Duplex stainless steel quality - ASTM A923 vs ISO 17781

Two standards are available for users when they are considering applying supplementary testing to duplex stainless steels: ASTM A923 and ISO 17781. ASTM A923 was a strong first attempt to formalise supplementary testing, while ISO 17781 is a newer contribution.

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History

Modern duplex stainless steels were developed in the 1970s and really came into their own in the 1990s and onwards. They quickly became a corrosion resistant alloy (CRA) of convenience in the oil and gas industry for seawater cooling/firewater systems and mildly sour process fluids.

Duplex stainless steels (DSS) are roughly 50/50 austenite and ferrite and it is necessary to have good control of the composition and the heat treatment to obtain satisfactory properties in both phases. Poor control of these can lead to the precipitation of third phases, such as nitrides, sigma, chi and alpha prime. These are all deleterious and can reduce both toughness and/or corrosion resistance. Similarly, poor control during welding of DSS can also result in the precipitation of third phases and poor properties of the joint.

ASTM 'product' specifications and ASME fabrication codes do not include microstructure, impact and corrosion tests that individually and collectively indicate the presence of deleterious phases in these steels or their welded joints. Since the mid 1980s, more sophisticated users have developed their own 'material' and 'fabrication' specifications that call up these tests as supplementary requirements to the product specifications and weld procedure qualification codes in order to assess the quality of the steel and the procedures used to weld it. This was mostly satisfactory in the 1990s when the major users, such as oil companies, and the major engineering design houses were writing testing specifications for these alloys and insisting on compliance. However, the use of DSS spread to other industries, such as chemical process, desalination, power, mineral processing etc. As the market for DSS expanded, more manufacturers around the world began offering duplex alloys as part of their portfolio. Similarly, more fabrication shops were offering to weld DSS too. A number of these new users either do not realise the importance of supplementary testing, or they consider it an unnecessary cost. So they relied on ASTM and ASME requirements alone and manufacturers and fabricators supplied accordingly.

The result has been that poor quality duplex has been supplied to some projects, either as parent metal or as fabrications, which have failed prematurely, usually by corrosion. There have been numerous reports in the literature of failures of both 22%Cr duplex and superduplex due to poor quality material. Some of the failures due to poor quality have cost millions of dollars.

There are two standards available to the user that can be considered and decided upon when trying to apply supplementary testing to DSS: ASTM A923 and ISO 17781. ASTM A923 was a strong first attempt to formalise supplementary testing and ISO 17781 is a much more recent contribution.

ASTM A923

ASTM A923, is designed to detect sigma phase in 22%Cr duplex and superduplex[1]. It does not address nitrides or alpha prime. (Later a second standard was written, ASTM 1084, for lean duplex). It quickly became apparent that ASTM A923 had some serious drawbacks. Test A is an etched microsection, but the sample is only etched in NaOH, which will not show nitrides. In our opinion, some of the comparative micrographs in A923 described as "possibly affected" are in fact definitely "affected" and the concept of using Method A alone as a "rapid screening test" is seriously flawed. This is because of how intermetallic phases form during conventional heat treatment, and how failures in heat treatment processes can cause localised precipitation of intermetallic phases rather than widespread formation. It is also the case that metallographic examination can be subjective, especially for welds, and it is influenced by sample preparation, etching and metallographer interpretation. For these reasons taking the results of microstructure checks, impact tests and corrosion tests as a collective is the best way forward.

Test method B is a Charpy impact toughness test, at minus 40°C. The standard is clear that the toughness acceptance criterion for each grade is only used to detect the presence

