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The Influence of Interstitial Solute Level on the Charpy Toughness Properties of a 40% Cr–Fe Stainless Steel

A. C. T. M. Van Zwieten

Division Materials Science Technology, CSIR, Pretoria, Republic of South Africa

&

J. H. Bulloch*

Head Office, Electricity Supply Board, Lower Fitzwilliam Street, Dublin 2, Republic of Ireland

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ABSTRACT

The present report describes a study aimed at assessing the influence of interstitial solute concentrations, in the form of carbon, nitrogen and oxygen, on the mechanical properties of a 40% Cr–Fe stainless steel. It is observed that carbon and nitrogen dramatically reduced the impact toughness properties while oxygen has only a small detrimental effect. Above a certain level of carbon and nitrogen the toughness was insensitive to the amount of interstitial solute. This was ascribed to the saturation of dislocation precipitation sites. The present toughness data support the proposed theory that the toughness of ferritic stainless steels is controlled by the precipitation of carbides and nitrides on dislocations and not by the structure and morphology of precipitates. Finally, the brittle sigma phase was not identified in the present study and a detailed analysis revealed only the presence of chromium-rich carbides and nitrides and some iron-rich oxides.

1 INTRODUCTION

Ferritic stainless steels, which contain 17–20% chromium with additions of molybdenum, niobium or titanium, represent an increasingly important group of materials.[1-3] In certain situations ferritic stainless steels

* To whom correspondence should be addressed.

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have certain advantages over their austenitic counterparts, viz. improved machinability, higher thermal conductivity, lower thermal expansion, and very importantly they offer immunity to chloride stress corrosion cracking. Moreover, there are an increasing number of applications where the higher cost of austenitic stainless steels, compared to that of the ferritics, makes them economically unsuitable.[4,5]

The 40% Cr–Fe alloy which is the subject of the present investigation can be classified as a super-ferritic stainless steel. The influence of interstitial type and level on the Charpy V-notch impact toughness properties of this particular alloy is investigated.

2 EXPERIMENTAL PROCEDURE

This section describes the experimental procedures developed and used in this project and includes a description of how the alloys were melted and the details of alloying and how acceptable interstitial levels were achieved. Details are given of the thermomechanical processing route to which the alloys were subjected. This section also describes all of the mechanical tests that were performed, namely tensile, hardness, Charpy impact and dynamic fracture toughness tests, and describes the techniques used in microscopic examination of the metals.

2.1 Alloying

2.1.1. *Base materials*

The base materials for all alloys were electrolytic iron flakes and electrolytic chromium chips. Table 1 gives the interstitial contents for these metals.

2.1.2 *Carbon-bearing alloys*

Carbon was added to Fe–40Cr as electrolytic graphite. The amount of carbon was calculated from the required weight percentage of carbon in the alloy plus an allowance of approximately 0·05% for reaction with

TABLE 1
Analyses of Base Material

	%*C*	%*O*	%*N*
Fe	0·006	0·055	<0·001
Cr	0·016	0·1	<0·014

TABLE 2
C, N, O Analyses of Experimental Alloys (in %wt)

Alloy	*C*	*N*	*O*	*Other*	*Description*
W1	0·007	0·006	0·036	—	Low interstitial
W2	0·047	0·005	0·023	0·05 V	Medium carbon
W3	0·073	0·005	0·023	—	High carbon
W5	0·01	0·006	0·05	—	Medium oxygen
W9	0·05	0·006	0·024	—	Medium carbon
W12	0·008	0·009	0·065	—	High oxygen
W15	0·01	0·06	0·06	—	Medium nitrogen
W16	0·01	0·08	0·06		High nitrogen

Note that in the text alloy W1 also is called 'high purity'

oxygen. On analysis, 0·05% vanadium was detected in one alloy and is suspected to have been added inadvertently as a piece of ferrovanadium. This alloy was retained for comparison and to determine whether vanadium would lessen the carbon effect. The analyses for these and all other alloys are shown in Table 2.

2.1.3 *Oxygen-bearing alloys*
Oxygen was added to the alloys by exposing the molten metal to various atmospheres containing oxygen after liquid state degassing. The amounts of oxygen and the time of exposure were determined by trial and error as no theory exists for diffusion of oxygen into Fe–40Cr. The medium oxygen alloy, W5, was subjected to 8 kPa argon and 0·4 kPa oxygen for 15 minutes before pouring. The high oxygen alloy, W12, was subjected to 8·5 kPa of a special gas mixture of oxygen and argon for 15 minutes. The mixture contained 13·5% oxygen and 86·5% argon.

2.1.4 *Nitrogen-bearing alloys*
Exposing the metal to atmospheres containing nitrogen proved to be unsuccessful in adding nitrogen to the alloy. Therefore, nitrogen was added in the form of a high purity, high nitrogen nitrided ferrochrome, the analysis of which is given in Table 3.

TABLE 3
Analysis of Nitrided Ferrochrome (in %wt)

Cr	*C*	*N*	*Si*	*P*	*S*
65	$<$0·1	3·3	$<$0·15	0·03	0·01

2.2 Melting of alloys

The melting procedure has been standardised[6] as follows. A prefired magnesia crucible in a 60 kW capacity vacuum induction furnace was charged with iron and chromium and preheated for 30 minutes while the vacuum chamber was evacuated to a pressure of approximately 10 Pa. The preheating period allowed for solid state degassing to take place. The melting was carried out under a partial pressure of argon of approximately 150 mbar (15 kPa). After melting, the chamber was once again evacuated and the metal was held in the molten state for 30 minutes to allow for liquid state degassing. During liquid state degassing, nitrogen and hydrogen diffuse out of the metal, while oxygen reacts with carbon to form CO, which is then outgassed.

The metal was poured into 8 kg cast iron moulds under a partial pressure of argon after having been given a boost of power to ensure fluidity. The argon was then pumped out and the metal was allowed to cool under vacuum.

