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QA/QC tools to ensure the quality of duplex fittings and other components

R. Francis[1], G. Warburton[1], G. Byrne[1] and J. Wilson[2]

[1]RA Materials, Blackburn, UK
[2]Rolled Alloys, Temperance, 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, 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. 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. Various electrochemical tests to assess individual item quality have also been proposed.

The present paper describes 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 is discussed.

1 INTRODUCTION

Modern duplex stainless steels have a roughly 50/50 austenite/ferrite phase balance, with a typical variation from 40% to 60% ferrite. After hot forming, duplex alloys are solution annealed at temperatures from 1050° to 1150°C and quenched. The cooling must be fast enough to avoid the formation of third phases, such as chi, sigma and alpha prime. These phases are known to reduce ductility and corrosion resistance. This means that the annealing temperature must be carefully controlled, the transfer time to the quench tank should be short and the quench tank must be large enough and cold enough to ensure that the metal cools fast enough.

The layout of components in the furnace is important, because if they are too tightly packed, they behave more like a single, thick block of metal instead of individual, small components. This reduces

the number of components that can be heat treated at a time, but guarantees that they will be at temperature for the right amount of time.

When duplex stainless steel enters the quench tank, a vapour film forms on the metal surface and this must be removed as much as possible to allow water access to the surface and increase quench efficiency. To this end, the flow of water into the tank is often from several direction and or water jets force water at the metal surface. In addition the metal component is often agitated, if large, to increase the rate of cooling.

The expanding use of duplex stainless steels means that they are increasingly being treated as commodity alloys and sufficient attention is not always paid to the heat treatment. In the last few years incorrect heat treatment has resulted in several problems in service that have been publicized. Statoil purchased some seam welded superduplex fittings which leaked in seawater service due to sigma phase from poor heat treatment [1]. These fittings were sold to several projects and a great deal of in-situ testing has been carried out to determine which fittings are faulty [2, 3]. Shell had problems with sigma phase due to poor heat treatment of superduplex flanges and weldolets on two North Sea projects, while ConocoPhillips have had a problem with 22% Cr duplex flanges with low toughness, again due to poor heat treatment [4].

Industry has now been alerted to the problem and the best way to detect material that has been poorly heat treated is currently under discussion. This paper describes the method that has been in use by RA Materials for 5 years and the results.

2 TEST TECHNIQUES

One obvious way to detect third phases is to saw off a piece of the component and prepare a microsection. However, this test is destructive and does not necessarily sample in the affected location.

In-situ metallography offers a non-destructive test for third phases, but it is time consuming and requires a skilled technician to carry it out. If numerous tests need to be carried out over a large area, it is very time consuming and costly.

The ferrite is magnetic and when third phases precipitate out of the ferrite, such as sigma and chi, the magnetic signature changes. Hence, measuring the ferrite content magnetically offers the possibility of a rapid, non-destructive method of detecting areas containing third phases. The best known of these devices is the Fischer Feritscope®, but opinion on its usefulness is divided. At one extreme, some companies believe that the numbers from the Feritscope can be used quantitatively to determine the ferrite content. At the other, some believe that the variability in readings makes the instrument useless and only in-situ metallography is reliable.

The following tests were carried out to determine how reliable the Fischer Feritscope MP30 magnetic measurements are and how they are affected by a number of factors.

3 FACTORS AFFECTING READINGS

All the tests were carried out on Zeron 100 superduplex stainless steel (UNS S32760) products taken from current stock. Most of the tests were carried out either on ½" od bar or 2" od bar, in the solution

annealed condition. Bars of various sizes and finishes were used in the tests on the effects of cold work.

Microsections were prepared of each bar and the ferrite content was determined by metallography. The results were:-

0.5” bar - 50% ferrite
2” bar - 47% ferrite

3.1 Surface Roughness

The 2” od bar was examined on the end face in four conditions. These were:

a) as sawn (hack saw)
b) as cut (slitting wheel)
c) abraded (120 grit silicon carbide)
d) polished (1µm diamond)

Ten readings were taken on the end face in each condition. The results are shown in Figure 1.

