

Effect of intermetallic content on pitting resistance of ferritic-austenitic stainless steels

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Qualification of welding procedures for ferritic-austenitic stainless steels normally requires demonstration that the weld area is substantially free from intermetallic phases.

However, uncertainty exists regarding an appropriate maximum permissible level.

Intermetallic phases up to 8% were induced in S32750 steel by varying short term isothermal heat treatments. It was shown that there was no direct correlation between intermetallic volume fraction at levels of concern in welding and pitting resistance in ferric chloride tests.

Hence, it was concluded that welding procedure qualification should be based on assessment of service properties rather than on microstructural examination.

INTRODUCTION

Intermetallic phases (sigma, chi, etc.) can form in ferritic-austenitic stainless steels on exposure to temperatures from about 500-1000°C (1,2). In superduplex stainless steels, the timescale over which precipitation can develop is of the same order as the thermal cycle experienced during a welding operation. Hence, intermetallics may form at welds, both in the heat affected zone (HAZ) and weld metal, and this can reduce the corrosion resistance and toughness (2).

Intermetallic precipitation may be especially marked either in welds made with high heat input to maximise joint completion rate (3) or in fairly thin material (below about 5mm) which can be welded in only one or two passes at a heat input that is high relative to the heat sink available (4). Given appropriate control, welding can be carried out reliably with little or no loss of properties from intermetallic formation, and the superduplex steels have found increasing use in oil and gas, petrochemical and other plant. Nevertheless, it is normal for welding procedure qualification (WPQ) specifications to require metallographic examination and demonstration of negligible intermetallic phase formation in the weld area. Complete freedom from intermetallic phases is virtually impossible to demonstrate metallographically, and thus many WPQ specifications require that intermetallic phases should be below a specific volume fraction, typically 1%.

Such maximum intermetallic levels essentially reflect what can be achieved without unacceptable restriction on welding conditions and productivity rather than what is necessary to obtain specific properties. The present work was therefore undertaken to examine the relationship between the volume fraction of intermetallic phases in a ferritic-austenitic stainless steel and the resultant corrosion resistance.

EXPERIMENTAL PROCEDURE

Sample preparation

A superduplex stainless steel pipe to UNS S32750 was used (Table 1). The base metal ferrite content was determined by point counting to be 47%. Samples 35x25x11mm were extracted for thermal cycling. Fairly short heat treatments were used, as experienced in a weld thermal cycle, and samples were heated to 800°C, 900°C or 1000°C, held at temperature for 2 or 5mins, and then water quenched. The temperatures and times used were selected to induce varying amounts of intermetallic formation. (1,2,5)

Metallographic examination

Through-thickness sections were taken, and prepared to a 1µm diamond finish, with electrolytic etching in 20% H₂SO₄ containing 0.1g/litre NH₄SCN. Examination was undertaken optically and using a scanning electron microscope (SEM). Phase proportions, including intermetallic contents, were determined from SEM backscattered images by point counting, a technique which enabled differentiation between sigma and chi phases: 1000 counts were made on each sample at x1850 magnification. Using energy dispersive X-ray (XRD) analysis, a "bulk" analysis was obtained from an area of about 2x2mm. Spot measurements of about 1µm diameter were made on austenite, ferrite and areas of intermetallic formation, and line scans were performed across the phases.

Pitting tests

Samples were tested in 6% ferric chloride solution to define a critical pitting temperature (CPT), generally following the procedure in ASTM G48-92. Above about 50-60°C, as may be required for superduplex steels, this solution becomes unstable, producing a colloidal hydroxychloride (6). Two ap-

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Element weight %									PI*
C	P	Si	Mn	Ni	Cr	Mo	Cu	N	
0.022	0.014	0.40	0.35	7.6	24.6	4.04	0.16	0.287	42.5
Other elements 0.001 S, < 0.01 Ti, 0.02 Nb									
*PI = % Cr + 3.3% Mo + 16% N									

Table 1 - Chemical composition of test Material.

proaches to avoid this effect were employed, viz addition of Na₂EDTA.2H₂O (as per IIV), (7,8) and acidification by HCl (as per ASTM) (9). The concentration of EDTA was 20g/l, with that of the HCl being 24ml of concentrated acid per 900ml of distilled water.

