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# QA/QC Tools to Ensure the Quality of Duplex Stainless Steel Components

Roger Francis
Rolled Alloys
Walker Industrial Park
Blackburn, BB1 2QE
UK

Glenn Byrne
Rolled Alloys
Walker Industrial Park
Blackburn, BB1 2QE
UK

Geoff Warburton
Rolled Alloys
Walker Industrial Park
Blackburn, BB1 2QE
UK

Jason Wilson
Rolled Alloys
Temperance
Michigan
USA

## ABSTRACT

It has long been understood that the heat treatment of duplex and superduplex stainless steels is critical to obtain the optimum structure and the desired properties. Over the last twenty years there have been a number of cases where inadequately heat treated components have been delivered by the manufacturer and then subsequently identified as defective further down the supply chain. In some cases the problem was identified and resolved prior to fabrication and installation, while in others fittings have leaked in service due to poor microstructure from incorrect heat treatment.

Common to all these cases is that the cast and batch production test certificate indicated that the goods met specification requirements in all respects. Hence the similitude between cast and batch specific test pieces and the production parts has been called into question. The use of additional testing when specifying these alloys is common but there is no agreement on what these tests should be.

There has been extensive discussion on how best to test individual components non-destructively to detect unsatisfactory material. Some have suggested that magnetic measurement of the ferrite content is adequate, whilst others believe the test to be insufficiently discerning, resulting in too many good parts falsely being identified as "suspect" and causing unnecessary remedial action.

The present paper describes the procurement specifications used by the authors' company to ensure adequate properties in service. The paper addresses the strengths and limitations of magnetic ferrite measurements and shows how the readings are affected by manufacturing route, product form, surface roughness and radius of curvature. The paper goes on to show how the test can be used to identify material that may contain sigma phase and that in-situ metallography is then required on these suspect

areas to either release the part or condemn the part to remedial heat treatment. The results of five years successful experience with this combination of tests are discussed.

Key words: Quality; Duplex Stainless Steel; Specifications; Standards

## INTRODUCTION

Duplex stainless steels are widely used by both the oil and gas and chemical and process industries. The compositions of the commonly used grades are shown in Table 1.

**TABLE 1**
**Composition of commonly used duplex stainless steels.**

| UNS No. | | COMPOSITION (wt%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Fe | Cr | Ni | Mo | N | Cu | W |
| S31803 | Min | Bal | 21 | 4.5 | 2.5 | 0.08 | - | - |
| | Max | | 23 | 6.5 | 3.5 | 0.20 | - | - |
| S32205 | Min | Bal | 22 | 4.5 | 3.0 | 0.14 | - | - |
| | Max | | 23 | 6.5 | 3.5 | 0.20 | - | - |
| S32750 | Min | Bal | 24 | 6.0 | 3.0 | 0.24 | - | - |
| | Max | | 26 | 8.0 | 5.0 | 0.32 | - | - |
| S32760 | Min | Bal | 24 | 6.0 | 3.0 | 0.2 | 0.5 | 0.5 |
| | Max | | 26 | 8.0 | 4.0 | 0.3 | 1.0 | 1.0 |

Bal = Balance

These alloys are nominally 50/50 austenite/ferrite and combine strength, ductility and corrosion resistance. To obtain these properties it is essential that these alloys are correctly heat treated after hot working. Over the last twenty years there have been a number of problems reported with both 22%Cr duplex and superduplex (25%Cr) alloys. These include reduced high temperature strength, low impact toughness and poor corrosion resistance.

In the last few years there has been an increase in the number of reported problems with duplex stainless steels due to quality issues. In some cases this has led to leakage in service and costly repairs.[1] Statoil[(1)] bought a large quantity of superduplex fittings, some of which were fitted on offshore platforms into both seawater and process lines. Some of the seawater fittings leaked due to the presence of sigma phase and a detailed survey was initiated to identify and replace the faulty fittings.[1] Conoco[(1)] reported problems with low impact toughness of 22%Cr duplex flanges due to poor heat treatment.[2] Several engineering and design companies have also experienced problems with both 22%Cr duplex and superduplex components due to poor manufacturing procedures.[3, 4] Figure 1 shows a microsection of a superduplex fitting that leaked on a Phillips[(1)] installation. The structure clearly shows large quantities of sigma (dark phase), which reduced the corrosion resistance.