2.3 Thermomechanical processing

The thermomechanical processing route was kept constant for all alloys. This was done so that no extra variables would be introduced into the test matrix. The processing route was that proposed in Ref. 7.

The alloys were rolled in a two-high reversing mill with a capacity of 50 tonnes. Ingots were rolled from a temperature of 1050 °C and their temperature was not allowed to drop below 650 °C in order to inhibit the formation of the brittle sigma-phase. Ingots were forged flat where necessary.

On completion of rolling, the ingots were water quenched. They were subsequently annealed at 950 °C for one hour and again water quenched.

Figure 1 shows a schematic representation of the thermomechanical processing procedure.

2.4 Mechanical testing

2.4.1 *Tensile tests*

Room temperature tensile tests were performed on all alloys in both the as-cast and wrought conditions. Standard Hounsfield specimens, cut in the transverse direction, were tested on an ESH servohydraulic testing facility with a capacity of 250 kN and at a strain rate of 0·1 mm/s.

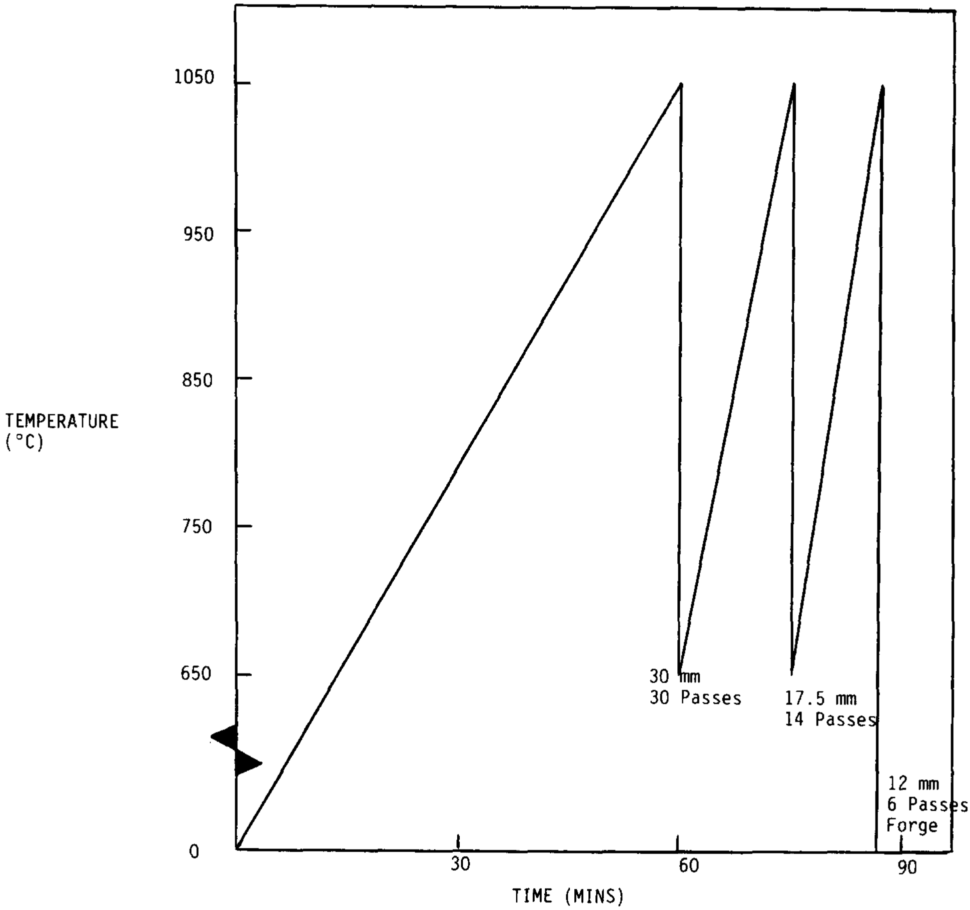

Fig. 1. The thermochemical processing route of the Fe–40Cr alloy.

2.4.2 *Hardness tests*

Hardness tests were carried out on a Vickers hardness testing machine in accordance with ASTM E92-82. A load of 30 kg was used.

2.4.3 *Charpy impact tests*

Standard transverse Charpy V-notch (CVN) specimens were tested in a Tinius Olsen testing machine. Tests were carried out in accordance with BS 151: Part 2: 1972 and ASTM 23–86. Testing temperatures ranged from −20 to 200 °C. Water coolant oil and dry ice in ethanol were used as heat transfer media. The ductile-to-brittle transition temperatures (DBTTs), where applicable, were taken as the temperatures corresponding to the energy values midway between the upper and lower shelf energies.

2.5 Optical microscopy

Specimens for metallographic examination were selected from each alloy, in both the as-cast and wrought conditions. Specimens were mounted and ground down on successive grades of silica carbide paper to 1000 grit. Final polishing was achieved by using an alumina lapping compound with a 1 μm finish. Two etchants were used, namely:

(a) Glyceregia consisting of 10 ml HCl and 30 ml glycerine to reveal the grain structure, carbides and nitrides. Glyceregia has poor wettability and it was difficult to obtain a uniform etch. Etching times varied.
(b) An electrolytic etch in a 40% NaOH solution for up to 30 seconds at 3 V to reveal the presence of the sigma-phase.

3 EXPERIMENTAL RESULTS

3.1 Microscopy

3.1.1 *Grain size*
Specimens from all alloys were examined using optical microscopy. Grain sizes were measured by counting the number of grains per 10 mm and are presented in Tables 4 and 5.

Tables 4 and 5 showed that alloying additions have little effect on the grain sizes of Fe–40Cr. The large grain sizes in the as-cast metal as recorded in Table 4 partly explain the poor toughness recorded. Some recrystallisation does occur during rolling, but the grains of the wrought metals are still extremely large (Table 5). These grains are large despite the heavy reductions per pass and using the lowest possible finishing temperature.