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of unacceptable third phases, rather than the minimum toughness to suit the actual application. We find that the Charpy impact toughness test had a rather low pass/fail criterion[2], which would not necessarily reject material with low levels of intermetallic particles in the microstructure. Indeed, when the standard was developed, Davidson[3] showed that 2205 plates meeting the 54J at minus 40°C acceptance level had already suffered a considerable loss in toughness and also some loss in corrosion resistance. The 54J acceptance criteria was applied because it was "regularly used for a wide range of process applications other than cryogenic applications"[3], and not because it was found to be related to some significant presence of intermetallic precipitates (IMP) in the microstructure. Our own work for superduplex stainless steels[2] showed that an acceptance level of 70J at minus 46°C was rather more discerning with respect to the presence of intermetallic phases. The problem is that low levels of acceptance such as in ASTM A923 Method B and other specifications, can allow materials that are predisposed to further precipitation of IMP to be fabricated by welding. In such cases they could suffer further and rapid IMP precipitation in the low temperature HAZ[4] and then be deployed in service. In such cases, if pre-existing rather than new weld procedure qualifications (performed on the susceptible material) are used it is unlikely that the problem will be discovered until it is too late. Finally, the corrosion test in ferric chloride solution, at 40°C was judged by some to be at too low a temperature for wrought and cast superduplex in the solution treated and water quenched condition, such that it could also pass material that might contain low levels of intermetallic phase. This was rectified to some extent by the inclusion of Supplementary Requirement S1 which gave the option of corrosion testing at 50°C. Again our own work on superduplex in the solution treated and water quenched condition shows a test temperature of 50°C to be much more discerning in terms of detection of intermetallic particles than testing at 40°C[2]. However, other contributors to the standard argued that the 50°C test temperature should be discretionary, applied only to the "arduous" applications rather than the "commodity" application that would be covered by the

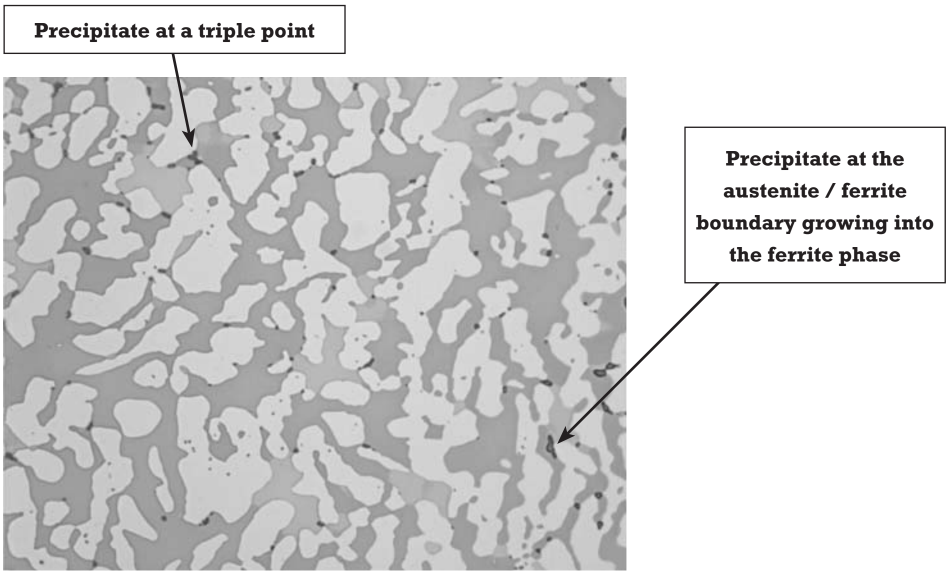

Figure 1. Showing typical locations of precipitates in a duplex stainless steel wrought microstructure.

40°C test temperature. In saying this, it is our experience that these grades are always deployed in arduous applications, so we find the concept of a commodity application difficult to rationalise.