This kind of problem is not peculiar to duplex stainless steels. Wintle[5] presented a number of cases where poor quality manufacturing led to problems in service for a wide range of corrosion resistant alloys.

[(1)]Registered trademark

In all of the problems with duplex stainless steels, the certification said that the material was satisfactory and met all the specification requirements. Clearly there was a lack of rigorous QA/QC at all stages from manufacture to installation. In many cases the problems were due to an inadequate heat treatment. This paper reviews the standards for duplex stainless steels and suggests what should be specified and tested to ensure the delivered items are fit for service.

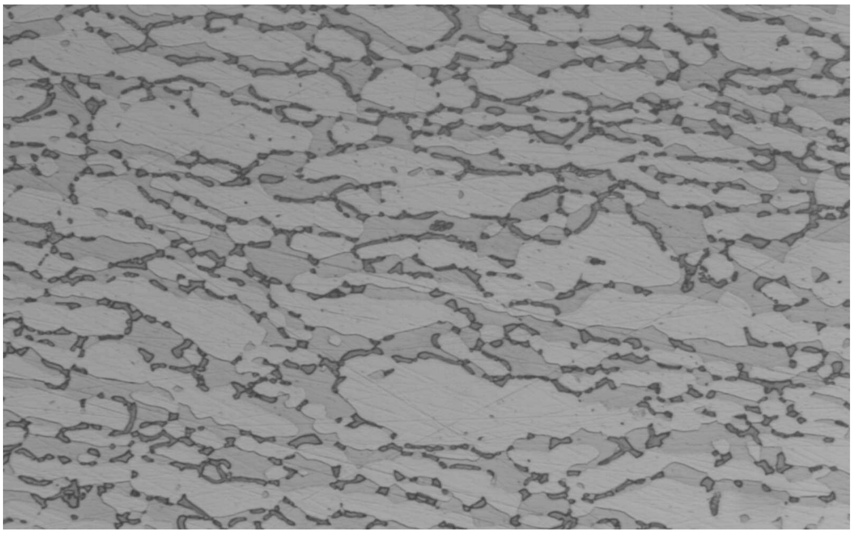

**FIGURE 1: Microsection showing sigma phase precipitates in a superduplex fitting. (electrolytically etched in oxalic acid then KOH; X500)**

## HEAT TREATMENT AND DELETERIOUS PHASES

Duplex stainless steels are usually delivered in the solution annealed condition and, after final heat treatment, the components are rapidly quenched, usually in a water tank. If the quench is too slow, it is possible for third phases to form, which can affect the subsequent properties.

If the metal is cooled too slowly in the range 1,000° to 750°C it is possible for nitrides to form and also sigma and chi phases. The latter are chromium and molybdenum rich intermetallic phases that deplete the surrounding matrix in these elements. This means that sigma and chi phases reduce both the toughness and the corrosion resistance. Because the sigma and chi phases tend to form as a smaller number of large particles, rather than a more uniform distribution of small ones, it needs only a small concentration to reduce both toughness and corrosion resistance significantly.[6, 7]

Nitrides can also affect both toughness and corrosion resistance, but they have a bigger effect on corrosion resistance.[8] Figure 2 shows the critical pitting temperature in the ASTM[(1)] G48 method E test as a function of nitride content, using an arbitrary scale developed by the authors.[8] This scale starts from zero and increases to 3 as the nitride content increases and the location changes.

Superduplex stainless steel, ZERON[(2)] 100, gained acceptance into NACE MR0175 under the UNS number S32760. A range of product forms was tested and all passed a sulphide SCC test at 80°C with 20kPa $H_2S$ and 120,000mg/L chloride at a pH~3.5. Tests on S32760 from another manufacturer failed under the same conditions due to the presence of nitrides, as shown in Figure 3.