TABLE 4
Grain Size for Alloys in As-Cast Condition

Alloy	*Purity*	*Condition*	*Grain size (μm)*
W1	High	As cast	625
W3	0·073% C	As cast	556
W5	0·05% O	As cast	588
W9	0·05% C	As cast	909
W12	0·065% O	As cast	556
W15	0·06% N	As cast	526
W16	0·08% N	As cast	667

TABLE 5
Grain sizes fqr Alloys in Wrought Condition

Alloy	*Purity*	*Condition*	*Grain size (μm)*
W1	High	Wrought	329
W3	0·073% C	Wrought	300
W5	0·05% O	Wrought	300
W9	0·05% C	Wrought	212
W12	0·065% O	Wrought	338
W15	0·06% N	Wrought	351
W16	0·08% N	Wrought	400

Furthermore, it is noted that while the oxygen-bearing alloys, W5 and W12, displayed superior toughness characteristics to the other alloys in the wrought condition, their grain sizes are similar to the carbon- and nitrogen-bearing alloys (Table 5). One may thus conclude that while reducing the grain size of Fe–40Cr by hot rolling does increase its toughness, this property depends more on the type and amount of interstitial present in the metal.

3.1.2 *Carbon-bearing alloys*

The carbon-bearing alloys displayed two features in their microstructures that were not observed in other alloys, namely: (1) Widmanstaetten carbides and (2) stringers of carbide precipitate. Apart from the expected extensive grain boundary carbide precipitation these alloys also contained Widmanstaetten carbides in the as-cast condition. These carbides precipitated both on the grain boundaries and intragranularly (see Fig. 2) and were unique to the carbon-bearing alloys.

Widmanstaetten carbides occur whenever a solid solution, homogeneous at one temperature, is made to become supersaturated at another temperature. In the majority of cases the precipitating crystals are thin plates forming on matrix planes of low indices, but in some instances they form needles, geometrical shapes or rosettes,[7] as observed in Fig 2.

Another feature unique to the carbon-bearing alloys is shown in Fig. 3. These stringers of precipitates were first presumed to be sigma-phase, but this theory was later rejected. EDAX analysis of several of these precipitates showed that they were chromium-rich precipitates, probably a carbide of the form $M_{23}C_6$. The carbides were observed to lie on the elongated grain boundaries of the as-rolled material before annealing. These carbides were not redissolved during the anneal and quench procedure.

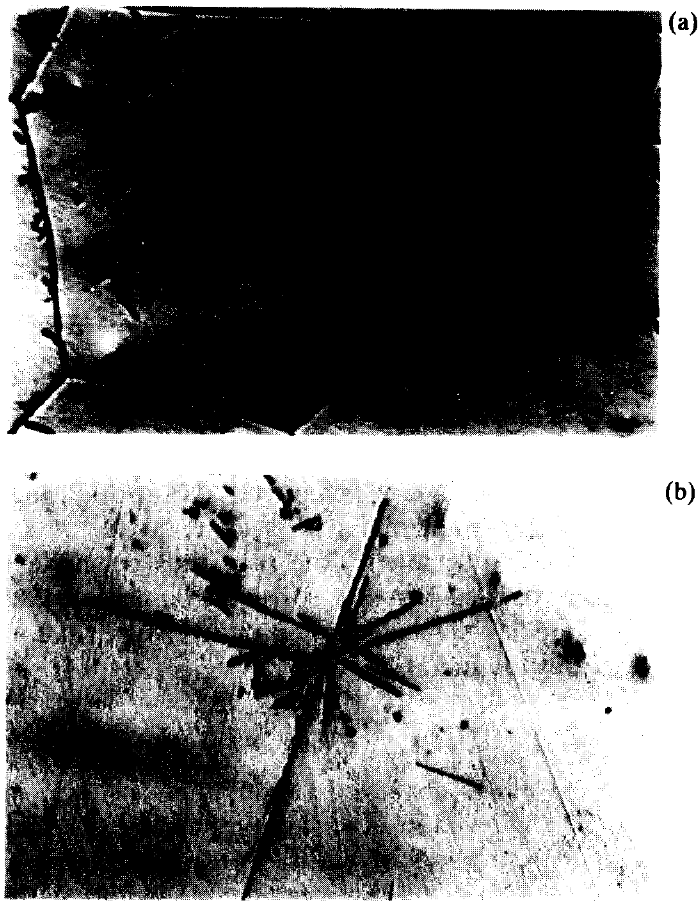

Fig. 2. Details of (a) intergranular (original magnification × 100) and (b) intragranular (original magnification × 260) Widmandtaetten carbide precipitation in the carbon-bearing alloys.

3.1.3 *Nitrogen-bearing alloys*

Extensive grain boundary precipitation was observed in these alloys, as shown in Fig. 4. This was accompanied by dispersed intraganular precipitation. EDAX analysis of these precipitates again revealed that they were chromium-rich, presumably Cr_2N or, because the 100 ppm carbon content is still high enough to cause carbide precipitation, $Cr_{23}C_6$, while the analysis of the adjacent matrix has a nominal FeCr composition.

3.1.4 *Oxygen-bearing alloys*

As with the low interstititial alloy, W1, the oxygen-bearing alloys revealed little grain boundary and intragranular precipitation (see Fig.

Fig. 3. Carbide stringers on the elongated as-rolled grain boundaries of the carbon-bearing alloys. (Original magnification × 200.)

5). The precipitates that were present in the material were either chromium carbides or nitrides, or iron oxides, as revealed by EDAX analysis. This lack of precipitation illustrated the fact that oxygen has a higher solubility in Fe–40Cr than do carbon and nitrogen.

3.2 Tensile tests

The average tensile test results of three tests per alloy in as-cast and wrought conditions are presented in Tables 6 and 7 respectively.

