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Deleterious phases resulting from the induction bending of thick-walled super-duplex pipework

Temper free induction bending can have a significant impact on the mechanical and corrosion-resistance properties of thick-walled super duplex pipe. Sections from induction bent pipe were solution annealed at 1120 °C for various periods to sequentially eliminate different deleterious phases. By comparing the results of modified DL-EPR analysis, optical microscopy, mechanical and corrosion testing before and after the various heat treatments, it was shown that the deterioration in properties was due to the precipitation of α' . It was also possible to determine the order in which α' , γ_2 and Cr₂N had precipitated, and thus to conclude that the unfavourable metallurgy was the result of inadequate post-bend cooling. A likely thermal history for the pipe is proposed that leads to the description of a modified temper free process.

Keywords: Induction bending; Super-duplex; Nitride precipitation; Alpha prime; Secondary austenite

1. Introduction

The process of induction bending involves applying a moment to a pipe whilst heating a short part of its length using an induction coil. At the point where the pipe leaves the zone heated by induction bending it is cooled using a water spray (refer to Fig. 1). At any given time, the length of the pipe exposed to the bending temperature is very short – typically 20 mm for Schedule 160 pipe and 25 mm for Schedule XXS+ pipe. As the pipe moves slowly through the induction coil the position at which bending occurs travels along the conduit. In this manner a single bend, or a continuous series of bends, can be produced.

In temper free (TF) induction bending, a cost-effective variant of the induction bending process, the expectation is

that no post-bend heat treatment will be required as the heat/cool cycle is such that the mechanical and corrosion resistant properties are undiminished by the process [1]. Super duplex stainless steel is a particularly attractive material for induction bending as, at the temperatures encountered in the heated zone (typically 1040 °C to 1150 °C), super duplex displays 90% reduction in yield strength when compared to the value at room temperature [2]. Previous research [3, 4] has also shown that thick-walled super duplex pipe can suffer a significant deterioration in both mechanical properties and corrosion resistance when subjected to TF induction bending.

In order to gain an understanding of the reasons for the previously observed deterioration in properties, the authors took samples from the same pipe which had been shown to have been adversely affected by the induction bending process, and subjected them to a more detailed analysis. This paper revisits the reduction in properties already published in [3] and then documents further work carried out by the authors. New research described in this paper includes a staged post-bend heat treatment regime which was employed to determine the minimum soak time required to restore the pipe's properties. Other novel developments include the use of optical microscopy, followed by a modified version of double loop electrochemical potentiokinetic reactivation analysis (DL-EPR) which were used to isolate the various contributions of the three deleterious phases which were found to be present (α' , γ_2 and chromium nitrides). This paper then proceeds to suggest the mechanisms by which the three deleterious phases may have formed, and the factors which may have influenced the precipitation of these phases. A possible thermal history which could have lead to the generation of α' , γ_2 and chromium nitrides during induction bending is suggested. This paper closes by suggesting process improvements which, if followed should prevent the generation of the three deleterious phases considered.

2. Testing philosophy

In a previous study [3] a total of 8 bends were produced in two pipes featuring very similar chemistry and identical OD's (6.625 inches or 168.3 mm), but different wall thicknesses (Schedule 160 with a wall thickness of 18.2 mm, and Schedule XXS+ with a wall thickness of 25.4 mm). Each pipe featured a series of bends, created consecutively, with the minimum time being allowed between each bend. This, it was felt, would best reproduce the conditions experienced in a production environment. Previous testing

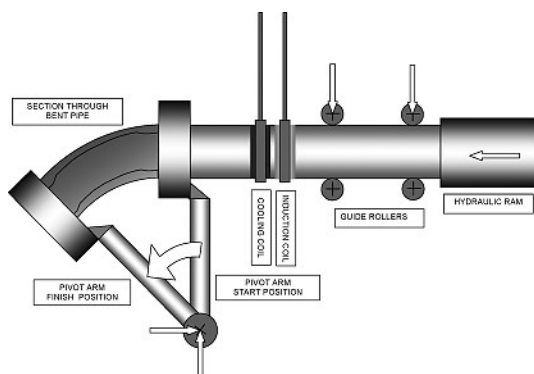


Fig. 1. Main components of an induction bending machine.

Table 1. Properties of parent pipe.

