generation DSSs became commercially available which helped overcome the problems at the welds. These new grades had nitrogen additions and better austenite/ferrite balances, which along with improved welding practices designed for the DSSs, led to the welds’ mechanical (strength and toughness) and corrosion properties being comparable to the annealed base metal. The DSSs most commonly used today in refineries include those with 22 %, 25 % and 27 % Cr. The 25 % Cr (super duplex grades) and 27 % Cr (hyper duplex grade) usually also contain more molybdenum and nitrogen, and so have higher PREN values than the 22 % Cr duplex steels.

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 higher minimum nitrogen, chromium, and molybdenum contents. In many cases, material is dual-certified as S31803/S32205. ASME and ASTM standards for duplex SS grades are given in Table 2 (in Section 1), while Table 3 (in Section 1) provides the mechanical properties. Type 316L and other austenitic SS are included in these tables for comparison.

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

a) potential environment-related failure mechanisms and preventative measures to avoid them;

b) typical material specification requirements used by refiners;

c) typical fabrication specification requirements used by refiners;

d) 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. The definitions of these terms have not been firmly established by the industry, and vary between literature references and materials suppliers. Table 1 shows how the various grades are being classified into “families” for the purposes of this report. The UNS numbers of the standard grades being used for corrosive refining services include:

— Lean DSSs: S32101, S32202, S32304, S32003, S82011, and S82441;

— Standard DSSs: S31803 and S32205;

— Super DSSs: S32520, S32550, S32750, S32760, and S32906;

— Hyper DSS: S32707.

The grades which are labeled as “lean” (including grades sometimes called “semi-lean”) have either lower Cr, Ni, or Mo than the standard grades, and are used in some process services that are less aggressive (primarily in corrosive environments to replace 304L SS). These alloys have also been used for storage tanks and structural applications, primarily for their higher strength as compared to carbon steel (CS). It is observed that new DSS alloys are being introduced and are likely to continue to be introduced. These new grades can be reasonably placed in the context of this discussion based on their composition.

The product forms within the scope are tubing, plate, sheet, forgings, pipe, and fittings for piping, vessel, exchanger, and tank applications. The use of DSSs for tanks is also addressed by API 650, Annex X. The Third Edition of this report (API 938-C) has added sections covering castings and hot isostatically-pressed (HIP) components for pumps, valves, and other applications. The limited use of DSSs as a cladding is also briefly covered within this document.

The majority of refinery services where DSSs are currently being used or being considered in the refining industry contain:

a) a wet, sour (H_2S) environment, which may also contain hydrogen, ammonia, carbon dioxide, chlorides, and/or hydrocarbons, which typically has a pH greater than 7;

b) water containing chlorides, with or without hydrocarbons—this includes many fresh water cooling water systems, and some salt water systems with higher alloy grades;

c) hydrocarbons with naphthenic acids at greater than 200 °C (400 °F), but below the maximum allowable temperatures in the ASME Code for DSSs (260 °C to 343 °C [500 °F to 650 °F], depending on the grade);

d) amines, such as MEA, MDEA, DEA, etc.; or

e) other environments, such as those containing caustic conditions.

The specific plant locations containing these services are described in a later section and the report scope will be limited to the first four environments. Although DSSs have good resistance to caustic environments, this service is not unique to or widespread in refining, and hence is not covered in detail in this report.