As-cast results for alloys W2 and W3, the 0·05% C–0·05% V and

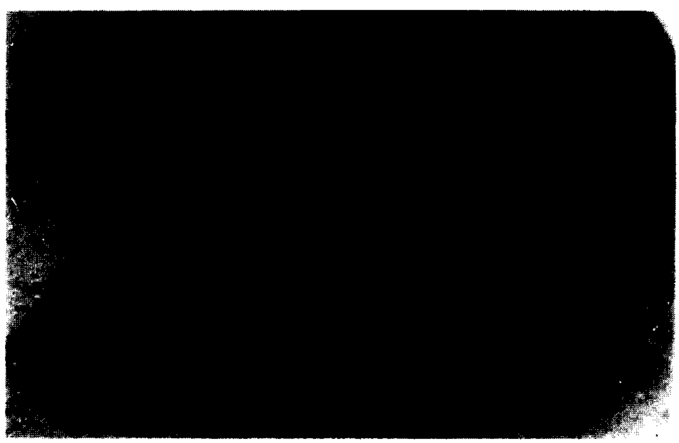

Fig. 4. Extensive grain boundary precipitation present in the nitrogen-bearing alloys. (Original magnification × 400.)

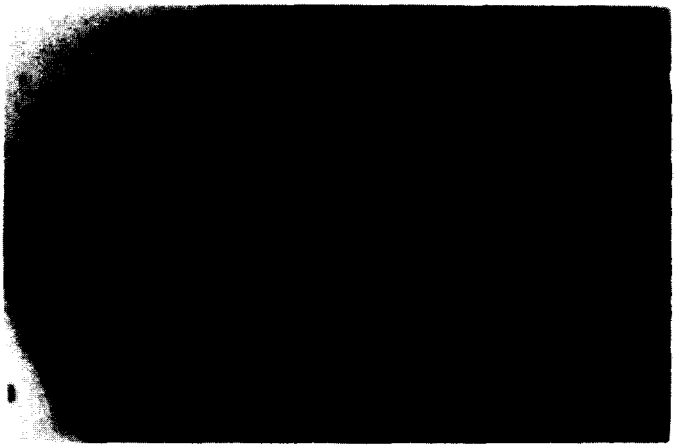

Fig. 5. Extent of precipitation in oxygen-bearing alloys. (Original magnification ×400.)

TABLE 6
Tensile Test Results for As-Cast Alloys

Alloy	*Purity*	σ_y *(MPa)*	$\sigma_{\ddot{o}\ddot{o}\acute{o}}$ *(MPa)*	*%RA*	*%ELONG*
W1	High	589	589	0·0	0·0
W5	0·05% O	412	412	0·0	2·9
W9	0·05% C	302	302	0·0	0·0
W12	0·065% O	480	480	1·4	0·0
W15	0·06% N	413	413	0·0	0·0
W16	0·08% N	454	454	0·0	0·0

TABLE 7
Tensile Test Results for Wrought Alloys

Alloy	*Purity*	σ_y *(MPa)*	σ_{uts} *(MPa)*	*%RA*	*%ELONG*
W1	High	521	565	3·5	6·0
W2	0·047% C 0·05% V	516	608	66·4	31·2
W3	0·073% C	483	552	2·8	6·1
W5	0·05% O	472	565	32·1	17·8
W9	0·05% C	456	490	6·7	3·2
W12	0·065% O	509	586	59·5	27·3
W15	0·06% N	673	716	6·2	3·1
W16	0·08% N	661	709	5·5	6·7

0·073% C respectively, are not available owing to a lack of material. However, the difference between wrought and as-cast yield strengths for nitrogen- and carbon-bearing alloys is an average 35%. Assuming this correlation is valid, one may thus predict the yield strengths of W2 and W3 to be approximately 361 and 414 MPa respectively. These as-case alloys would also not be expected to exhibit any significant tensile ductility.

From Table 7, it is seen that nitrogen has the tendency to increase the strength of Fe–40Cr. This phenomenon is well known and indeed about fifty years ago Newell[8] added nitrogen to his ferritic stainless steels in order to increase hardness and strength. These strengthening effects, obtained by the addition of nitrogen, are generally believed to be a result of solid solution hardening.[9] This effect is not clear in the as-cast condition where large columnar grains override the effects of nitrogen addition.

Table 7 also shows that, while the addition of oxygen to alloys W5 and W12 do not significantly affect the strength of the alloys as compared to the carbon-bearing alloys, it does increase the tensile ductility. This effect is ascribed to a higher solubility of oxygen in Fe–40Cr which prevents precipitation and increases toughness and tensile ductility. Also varying the carbon content in Fe–40Cr does not affect the tensile properties significantly compared to the high purity W1. However, the presence of vanadium does increase ductility and this may be ascribed to the stabilising properties of the element which in the amount present (0·05%) increases the static ductility.

3.3 Hardness tests

The average of five hardness measurements for all alloys in the as-cast and wrought conditions are given in Table 8. It is seen that, in general, the as-cast hardness values are slightly higher than the wrought hardness values while the hardness is seen to increase when nitrogen is added to the material (W15 and W16). This effect of nitrogen is one of solid solution hardening.

3.4 Charpy impact tests

3.4.1 *As-cast alloys*

The averages of three room temperature impact energies for all alloys in the as-cast condition are given in Table 9. These low impact energies were expected as the alloys were not heat treated after casting. As a result there was therefore no control of the precipitation. Interstitial

TABLE 8
Hardness Values (VPN 30)

Alloy	*Purity*	*As-cast*	*Wrought*
W1	High	224	196
W2	0·047% C 0·05% V	236	196
W3	0·073% C	226	196
W5	0·05% O	215	193
W9	0·05% C	248	198
W12	0·065% O	248	201
W15	0·06% N	250	264
W16	0·08% N	237	246

content makes little difference on the as-cast impact toughness properties of Fe–40Cr, with only the low interstitial W1 displaying a slightly higher Charpy impact toughness than the rest of the alloys.