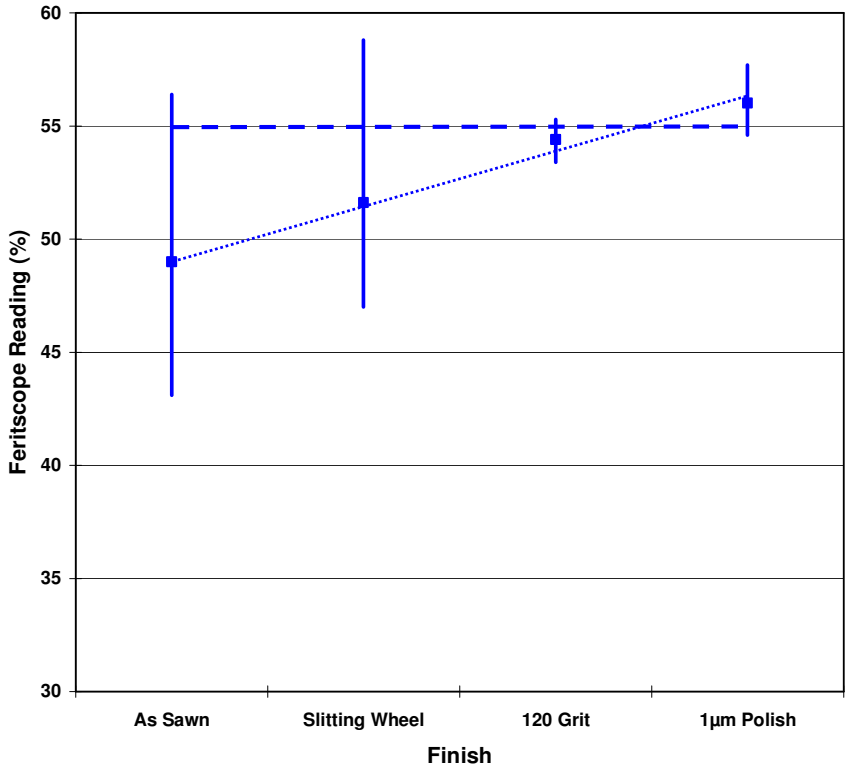

Figure 1 Effect of surface finish on Feritscope readings.

3.2 Radius of Curvature

Readings were taken from a single sample of the 2" bar and several millimeters at a time were machined from the diameter and the readings were repeated after each operation. This was done from a bar diameter of 50mm down to 12.5mm. As before, ten readings were taken on each curved surface. The machining operation meant that the surface finish and any surface cold work from machining were similar for each bar diameter. The results are shown in Figure 2 and as a fraction of the polished flat face reading in Figure 3.

3.3 Cold Work

When bar is produced it is straightened after heat treatment, which means that the surface has a small amount of cold work in it. To determine what effect surface cold work from the manufacturing process would have on the Feritscope readings, small amounts of metal were machined from the diameter of a piece of 2" od solution annealed bar. Initially these increments were 0.25mm, but the increment was increased as metal was removed, until the total reached 4mm. Ten Feritscope readings were taken after each machining operation. The results are shown in Figure 4.