1) American Society for Testing and Materials, Pennsylvania, USA
(2) Registered Trademark of Rolled Alloys, Michigan, USA

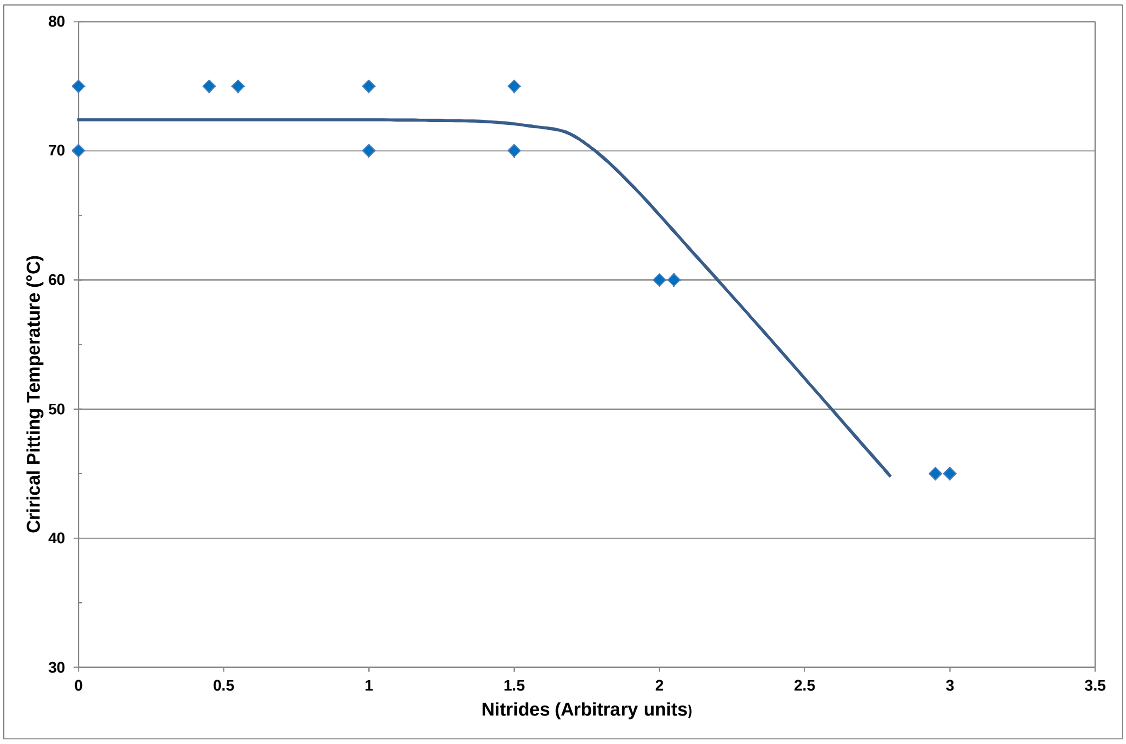


**FIGURE 2: Effect of nitrides on the critical pitting temperature of superduplex stainless steel in ASTM G48 method E**

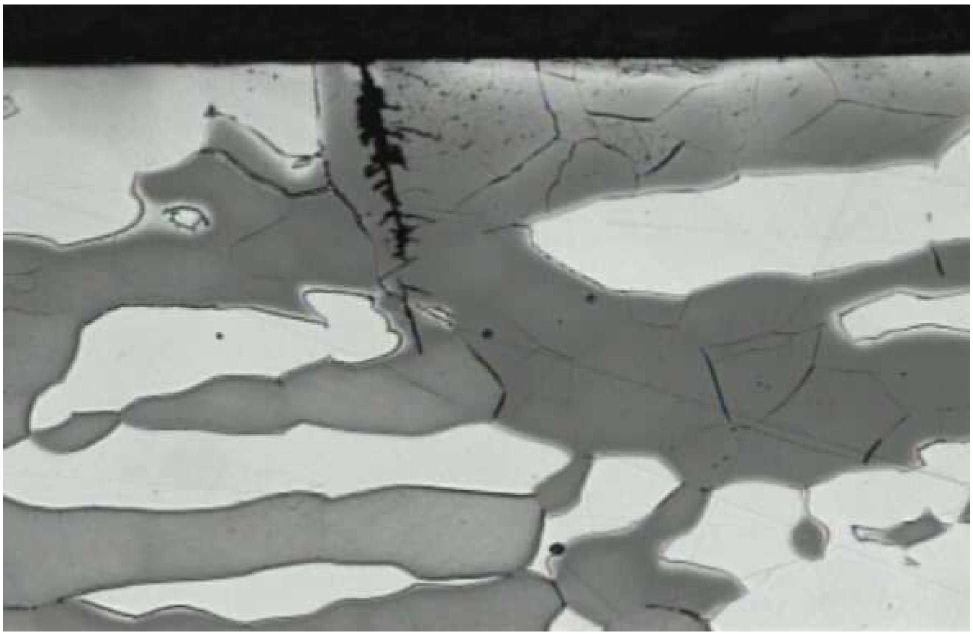

**FIGURE 3: Microsection of S32760 that failed a sulphide SCC test under NACE MR0175 conditions. (electrolytically etched in oxalic acid then KOH; X500)**