The fracture surfaces reveal very large columnar grains which were especially evident in the carbon and nitrogen-bearing alloys (see Fig. 6). These grains often spanned the width of the Charpy specimen and hence there were no barriers (e.g. grain boundaries) to a crack once it started to extend. The pure and oxygen-bearing alloys have large equi-axed grains (Fig. 7), which could help explain their somewhat marginally higher tougnness values.

3.4.2 *Wrought alloys*

Results of impact energy versus temperature presented in Figs 8 to 10 compared the results according to the alloying element while Figs 11 and 12 compared the data according to the interstitial level.

TABLE 9
As-Cast Impact energy (J)

Alloy	*Purity*	*Impact energy (J)*
W1	High	5
W2	0·047% C 0·05% V	2
W3	0·073% C	2
W5	0·05% O	3
W9	0·05% C	3
W12	0·065% O	4
W15	0·08% N	2
W16	0·08%N	2

Fig. 6. Large columnar grains evident on the fracture surface of the carbon-bearing as-cast Charpy specimen.

Fig. 7. Equi-axed grain structure evident on the fracture surface of the oxygen-bearing as-cast Charpy specimen.

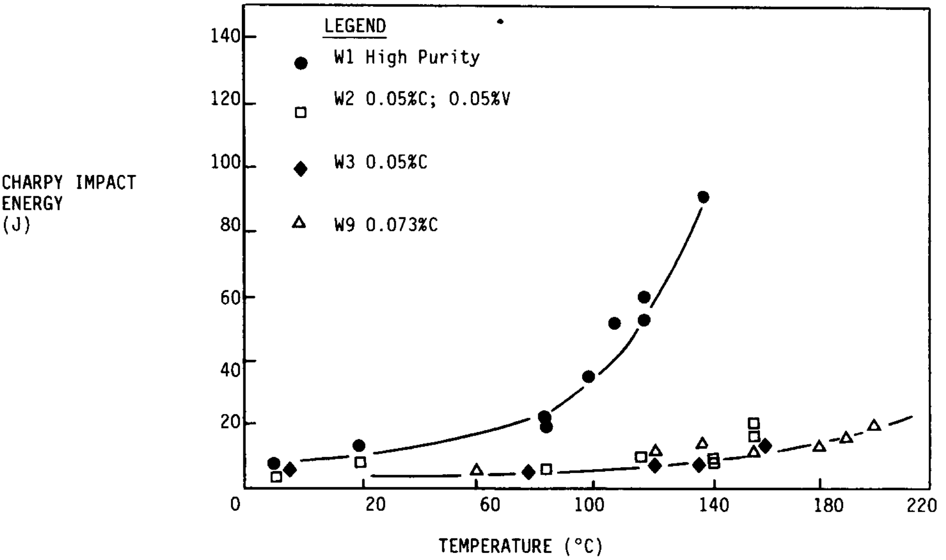

Fig. 8. Impact energy as a function of temperature for the carbon-bearing alloys.

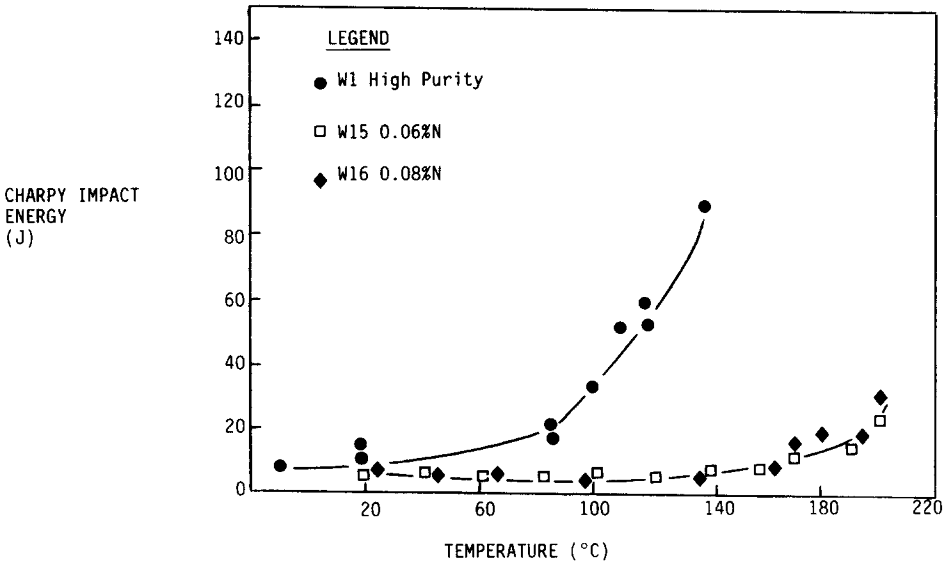

Fig. 9. Impact energy as a function of temperature for the nitrogen-bearing alloys.

