



## Some Considerations on the Toughness Properties of Ferritic Stainless Steels—A Brief Review

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### ABSTRACT

*The present paper has attempted to briefly review the factors that influence the toughness properties of ferritic stainless steels. The structure and constitution of ferritic stainless steels were discussed together with the effects of second phase particles on the toughness aspects. Generally the presence of second phases such as carbides, nitrides and oxides, as well as the chromium-rich ferrite, precipitates and sigma-phase,  $\sigma$ , can cause a significant decrease in the toughness of ferritic stainless steels.*

*The influence of structural parameter or microstructural grain size on the toughness considerations, although well documented, are not always clearly understood. This is the result of other varying factors which can obscure the true effects of grain size.*

*Thermomechanical processes, such as cold working, hot working and controlled rolling, can significantly influence toughness properties as a direct result of their effects on grain size and the precipitation of carbides, nitrides and sigma-phase.*

*Finally, the detrimental effects of interstitial elements on the toughness of ferritic stainless steels can be controlled by the addition of stabilising elements, e.g. titanium and niobium.*

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## 1 INTRODUCTION

Stainless steels may be categorised into several main types:<sup>1</sup>

- Martensitic steels contain 12–17% Cr, 0.4% Ni and 0.1–1% C with additions of elements such as molybdenum, niobium, tungsten, etc., which increase their tempering resistance. Their uses are widespread in structural applications, viz. chemical plant, turbine engines and, in the higher carbon variants, for tools, bearings and cutlery.
- Controlled transformation steels contain 14–17% Cr, up to 7% Ni and many different alloying additions such as molybdenum, aluminium, titanium, copper, etc. These steels are austenitic after heat treatment and can be formed readily. They are then transformed by various treatments and age hardened or tempered to give high proof stresses. These steels are widely used in the aircraft and aerospace industries.
- Precipitation-hardening steels contain more chromium than the controlled transformation steels and have to a large extent replaced them because of difficulties in controlling the transformation behaviour.
- Austenitic stainless steel is the most widely used type and contains 18–25% Cr, 7–20% Ni and less than 0.03% C. They are frequently alloyed with Mo, Nb or Ti to provide creep resistance or stabilisation against intergranular corrosion. Because they are predominantly austenitic at all temperatures, they can be hot-worked readily. However, some measure of control over delta ferrite must be exerted by compositional variations which is essential for good weldability, whilst similar control over the formation of martensite is essential to optimise formability. This control is necessary because delta ferrite, once formed, is very difficult to remove. These steels have excellent high temperature strength, are very shock resistant and are resistant to scaling. Consequently, they are used in a wide range of applications ranging from severe corrosion conditions to medicine dispensing. Unfortunately the austenitic steels are liable to stress corrosion cracking and their application is thus limited in this respect.
- Duplex stainless steels contain approximately equal amounts of alpha and gamma phases, which not only gives an improved combination of toughness and stress corrosion resistance but also increases strength.
- Ferritic stainless steels contain between 14 and 35% Cr with

additions of molybdenum, niobium or titanium. Recently, very low (C + N) content have been specified; the super-ferritic steels. The higher alloy compositions can also include up to 4% Ni, provided this does not alter their fully ferritic structure. Ferritic stainless steels have been known for almost 50 years, but have found far less application than their austenitic counterparts. Reasons for this are numerous and include lack of ductility, susceptibility to embrittlement, notch sensitivity and poor weldability.

However, there are many applications for stainless steels in which the unique properties of the austenitics are not required. Additional applications exist where the ferritics have property advantages over the austenitics, including improved machinability, higher thermal conductivity, lower thermal expansion and, most importantly, immunity to chloride stress corrosion cracking. Moreover, there are an increasing number of applications where the higher cost of austenitic stainless steels compared with that of the ferritics makes the austenitics economically unsuitable.<sup>2,3</sup>