	Chemical Analysis (wt.%)											
	C	Mn	P	S	Ni	Cr	Mo	N	Cu	W	Si	Fe
Schedule XXS+	0.020	0.44	0.023	0.0003	7.03	25.37	3.60	0.255	0.54	0.69	0.52	61.52

	Mechanical/Corrosion/Microstructure Test Results						
	0.2% PS (N mm ⁻²)	UTS (N mm ⁻²)	El (%)	Hardness	Impact (J)	Corrosion	Ferrite Content (%)
Specification Requirements Schedule XXS+	550 min 558	800 min 800	25 39.4	32 HRC max 24	Ave 45 J at -46 °C 291	4.0 g m ⁻² 0.067	35 to 55 49.7

had shown that all of these bends had suffered a significant deterioration in corrosion resistance and mechanical properties, especially impact toughness [3]. In addition it had been shown that all of the bends contained high levels of chromium nitride, and a lesser amount of secondary austenite precipitation. The same pipes from the same batch were used in this research (UNS S32760). Table 1 provides the typical composition of the *parent pipe* – i. e. the straight pipe in its pre-bent condition.

In order to develop a remedial action it was first necessary to isolate the contribution of the various deleterious phases to the deterioration of properties. It is known that the three phases possess different levels of thermodynamic stability. By selecting samples from the as-bent pipe which displayed very low impact toughness and high levels of nitrides and secondary austenite. By solution annealing these samples at 1120 °C for 15, 30, 45 or 60 min respectively and following this with a water quench, it was hoped that each of the precipitates could be eliminated sequentially, thus allowing the authors to establish the effect on the properties of each of the deleterious phases.

Impact toughness and residual precipitate levels were determined following heat treatment for each soak time (methods as per Sections 3.3 and 5.1 respectively). The heat-treated sample with the lowest soak time, which provided impact toughness values above the minimum required by NORSOK M-630 D51 Rev 3 [5] was selected for more rigorous examination. This sample was subdivided to provide a hardness test specimen, a tensile test specimen, a corrosion resistance sample, a DL-EPR specimen, a microscopy sample and two more impact toughness specimens.

The initial results showed that the impact toughness had been restored after just 15 min solution annealing at 1120 °C followed by water quench, but that, even after soaking for an hour the bent pipe still displayed a high level of chromium nitride precipitates. It was thus decided, by way of comparison, that both the 15 min and 1 h specimens be subjected to the full range of testing.

3. Mechanical testing

Mechanical testing included hardness, tensile and impact testing. The results are compared to and contrasted with figures previously obtained for as-bent samples [3, 4] and with values obtained from the original mill certificates for the pipe.

Table 2. Hardness testing (HV10) – comparison of results.

Heat Treatment Condition	Hardness Testing (HV10)		
Parent Pipe	–	24 HRC	–
As Bent	327	325	322
Solution Annealed for 15 min	300	308	306
Solution Annealed for 1 h	272	276	272

Max Permissible Hardness = 330 HV10 [5]

3.1. Hardness testing

A Vickers (HV10) hardness survey was carried out in accordance with BS EN 6507-1 1997 [6] using a 10 kg load (see Table 2). NORSOK M-630 requires the hardness strikes to be below or equal to 330 HV10. Previous research [3] had showed that the majority of the readings from the as-bent samples were in excess of this maximum. The excessive hardness was not confined to any one bend, nor was it peculiar to any particular part of any of the bends; high hardness was found near the pipes' inner and outer surfaces and right across the wall sections. Interestingly, high hardness was encountered even in the bend tangents which, it should be noted, had not been subjected to direct induction heating.

The material which had received a post-bend solution annealing at 1120 °C for an hour gave hardness results below the 330 maximum set down by NORSOK M-630, and 50 points below that of the as-bent sample (refer to Table 2). The material which had received a post-bend solution annealing at 1120 °C for 15 min also gave hardness results below the 330 maximum set down by NORSOK M-630 and 20 points below that of the as-bent sample (refer to Table 2).

3.2. Tensile testing

Tensile testing was carried out in accordance with BS EN 10002 Part 1 2001 [7]. The test results given in Table 3 show that the as-bent samples exceeded all of the minimum requirements laid down in the relevant specification, the exception to this was the minimum elongation, which was slightly below that required by NORSOK M-630. The ultimate tensile stress (UTS) results for the as-bent samples greatly exceed the minimum requirement; high UTS values can be indicative of metallurgical problems.

Table 3. Tensile testing – comparison of results

Heat Treatment Condition	Measure			
	RP 0.2% (N mm ⁻²)	UTS (N mm ⁻²)	% El	% RA
Specification	550 min	800 min	25 min	–
Parent Pipe	558	800	39.4	–
As Bent	835	1075	23.0	33.0
Solution Annealed for 15 min	622	839	37.0	66.0
Solution Annealed for 1 h	635	849	37.5	71.0

Samples heat treated for both 15 min and 1 h showed a reduction in the 0.2% proof stress (PS) and the UTS and an increase in % elongation when compared to the as-bent samples. In each case the results were better than the minimum values laid down in NORSOK M-630, and were broadly in line with the performance recorded in the mill certification for the parent pipe.