The samples were prepared to a 600 grit finish. The exposure period at any one temperature was 23 hours. Testing was initiated at +25°C, the temperature being increased in steps of +2.5°C, and was discontinued once pitting was visible: this generally corresponded to a weight loss exceeding 5mg. This temperature was taken as the CPT. Test surfaces were not reground between exposure periods, but were washed, degreased, and dried.

Short term testing to identify pit initiation regions was undertaken. The 900°C/2min sample was prepared to a 1µm diamond finish, lightly etched to reveal the microstructure, and exposed to ferric chloride solution containing EDTA at 50°C, followed by examination using light microscopy and the SEM.

RESULTS

Metallographic examination

The as-received microstructure consisted of elongated islands and small clusters of austenite in a ferrite matrix. After heat treatment at 800°C/5mins, small amounts of intermetallic phase were visible at ferrite/austenite boundaries and within the ferrite (Fig.1a). Raising the temperature to 900°C substantially increased the intermetallic content (Fig.1b), but at 1000°C only isolated pockets of intermetallic were evident. Table 2 gives results of point counting on back-scattered electron images. The greatest intermetallic proportion, nearly 8%, was in material heated to 900°C for 2mins, whilst 1-1.5% was recorded in both the 800°C and 1000°C samples. Small "white" islands were noted in the SEM images, often within the major intermetallic constituent, up to about 0.5% being found in 900°C samples.

Table 3 gives compositions of the phases in the 900°C/2min sample as determined by EDX analysis. The ferrite was enriched in Cr and Mo and lean in Ni relative to the austenite. Of the two intermetallic phases identifiable from the SEM back scattered images, the dominant constituent had Cr and Mo contents of 29.4% and 9.7% respectively, consistent with sigma phase (3). The minor phase had 13.8%Mo, while the Cr content was less than in the sigma, indicating it to be chi phase (3).

Line scans on as-received material showed the compositional differences in Table 3, as the ferrite to austenite interface was traversed; there was no compositional change within individual ferrite or austenite regions. Figure 2 shows a line scan on the 900°C/2min sample from ferrite into sigma, and back into ferrite: the Cr and Mo contents change as the sigma particle is traversed. Chi phase is also visible. There was no clear evidence of alloy depleted regions adjacent to intermetallic particles, with scans at right angles from either ferrite or austenite into the intermetallic.

Pitting tests

Visual observation of pitting coincided fairly well with increased weight loss, and values of CPT obtained visually are given in Table 4. The lowest pitting temperatures determined were 40-45°C for samples heated at 900°C and exposed to the HCl solution. Identical samples exposed to the EDTA solution gave a slightly higher pitting temperature of 50°C. The samples heated to 800°C/5min produced higher pitting temperatures than the 900°C series, 55°C in EDTA and 57.5°C in HCl solutions, while both as-received and 1000°C/5min specimens gave CPTs of 80°C. Initiation of pitting attack in the 900°C/2min sample after