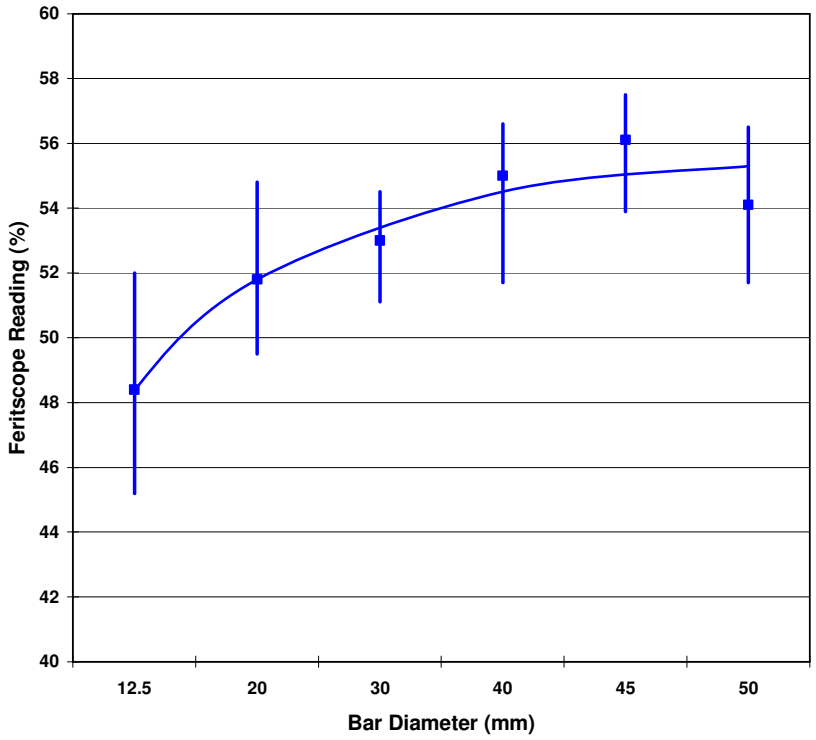

Figure 2 Feritscope readings as a function of bar diameter.

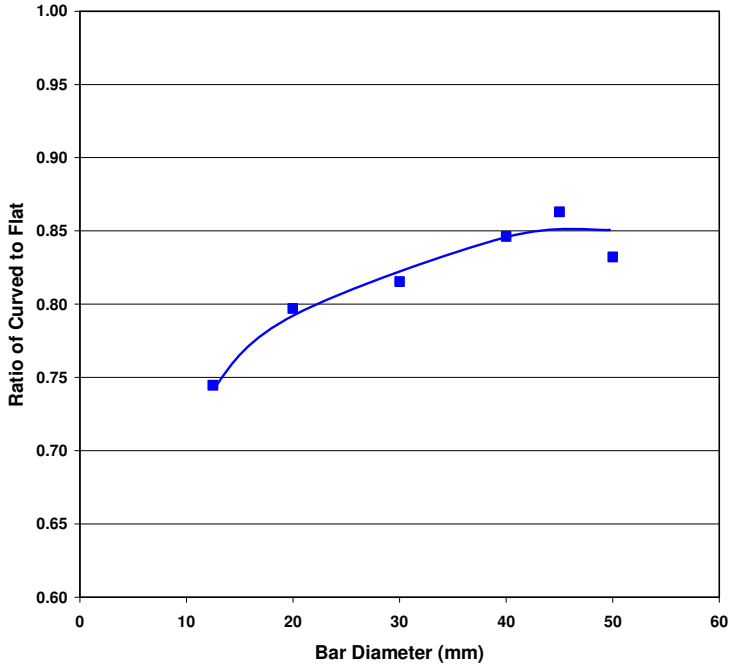

Figure 3 Effect of bar diameter on Feritscope reading ratio.

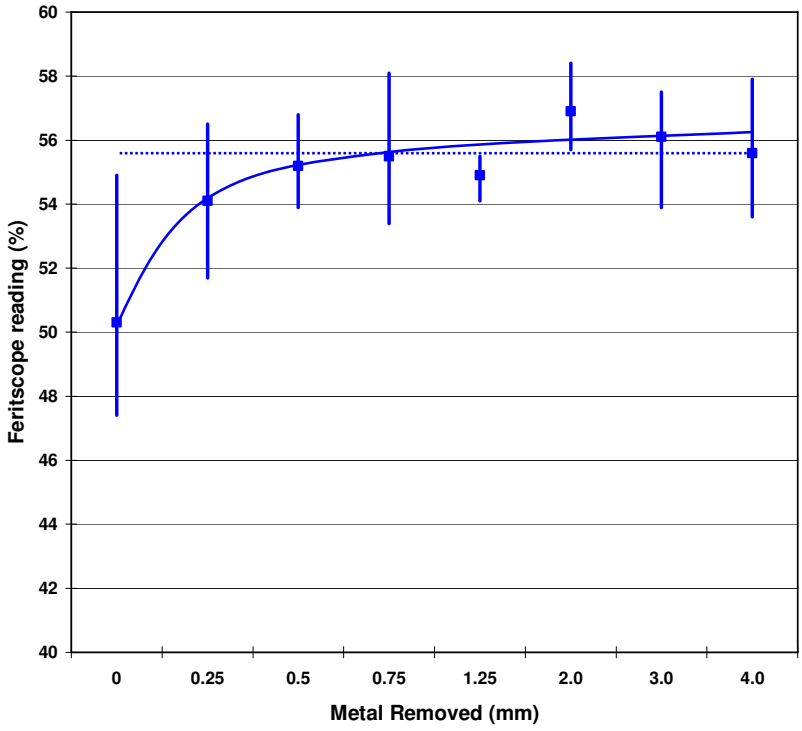

Figure 4 Effect of removing metal from diameter of 2” bar.