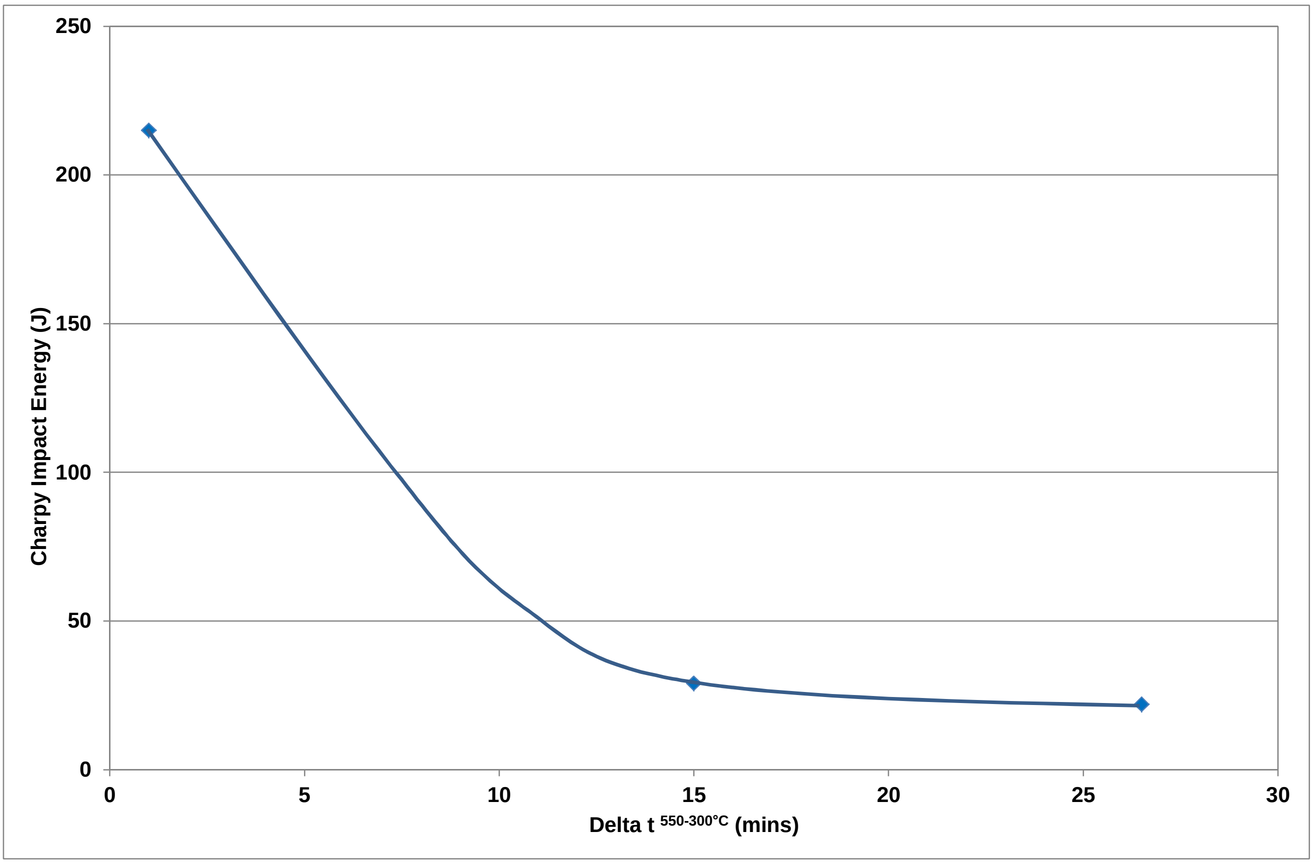


**FIGURE 4: The effect of alpha prime phase on impact toughness.**

Alpha prime phase can form if a duplex alloy is cooled too slowly through the temperature range 550° to 300℃. This phase is an intermetallic, but it i s very fine and cannot be seen by optical microscopy. Alpha prime phase does not normally have a significant effect on corrosion resistance, but it significantly reduces impact toughness, as shown in Figure 4. Alpha prime phase requires a longer time to form than sigma or chi phases. It is most often seen in thick section components that are removed from the quench tank too soon, when the centre of the component is still well above 300℃. The alpha prime then precipitates while the component is slowly cooling in air.