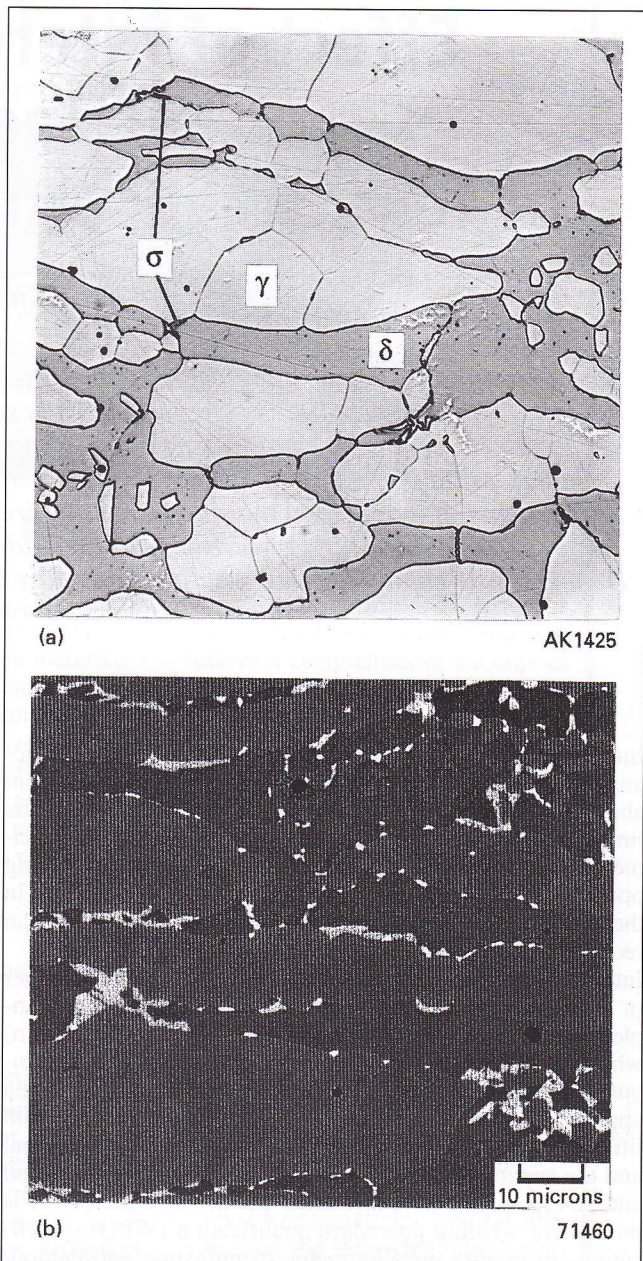


Fig. 1 - Intermetallic formation:
 (a) 800°C/5min; optical image: x800
 λ = austenite
 δ = ferrite
 σ = intermetallic
 (b) 900°C/2min; SEM image: ~x1000
 intermetallic - white
 ferrite - dark grey
 austenite - light grey.

Sample condition	Phase type %		
	Sigma	Chi	Undefined ⁽¹⁾
As received	0	0	0.4
800°C/5min-WQ	1.3	0.1	0.2
900°C/2min-WQ	6.5	0.5	0.3
900°C/5min-WQ	7.6	0.3	0
1000°C/5min-WQ	1.3	0.1	0.1

⁽¹⁾ structure not resolved

Table 2 - Second phase proportions determined by point counting.

Location of measurement	Element wt%		
	Cr	Ni	Mo
Parent (Bulk) ⁽¹⁾	24.5	7.5	4.3
Ferrite ⁽¹⁾	26.4	5.3	5.3
Austenite ⁽¹⁾	23.4	8.8	3.2
Sigma ⁽¹⁾	29.4	4.6	9.2
Chi ⁽²⁾	27.0	4.6	13.8

⁽¹⁾ Spot measurement (average of 6 areas)
⁽²⁾ Line scan

Table 3 - Phase composition determined by EDX analysis (900°C/2min).

Thermal cycle	Critical pitting temperature, °C	
	EDTA	HCl
As-received material	80	>80
800°C/5min WQ	55	57.5
900°C/2min WQ	50	40
900°C/5min WQ	50	45
1000°C/5min WQ	80	80

Table 4 - Critical pitting temperatures, assessed visually.