As a further check, the readings on the flat end surfaces of both solution annealed and fastener grade bars were compared. The fastener grade material typically has 5% to 7% cold work to increase its strength for offshore fasteners. The results are shown in Table 1.

Table 1 Mean Feritscope® readings for solution annealed and cold worked bar.

BAR DIA. (mm)	MEAN FERITSCOPE READING (%)			
	Curved Surface		Flat Surface	
	SA *	FLT +	SA *	FLT +
12.5	43.7	45.5	61.1	48.4
25	52.0	50.0	59.4	50.5
28.6	-	44.5	-	46.1
32	53.1	-	59.3	-

* Solution annealed

\+ Cold worked

3.3 Pickling

In order to determine the effect of pickling on the Feritscope readings, a sample of the 0.5" od bar was pickled for 2 hours at 50°C in a nitric/hydrofluoric acid mixture, according to RA Materials procedure PP001. This had no effect on the Feritscope readings. A sample of 0.5" od bar was then treated first with a softening solution at 50°C for 3 hours followed by the nitric/hydrofluoric acid pickle for 1 hour, according to RA Materials procedure PP002. The softening solution is a sulphuric/hydrofluoric acid mixture designed to remove heavy scaling. This sample also gave identical Feritscope readings to the as-manufactured bar.

However, samples are normally pickled after a solution anneal at 1050°C to 1120°C, depending on the grade of duplex stainless steel. A piece of 0.5" od bar, 100mm long was heat treated at 1120°C for 1 hour followed by a water quench. Feritscope readings were then taken on the curved surface of the as- quenched bar, while still covered in oxide. The bar was then pickled at 50°C for 1½ hours. Some oxide still remained and the Feritscope readings were taken on the curved surface. The bar was then pickled for a further 3 hours at 50°C (4½ hours total) which removed more oxide,

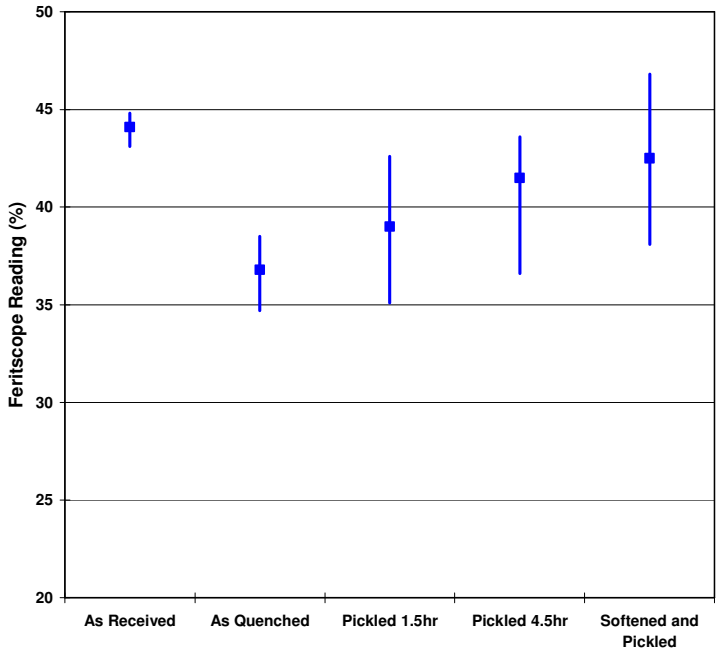

Figure 5 Feritscope readings after various treatments of 0.5" bar.

