

Use of Duplex Stainless Steels in the Oil Refining Industry

API TECHNICAL REPORT 938-C
SECOND EDITION, APRIL 2011



AMERICAN PETROLEUM INSTITUTE

Use of Duplex Stainless Steels in the Oil Refining Industry

Downstream Segment

API TECHNICAL REPORT 938-C
SECOND EDITION, APRIL 2011



AMERICAN PETROLEUM INSTITUTE

Special Notes

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

Neither API nor any of API's employees, subcontractors, consultants, committees, or other assignees make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or usefulness of the information contained herein, or assume any liability or responsibility for any use, or the results of such use, of any information or process disclosed in this publication. Neither API nor any of API's employees, subcontractors, consultants, or other assignees represent that use of this publication would not infringe upon privately owned rights.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any authorities having jurisdiction with which this publication may conflict.

API publications are published to facilitate the broad availability of proven, sound engineering and operating practices. These publications are not intended to obviate the need for applying sound engineering judgment regarding when and where these publications should be utilized. The formulation and publication of API publications is not intended in any way to inhibit anyone from using any other practices.

Any manufacturer marking equipment or materials in conformance with the marking requirements of an API standard is solely responsible for complying with all the applicable requirements of that standard. API does not represent, warrant, or guarantee that such products do in fact conform to the applicable API standard.

All rights reserved. No part of this work may be reproduced, translated, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 1220 L Street, NW, Washington, DC 20005.

Copyright © 2011 American Petroleum Institute

Foreword

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

This document was produced under API standardization procedures that ensure appropriate notification and participation in the developmental process and is designated as an API standard. Questions concerning the interpretation of the content of this publication or comments and questions concerning the procedures under which this publication was developed should be directed in writing to the Director of Standards, American Petroleum Institute, 1220 L Street, NW, Washington, DC 20005. Requests for permission to reproduce or translate all or any part of the material published herein should also be addressed to the director.

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

Suggested revisions are invited and should be submitted to the Director of Regulatory and Scientific Affairs, API, 1220 L Street, NW, Washington, DC 20005.

Contents

	Page
1	Scope 1
2	Normative References 1
3	Terms, Definitions, and Acronyms 6
3.1	Terms and Definitions 6
3.2	Acronyms 6
4	Metallurgy of DSS 8
4.1	Background 8
4.2	Solidification 8
4.3	Problems to be Avoided During Welding 8
4.4	Low and High Temperature Properties 10
5	Potential Environmentally-related Failure Mechanisms 12
5.1	Chloride Pitting and Crevice Corrosion 12
5.2	Chloride Stress Corrosion Cracking (CSCC) 15
5.3	Hydrogen Stress Cracking/SSC 17
5.4	Ammonium Bisulfide Corrosion 18
5.5	Naphthenic Acid Corrosion 19
5.6	475 °C (885 °F) Embrittlement 20
6	Material Specifications 22
7	Fabrication Requirements 23
7.1	Typical Specification Requirements 23
7.2	Dissimilar Metal Welding 25
7.3	Cold Working, and Hot, and Cold Bending 25
7.4	Hydrostatic Testing 25
7.5	Tube-to-tubesheet Joints 26
7.6	NDE Methods 26
8	Examples of DSS Applications within Refineries 26
	Annex A (informative) Example of Special Material Requirements for DSS 34
	Annex B (informative) Example of Special Welding Procedure Qualification Requirements for DSS 36
	Annex C (informative) Example of Special Welding and Fabrication Requirements for DSS 40
	Bibliography 43
Figures	
1	Comparison of the Proof Stress and Pitting Resistance of Duplex and Austenitic SS 4
2	Possible Precipitations in DSS 9
3	Effect of Weld Metal Oxygen Content on the Toughness of the Weld 10
4	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 12
5	CPT for 22 % Cr and 25 % Cr DSS Alloys Compared to Austenitic SS Alloys in 6 % FeCl₃, ASTM G48 Test Method A 13
6	CPTs at Various Concentrations of Sodium Chloride (at +300 mV vs. SCE, Neutral pH) 14
7	CCTs for 22 % Cr and 25 % Cr DSS Alloys Compared to Austenitic SS Alloys in 6 % FeCl₃, ASTM G48 Test Method B 14

Contents

Page

8	CSCC Resistance of 22 % Cr and 25 % Cr DSS Alloys Compared to Austenitic SS Alloys in Oxygen-bearing Neutral Chloride Solutions	16
9	Results of SCC Tests of 22 % Cr and 25 % Cr DSS Alloys Compared to Austenitic SS Alloys in Constant Load Tests in 40 % CaCl₂, 1.5 pH at 100 °C with Aerated Test Solution	16
10	Suggested Chloride and pH₂S Limits for Cold Worked (34 HRC to 35 HRC) 22 % Cr (S31803) and a Super DSS (S32760) (pH < 4) (1 psi = 6.89 kPa)	18
11	Impact Energy Curves for Alloys Aged at 300 °C or 325 °C: a) Quench Annealed S32750; b) 45 % Cold Worked S31803 [$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$]	21
12	Embrittlement of UNS S32304, S32205, and S32507 after Long Time Annealing	22