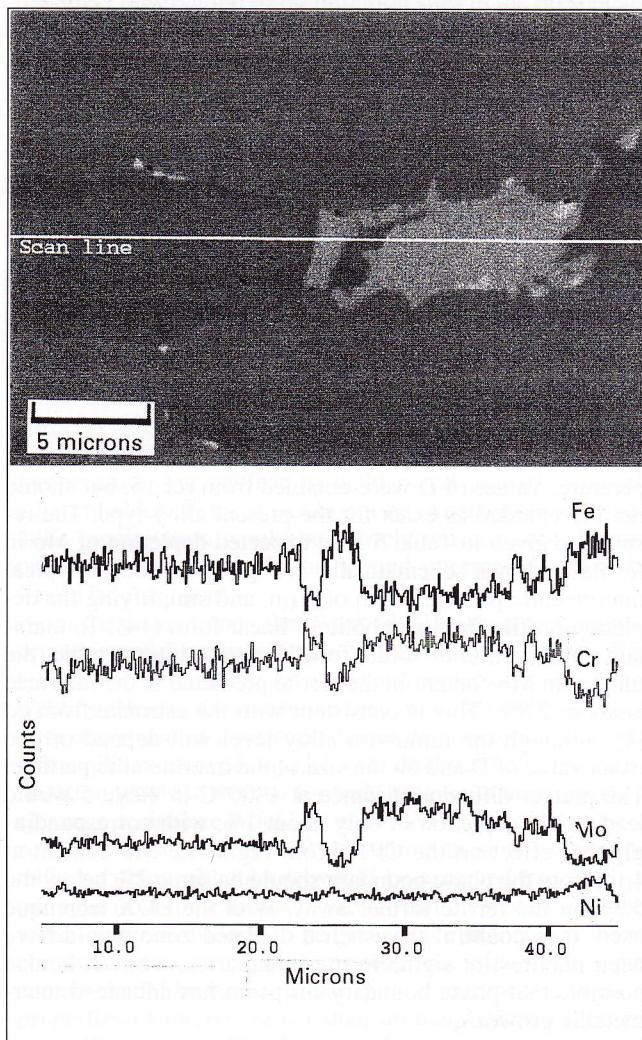


Fig. 2 - Alloying element distribution illustrated by line scan across intermetallic region: scan direction from ferrite → sigma → ferrite.

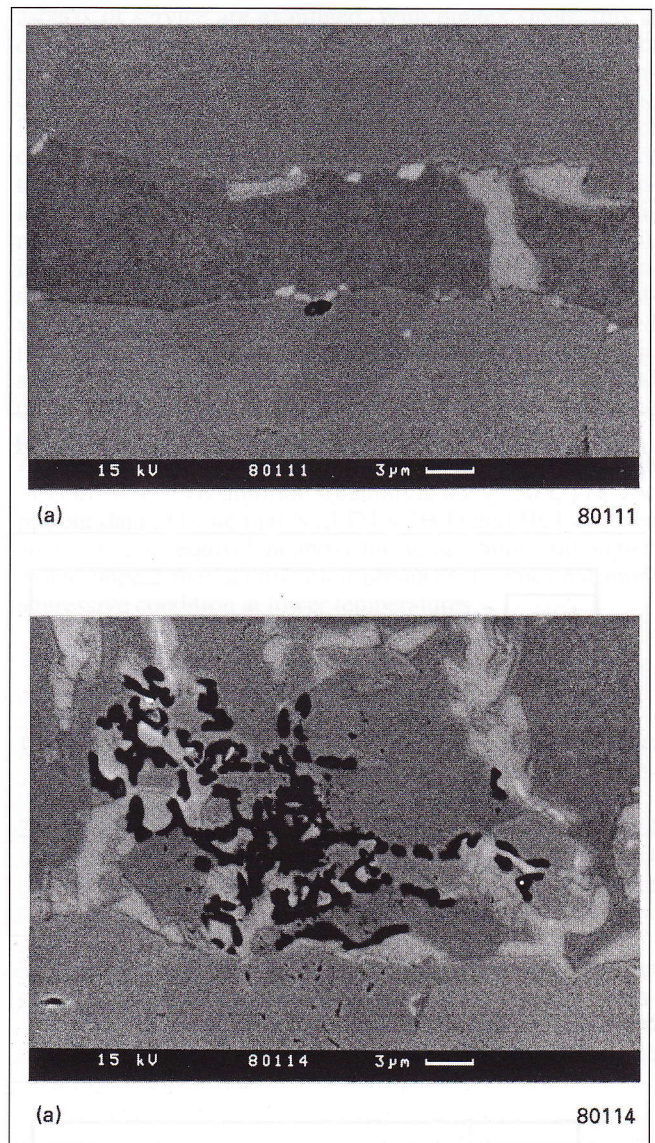


Fig. 3 - Pit initiation sites: nominal magnification x3000 (a) in austenite adjacent to chi particle (b) in ferrite at sigma particles.

short term exposure to EDTA solution at 50°C took place at intermetallic phase boundaries, at both sigma and chi particles (Fig.3). Pits initiated at a number of locations in the sample. The most common sites were at intermetallic/austenite boundaries, but the largest "areas" of pit initiation were at groups of intermetallic particles which had formed in the ferrite. As far as could be discerned, pit growth took place in the austenite or ferrite with relatively little attack on the intermetallic particle.

