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THE SELECTION OF SUPERDUPLEX STAINLESS STEEL FOR OILFIELD APPLICATIONS

G. Byrne, R. Francis, G. Warburton
Weir Materials and Foundries,
Park Works, Newton Heath, Manchester, M40 2BA, U.K.
and
M. Maligas
FMC Technologies,
Houston, Texas, USA.

ABSTRACT

The combination of high strength and corrosion resistance makes super duplex stainless steel attractive for a number of applications both in sour process fluids and seawater. Several superduplex alloys exist and each has its own proprietary chemical composition and UNS designation. This paper considers one such UNS designation and shows that a wide range of properties is possible. Superduplex materials are normally specified with a minimum PREN value. To achieve this value, chemical composition is critical and likewise careful processing is necessary to achieve optimum properties including toughness and corrosion resistance. This paper discusses the setting of adequate alloy qualification criteria within the context of a range of international and company standards.

Keywords: superduplex stainless steel, mechanical properties, corrosion, specifications.

INTRODUCTION

The first widely available super duplex stainless steel was developed by Gradwell and co workers[1] in the mid 1980's. This alloy was called Zeron 100® and was developed as a casting alloy for pump applications in the oil and gas industry. The performance of the steel in this application generated a demand for the alloy in wrought product forms also. This demand was serviced by Weir who, together with other European manufacturers, developed the manufacturing procedures required to obtain the desired quality of product.

As demand for the steel grew, clients called for ASTM, NACE, British Standards and other codes to include and cover the Zeron range of products. Moreover, with the introduction of the EC Procurement Directive in 1993, it became an exception for clients to specify any trade name in requests for quotation and a generic description for the alloy was required for the business to continue. In 1993-94 ASTM considered the properties of several heats of ZERON 100 in a range of product forms and on the basis of this designated the code UNS S32760 to the alloy and introduced this number into several standards.

In 1994 UNS S32760 was included in NACE MR0175, again based upon the performance and properties of the proprietary alloy. Finally, in 1997, UNS S32760 was listed in ASME complete with applicable design stresses. These listings were again based upon the properties of the proprietary alloy.

Subsequently, other steelmakers began to manufacture UNS S32760 and to offer this grade to the market. During the period of manufacture and deployment of these steels it became apparent that the properties and performance normally expected was not always realised. The properties that began to deteriorate included elevated temperature tensile properties, low temperature toughness properties and, in Norway, performance in ferric chloride (ASTM G48 Method A) at 50°C. Similar behaviour was also being experienced by UNS S32750, which is also a super duplex stainless steel. The variation in performance seemed intermittent and ad-hoc.

It is believed that the problem stems from the fact that within the UNS composition and ASTM processing limits for S32760, a wide range of properties are possible. A production route that differs significantly from that used for the proprietary material that was tested for entry into standards can produce substantially inferior properties. This paper discusses the application of standards and specifications to ensure adequate material quality.

The Alloy

The composition limits of UNS S32760 are shown in Table 1. It is clear that within these limits a wide range of compositions is possible. The melting specification for the alloy defined by the authors' company is designed to produce an alloy with a 50/50 austenite/ferrite phase balance. This combines the strength of the ferrite with the ductility of the austenite. The minimum mechanical properties at room temperature are shown in Table 2. Some standards include a maximum hardness value, such as ASTM A240 (plate and sheet). The NACE standard MR0175 used to include a maximum hardness of HRC 28, but this had been removed in the 2003 edition and there are now no hardness limits for solution annealed material. This is a recognition of the fact that hardness is only relevant to cold worked material, where high levels of cold work significantly reduce the resistance to sulphide stress corrosion cracking (SSCC).

The alloy has good impact toughness with most product forms producing a Charpy energy over 100J at low temperatures. However, non-optimized alloys can give very low impact toughness, as is described in the next section. Impact toughness requirements for S32760 are not specified in any of the ASTM standards. Our company specification calls for a minimum of 70J at -46°C, as do several user company specifications. ASME requires a minimum lateral expansion of 0.38mm at a temperature that is specified by the project. The Norwegian Oil and Gas standard, NORSOK, requires an average of 45J at -46°C with a minimum of 35J for any single value.

Impact toughness measurements can serve two purposes. One is to guarantee a minimum level of toughness at a low temperature that can occur in service. The other is as a quality control check. This latter use is discussed in more detail below.