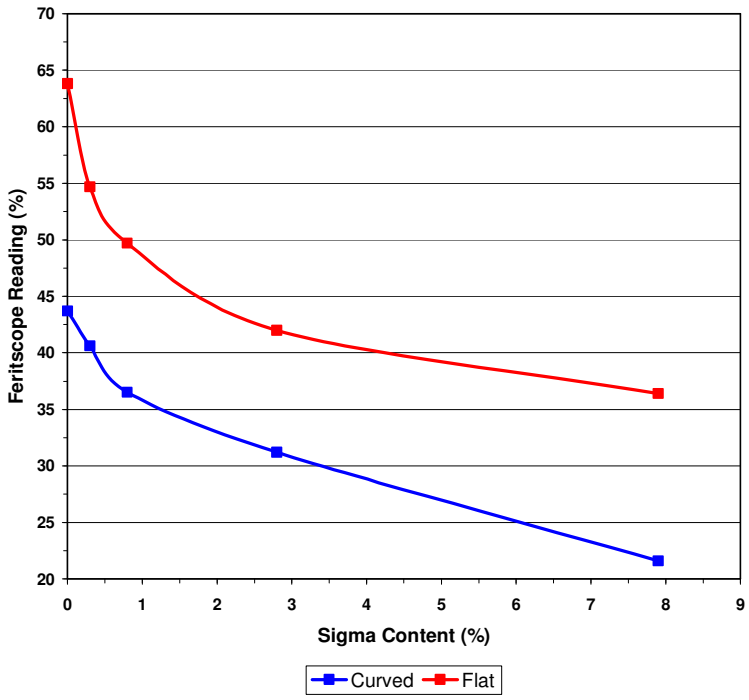

Figure 6 Variation of Feritscope reading with sigma content.

but some still remained. Feritscope readings were again taken on the curved surface. Finally, the bar was cleaned in softening solution and then pickled, both at 50°C, as described above. The bar was now free of oxide and Feritscope readings were again taken on the curved surface. The results are shown in Figure 5.

4 DETECTION OF THIRD PHASES

To determine how Feritscope readings change in the presence of third phases, compared with the other factors described above, some 100mm long samples of 0.5" od bar were heat treated to induce sigma/chi phase. A thermocouple was wired onto the side of the bar and it was placed in a furnace set at 850°C. When the temperature of the bar reached 800°C the clock was started. Samples were exposed for 1, 3, 5 and 10 minutes. The sigma/chi phase was determined by LECO image analyzer from a microsection from each bar. The content was taken as the mean of ten fields. Ten Feritscope readings were taken on the curved surface of each bar. The results are shown in Figure 6.

5 DISCUSSION

The results in Figure 1 show that the scatter in Feritscope readings is greatest with the roughest surfaces. Because of this, it could be argued that a mean value of 55% could be drawn through all the readings. However, taking the mean values for each finish, there is a trend of increasing Feritscope reading as the surface becomes smoother. This increase is about 7% from the roughest to the smoothest and it is not a particularly big change as Feritscope readings go. The readings also get higher than the actual ferrite content as the surface becomes smoother.

Figure 2 shows the effect of bar diameter on the Feritscope readings. The effect is most noticeable at small bar diameters and at 12.5mm, the reading is ~7% lower that at 50mm diameter. The change of reading with curvature in Figure 2 is of the same magnitude as reported by Fisher in the Feritscope operating manual. Again the readings are higher than the actual ferrite content. Figure 3 shows the data as the ratio of curved to flat surface reading and this shows the same trend as in Figure 2. The ratio would be expected to approach unity as the bar diameter increased, but this does not seem to happen as the curve appears to be leveling off at 50mm diameter. However, this is probably due to surface cold work, as described below.

The results in Figure 4 show a slight increase in Feritscope reading between the surface and the interior. The results also show that the surface effect only extends to a depth of ~0.3mm from he surface. Other surface treatment processes, such as shot peening, show a similar range of penetration from the surface. The change in reading is not large, being only about 6%. The lower readings at the surface suggest that the method of production introduced a moderate level of cold work just in the surface layer.

In Table 1 it is noticeable is that the readings on the curved surface for the same size of bar were similar for both solution annealed and FLT bar, but the readings on the flat surface were lower for the FLT bar. This suggests that cold work reduces the Feritscope reading. The reason that the machined 2" bar and the FLT bar give similar readings on the curved surface is that the machining introduces a level of surface cold work similar to that in FLT cold worked bar. 5% to 7% cold work reduced the ferrite readings by about 10%.