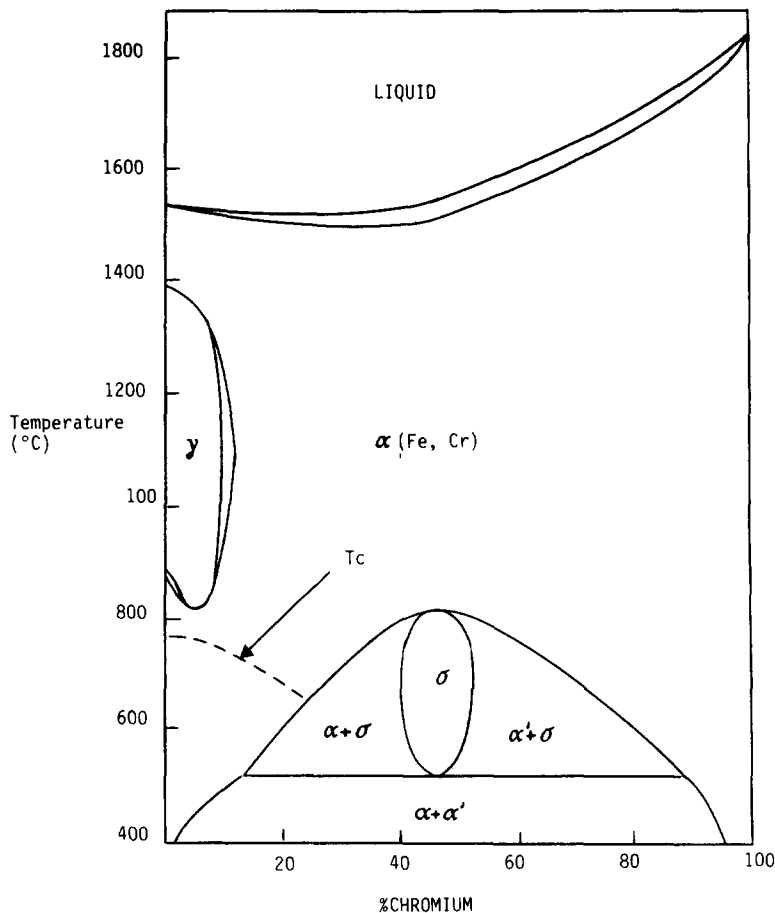
An iron–40% chromium alloy has been the subject of recent research and can be classed as a super-ferritic stainless steel. It is similar to commercial ferritic stainless steels in all respect except for its chromium content, which is significantly higher than the common highest value of 26%.

The present paper aims to give a brief overview of the state of the art of high purity iron–chromium alloys and ferritic stainless steels and an assessment of their general mechanical properties, concentrating mainly on toughness considerations.

## 2 STRUCTURE AND CONSTITUTION OF FERRITIC STAINLESS STEELS

Ferritic stainless steels are structurally fairly simple. At room temperature they consist of alpha ( $\alpha$ ) solid solution having a body centred cubic (BCC) crystal structure. The alloys contain very little carbon in solution; most of the carbon appears as finely distributed chromium carbide precipitates. A typical phase diagram of the iron–chromium system is shown in Fig. 1.

Chromium is a member of a group of elements called ferrite formers which extend the alpha-phase field and suppress the gamma-phase field. This property results in the formation of the gamma loop as seen in Fig.