3.3. Impact testing

Impact testing was performed in accordance with BS EN 10045 Part 1 1990 [8] using samples of size 10 mm × 10 mm × 2 mm with a V-notch to KV150. Tests were performed at room temperature. Samples were taken in the longitudinal direction. Results are given in Table 4.

NORSOK M630 requires that values are above the minimum of 45 J average at –46 °C. It had been the intention of the authors to carry out a second set of impact testing at –46 °C as required by NORSOK. However, even at ambient temperatures, the Charpy impact values from the as-bent pipe were catastrophically low. This indicated that a significant deterioration in material properties had occurred, and it was not therefore deemed necessary to repeat the testing at –46 °C. Impact results for the heat-treated samples showed a huge improvement; from an average of 7 J before heat treatment to 270 J after 1 h heat treatment, and 300 J after 15 min.

3.4. Summary of mechanical testing

Although the induction bends produced samples which were acceptable in terms of 0.2% PS, UTS and % reduction in area (RA), they were outwith acceptable limits in several respects, most notably high hardness and low ductility. Hardness values above 330 HV10 can leave duplex steels susceptible to hydrogen induced stress cracking (HISC)

Table 4. Impact testing – comparison of results.

Heat Treatment Condition	Absorbed Energy (J) at 20 °C			
	1	2	3	Average
Parent Pipe	–	291	–	291
As Bent	6	7	7	7
Solution Annealed for 15 min	300	303	297	300
Solution Annealed for 1 h	270	268	273	270

Table 5. Corrosion testing – comparison of results.

Heat Treatment Condition	Pitting	Weight Loss (g m ⁻²)
Parent Pipe	None	0.067
As Bent	Extensive Pitting	150
Solution Annealed for 15 min	None	0.000
Solution Annealed for 1 h	None	0.049

Maximum permissible weight loss is 4.0 g m⁻² and no visible pitting at ×20 magnification [5]

[6]. Low impact toughness also causes concern; the extreme brittleness can lead to failures in service and are, additionally, indicative of metallurgical problems. Solution annealing the induction-bent material for 15 min at 1120 °C followed by water quenching, restored all of the mechanical properties to values in line with the parent material. There was no benefit, (nor was there any deficit), in prolonging the soak time to 1 h.

4. Corrosion testing

Samples were prepared and tested according to ASTM G48-03 [9] method A; 24 h at 50 °C. NORSOK M-630 allows a maximum weight loss of the 4.0 g m⁻² and permits no visible pitting at a magnification of ×20. Table 5 shows that the as-bent samples fail to meet the NORSOK standard. By comparison the samples which were solution annealed both for 15 min and 1 h produced corrosion rates which fell within the NORSOK M630 acceptance criteria.

5. Microscopic examinations

5.1. Procedure for microscopy

Samples were taken from the as-bent specimen, from the 15 min heat treatment specimen, and from the 1 h heat treatment specimen. The samples were polished, and prepared to a 1 micron finish. Each piece was then electrolytically etched in potassium hydroxide to reveal the microstructure. Ferrite/austenite phase balance checks were carried out by a point counting technique to ASTM E562 [10]. Micrographs of each sample were produced at ×500 and ×1000 magnification.

5.2. Results of microscopy

NORSOK [7] allows the percentage of ferrite to lie between 35.0% and 65.0%. Table 6 shows that all the samples provided acceptable results, as regards the absence of intermetallic phases and percentage ferrite in an as-bent condition.

Table 6. Phase balance and the presence of intermetallic phases.

Heat Treatment Condition	% Ferrite	Intermetallic Phases
Parent Pipe	49.7	None
As Bent	51.2	None
Solution Annealed for 15 min	51.0	None
Solution Annealed for 1 h	51.6	None

% Ferrite must lie between 35.0 and 65.0 [10]

The micrographs of the as-bent sample showed some secondary austenite, and large amounts of chromium nitride precipitation, the degree of precipitation being so severe that it exceeded the maximum level of 3 on the scale developed by Byrne et al. [11].

Byrne et al. describe level 3 nitride precipitation as ‘*Extensive ferrite grain boundary network and large quantities of precipitates within the grains*’. For the purposes of this paper the authors now introduce nitride number 4 which they describe as ‘*Grain boundary network covering the complete ferrite phase, and large quantities of precipitates completely dominating the grains*’. An example of an as bent sample exhibiting this level 4 nitride precipitation is given in Fig. 2.