DISCUSSION

Effect of intermetallics on pitting resistance

In both test solutions, the lowest values of CPT were obtained from specimens heat treated at 900°C which contained the highest intermetallic volume fractions. The present results are combined with data obtained from other work (4, 10) in Fig. 4, and clearly high intermetallic contents have a significant adverse effect on pitting behaviour. However, from Tables 2 and 4, heat treatment at 1000°C and 800°C both produced an intermetallic volume of fraction of 1.4%, yet the former temperature had no adverse effect on corrosion resistance, whereas the latter reduced the CPT by some

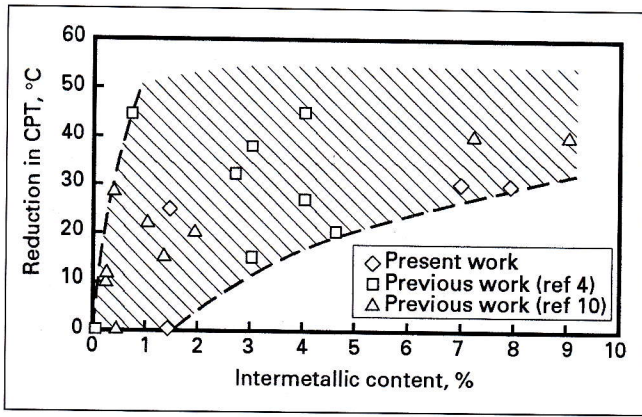


Fig. 4 - Relationship between intermetallic content of superduplex steels and reduction in CPT.

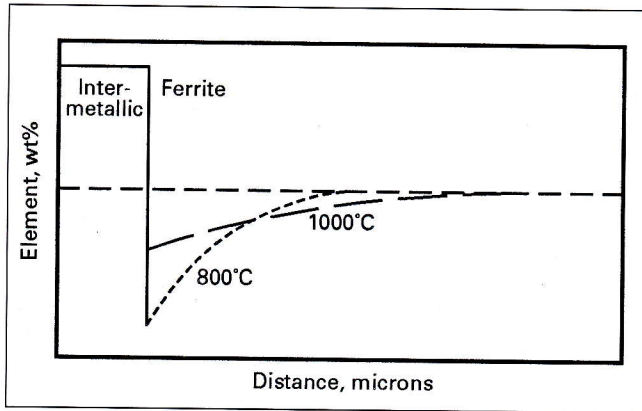


Fig. 5 - Schematic illustration of depleted zone width adjacent to an intermetallic particle, and minimum local alloy content, following intermetallic growth at 800°C and 1000°C.

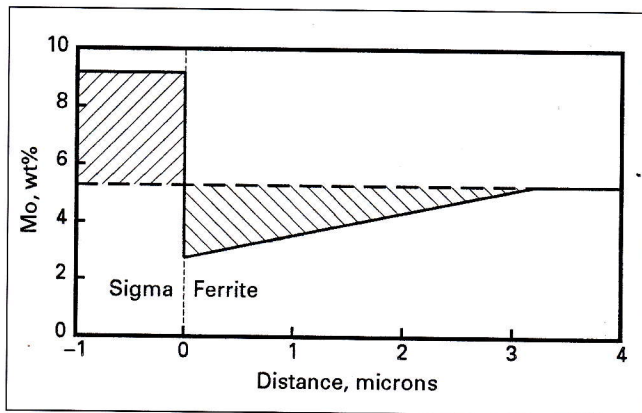


Fig. 6 - Simplified Mo concentration profile across sigma/ferrite boundart in 900°C/5min sample; note that hatched areas are equal.

25°C. While the present results were obtained on isothermally heat treated material, it must be concluded that, at fairly low intermetallic levels as might arise during welding, there is no direct relationship between volume fraction of intermetallic phases and corrosion resistance as indicated by a critical pitting temperature in ferric chloride.

There has been relatively little attention paid to the detailed mechanism by which passive film stability is reduced by intermetallic phases. The results in Table 2 and 3 indicate the major intermetallic constituent to be sigma phase consistent with other work, (2, 5, 10, 11) but the key feature is that, relative to the ferrite and austenite, all intermetallics have in-

creased contents of chromium and molybdenum. Hence, it has been tacitly assumed that alloy element depletion occurs, as experienced in the problem of "weld decay" from chromium carbide formation in austenitic steels for example. Intermetallic particles grow into the ferrite phase, presumably in consequence of the more rapid diffusion of substitutional elements than in austenite, and previous consideration of the development of an alloy depleted zone has been based on this zone forming preferentially in the ferrite (5). However, from the present tests, pit initiation most frequently took place on the austenite side of intermetallic particles. Potgeiter also reported chloride pit initiation in both austenite and ferrite, from electrochemical tests on UNS S31803 steel containing 6% sigma (12). Evidently, intermetallic particles do grow into the austenite, or at least elemental diffusion occurs across the austenite/intermetallic boundary.