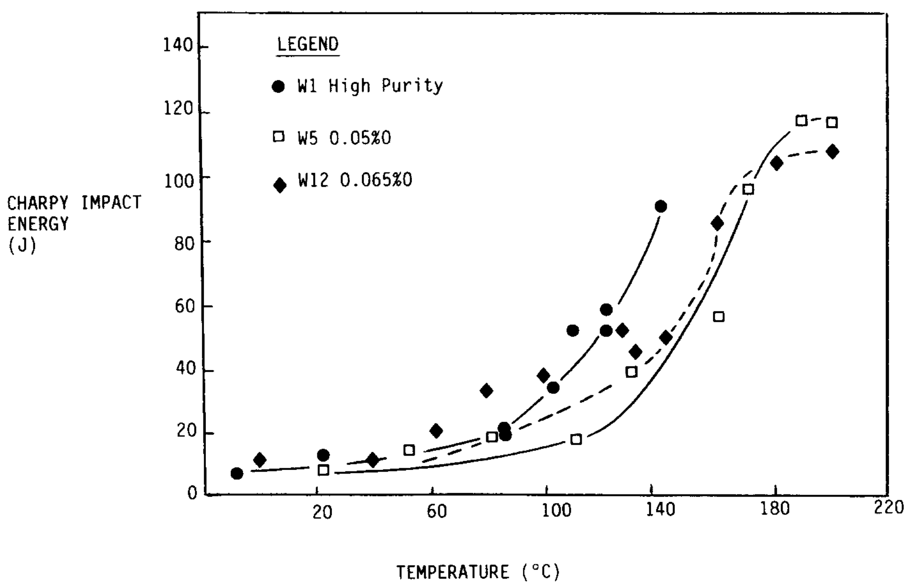

Fig. 10. Impact energy as a function of temperature for the oxygen-bearing alloys.

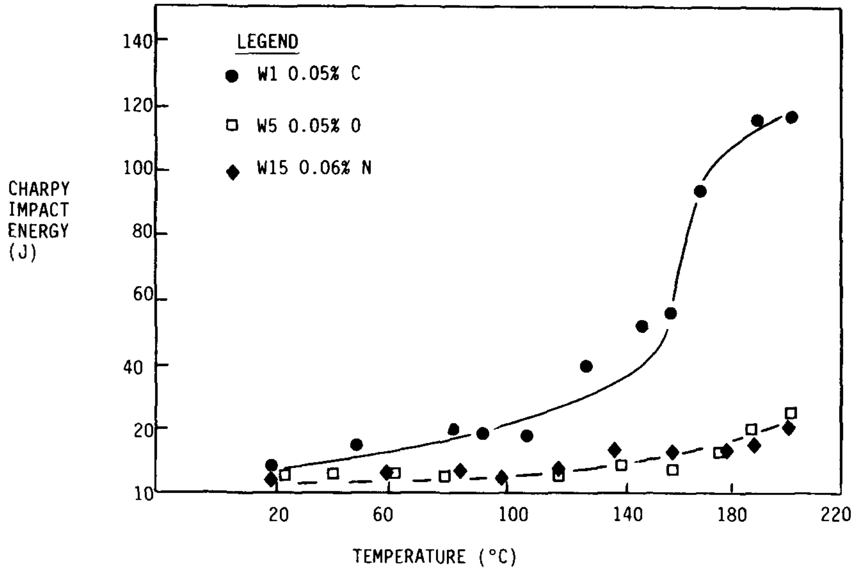

Fig. 11. Impact energy as a function of temperature for the medium interstitial solute alloys.

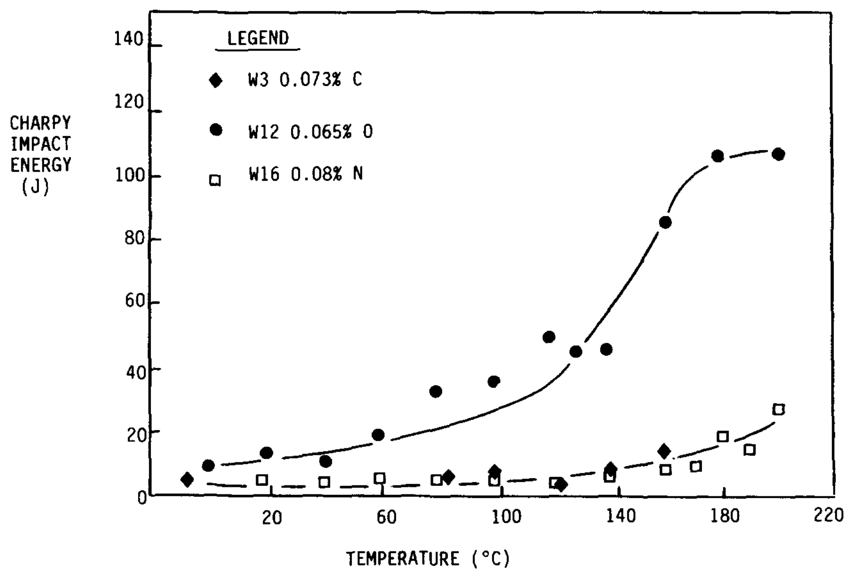

Fig. 12. Impact energy as a function of temperature for the high interstitial solute alloys.

The impact energies for all alloys are significantly lower than those quoted by Hermanus[6] and DeMarsh.[10] Even in the case of the low interstitial alloy W1, the apparent DBTT is much higher than that quoted by the above researchers. A discussion on this difference is presented later.

From Figs 8 and 9 it is evident that whereas the DBTT of W1, the low interstitial alloy, appears to occur at approximately 130 °C, both carbon-bearing (W2, W3 and W9) and nitrogen-bearing (W15 and W16) alloys only then start to exhibit an increase in toughness at such a temperature. It is thus seen that an increase in either carbon or nitrogen content seriously affects the toughness of the present Fe–40Cr alloy. This confirmed the finding of other researchers who found a similar effect on lower chromium content alloys.[11–14]

Figure 8 indicated that the presence of vanadium in W2 has very little effect on the Charpy impact toughness of Fe–40Cr. However, it must be remembered that the amount of vanadium present was small and may not have been sufficient to stabilise the metal sufficiently to increase the dynamic ductility and toughness. It has already been shown that vanadium does increase the static ductility. It can thus not be taken as conclusive that vanadium has no effect on the toughness of Fe–40Cr.