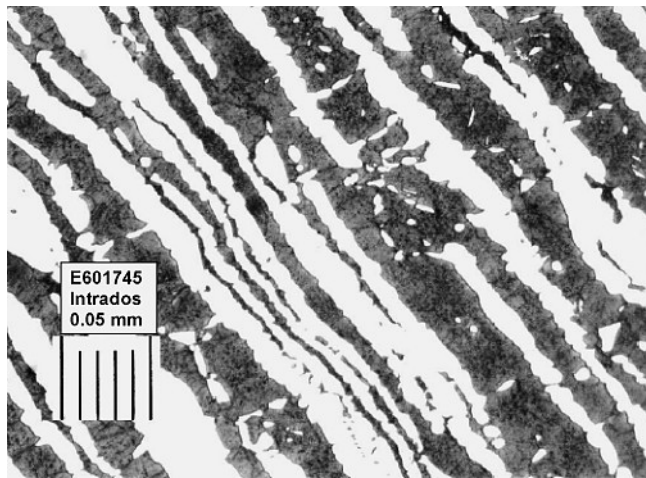


Fig. 2. Micrograph of as-bent sample showing level 4 nitride precipitation. Secondary austenite appears as small white areas within the light grey ferrite phase. Primary austenite occurs in linear bands running diagonally across the micrograph, whereas the secondary austenite has no prescribed orientation.

As-bent samples showed both secondary austenite, and chromium nitride precipitation exclusively within the ferrite matrix (refer to Tables 7 and 8). Solution annealing at 1 120 °C for 15 min seems to have had no effect on reducing the level of secondary austenite present, although it does seem to have reduced the degree nitride precipitation (see Fig. 3 and Table 7). Solution annealing for an hour significantly reduced the secondary austenite. It also reduced the level of nitrides. The level of nitride precipitation was reduced from 4 to 2.5 on the Weir scale after 15 min; longer soak times seem to have only a marginal additional benefit vis-à-vis the further reduction in the level of nitride precipitation (see Fig. 4 and Table 7). No other deleterious phases were observed in any of the samples.

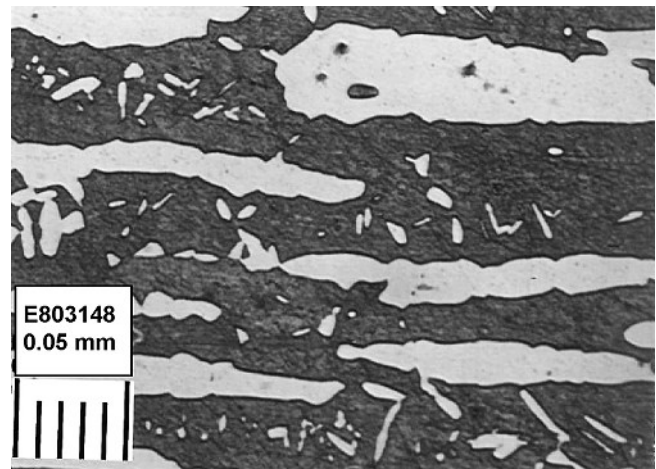


Fig. 3. Micrograph of pipe heat treated at 1 120 °C for 15 min followed by water quench. Secondary austenite appears as small white areas within the light grey ferrite phase. A high degree of nitride precipitation is visible in this micrograph, appearing as black or dark grey speckles within the light grey ferrite phase.

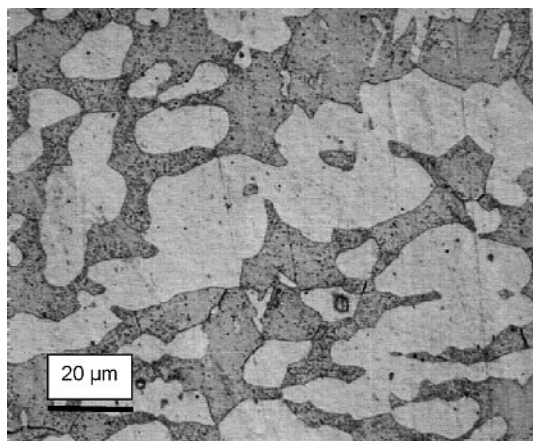
Table 7. Deleterious phases present after bending and following heat treatment.