The above discussion demonstrates the need to carry out a careful heat treatment, both to dissolve any third phases that formed during hot working and also to prevent them forming on quenching. This means that, not only is the temperature of the heat treatment important, but so is the time at temperature. In addition, the transfer time from the furnace to the quench tank, the size of the quench tank and the water temperature during the quench are all important.

## STANDARDS

Duplex stainless steels in the oil and gas sector are usually procured to ASTM product specifications, e.g. ASTM A815 for fittings. These standards require only a composition to the UNS specification (often quite wide), minimum tensile properties and a temperature range for heat treatment. The temperature of the heat treatment controls the phase balance, so this must be carefully balanced with the composition. The ASTM standards make no mention of the time at temperature, the transfer time or the speed of quench, all of which strongly affect the microstructure.

In an effort to ensure freedom from third phases in duplex stainless steels, ASTM A923-08 was introduced.[9] This specification is mostly focused on the avoidance of sigma and chi phases and makes no mention of nitrides or alpha prime. ASTM A923-08 offers three methods of evaluating alloys. The first is by examination of a microsection etched to show third phases. The second method is by impact toughness testing, as shown in Table 2. Not all the superduplex alloys are listed and no criteria are set for any superduplex alloy. The test temperature is -40℃ and with most oil and gas specifications requiring testing at -46° or -50℃, this is clearly too high, as it may pass alloys that are not tough enough at service blow-down temperatures. In addition, the increasing number of high temperature/high pressure wells means that blow down temperatures are decreasing, and good impact toughness is being increasingly required at -60° or -70℃. Henc e, the impact toughness temperature requirement is not rigorous enough for most current oil and gas projects.

**TABLE 2**
**Impact energy requirements from ASTM A923.**

| UNS No. | TEMPERATURE (℃) | MIN. IMPACT ENERGY (J) |
|---|---|---|
| S31803 | -40 | 54 |
| S32205 | -40 | 54 |
| S32750 | -40 | By Agreement |
| S32760 | No Entry | No Entry |

**TABLE 3**
**Corrosion rate requirements from ASTM A923.**

| UNS No. | TEMPERATURE (℃) | MAX. CORR. RATE (mdd) |
|---|---|---|
| S31803 | 25 | 10 |
| S32205 | 25 | 10 |
| S32750 | 40 | 10 |
| S32760 | No Entry | No Entry |

The third test is a ferric chloride corrosion test, similar to ASTM G48, as shown in Table 3. Again, not all superduplex alloys are listed, and the test conditions are felt to be inadequate. While 25℃ is satisfactory for 22%Cr duplex alloys, 40℃ is not s uitable to detect nitrides in superduplex (Figure 2) and a higher temperature is required.[8] In addition, the pass/fail criterion is regarded as rather onerous, in that, while it is satisfactory for plate or bar, welded products might have a problem meeting it.

Another commonly used standard is NORSOK[10], which requires impact toughness testing at -46℃, with a minimum average of 45J and a minimum single value of 35J. This is believed by the authors to be inadequate for parent metal, because most products are welded into position and the toughness after welding is much less than that of parent metal.[11] Hence, a parent metal just meeting the NORSOK minimum toughness values will probably have inadequate toughness after welding. NORSOK also requires a ASTM G48A corrosion test at 50℃ for 24 hours, with a requirement of no pitting and a weight loss less than 4g/m$^2$ (40mdd). In the authors' experience, this test can easily detect sigma, chi and nitrides.