The results in Figure 5 show the effect of heat treatment and pickling 0.5" od bar. The lower readings in the as-quenched condition are not surprising as the oxide will separate the probe from the metal surface and reduce the reading. The results also show that the readings increase towards that of

as-manufactured bar as the quality of the pickle is improved. These tests show that pickled surfaces do have lower readings than ground ones, although in this instance the reduction was only ~5% for the worst pickled surface. However, larger components often require longer solution annealing times than one hour, which will result in a thicker oxide. This will be more difficult to remove and could result in a bigger reduction in the Feritscope reading, if the oxide is not fully removed. This means that low readings on pickled surfaces can be indicative of a poor quality pickle. The solution annealing will have removed any cold work, although curvature effects may still be important.

Figure 6 shows the change of Feritscope reading with sigma content, as determined by metallography. There is a clear decrease in the reading with increasing sigma content and the decrease is ~7% for 0.8% sigma and ~22% for 7.9% sigma, on a curved surface and even greater on a flat surface (14% and 27% respectively).

The foregoing tests show that surface roughness, radius of curvature, cold work and the quality of pickling can all reduce the Feritscope reading. In commercial product forms, with different production routes, sizes, finishes etc. there is clearly no absolute value of Feritscope reading that can be relied on to give an accurate guide to the ferrite content. However, for any given component, the presence of third phases will produce a significant local reduction in Feritscope reading. Hence, the best way to use the Feritscope is to do random checks over the whole surface of the component and to do alternative tests, such as in-situ metallography, on any areas where the Feritscope reading is substantially lower than the typical value.

6 SERVICE EXPERIENCE

For the past five years or so RA Materials has been 100% testing of all material coming into the warehouse, particularly pipe fittings. By doing random checks over the surface of each item, it is possible to see whether there are any areas giving low values compared with the average value in areas giving higher values. Areas with low readings can be marked and then checked by in-situ metallography. This means that the ferrite readings can be done quickly by an inspector, who requires only a little training in the use of the instrument. Experienced technicians are only brought in to do in-situ metallography when low readings are found. This check is still required because there are reasons other than third phases that can cause low readings.

One example is a thin surface layer enriched in austenite. This can occur when a pickling bath is growing “tired” and new acid is needed. This can be more aggressive to ferrite and can leave a very thin surface layer enriched in austenite. In-situ metallography readily identifies if this is the cause of low readings. Low ferrite readings can also be caused by austenite being smeared over the surface during some mechanical finishing operations. Again, in-situ metallography can readily identify if this is occurring.

Items where sigma or chi phases are identified can then be returned to the manufacturer for re-heat treatment. Service experience has been very good with Zeron 100 components, but supply experience has been very varied, requiring hands on 100% checking. Inadequate fittings are regularly found, irrespective of manufacturer and level of qualification or reputation.

A case history serves to demonstrate the point. RA Materials cut up some lengths of 6” XXS pipe for a customer, and was required to re-grade these with a third party witness to the testing. The Charpy impact toughness values were low and so the cut lengths were tested with a Feritscope and areas with low readings were found intermittently all along the pieces, except the regions that were originally

pipe ends. In-situ metallography demonstrated that the areas with low readings did indeed contain sigma and the cut lengths were then re-heat treated along with a sacrificial piece for test samples. Correctly heat treated material then gave the desired properties and was supplied. The reason for the sigma was a change in the manufacturer's heat treatment practice. This was not picked up on original testing, because the test pieces were cut from a pipe end, which was free of sigma. This demonstrates the ability of the Feritscope and in-situ metallography to detect sigma phase prior to supply.

7 CONCLUSIONS

1. The Feritscope readings are affected by surface finish, radius of curvature, cold work and inadequate pickling.
2. The readings decrease significantly in the presence of sigma/ chi phases, when tested on both flat and curved surfaces.
3. By testing at several places on a component, it is possible to determine if there are any areas of low reading, where third phases may be present. This can then be confirmed by in-situ metallography.
4. Use of this method by RA Materials for the last 5 years has successfully identified faulty items that require re-heat treating.

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