Heat Treatment Condition	Intermetallic Phases	Nitride No. (Measured on the modified Weir Scale)	γ_2 (% of ferrite phase occupied by γ_2 as measured in micrographs)
Parent pipe (prior to being subjected to induction bending)	None	None	–
As Bent (no heat treatment)	None	4	10% of Ferrite Phase
Solution Annealed for 15 min	None	2.5	10% of Ferrite Phase
Solution Annealed for 1 h	None	2	0% of Ferrite Phase

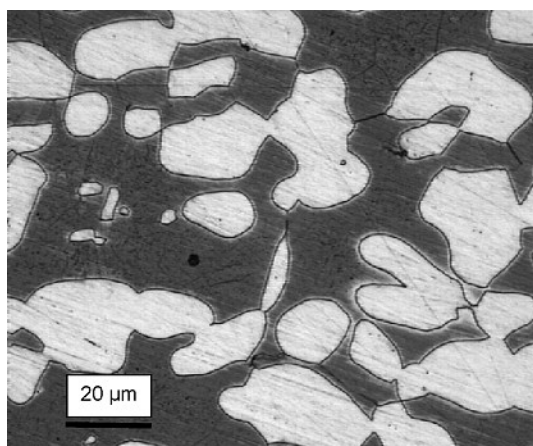
Table 8. Nitride numbers (after [11]).

Nitride No.	Description
0	No nitrides visible
1	Some ferrite grain boundaries visible, but not as an extended network
2	Substantial amount of ferrite grain boundaries visible, forming a network in many places. A few dark precipitates within the grains.
3	Extensive ferrite grain boundary network and large quantities of precipitates within the grains.
4	Grain boundary network covering the complete ferrite phase, and large quantities of precipitates completely dominating the grains.

Where fields show roughly equal divisions between two nitride numbers then they are allowed an intermediate value.



(a)



(b)

Fig. 4. (a) Micrograph of pipe heat treated at 1120 °C for 1 h followed by water quench – induction bend sample before heat treatment. (b) Micrograph of pipe heat treated at 1120 °C for 1 h followed by water quench – induction bend sample after solution for 1 h followed by water quench.

5.3. Discussion of results of microscopy

(a) Secondary austenite

Previous research showed that although secondary austenite (γ_2) was found in the induction bent pipe, it was not present in all samples. When it did occur it was not of a fully developed Widmanstätten form. Instead, the majority of γ_2 present appeared to be of a type which results from a diffusionless transformation from the ferrite matrix in which it sits (see Fig. 2). The micrographs do not show any evidence that the γ_2 was a eutectoid of $\gamma_2 + \sigma$.

(b) Nitrides

When super duplex is cooled rapidly from a high temperature, supersaturation of nitrogen can occur in the ferrite phase. The free nitrogen then bonds with chromium to form Cr_2N or, more rarely, CrN . Cr_2N particles tend to precipitate initially along the d/d grain boundaries and then in an intergranular fashion [12]. This description fits the pattern of nitride precipitation seen in the micrographs. It is suggested therefore that the form of the nitrides present in this case is most likely to be Cr_2N .

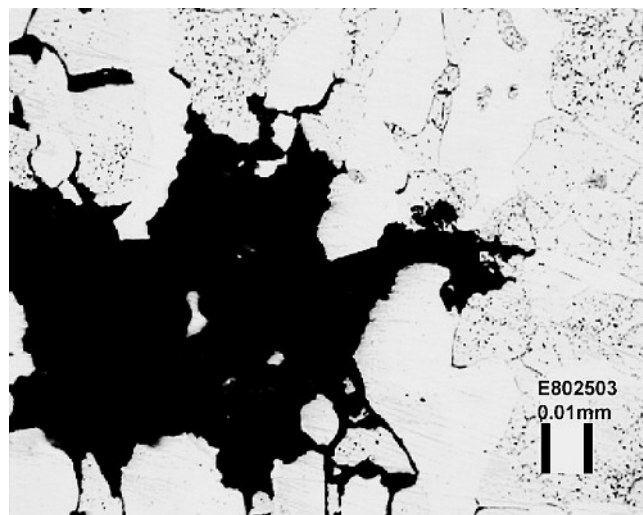


Fig. 5. Micrograph of as-bent pipe following G48-A test.

(c) Micrographic analysis of corrosion

A micrograph was taken of the G48-A sample (refer to Fig. 5). The degree of corrosive attack was significant. Both inter- and intragranular corrosion was observed, this being confined to the ferrite phase. Two of the deleterious phases being considered, Cr_2N and α' , tie up chromium within the ferrite phase, preventing it from forming a protective film of chromium oxide which would, if present, have protected the ferrite. Nitrides have been observed to have a greater effect on corrosion resistance than on impact toughness when present in large quantities [12].

6. Electrochemical potentiokinetic reactivation

From the outset, the presence of α' was suspected in the as-bent samples because of the very low impact toughness results; however α' is difficult to detect. Transmission electron microscopy (TEM) has been found to be successful where samples have been exposed in the critical temperature range (300–600 °C) for several hours [13], but the exposure time in this case was known to have been minutes rather than hours, so TEM was not felt to be appropriate. Attempts have been recorded of using changes in the magnetic behaviour of the super duplex to establish whether or not α' is present, but these findings from different research teams have been inconsistent [14]. In this study the authors elected to use a variant of DL-EPR in order to establish the presence, or otherwise, of α' .