Figure 8 showed that the increase in carbon content from approximately 0·05% wt in alloy W9 to approximately 0·075% wt in alloy W3 does not significantly change the impact properties of Fe–40Cr, whereas a marked difference is observed when the carbon content is increased from 0·0007 (W1) to 0·05%. A similar phenomenon is observed when the nitrogen content is varied (Fig. 9). These observations lead to the conclusion that, above a certain interstitial level, the toughness of Fe–40Cr may be independent of the levels of carbon or nitrogen present. The authors know of no reported literature that has tested this theory, nor are the effects of varying amounts of carbon and nitrogen on the upper shelf toughnesses known. Furthermore, from Figs 11 and 12 it can be seen that the effect of both nitrogen content and carbon on the toughness properties of Fe–40Cr are effectively identical. The impact toughness data coincide despite the difference in interstitial element and despite the difference in the structure of their precipitates.

From Fig. 10, it is seen that oxygen has a much less deleterious effect on impact toughness than do carbon and nitrogen. Indeed, increasing the oxygen content from 0·026 to 0·065% caused a maximum temperature shift of 40 °C due to a carbon or nitrogen content increase, as observed in Figs 8 and 9. Furthermore, whereas an increase in oxygen content certainly decreased the impact energy of Fe–40Cr, the difference in toughness behaviour between the 0·05% oxygen alloy

(W5) and the 0·065% oxygen alloy (W12) is difficult to ascertain because of overlapping results. It would seem that the high-oxygen alloy, W12, may have slightly better impact toughness properties than W5, but this is probably due to heat treatment effects.

4 DISCUSSION

Hermanus[6] and DeMarsh[10] quoted DBTT values that were significantly lower than those emerging from the present study. Whereas the above researchers sometimes recorded negative DBTTs, the lowest recorded in this study was approximately 130 °C. Indeed, even for the low interstitial alloy, W1, the DBTT is much higher than that quoted by the above researchers. This difference was attributed to the thermo-mechanical processing procedure as well as subsequent heat treatment. Although a short study has been done to optimise the rolling and annealing procedure,[7] the conclusions of this study differed from the optima found by Hermanus and DeMarsh. The thermomechanical processing route used in this study was selected from the recommendations of the study performed about six years ago[7] and was therefore not necessarily the best. It follows, therefore, that the results quoted in this work should be regarded rather more qualitatively than quantitatively.

Keeping the thermomechanical processing route constant, as the interstitial level is increased, will lead to the occurrence of high temperature embrittlement. Rapid cooling rates from high temperatures, as employed in this study, enhance the toughness of low interstitial alloys[3] since it prevents carbide precipitation. This was borne out by optical microscopy where few carbides were detected in the low interstitial alloy. However, as the interstitial level increased to high levels, rapid quenching raised the DBTT. Baerlecken *et al.*[15] proposed that this increase in DBTT was connected with the structure and morphology of the precipitates, while Demo[16] suggested that it was due to the formation of precipitates on dislocations. The effect of interstitials on the toughness of Fe–40Cr can be reduced by slow cooling from intermediate temperatures, the reason being that during a slow cool, coarser precipitates form, and these are not as effective in raising the lattice friction stress or in locking dislocations as the finer precipitates resulting from a rapid quench. Alternatively, during a slow cool, the longer time given to relieve supersaturation could result in the diffusion of interstitial elements to the grain boundaries rather than precipitation on dislocations.

Wolff[17] observed that the toughness of Fe–40Cr could be increased by an intermediate anneal in the 750–850 °C range before annealing and quenching from 1050 °C. Using transmission electron microscopy he found that this intermediate anneal resulted in a uniform distribution of free dislocations and a sparse distribution of large spheroidal precipitates which acted as generation sites for free dislocations and as stabilisers of interstitial solutes which would otherwise embrittle the material. However, the density of free dislocations which improved the toughness of Fe–40Cr seemed to be related to the amount of second phase present in the material and Wolff considered it likely that an optimum thoughness could exist. It is therefore possible that with large amounts of second phase present, as in the present study, the large number of free dislocations would lead to work hardening and as such an intermediate anneal would have no beneficial effect on toughness.

It is therefore apparent that no single universal optimum thermomechanical processing route exists for ferritic stainless steels. This processing route depends on the amount of interstitial phase present in the metal. For the results presented in this study to reflect the best obtainable for the particular alloys, seven optima would have had to be established; this was clearly beyond the scope of this study. The thermomechanical processing route was therefore kept constant for all alloys and the results merely reflect trends in the mechanical behaviour of high interstitial alloys.

4.1 The 'sigma-phase question'

Throughout this study sigma-phase (σ) was never positively identified in any of the alloys tested. This stands in contradiction to the work of DeMarsh,[10] who claimed to have identified this phase in his study. EDAX analysis performed on many precipitates showed that they were chromium-rich and were probably carbides of the form $M_{23}C_6$ or nitrides of the form Cr_2N or $Cr_2(C, N)$; sigma has a nominal FeCr composition.

Carbon, nitrogen or oxygen additions have not been known to increase the rate of formation of sigma-phase, which is usually very slow to form. The known accelerators for the formation of sigma-phase are molybdenum, silicon, nickel and manganese, none of which was present in the alloys in the particular study.

Newell[8] observed that the presence of sigma-phase in an alloy is accompanied by an increase in hardness. From Table 8 it can be seen that the hardness of these alloys was constant, except for the nitrogen-bearing alloys. However, the increase in hardness here is due to solid solution hardening rather than to the presence of sigma-phase.

All the alloys in this study were annealed well above the temperature of stable sigma formation and were subsequently water quenched. No time was therefore allowed for the formation of this phase. It would thus have been surprising if sigma has been detected in any of the alloys used in this project and it would seem that Hermanus and DeMarsh misidentified the precipitates present in their alloys.

4.2 The effects of carbon, nitrogen and oxygen on toughness

The results presented earlier were vary much as predicted by the literature. It has been known for about forty years[8] that carbon and nitrogen can adversely affect the toughness of ferritic stainless steels. The effect of oxygen is less widely known. Some interesting points that have come out of this study, however, merit further discussion.