ASTM A923 and welds

In addition, ASTM A923 does not address welds well; in particular, how to take samples, and this impacts on suitable pass/fail criteria. ASTM A923 allows testing of both machined flat, rectangular samples cut from welds, with polishing of all faces and also testing of samples with surfaces in the "as fabricated" condition and only cut edges polished. Both NORSOK[5] and TWI/ International Institute of Welding (IIW)[6] only require a cut out of the weld and polishing of cut faces, which means that both the as-manufactured and as-welded surfaces including the weld root run are tested. These areas are what a user wants to know about. The NORSOK requirement for a brief pickle prior to testing is supposed to remove test to test variability because it gave a distinct transition between the passive state and active pitting[7], but this might also remove some surface defects like poor pickling or areas of nitrogen loss in the root of welds where corrosion could initiate[2]. For this reason, the authors prefer to test the mill finished and as welded and cleaned condition (without pickling of the sample, unless pickling is going to be applied post welding). These two test methods have different weight loss acceptance criteria too. ASTM 923 allows no more than 10mg/ decimeter^2/ day (10mdd), which equates to 1g/m^2 in a 24-hour test while the TWI method has a maximum weight loss of 4g/m^2. The lower weight loss in ASTM A923 is justified in terms of it being "discernable, measurable and not reliant on the subjectivity of visual determination of pitting"[3], but not in terms of presence of IMP's. When using ASTM A923 it is possible that all the as-manufactured faces have been removed by grinding and only the bulk metal is being tested. Whereas, when as-manufactured, or as-welded, surfaces are tested higher weight loss limits are appropriate[6]. It has been found that for weight losses exceeding 4g/m^2 the rate of weight loss increases rapidly, indicating stable pitting. As such a weight loss of 4g/m^2 and lower is considered acceptable. Further, the TWI method was developed on the basis of evaluating round robin testing of welds in a number of different laboratories. As far as the authors are aware, no such testing has been done to justify the use of ASTM A923 Method C test for welds. Indeed, users have reported problems when trying to apply A923 corrosion test requirements as part of weld procedure qualification[8]. For this reason, the authors prefer the TWI method and its 4g/m^2 weight loss limit.

ASTM A923 and its acceptance levels are based more on what a manufacturer would wish to supply rather than what an end user may need. When criticised because the test methods failed to detect problems associated with nitrides, ineffective pickling of parts, or nitrogen loss from the root runs of welds say, the custodians of the standard fall back on to the scope of the standard, arguing that it was dedicated only to the detection of intermetallic phases that cause significant loss in toughness or corrosion resistance, recognising that the test methods will not necessarily detect loss of toughness or corrosion resistance attributable to other causes. The standard has been modified over the years, but changes were slow to come about and did not always meet oil and gas companies' requirements. Hence, the oil industry users sat down to write a more robust standard based on their own requirements, under the auspices of ISO. This became ISO 17781[9], first issued in 2017.

What's in the ISO standard

The ISO standard addresses the quality of all grades of DSS, lean duplex, standard duplex, superduplex and hyper duplex, as well as welds of these alloys. It covers all major production routes, including wrought, cast and HIP. The document describes in detail how test samples should be taken, particularly for thicker section products, so that the tests represent the thickest material. The standard requires three different tests.

The first is a microsection and the standard says where and how it should be sectioned, and how it should be polished and etched. The most common etch is a two stage, in 10% oxalic and 20% to 40% NaOH or KOH. These etches will show nitrides, sigma and chi phases. This double etch must be specified, as a single NaOH etch is also an option. We find the double etch good for 22% and 25% Cr duplex grades. Outokumpu argue that the oxalic acid etch encourages transpassive attack, which exaggerates the apparent size of precipitates and causes "ditching" of grain boundaries, so they do not recommend it for etching of 2507. They recommend etch V2A, (50ml hydrochloric acid, 5ml nitric acid and 50ml water)[10].

The microsection is examined firstly at low magnification, scanning the whole area of the sample. Any areas that are then thought to be possibly affected are then examined at high magnification to confirm that they are not etching artefacts but are indeed third phases. This is usually done by considering the location of the particles. Intermetallics tend to precipitate at the austenite/ferrite grain boundaries and grow in to, and consume the ferrite phase. Locations like grain triple points and interdendrictic spacings in castings or welds are prime locations for precipitation. Figures 1 and 2 illustrate this.