Solution annealed material has good corrosion resistance, with a typical critical pitting temperature (CPT) of 70°C to ASTM G48C. Most standards do not require a corrosion test, but one has been required by some user company specifications and a resistance to pitting at 50°C in the ASTM G48A test is required by NORSOK.

Alloy Properties in Production

The production of most components involves the hot working of billet followed by solution annealing and quenching. Not only does the composition of the billet affect the final properties, but also the temperature of the heat treatment and the speed of the quench. ASTM A473 (forgings) specifies a minimum temperature for solution annealing of 1100°C, but no maximum. The standard also specifies a water quench or rapid cool, but does not define how fast the cooling should be. These are critical for obtaining the correct properties, particularly with thicker sections. The consequences of getting these wrong are discussed below.

Phase Balance

The phase balance of the wrought alloy is critical to performance. Although the aim is 50/50 austenite/ferrite, many standards permit a wide variation. For instance NACE MR0175 permits the ferrite content to vary from 35% to 65%. However, a change from the optimum value has a number of consequences.

When the alloy is cooling and forms austenite, some elements preferentially partition to the ferrite and some to the austenite. For example chromium and molybdenum tend to partition to the ferrite while nickel and nitrogen partition to the austenite. The presence of nitrogen also modifies the partitioning behaviour.[2]

An increase in the ferrite content from optimum decreases the net chromium and molybdenum content in the ferrite, reducing corrosion resistance. At the same time the reduced fraction of austenite means that the nitrogen solubility limit can be passed and nitrides are precipitated. The result of this is to decrease impact toughness. Bousquet et al[3] report tests on UNS S32750 (another superduplex), where a forging with a high ferrite content (58.3%) had its CPT in the ASTM G48C test reduced by 10°C compared with material with a ferrite content of 54%, due to the formation of precipitates.

A decrease in the ferrite content from optimum means that the chromium and molybdenum in the ferrite increases. This means that a faster quench is required after solution annealing to avoid the formation of sigma and chi phases. The increased fraction of austenite means that its overall concentration of chromium, molybdenum and nitrogen is reduced, thus reducing corrosion resistance. In addition the higher austenite fraction also lowers the alloy strength.

Third Phases

Figure 1 shows a typical CCT (continuous cooling transformation) diagram for S32760. It can be seen that relatively fast cooling is required to avoid the formation of nitrides, chi and sigma phases. Even in thick sections it is usually possible to cool below 750°C fast enough to avoid the formation of these phases with an adequately designed quench tank. It is important that the processing facilities (heat treatment, quench volume, temperature control, general processing etc.) in any plant are matched to the size of the component being manufactured.

Figure 1 shows the typical CCT diagram for S32760, and if the quench is fast then sigma and chi phases will not form. However, with a slack quench it is possible to prevent the formation of third phases, but elemental segregation has already occurred. This means that only a small further time at temperature, e.g. during welding, will result in the production of third phases and loss of properties. In effect a slack quench consumes a substantial portion of the incubation time for the formation of third phases.

It can be seen from Figure 1 that between 550°C and 350°C alpha prime phase can form if the quench through this temperature range is too low. A fast enough quench can be more difficult to achieve with thick section forgings in this region. Alpha prime cannot be seen by optical microscopy, and so is difficult to detect.

All of these phases will reduce impact toughness. The greater the quantity of third phase, the greater the reduction in impact toughness. The authors have investigated a large forging of S32760 that had an impact toughness of only 6J at -46°C. This was because the ferrite had entirely transformed into sigma/chi phase due to a totally inadequate heat treatment and quench (Figure 2). This is an extreme example of the effects of inadequate heat treatment and quench.

Byrne et al[4] investigated several commercial heats of S32760 which had a range of nitride contents from none to a large quantity. Figure 3 shows the decrease of impact toughness at –46°C with increasing nitride content. The impact toughness was significantly reduced when the nitride content was high.

Alpha prime is difficult to detect other than by its effect on impact toughness. Bousquet et al[3] showed how small changes in the cooling time from 550° to 300°C of S32750 could decrease the impact toughness due to the formation of alpha prime. The charpy impact energy at –46°C decreased sharply as the time spent in the critical temperature range increased (Figure 4).