Wright[12] reported that an increase in oxygen content from 90 to 535 ppm in an Fe–26Cr alloy had essentially no effect on the DBTT. The present study has shown that an increase in oxygen content from 200 to 650 ppm in Fe–40Cr similarly has very little effect on the Charpy impact energy. Far fewer precipitates were observed in these alloys after quenching than in the carbon- and nitrogen-bearing alloys. This retention of interstitials in solution tends to have a beneficial effect on toughness and has been reported by Plumtree & Gullberg[19] and Grubb & Wright.[20]

Whereas Honda & Taga[21] observed that oxygen in body centred cubic (BCC) metals promoted the occurrence of intergranular failure, extensive fractography revealed no such phenomenon in the alloys used in the present study. The above researchers also found, however, that when the carbon content reached a critical level the fracture mode changed to transgranular cleavage. Above this critical carbon content no amount of oxygen addition could cause the fracture mode to revert back to intergranular faulure. Although they worked with carbon contents in excess of those achieved in W5 and W12, they worked on a different BCC material, and it is possible that the critical carbon level is material dependent and was exceeded in the Fe–40Cr alloy.

Semchyshen *et al.*[22] discovered that increasing the nitrogen content from 0·010 to 0·057% in an Fe–17Cr alloy did not result in a significant reduction in toughness, while increasing the nitrogen content from 0·006 to 0·06% in an Fe–40Cr alloy in the present study caused a dramatic decrease in toughness. However, two importance differences exist in the parameters of tests performed on these alloys. Firstly, the Fe–17Cr alloy was heat treated at 815 °C instead of 950 °C as in the case of the Fe–40Cr alloy. The 17% chromium level lies outside the sigma formation range and heat treatment at 815 °C was thus possible. This heat treatment prevented high temperature embrittlement which was the main cause for loss of toughness in the alloys assessed in this study. Secondly, the alloys tested by Semchyshen *et al.* contained 0·004% carbon as opposed to the 0·01% in the present alloys. The above researchers found that as the carbon content increased, the degrading effect of increased nitrogen content was more clearly evident. The present study shows that in Fe–40Cr, at carbon levels of 100 ppm, the effects of nitrogen and carbon are equally detrimental to toughness. Baerlecken *et al.*[15] found that the toughness of ferritic stainless steels was connected with the structure and morphology of the precipitates, while Semchyshen *et al.*[22] found that high temperature embrittlement is caused by precipitates of chromium-rich carbonitrides on the grain boundaries. However, when one compared the nature of precipitates observed in the carbon- and nitrogen-bearing alloys, these theories did not seem to hold. Carbon-bearing alloys contain precipitates that had formed on the elongated grain boundaries of the as-rolled material and had not redissolved on subsequent annealing. Grain boundary precipitation in these alloys was much less severe. Nitrogen-bearing alloys display severe grain boundary precipitation with randomly distributed intragranular precipitates. However, the toughness behaviour of the two types of alloys is similar.

Demo[16] offers an alternative explanation for the high temperature embrittlement of ferritic stainless steels. He proposed that the precipitation of chromium-rich carbides on the dislocations in the grain body and not on the grain boundaries is responsible for the severe loss of toughness in high interstitial alloys when heated to high temperatures. He associated the poor ductility of chromium–iron alloys subjected to high temperature exposure to fine, dispersed precipitates in the matrix preventing easy movement of dislocations, similar to a precipitation hardening effect. Furthermore, Plumtree & Gullberg[11] proposed that increasing amounts of second-phase inhomogeneously distributed throughout the matrix lowers the effective surface energy of the crack, thus promoting susceptibility to brittle failure.

When one considers the toughness behaviour of the carbon- and nitrogen-bearing alloys and relates this to the precipitates observed, it would appear that the results of the present study support the theory proposed by Demo. This theory may also serve to explain the similar toughness values obtained in medium and high interstitial alloys. Precipitation on dislocations can only occur while such dislocation sites are available and a distinct saturation point will be reached when the sites are filled. After this saturation point has been reached, the interstitial content, quenching from high temperatures, causes the dislocation sites to become saturated. Since high temperature embrittlement is only caused by precipitation on dislocations, and not on grain boundaries, raising the interstitial level would not affect the toughness since it would not increase precipitation on the embrittlement areas.

5 CONCLUSIONS

In this project alloys of Fe–4040Cr were made up with varying carbon, nitrogen and oxygen contents. The metallographic and mechanical properties of the alloys were measured and included Charpy V-notch, tensile and hardness tests. It was found that:

(1) The actual values of DBTT as recorded in this study were very high, the lowest recorded being approximately 130 °C. Other researchers have found DBTTs as low as −10 °C. This strongly relates to thermomechanical processing routes, which ideally should be optimised for each alloy type but which were kept constant for the present study.
(2) The introduction of oxygen into Fe–40Cr has very little effect on the toughness properties of the alloy.
(3) Above a certain level of carbon or nitrogen content, the toughness of Fe–40Cr was independent of the amount of interstitial present. This phenomenon was ascribed to the saturation of dislocation precipitation sites above a certain interstitial level.
(4) At high levels of carbon and nitrogen content, these two interstitial elements have the same effect on the toughness of Fe–40Cr.
(5) The results emanating from this study support the theory proposed by Demo, viz. that the toughness of ferritic stainless steels was not related to the structure and morphology of the precipitates, but rather that high temperature embrittlement was due to the precipitation of carbides and nitrides on dislocations.
(6) At high carbon levels annealing at 950 °C for one hour was not sufficient to redissolve carbides precipitated on the elongated grain boundaries of the as-rolled material.
(7) Despite the reports of other researchers the brittle sigma-phase was not identified in the alloys tested in this study. Analyses performed on the precipitates present revealed only the presence of chromium-rich carbides and nitrides, and some iron-rich oxides. Indeed, the kinetics of sigma formation is too slow for it to form after one hour at 950 °C.

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