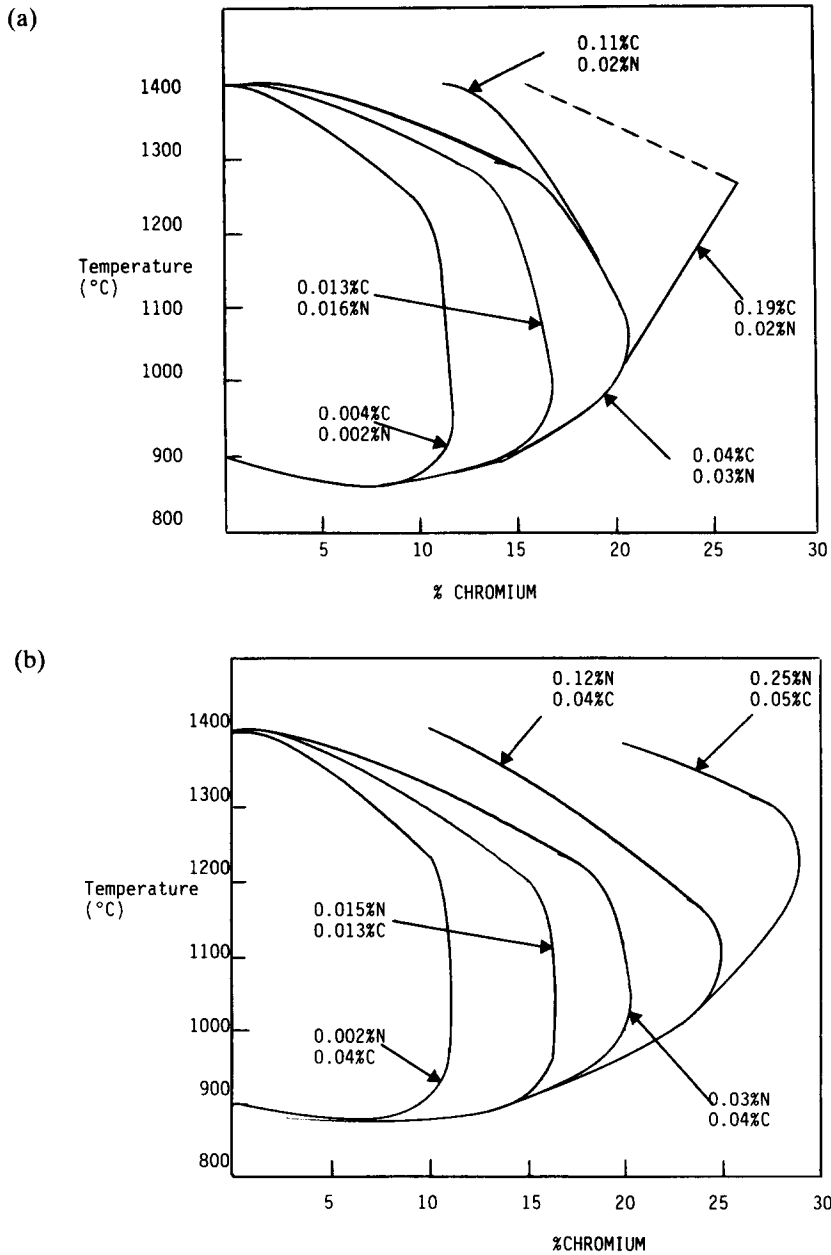
**Fig. 1.** The iron–chromium system.

1, which in the absence of carbon and nitrogen extends to chromium contents of about 12–13%. At higher chromium contents, transformation to gamma is no longer possible and the metal will remain ferritic up to melting temperatures. Between the gamma loop and the alpha-phase field, there is a narrow transition region where an alloy at temperature will have both alpha- and gamma-phases.<sup>4</sup>

Baerlecken *et al.*<sup>5</sup> showed that the addition of stabilising elements, particularly carbon and nitrogen, caused the outside boundary of the two-phase field to shift to higher chromium levels (see Fig. 2).

### 3 BCC BEHAVIOUR OF IRON AND IRON–CHROMIUM

The fact that the crystal structure of ferritic stainless steels is body centred cubic accounts for much of the brittleness observed in these



**Fig. 2.** Shifting of the boundary line  $(\alpha + \gamma)/\gamma$  in the Fe-Cr system through additions of (a) carbon and (b) nitrogen.

alloys.<sup>6,7</sup> As the temperature is decreased, BCC metals display a substantial increase in lattice friction stress. This increase manifests itself in an increase in the ductile-to-brittle transition temperature (DBTT), in accordance with the Cottrell model, as reported in Petch's paper,<sup>8</sup> which states that the DBTT occurs when

$$\sigma_y k_y d^{1/2} = k_y^2 + \sigma_0 k_y d^{1/2} > C \mu \gamma \quad (1)$$

where

$\sigma_y$  = flow or fracture stress, or both

$k_y$  = Hall–Petch slope

$d$  = grain size

$\sigma_0$  = lattice friction stress

$\mu$  = shear modulus

$\gamma$  = effective surface energy of an implied crack

$C$  = constant

However, the basic cause of BCC brittleness is the sensitivity of these metals to interstitials. While high purity metals may be ductile at very low temperatures, slightly less pure alloys have relatively high DBTT values.<sup>6</sup> Interstitials cause embrittlement by locking dislocations. This can be demonstrated by cold-working. It is observed that as the amount of cold work increases, the DBTT also increases. According to the Cottrell model this phenomenon may be explained by the fact that the locking of dislocations during cold-working causes the flow stress to increase.<sup>5</sup>

However, the solubility level of interstitials in BCC metals are sufficiently low (Fig. 3) that it is rarely possible to distinguish between solute embrittling effects and the effects of second-phase precipitates.<sup>9</sup> The precipitates, in fact, become more important than the solute when the amount of interstitial elements significantly exceeds the solubility limit.