Corrosion resistance is not significantly affected by alpha prime, although chi, sigma and nitrides all reduce the corrosion resistance. They do this because they contain increased quantities of chromium and/or molybdenum that depletes the surrounding matrix, thus reducing its corrosion resistance. Although alpha prime also contains increased levels of chromium, the particles are so small that the depleted zone is also very small. No effect on corrosion resistance is seen until the concentration is much greater than that at which toughness is dramatically reduced.

Francis et al[5] described tests on C-rings of S32760 containing up to 2.5% sigma phase in a 30,000 mg/l chloride brine with 0.2 bar H_2S and 20 bar CO_2 at 90°C. No SSCC was observed on any sample. However, Bowden et al[6] found a reduction in impact toughness with 2.5% sigma. Subsequently Francis et al[7] have suggested that a sigma content of ~ 4% would be required to significantly affect corrosion resistance.

Byrne et al[4] showed that nitrides reduced the CPT in the G48C test from 70°/75°C to 45°C at the highest nitride content (Figure 5). They also showed that S32760 with a high nitride content failed an SSCC test under the same conditions that had been used to gain the alloy entry to MR0175 (Figure 6). This is a significant worry in the safety conscious oil and gas industry.

Woollin et al[8] also tested several commercial tests of S32760 and found material with nitrides suffered pitting in a sour brine, when nitride-free material did not. The corrosion results from Byrne et al[4] and Woolin et al[8] are summarized in Table 3.

Woollin et al[8] also reported cracking of S32760 without nitrides. However, the test conditions take the alloy outside the safe envelope for S32760, as defined by the authors[5], so the SSCC is not surprising (Figure 7).

DISCUSSION

The previous data have demonstrated that superduplex stainless steels are not commodity alloys, but require careful control during processing to ensure that the desired properties are achieved. This is not adequately defined by any of the ASTM standards for the various product forms, e.g. A240 (plate) and A473 (forgings). ASTM A923 defines methods for testing for detrimental third phases in duplex stainless steels. However, at present, acceptable criteria are only listed for 22% Cr duplex (S31803 and S32205). These criteria are not fitness for purpose tests, and in the authors' opinion the pass values are set too low and 22%Cr to these minima may give problems in manufacturing or in service.

While phase balance and third phases affect the properties of the alloy, there are no hard and fast rules as to what these should be to obtain the desired properties.

It is important to ensure that the parent metal has more than just adequate properties for a specific project. The reason for this is that most components are welded, either during manufacture or installation. This generally results in a lowering of impact toughness and corrosion resistance compared with parent metal. Hence, parent metal must have properties that will be satisfactory even after welding.

It is clear that chi, sigma and alpha prime phases affect impact toughness at levels below that at which corrosion resistance is affected. The authors believe that a minimum charpy impact toughness energy of 70J at -46°C for parent metal will ensure that qualification of welding procedures to meet normal Charpy impact energy requirements should not prove troublesome.

The data above show that the presence of nitrides has a greater effect on corrosion resistance than impact toughness, i.e. even the highest level of nitrides produced a charpy impact energy greater than 70J at -46°C. However, this material did not meet the NORSOK ASTM G48A requirement at 50°C. Not only can a G48 test at 50°C detect high nitride levels, but it can also detect surface chromium depletion due to inadequate pickling after heat treatment[9].

Finally, a microsection is also always useful because it enables the rapid measurement of the phase balance and, with careful etching, it can also show chi, sigma and nitride phases. This is essential, if the material has failed the G48 or impact toughness test, to determine whether reheatreatment might restore the properties, and what the most appropriate heat treatment would be.

The authors believe that these minimum properties give a guarantee of good performance under most conditions likely to be experienced in the offshore oil and gas industry. Although each of these is required separately by some standards, e.g. NORSOK, no current standard requires all three of them. In conjunction with this it is advisable to pre-qualify prospective vendors to prevent problems during production, when there are often severe time constraints. Such a practice is part of NORSOK M650, where special materials, which include superduplex, require pre-qualification of vendors.

CONCLUSIONS

1. The composition limits of all superduplex stainless steels provide for a wide range of possible properties.

2. The final properties are influenced not only by the initial composition, but by subsequent hot working, heat treatment and quenching.