In addition to these standards, it is common, at least among major companies, to have an approved vendor list for corrosion resistant alloys. It is also a requirement under NORSOK M-650 for special materials (CRA's). Although suppliers are rigorously audited to gain admittance to the approved vendors list, regular checks and audits are often not carried out, such that current manufacturing procedures may no longer be adequate. NORSOK M-650 makes no provision for regular auditing and the problems described with fittings in the Introduction[1] were from a NORSOK approved vendor. Hence, while having an approved vendors list is useful, it is important that it includes provision for regular auditing to ensure that quality is being maintained.

## THE SOLUTION

The authors' company recognized the inadequacies of standards and specifications to ensure adequate material quality and instigated its own requirements for superduplex stainless steel some 10 years ago. These are:

1. Impact toughness ≥ 70J average at -50℃.
2. ASTM G48A test for 24 hours at 50℃ (no pitting and weight loss < 4g/m$^2$).
3. Microsection at X500 (electrolytically etched in oxalic acid, then KOH).

The requirements for 22%Cr duplex are the same, except the ASTM G48A test temperature is 25℃.

The impact toughness test guarantees that, even after welding, there will be adequate toughness for most oilfield applications. Passing the corrosion test shows that third phases are not present in sufficient amounts to significantly affect the corrosion resistance. The corrosion test can also detect nitrides, which may cause pitting or just a high weight loss[8]. The weight loss criterion is also useful because it can detect surface chromium depletion due to inadequate pickling after heat treatment and quenching, even though this does not cause pitting. If the chromium denudation is very shallow, pitting does not occur because of the sound metal beneath the denuded zone. The weight loss may also be due to inadequate scale removal.

The microsection enables the phase balance to be determined and also what third phases are present, if any. This is particularly helpful if the material has failed test 1 or 2, as it helps to determine the most appropriate heat treatment to restore the properties.

## IMPORTANCE OF CHECKS

The materials test requirements described above are not sufficient alone to ensure adequate quality is maintained. Hence, it is necessary to initiate QA/QC checks to verify that materials are acceptable. One of the problems described in the introduction[1] was due to fittings being heaped into a basket for heat treatment (Figure 5) instead of being stacked separately. Testing at some stage in the delivery process would have shown the fittings to be sub-standard.

There are a number of ways that material can be tested. Positive Material Identification (PMI) will only show that it is the correct alloy composition. Cutting off a piece for a microsection will work, but it is destructive. In-situ metallography is capable of identifying third phases non-destructively, but it is time consuming and also requires a skilled technician.

**FIGURE 5: Poorly stacked fittings in a heat treatment basket.**

The authors evaluated the use of the feritscope, which is a magnetic method of determining ferrite content rapidly and does not require a skilled operator. The results showed that the readings are influenced by a number of factors; surface roughness, radius of curvature, cold work and pickling, as well as the presence of sigma or chi phases.[12] The first four of these could produce variations in ferrite readings of up to 10%. The decrease due to sigma/chi phases was up to 28% ferrite for flat products and 22% for 0.5 inch diameter round bar, as shown in Figure 6. These results show that, while large volumes of sigma are readily detected, smaller concentrations give decreases in ferrite readings that could be due to other causes. Besides the factors listed above, low ferrite readings can also be caused by surface austenite enrichment, due to pickling in a bath where the acids are becoming depleted. When pickling baths become depleted through use, they can cause selective attack of the ferrite phase.

For the past six years all duplex and superduplex materials entering the authors' company's warehouse have been tested with a feritscope. While this is not an absolute measure of the ferrite content, it has been shown that it can identify areas of low ferrite reading that may potentially be due to sigma or chi phases[12]. Random checks are carried out over the entire surface to establish a typical reading for the surface (for example 6 to 10 readings on a NPS6 elbow) and additionally to identify any areas giving unusually low readings. The areas with low ferrite readings are then checked by in-situ metallography, because there are other possible reasons for low readings in addition to third phases. Items which are confirmed as having third phases present can then returned for re-heat treatment. Since this practice was instituted, there have been no reports from service of duplex or superduplex components failing due to sigma phase.

## CASE HISTORY

A case history serves to show how this works in practice. Some lengths of 6in XXS pipe were cut and hardness checks were performed on the cut lengths. The hardness values were high and feritscope readings were low where the hardness was locally high. In-situ metallography confirmed sigma phase in patches along the length, but not at the original pipe ends. Re-heat treatment removed the sigma phase and restored the properties of the pipe to normal values.