Development of a depleted zone

The influence of temperature on intermetallic formation and resultant corrosion resistance will reflect the diffusion rates of substitutional elements, the equilibrium interfacial compositions, and the associated minimum alloy content developed around an intermetallic particle. The situation is illustrated by Fig.5. The EDX scans showed the enrichment in chromium and molybdenum at intermetallic particles. Pitting resistance of stainless steels can be related to composition by an empirical relationship of the form:-

$$\text{Pitting index (PI)} = \%Cr + 3.3\%Mo + 16\%N \quad [1]$$

The observed 30-40°C reduction in CPT due to intermetallic phases relative to parent material performance implies a decrease in local alloy content of at least 10 pitting index points (13). The precise depletion will depend on the composition of the intermetallic particle, but such loss in corrosion resistance will correspond roughly to reduction in chromium and molybdenum of about 1% and 3% respectively. This assumes no significant effect of nitrogen in intermetallic formation.

For the isothermal heat treatments used, mean diffusion distances (x) were calculated (14) for chromium and molybdenum in both ferrite and austenite, from the relationship:-

$$x = 2\sqrt{Dt} \quad [2]$$

where D is the diffusion coefficient and t is the time at temperature. Values of D were obtained from ref 15, but should not be regarded as exact for the present alloy type. The results are given in Table 5. The expected depletion of Mo in ferrite is shown schematically in Fig.6, assuming a typical intermetallic particle width of 1µm, and simplifying the depletion profile from parabolic to linear form (14). To maintain conservation of solute from ferrite to intermetallic, the minimum Mo content in the ferrite predicted at the interface is about 2.8%. This is consistent with the estimate from eq [1], although the minimum alloy level will depend on the exact value of D and on the size of the intermetallic particle. The greater diffusion distance at 1000°C in Table 5 would lead to Mo depletion of only about 1%, with correspondingly less effect on the CPT. From Fig.6, the Mo content at 1µm from the phase boundary should be some 2% below the 5.3% in the ferrite further away. With the EDX technique used, it is doubtful that such a depleted zone would have been manifest at sigma/ferrite boundaries, while it is also possible that phase boundary diffusion has enhanced intermetallic growth.

Studies using the scanning transmission electron microscope by Thorvaldsson and his co-workers (5, 10) indicated reduction in ferrite Cr and Mo contents to about 22% and 2% respectively, in material immediately adjacent to sigma par-

Element	Phase	Distance, mm		
		800°C	900°C	1000°C
Cr	Ferrite	1.1	2.2/3.4*	8.8
	Austenite	0.06	0.12/0.16	0.42
Mo	Ferrite	0.84	1.9/3.1	8.2
	Austenite	0.10	0.20/0.32	0.84

* 2min/5min

Table 5 - Calculated diffusion distances for Cr and Mo in ferrite and austenite.

ticles, the minimum occurring over a distance of some 0.1mm. From eq [1], this depletion would certainly induce significant loss of chloride pitting resistance. Moreover, Nilsson found that local depletion in Cr and Mo could be sufficient to induce ferrite transformation to secondary austenite (10), and considered this reaction (together with Cr₂N formation) to contribute to the poor CPTs obtained in S32570 material aged at low temperatures (750°C) which had intermetallic contents well below 1%.

Nilsson et al also considered (10) alloy element depletion in austenite to be unlikely, at least over timescales relevant to welding, because of the slow diffusion rate. However, from the direct observation of pit initiation sites in the present and other work (12), depletion has occurred at austenite/intermetallic interfaces, although the diffusion distances in Table 5 are significantly smaller than the EDX analysis region, and observation of a depleted zone would not be anticipated. Pit initiation studies on stainless steels have indicated that pits can grow from nuclei as small as 10nm up to perhaps 1µm, depending on the severity of the corrosive medium (16, 17), and hence depleted zones of the size indicated by Table 5 should be quite adequate to induce passive film breakdown and stable pitting in ferric chloride.