The presence of carbon or nitrogen, in amounts in excess of the solubility limit, serve to increase the DBTT still further. This embrittling effect is closely linked to the number and size of carbides and nitrides formed at the grain boundaries. Thick precipitate films act as strong barriers to slip propagation across the grain boundaries and raise  $k_y$ . Grain boundary carbide and nitride precipitation are suppressed by quenching from above the solution temperatures when the interstitial content is low. However, the resulting fine intragranular precipitation may increase the DBTT by increasing the lattice friction stress ( $\sigma_0$ ).

The addition of chromium in large quantities has a relatively minor

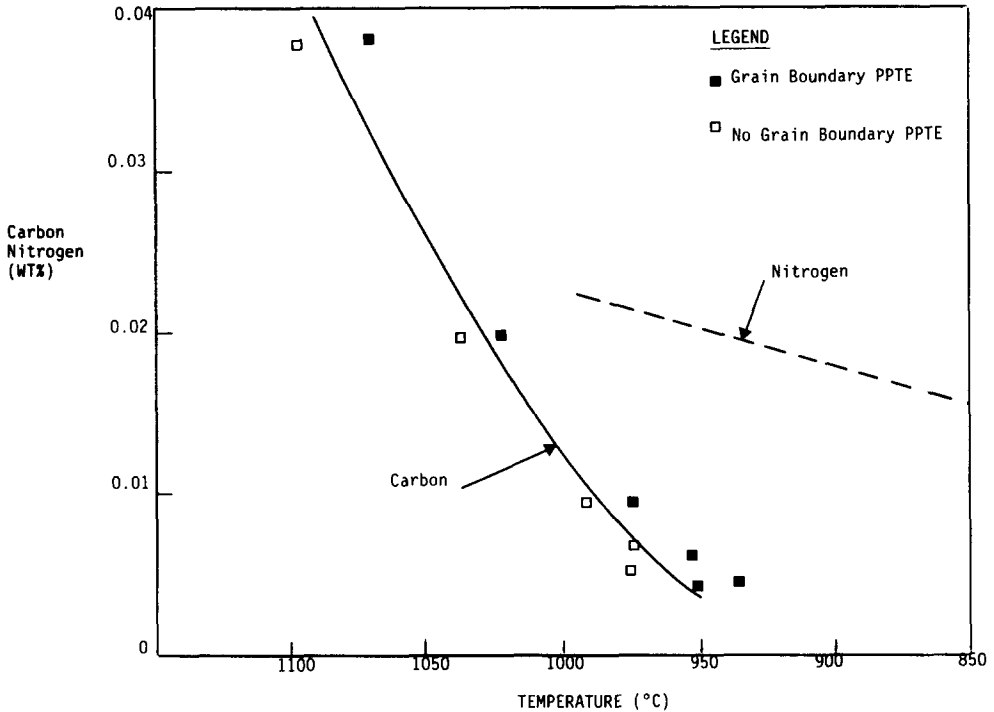


Fig. 3. Solubility of carbon and nitrogen in a 26% Cr steel with temperature.

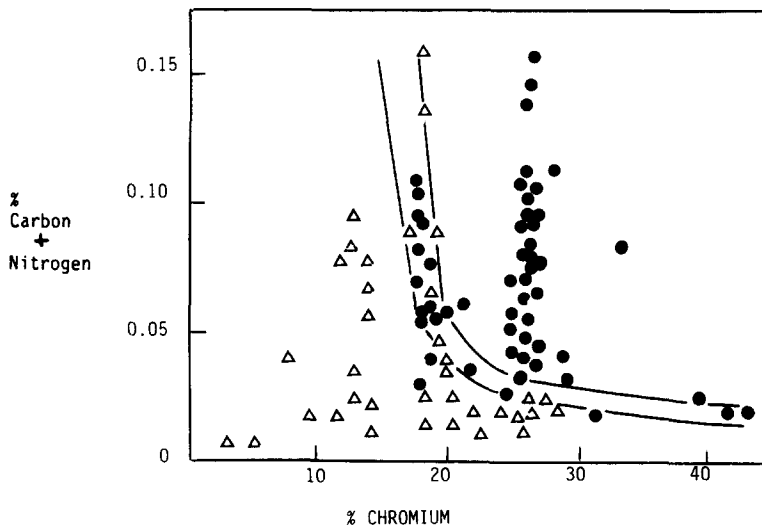
effect on the DBTT values of iron. It is, of course, difficult to separate the effect of chromium as a solid solution strengthening element from its effect as a carbide and nitride former.