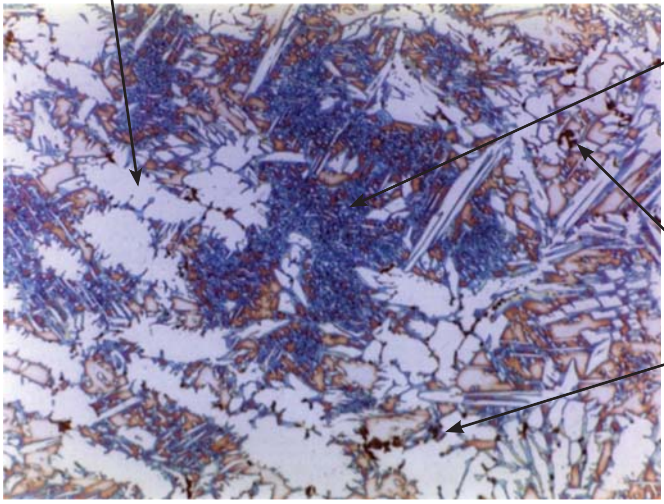

Figure 2. Showing typical location of precipitates in the root run of a duplex stainless steel weld.

The occasional third phase particle is not necessarily a fail, provided the material passes the other two tests. In these circumstances it is suggested that the microstructure of the corrosion and impact test samples be checked to ensure similitude between these and the original microstructure check sample. The microsection is also used to determine the phase balance, and the ferrite content must be in the range 35 to 60% for parent metal and 30 to 70% for welds in the as-welded condition.

The second test is a Charpy impact toughness test, with the test temperature specified for different duplex grades. The standard is also particular about where the samples are taken and their orientation. This is because the toughness varies significantly depending on whether it is orientated in a longitudinal or transverse direction with respect to the grain structure of the steel. For parent standard duplex and superduplex the test temperature is -46°C. The pass/fail criteria are specified for different product forms of the different grades, and some of these are split into two, with higher energies required for more demanding applications. As-welded joints have their own special requirements.

The third test is an ASTM G48 type corrosion test for higher alloys and an ASTM 1084 type for lean duplex alloys. The test temperature is specified for each grade and the pass/fail criteria include a maximum weight loss, in addition to having no visible pitting at x 20 magnification. This is because nitrides or ineffective acid pickling of the material can cause a high weight loss without showing any pitting. The standard also includes tests for as-welded welds with specific requirements on sample location and preparation, as well as different temperatures and pass/fail criteria for each grade. Table 1 summarises the test

Table 1. Test requirements for some duplex stainless steel welds (taken from ISO 17781).

ALLOY		TEST		
		TOUGHNESS	CORROSION	MICROSECTION
Lean Duplex	Test	Charpy impact test at 20°C	ASTM A1084 for 24h+	Polished and double etched*
	Pass	45J Min average; 35J single minimum	No pitting at ×20; Wt. loss < 4g/m²	Ferrite 30 to 70%; No significant third phases
2205	Test	Charpy impact test at −46°C	ASTM G48 at 22°C for 24h	Polished and double etched*
	Pass	50J Min average; 40J single minimum	No pitting at ×20; Wt. loss < 4g/m²	Ferrite 30 to 70%; No significant third phases
Superduplex	Test	Charpy impact test at −46°C	ASTM G48 at 35°C for 24h	Polished and double etched*
	Pass	50J Min average; 40J single minimum	No pitting at ×20; Wt. loss < 4g/m²	Ferrite 30 to 70%; No significant third phases

** Double etching = electrolytic etching first in oxalic acid and then in NaOH.*

+ No temperature specified

requirements for some duplex welds. The tests are the same for parent metal, but the test conditions and pass/fail criteria are higher, and they vary with the product form.

The importance of the tests

The tests in ISO 17781 were designed to prevent sub-standard material being supplied to the oil and gas industry. However, there have been failures of DSS due to poor quality in many other industries. The authors have seen failures in the desalination, mineral processing and chemical industries. The document is quite demanding in its testing requirements and pass/fail criteria, but this is based on the experiences of the oil and gas industry and what it takes to be sure that the alloy will not fail prematurely. Failures due to poor quality microstructures have cost tens of millions of dollars to rectify in some instances[11-13], so a little extra money spent up front on quality is felt to be justified.

Because of the experiences that drove this standard to be created, there is no reason for it not to be adopted by other industries when purchasing, or fabricating, duplex stainless steels.

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