Potentiodynamic polarisation scans have been used in the past to investigate, for example, changes in the corrosion resistance of 304 stainless steel due to chromium carbide precipitation along the grain boundaries [15]. Hutchings [16] developed a variant of this technique specifically designed to target deleterious phases in super duplex steels, and it is Hutchings variant which was used in this analysis.

6.1. Description of modified DL-EPR

In a standard DL-EPR the sample is allowed to stabilise at the open circuit potential. The sample is then scanned dynamically from the open circuit potential up to a pre-de-

terminated maximum, after which the sample is then scanned back down to the original open circuit potential. The technique used in this case varied from the standard DL-EPR in the following ways:

(a) Solution

A typical solution for checking the sensitisation of 304 stainless steel would be 0.5 M H₂SO₄ + 0.01 M KSCN. In this case 5 M HCl was used. The strength of the acid meant that the sample could not be exposed to the solution for prolonged periods. This had an impact on the sweep rate (which had to be increased) and to the time allowed for passivation (which had to be severely reduced).

(b) Sweep rate

ASTM G108 [17] requires a standard sweep rate of 1.67 mV s⁻¹. Here a sweep rate of 4 mV s⁻¹ was selected, this much more rapid rate being required in order to produce distinct peaks for the ferrite and austenite phases.

(c) Sweep range

The starting point for a standard DL-EPR is the passivation potential, typically around -400 mV. However, in this case it was decided to begin well below the expected passivation potential due to uncertainties over the range of the full active region; the range used was -800 mV to +200 mV. Unlike a standard DL-EPR the authors chose not to passivate the sample at the open circuit voltage, nor to hold it at the top end of the sweep; this was necessary due to the concentration of the solution.

(d) Reference electrode

The reference electrode selected was a saturated calomel electrode (SCE).

(e) Diagrammatic representation

The standard way of displaying the results of a DL-EPR is by means of an Evan's diagram. The Evan's diagram shows both forward and reverse scans on the same graph, the y-axis giving potential with log₁₀ of the current density appearing on the x-axis. In this case, in order to clearly show separate peaks for the ferrite and austenite phases, it was necessary to display the actual current density rather than the log of the value. In addition, to aid clarity, current density is placed on the y-axis and Potential on the x-axis.

6.2. Results

The modified DL-EPR reactivation curve of an ideal super duplex forging will show two peaks, these representing the ferrite and austenite phases. The Modified DL-EPR graph of the as-bent sample (see Fig. 6) shows a single peak. The peak has a large maximum current density, and the area below the curve is much larger than for the idealised super duplex sample.

For the samples which were solution annealed for both one hour and for 15 min, two phase peaks, ferrite and austenite, were observed (refer to Fig. 7). The shape of these

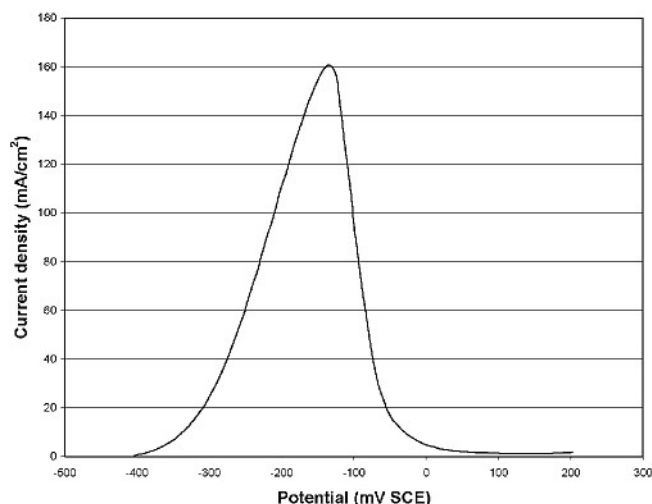


Fig. 6. DL-EPR plot of as-bent pipe.