3. Failure to control these properly 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, even after fabrication.

5. It is suggested that, in addition to composition and mechanical requirements, a microsection, a minimum charpy energy of 70J at -46°C and no pitting in a G48A ferric chloride test at 50°C are required.

6. Pre-qualification of vendors can prevent problems later in the project when time is short.

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Table 1
Composition limits of UNS S32760.

	COMPOSITION (wt%)											
	C	**Si**	**Mn**	**S**	**P**	**Cr**	**Ni**	**Mo**	**W**	**Cu**	**N**	**Fe**
Min	-	-	-	-	-	24.0	6.0	3.0	0.5	0.5	0.2	Bal
Max	0.03	1.0	1.0	0.01	0.03	26.0	8.0	4.0	1.0	1.0	0.3	

Bal = balance
PREN % Cr + 3.3 x % Mo + 16 x % N
PREN > 40

Table 2
Minimum mechanical properties for UNS S32760 at room temperature.

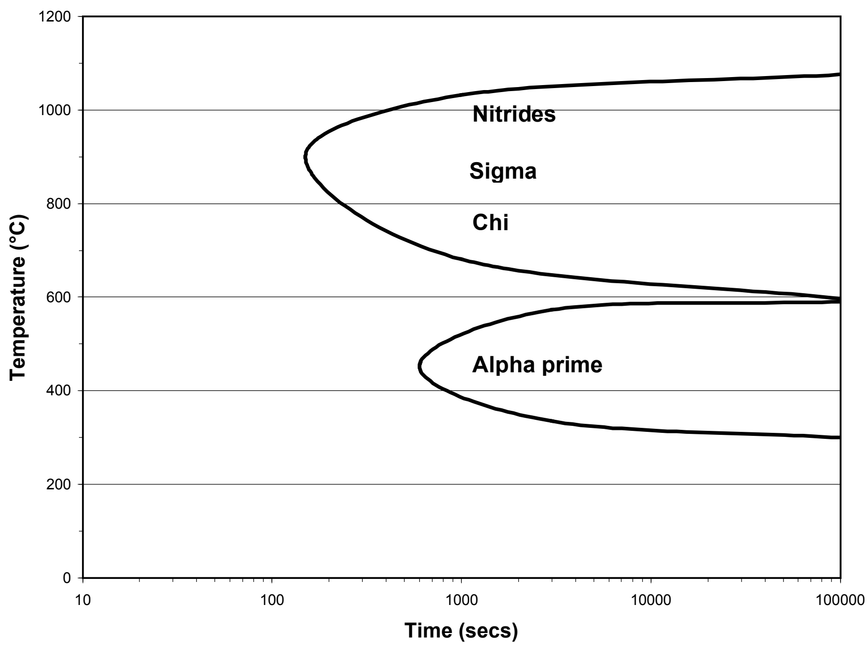
0.2% Proof Stress	550 MPa
UTS	750 MPa
Elongation	25 %
Hardness	270 HBr *

* ASTM A240.

Table 3
The effect of nitrides on the corrosion of S32760 in sour service.

CONDITION	ENVIRONMENT H_2S (bar)	CO_2 (bar)	Chloride (mg/l)	Temp (°C)	CORROSION	REF
no nitrides	0.2	20	120.000	80	none	MR0175
no nitrides	0.2	20	120,000	80	none	4
nitrides	0.2	20	120,000	80	SSCC	4
no nitrides	0.2	40	60,700	85	none	8
nitrides	0.2	40	60,700	85	pitting	8
no nitrides	0.2	40	60,700	100	none	8
nitrides	0.2	40	60,700	100	pitting	8