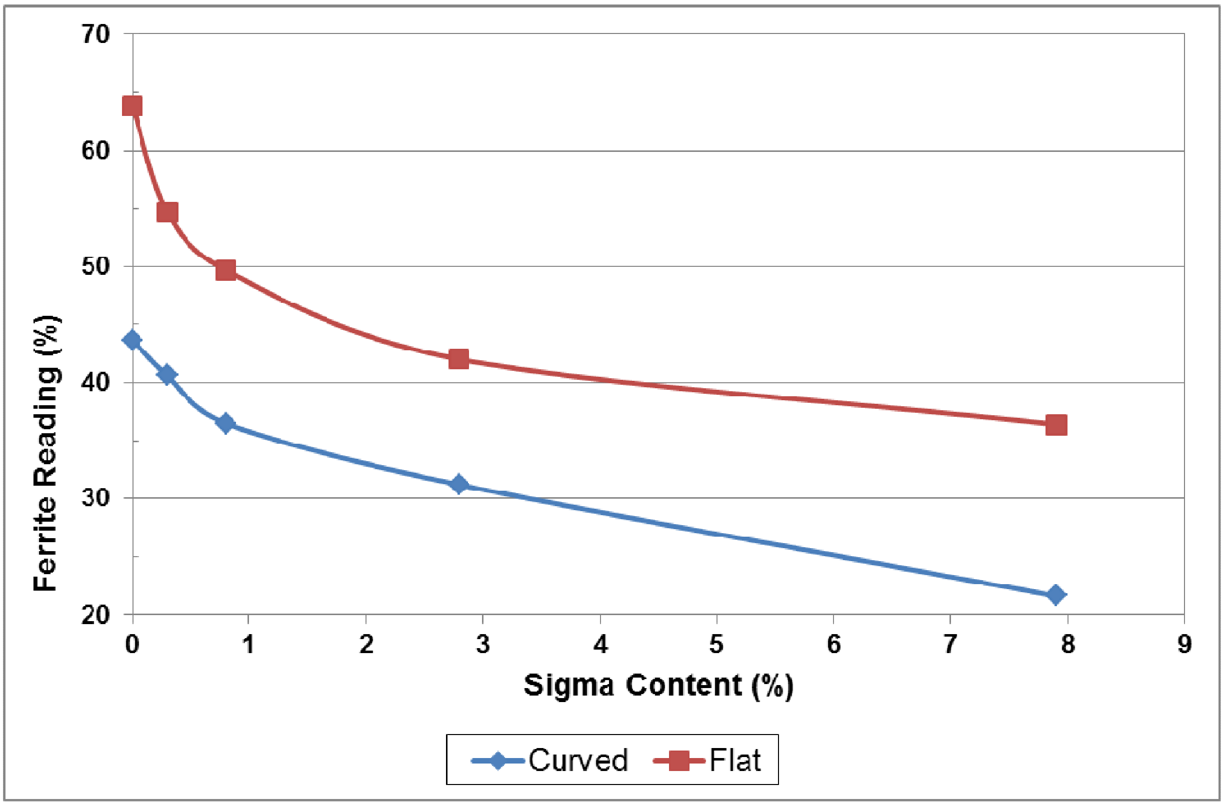


**FIGURE 6: Effect of sigma content on feritscope readings.**

The sigma was produced due to a change in the manufacturer's heat treatment practice, which was not notified to our company. This was not detected on initial testing because the samples were cut from the pipe ends, which were free of sigma phase. This demonstrates the value of the feritscope combined with in-situ metallography.

## CONCLUSIONS

1. The composition limits for duplex and superduplex stainless steels permit a wide range of possible properties.
2. The final properties are influenced not only by the composition, but also by the heat treatment and quenching.
3. Failure to control these adequately can result in a significant loss of impact toughness and/or corrosion resistance.
4. Current standards do not adequately define material properties, such that a component will be satisfactory in service.
5. It is suggested that ASTM requirements be supplemented with an impact toughness test, a corrosion test and a microsection.
6. Areas containing sigma and chi phases can be identified by checking components with a feritscope. In-situ metallography is needed to confirm this.
7. Pre-qualification of vendors can prevent problems later in the project when time is short. However, it is important that approved vendors are audited regularly.

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