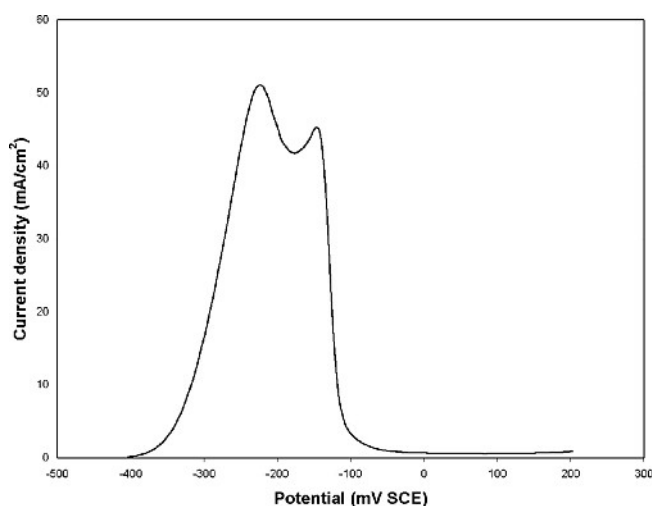


Fig. 7. DL-EPR plot of pipe heat treated at 1120°C for 1 h followed by water quench.

curves is very similar to that which would be expected for an ideal super duplex. The same samples gave a Weirs' scale nitride count [11] of 2.5 and 2 for the 15 min soak, and 1 h soak respectively. The results of the DL-EPR for the solution annealed specimens taken together with the improvement in impact test result following heat treatment strongly suggest that shape of the single peak curve observed prior to heat treatment, and the poor initial Charpy impact results, were due mainly to the presence of α' rather than nitrides.

7. Solution annealing

The effect of the solution annealing was to restore the mechanical properties and corrosion resistance to their pre-bend levels. The shape of the modified DL-EPR curve for the samples solution annealed at 1120°C for one hour and 15 min were seen to be similar to the shape expected for an ideal duplex steel. Optical microscopy for the 15 min sample showed some reduction in secondary austenite, a reduction in the level of nitrides. Optical microscopy for the 1 h sample showed that secondary austenite had been eliminated, but it also showed that there had been no further re-

duction in the level of nitrides. Neither heat treatment regime showed a generation of other deleterious phases. Despite the fact that chromium nitride levels remained high after solution annealing, the material was returned to a usable condition even after subjecting it to a soak time of just 15 min.

8. Probable cause of the loss of properties

The fact that all of the properties were restored while the level of nitride precipitation remained not insignificant, suggests that the drop in properties seen in as-bent pipe was due to something which was detectable when using modified DL-EPR, but which was not visible using optical microscopy. It is proposed therefore that α' was the main culprit.

9. Thermal history

Before suggesting a possible time-temperature profile for the induction bent pipe it is worthwhile considering a brief summary of the facts that have been established.

- The pipe before induction bending possessed good impact toughness and corrosion resistance. It can be concluded therefore that the drop in properties occurred during, or immediately following, induction bending.
- No nitrides were present in the pipe before induction bending therefore the significant nitride precipitation seen in the as-bent samples must have resulted from the induction bending process.
- The form of chromium nitride which was seen in the post-bend micrographs appears to be Cr_2N , which tends to form between 700 and 900 °C [12].
- α' precipitates between 300 and 600 °C [13]. The precipitation rate is temperature dependent, taking thousands of hours at 300 °C but only a few minutes at 600 °C [18].
- No secondary austenite was present in the pipe before induction bending therefore the secondary austenite seen in the as-bent samples must have resulted from the induction bending process.
- The majority of γ_2 appears to have resulted from a diffusionless transformation from the ferrite matrix. This type of γ_2 forms below 650 °C [19].
- Fully formed Widmanstätten type γ_2 was not observed. Widmanstätten type γ_2 tends to occur between 650 and 850 °C [20].
- The micrographs do not show a eutectoid of $\gamma_2 + \sigma$, a form which tends to occur between 700 and 900 °C [21].
- No σ -phase was found before or after induction bending. σ -phase tends to form between 650 and 1000 °C with particular sensitivity occurring around 900 °C.
- Nitrides, together with deterioration in mechanical properties and corrosion resistance, occurred even in areas of the pipes which had not been subjected to direct induction heating. This suggests that a significant amount of heat was transferred to areas not directly exposed to induction heating by conduction.
- During induction bending maximum outer wall temperatures were recorded at 1154 °C, the range being between 1040 and 1154 °C. The time which any given point on the pipe took to pass through the heated zone was approximately 30 s for Schedule 160 pipe, and 45 s for XXS+ pipe. The time for the execution of indi-

vidual bends varied from 6 min for a 60° Schedule 160 bend with a radius of 1.5D, to 14 min, for a 60°, Schedule XXS+ bend with a bend radius of 3D. The total heated time for the pipes which were the subject of the parametric study was 38 min for the Schedule 160 pipe and 30 min for the Schedule XXS+ pipe. The total time taken to complete the bending process was approximately 1.5 h and 1 h for the Schedule 160 and Schedule XXS+ pipes respectively, assuming a set-up time of 10 min between individual bends.

From consideration of the above, some propositions can be made about the order in which the various microstructural changes took place.