FIGURE 1
Typical CCT curve for S32760 superduplex stainless steel



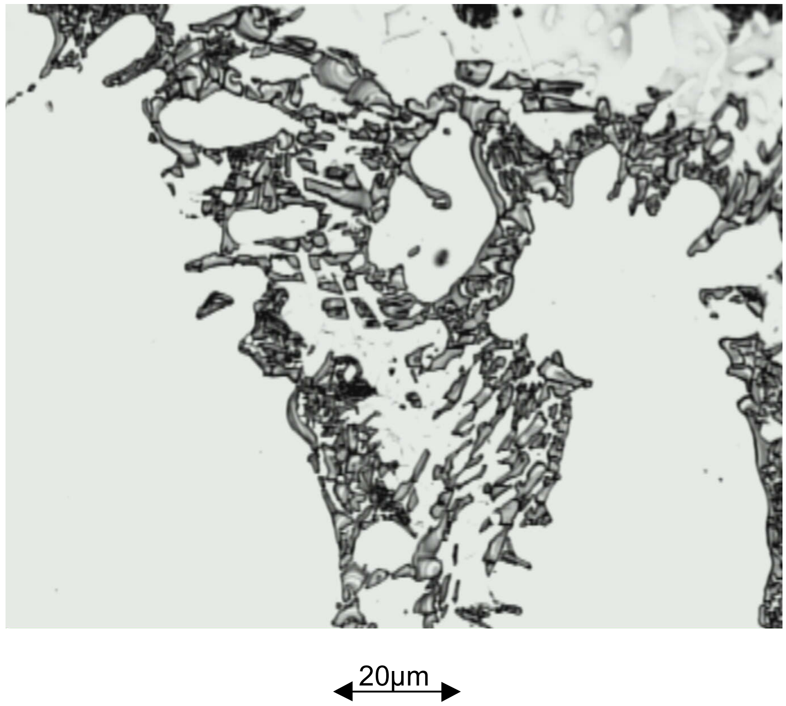


FIGURE 2
Two phase microstructure of sigma and austenite due to improper heat treatment and quench.