Tables

1	Chemical Compositions of Commonly Used DSS and Other Alloys Composition, Mass %	2
2	ASME and ASTM Specifications for DSS	4
3	Mechanical Properties of Various Duplex and 316L SS	4
4	ASME Code Maximum Allowable Temperatures, °C (°F)	11
5	Partitioning of Alloying Elements Between Phases	19
6	Case Histories of DSS Uses Reported in NACE International Refin-Cor	27
7	Case Histories of DSS Uses Reported by Other Sources	30
8	Summary List of DSS Refinery Applications to Date	33
B.1	Additional Specimens for PQR Test Weld	37
C.1	Welding Consumables	40

Introduction

Duplex stainless steels (DSS) are finding increasing use in the refining industry, primarily because they often offer an economical combination of strength and corrosion resistance. These stainless steels (SS) 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. The benefits expected from the use of DSS are maintained even to a ratio of 75/25 ferrite/austenite volume fraction (except for possible problems with weldability). Most refinery applications where DSS are used are corrosive, and DSS or other higher alloys are required for adequate corrosion resistance. However, some plants are also starting to consider DSS as a “baseline” material. [1] They are using it in applications where carbon steel may be acceptable, but DSS have been shown to be more economical considering their higher strength and better long-term reliability.

DSS 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). Figure 1 shows a comparison of some DSS with various austenitic SS showing the difference in strength and chloride corrosion resistance [expressed as pitting resistance equivalent number (PREN)]. [2] This chart shows the excellent combinations of higher strength and corrosion resistance available with DSS. It also shows that there are “subfamilies” of specific grades within both the DSS and austenitic families. This is also illustrated in Table 1.

DSS 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] Hence, the initial applications were almost exclusively heat exchanger tubing, particularly in corrosive cooling water services, and shafting or forgings. In the 1980s, second generation DSS became commercially available which helped overcome the problems at the welds. These new grades had nitrogen additions, which along with improved welding practices designed for the DSS, led to the welds’ mechanical (strength and toughness) and corrosion properties being comparable to the annealed base metal. The DSS most commonly used today in refineries include those with 22 % and 25 % Cr. The 25 % Cr (super duplex grades) usually also contain more molybdenum and nitrogen, and so have higher PREN values than the 22 % Cr duplex steels.

Table 1 lists the chemistries and UNS numbers of various common DSS, including some first generation DSS for comparison. Note that UNS S32205 is a “newer version” of UNS S31803 and is produced with higher nitrogen, chromium, and molybdenum contents. ASME and ASTM standards for these grades are given in Table 2, while Table 3 provides the mechanical properties. Type 316L and other austenitic SS are included 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 DSS within refineries.

Use of Duplex Stainless Steels in the Oil Refining Industry

1 Scope

This report covers many of the “lean,” “standard,” and “super” grades of duplex stainless steels (DSS) 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 S31803 and S32205, while the super grades include S31260, S32520, S32550, S32750, S32760, S39274, and S39277. The grades which are labeled as “semi-lean” include S32304 and UNS S32003, have either lower Cr or Mo than the standard grades, and are used in some process services that are less aggressive. These alloys and lean duplexes, such as S32101, have also been used for storage tanks and structural applications primarily for their higher strength 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 DSS for tanks is addressed by API 650, Appendix X. Later revisions of this report may consider expanding the scope to include castings and other product forms for pumps, valves, and other applications. Use of DSS as a cladding is also not included within the scope of this document.

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

- a) a wet, sour (H₂S) environment which may also contain hydrogen, ammonia, carbon dioxide, chlorides, and/or hydrocarbons;
- b) water, containing chlorides, with or without hydrocarbons; or
- c) hydrocarbons with naphthenic acids at greater than 200 °C (400 °F) but below the maximum allowable temperatures in the ASME Code for DSS (260 °C to 343 °C [500 °F to 650 °F] depending on the grade).

The specific plant locations containing these services are described in a later section and the report scope will be limited to these environments.

2 Normative References

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

API Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*

API Standard 650, *Welded Tanks for Oil Storage*

API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*

ASME *Boiler and Pressure Vessel Code (BPVC)*¹, Section VIII : Pressure Vessels; Division 1, Division 2

ASME *BPVC*, Section IX: “Welding and Brazing Qualifications”

ASME B31.3, *Process Piping*

¹ ASME International, 3 Park Avenue, New York, New York 10016-5990. www.asme.org.