Implications

In a welded joint, the temperature experienced at any point will vary continuously. Nucleation of intermetallic particles will take place at low temperatures on heating in the HAZ away from the fusion boundary and also at high temperatures on cooling in weld metal and immediately adjacent HAZ. Thus, it would not be expected that intermetallic precipitation would be entirely uniform, nor that any pattern of element depletion around intermetallic particles would be consistent.

From the present and other work (4, 10, 18), corrosion resistance is not directly relatable to the volume fraction of intermetallic particles at levels of particular concern during welding. Hence, the common stipulation that welding procedure qualification testpieces should display a maximum intermetallic content of, say, 1% is of doubtful value. A similar situation would arise also for weld area toughness insofar as cleavage resistance would be governed by the maximum size of nucleating defects (19), assuming these to be intermetallic particles, although it would be accepted that, with an increase in volume fraction, the maximum size of any individual particle is likely to be greater. It can therefore be recommended that acceptance or otherwise of a welding procedure should be based primarily on direct measurement of properties of interest rather than on metallographic examination for intermetallic phases.

This is not to say that a requirement for some form of intermetallic examination has no value. Qualification of a welding procedure implies that weldment properties for all

aspects of service are examined. With duplex steels, this is certainly the case in terms of pitting resistance and impact toughness, but procedure qualification is rarely, if ever, undertaken to demonstrate suitability for sour H₂S conditions, for example. Thus, if service is likely to entail properties not directly covered by WPQ specification, it would be prudent to require some form of metallographic examination to confirm that welding conditions are sufficiently stringent to minimise intermetallic precipitation. Even given such control, it should be recognised that there may be discernible reduction in CPT with intermetallic contents too low to be resolved metallographically (5,10). Conversely, Potgeiter showed that some 20% intermetallic phase was required to affect the sulphuric acid corrosion resistance of UNS S31803 material (12), further illustrating the potential unreliability of relating corrosion resistance to intermetallic content.

At present, there is debate regarding the optimum approach to stabilising ferric chloride solutions at above 50°C (7). The present data indicate that Na₂EDTA.2H₂O and HCl addition are reasonably equivalent above this temperature, although it would appear that acidification produces a somewhat more aggressive condition at lower temperatures.

CONCLUSIONS

1. Chloride pitting resistance of ferritic-austenitic stainless steels is reduced significantly by high intermetallic contents (e.g. >5%).
2. However, there is no direct correlation between critical pitting temperature and intermetallic volume fraction at levels of about 1.5% as more commonly associated with welding.
3. Weld procedure qualification (WPQ) should be based on direct measurement of properties of interest; metallographic examination for intermetallic phases may be of value in respect of service properties not covered by the WPQ specification.

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REFERENCES

- 1 Charles J A: Proc 'Duplex '91', 1991, Beaune, France, les Editions de Physique, 3-48.
- 2 Karlsson L: Proc Duplex Stainless Steels '97, 1997, Maastricht, The Netherlands, KCI Publishing BV, 1 43-58.
- 3 Gooch T G: Welding Journal 1996, 75 (5) 135s-154s.
- 4 Gunn R N: Vide ref 2, 1 335-345 and TWI Members Report 505/1995.
- 5 Thorvaldson T, Eriksson H, Kutka J and Salwén A: Proc Stainless Steels '84, 1984, Gothenburg, Sweden, Institute of Materials, London, UK, 101-105.
- 6 Olsson C-O A and Arnvig P-E: Corrosion Science 1995, 37 (8) 1201-1210.
- 7 Doyen R and Potty A: IIW Doc-II-1270-95.
- 8 Recommended practice for pitting corrosion testing of duplex stainless steel weldments by the use of ferric chloride solutions. TWI Doc. 5632/19/93.
- 9 ASTM Task Group G01.05.07: Draft revision of ASTM Standard G48-xx.
- 10 Nilsson J-O, Wilson A, Josefsson B and Thorvaldsson T:

- Proc Applications of Stainless Steel 92, Stockholm, Sweden, Jernkontoret, 1 280-289.
- 11 Kondo K, Ueda M and Ogawa K: Proc Innovation Stainless Steel 1993, Florence, Italy, AIM, 2.191-2.196.
 - 12 Potgeiter J H: Brit Corr Journal 1992, 27 (3) 219-223.
 - 13 Suutala N and Kurkela M: Vide ref 5, 240-247.
 - 14 Porter D A and Easterling K E: 'Phase transformations in metals and alloys'. Second edition, Publ Chapman and Hall, London, UK, 1992.
 - 15 Smithells Reference Book, 6th edition, Butterworth & Co (Publishers) Ltd, London, UK, 1983.
 - 16 Pistorius P and Burstein T: 1992. Phil Trans Roy Soc, A341, 531-559.
 - 17 Mattin S P: 'Nucleation of corrosion pits on stainless steel'. 1994. PhD dissertation, Cambridge University, Cambridge, UK.
 - 18 Francis R: 'Discussion on ref 11, Brit Corr Journal, 1992, 27 (4) 319-320.
 - 19 Knott J F: 'Fundamentals of fracture mechanics'. Butterworths (Publishers) Ltd, London, UK, 1973.

— A B S T R A C T —

**EFFETTO DEL CONTENUTO DI INTERMETALLICI
SULLA RESISTENZA AL PITTING
NEGLI ACCIAI FERRITICO/AUSTENITICI**

Gli acciai inossidabili superduplex sono sensibili a precipitazione intermetallica durante le operazioni di saldatura, sia nella zona termicamente alterata (heat affected zone HAZ) che in corrispondenza del metallo saldato. La preoccupazione che si possono verificare prestazioni in servizio, le norme relative alla qualificazione della procedura di saldatura (WPQ) richiedono solitamente che le fasi intermetalliche siano al di sotto di una frazione specifica del volume, tipicamente dell'1%. Tali massimi riflettono quello che può essere raggiunto senza restrizione inaccettabile alle condizioni di saldatura e alla produttività piuttosto che quanto è necessario per ottenere prestazioni soddisfacenti in servizio: quindi, il presente lavoro è stato eseguito per trovare una correlazione fra contenuto di fase intermetalliche e resistenza a corrosione da pitting.

Campioni di tubo di acciaio superduplex UNS S32750 sono stati sottoposti a trattamento termico isotermino a 800, 900 e 1000°C, seguito da tempra in acqua, al fine di indurre una gamma di contenuti intermetallici. Sono state eseguite prove metallografiche e analisi dispersiva ai raggi X (EDX), ed è stata determinata la frazione in volume delle fasi intermetalliche mediante conteggio dei punti usando micrografie ottenute al microscopio a scansione elettronica. I campioni sottoposti a trattamento termico sono stati esaminati in soluzioni al 6% FeCl₃ stabilizzate con EDTA o HCl, per dete-

rminare temperatura critica di pitting (CPT). Sono stati ottenuti contenuti intermetallici fino a circa 8%. Le particelle intermetalliche sono state arricchite in Cr e Mo, ma, utilizzando l'EDX, non si è riscontrata alcuna evidenza di zone di lega impoverite. Ciò è stato consistente con i profili calcolati di impoverimento dell'elemento.

La CPT del metallo base da 80°C è stata ridotta a 50°C in campioni trattati a 900°C con 6-8% di fasi intermetalliche. L'inizio del pitting si è verificato lungo i bordi della fase intermetallica, sia ferrite che austenite. Un contenuto intermetallico di 1,4% è stato ottenuto mediante trattamento termico a 800 e 1000°C; per il ciclo 800°C il CPT è sceso di 25°C, mentre non è stato osservato alcun effetto negativo per il trattamento a 1000°C. Questa differenza di comportamento è stata valutata essere il risultato della dipendenza del profilo di impoverimento dell'elemento dalla temperatura di formazione intermetallica.

Si è concluso che la resistenza al pitting in ambiente di cloruri degli acciai inossidabili ferritico/austenitici risulta significativamente ridotta dai contenuti elevati di intermetallici (es. > 5%).

Tuttavia, non vi è alcuna correlazione diretta tra temperatura critica di pitting e frazione di volume intermetallico a livelli più comunemente associati alla saldatura. Quindi, per la qualificazione delle procedure di saldatura, è preferibile misurare direttamente le proprietà di interesse pratico, anche se l'analisi metallografica rimane valida se le condizioni di servizio comportano caratteristiche del materiale non coperto dalle prove WPQ.