FIGURE 3
Effect of nitrides on Charpy impact toughness energy
at -46°C

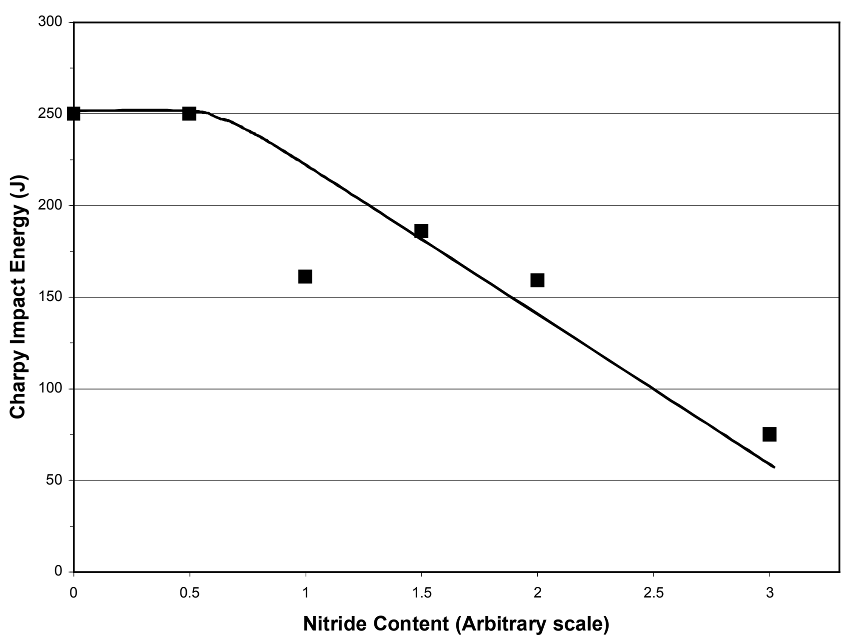


FIGURE 4
Effect of alpha prime on Charpy impact toughness energy at -46°C

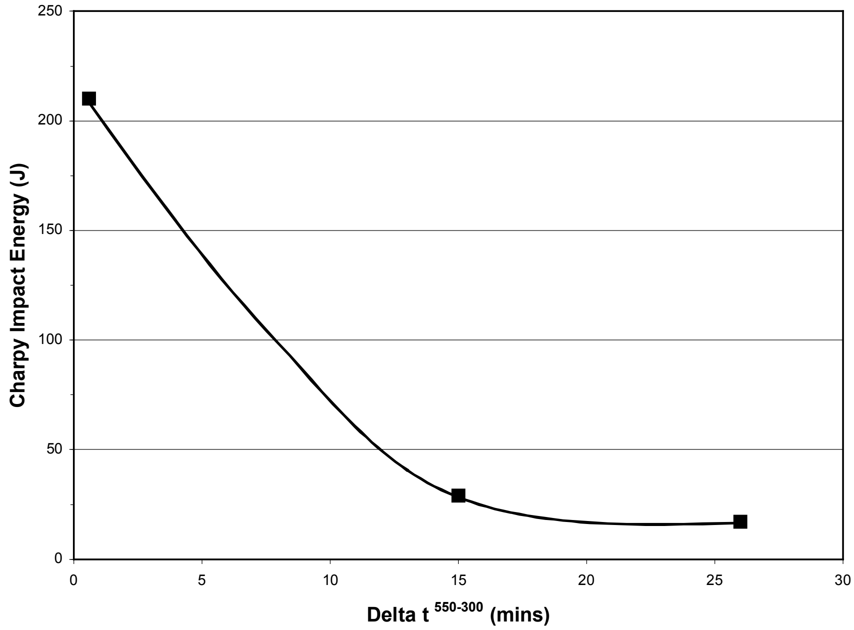
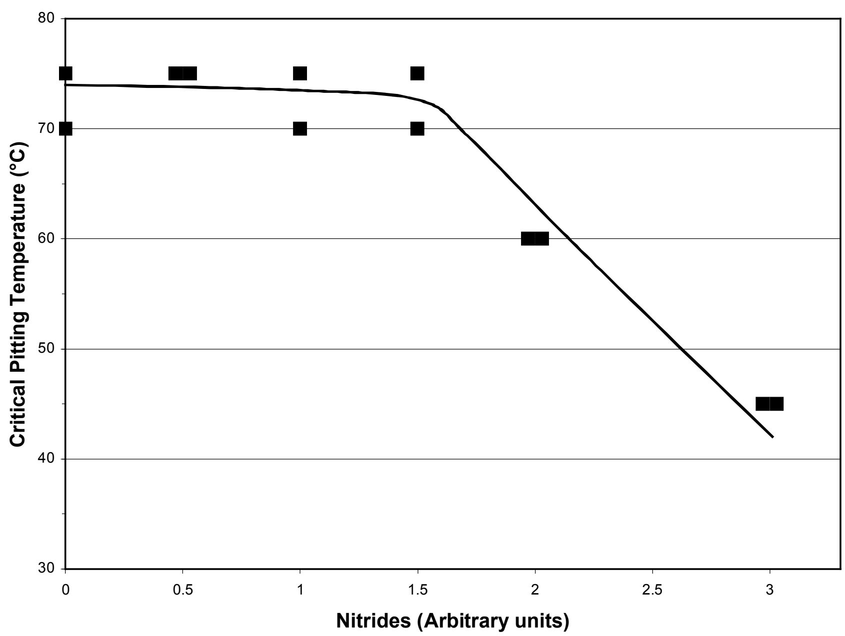
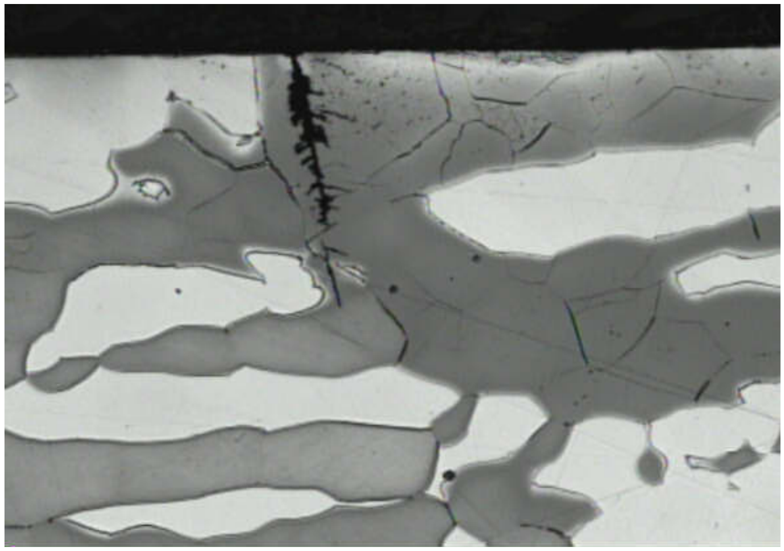


FIGURE 5
The effect of nitrides on the critical pitting temperature (ASTM G48C)





20µm

FIGURE 6
Microsection of S32760 with high nitrides showing SSCC under MR0175 conditions.

FIGURE 7
SSCC limits for S32760 at pH=3.5 from Ref 5 with Ref 8 data