Proposition 1:

Cr_2N precipitates were not present in any areas of the pipe prior to induction bending, and that during induction bending no portion of the pipe had any significant Cr_2N precipitation prior to that part of the pipe arriving at the heating zone.

Justification:

At the temperature at which induction bending is conducted the majority of the super duplex would exist as ferrite phase. Had the level of nitride precipitation seen in the post-bend samples been present before the pipe arrived at the heating zone then much of the nitrogen present would have been, and would have remained, tied up as Cr_2N , as any point of the pipe is exposed to the heat of induction bending for too short a time to allow the dissolution of the Cr_2N . Nitrogen is an austenite stabiliser, and therefore as the material cooled back down after leaving the heated zone, it is likely that the resultant alloy, deprived of nitrogen, would have displayed more ferrite than austenite [11]. It has been shown in this study that the induction bending did not upset the phase balance, suggesting that nitrides were not present to any great extent prior to the pipe being induction bent.

Proposition 2:

Nitride precipitation did not take place during the immediate post-bend cooling period.

Justification:

Where nitrides precipitate while super duplex is being cooled from temperatures close to its solidus temperature then the chromium nitrides will tend to co-precipitate with γ_2 . Nitrides will tend to precipitate along grain boundaries, low energy interfaces develop, and these can destabilise the ferrite encouraging the formation of γ_2 [22]. Microscopy showed that γ_2 was not present in every sample following induction bending. It is suggested that the Cr_2N was not a co-precipitant with γ_2 but that it precipitated first. The comparative lack of γ_2 may then be explained because nitrogen which would have encouraged γ_2 growth was locked up as Cr_2N , and therefore not available to act as an austenite stabiliser.

Proposition 3:

Cr_2N precipitated before the α' .

Justification:

The relationship between α' and Cr_2N is an interesting one. Because α' and Cr_2N often occur together there has been some discussion over the possible role of Cr_2N in α' precipitation. Gunn [13] suggests that α' and Cr_2N are often co-

precipitants, however work by Strutt [15] suggests that nitrides can act as heterogeneous nucleation sites for α' . Assuming that Strutt's argument holds, then in this case the precipitation of Cr_2N ahead of the precipitation of α' would explain the severe α' precipitation which was encountered.

Based on the three propositions above the following thermal history is proposed for the pipe:

1. The first part of the induction bending process worked as planned, the pipe remaining below the critical temperature for deleterious phase generation until it reached the heated zone at which point the temperature rapidly ramped up. Bending took place as normal, but the subsequent post-bend cooling was insufficiently fast to bring the temperature of the pipe down below the critical range right through the wall section. As a result, after post bend cooling the area of the pipe which already been cooled was reheated by conduction from a heat sink (most likely the thick wall section at the bend's intrados) to a temperature above 700°C (which would allow Cr_2N precipitation) but well below 900°C (the critical temperature for the formation of σ -phase, no σ -phase having been found). The pipe must have been maintained at this temperature for some time in order to account for the level of nitrides which precipitated. It seems likely that the temperature then gradually fell allowing diffusionless transformation of some of the ferrite to γ_2 (but recall the argument that the significant presence of Cr_2N prevented large scale γ_2 precipitation) at a temperature below 650°C .
2. Further reduction of temperature into the 300 to 600°C range would then encourage the precipitation of α' . Several minutes would be required at the upper end of this temperature range in order to account for the apparently high level of α' precipitation. The pre-existence of Cr_2N may well have acted as nucleation sites for α' , decreasing the time required for α' precipitation, and at the same time encouraging a higher degree of α' precipitation than would otherwise have been present.

10. Recommended process improvements

It has been shown that it is possible to restore the mechanical properties and the corrosion resistance of the induction bent samples by employing a heat treatment of 1120°C for as little as 15 min, followed by a water quench. A similar technique could be applied to finished pipework, however there are practical barriers to this. It is expensive and time consuming to have to carry out heat treatment in a production environment, and ovens and quenching baths of an appropriate capacity would be expensive to build and maintain. Super duplex pipes may deform under their own weight during heat treatment due the massive loss of strength experienced by the material at the temperatures required for solution annealing [2]. Even assuming that quench baths of an appropriate size were available, it would prove extremely difficult to replicate the rate of cooling achieved in the small samples used in this testing in thick-walled, convoluted pipes.

Rather than relying on post-bend heat treatment, a more appropriate long term solution is to improve the cooling during induction bending. Possibilities include continuous water quenching of the pipe, both on the outside and in the bore, from the point where the bending takes place, right

along the pipe. This water spray must be maintained until all the bends have been completed, and for some time thereafter. In addition it may be necessary to manufacture the pipe in a series of discreet steps; the process being suspended between bends in order to let the pipe cool down.

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