#### 4 SECOND-PHASE EFFECTS IN FERRITIC STAINLESS STEELS

The second-phase effects that are of primary importance to the DBTT of ferritic stainless steels are those of the carbides, nitrides and oxides and of martensite and the alpha-, sigma- and chi-phases.

##### 4.1 Carbides, nitrides and oxides

Until about forty years ago, the addition of chromium *per se* was regarded as the major factor in the embrittlement of iron-chromium



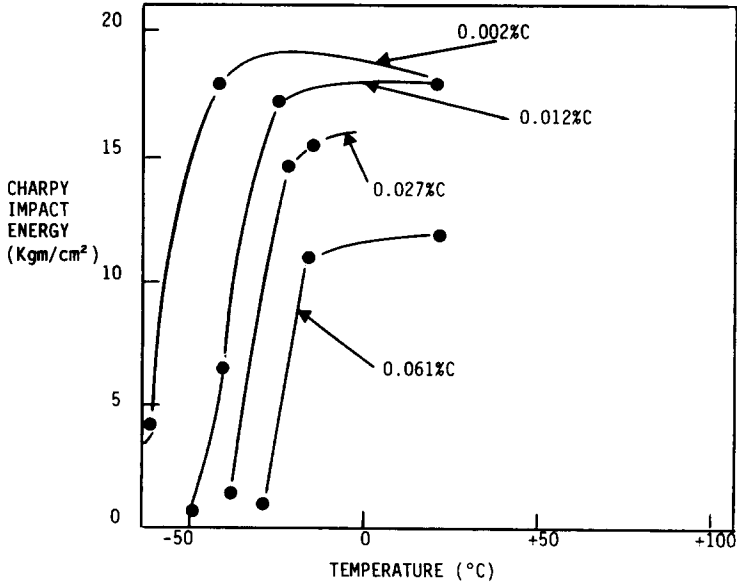
**Fig. 4.** Influence of carbon and nitrogen on the toughness of Fe-Cr alloys:  $\Delta$ , high impact strength alloys;  $\bullet$ , low impact strength alloys.

alloys. Nitrogen was regarded as beneficial because of its ability to refine the grain structure and to inhibit grain growth at elevated temperatures. Therefore nitrogen was often added to the alloy.<sup>10</sup> However, in 1951, Binder & Spendelow<sup>11</sup> proposed that it was not the presence of chromium but the presence of interstitial carbon and nitrogen that accounted for the lack of toughness in these alloys. These investigators found that toughness can be increased by reducing the combined (C + N) levels (Fig. 4).

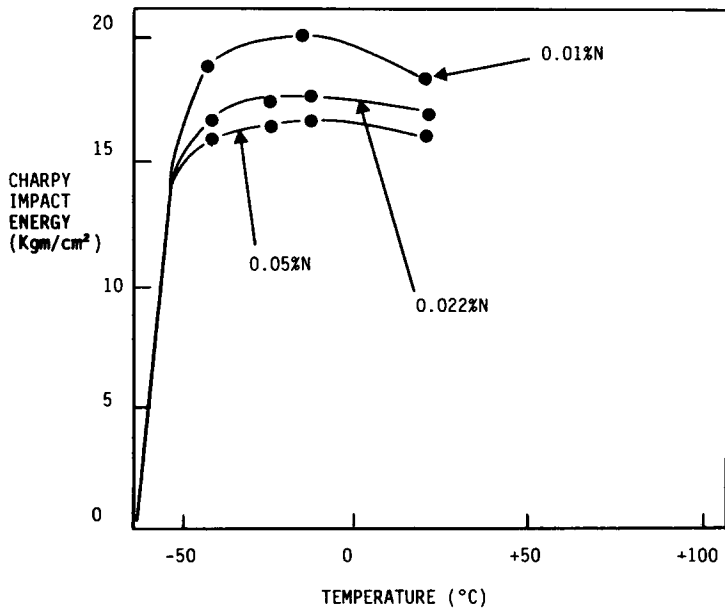
Semchyshen *et al.*<sup>12</sup> Mueller<sup>13</sup> studied the effect of varying carbon and nitrogen contents in alloys with several different base compositions. Figure 5 shows the effect of carbon content on the impact energy of 17% Cr alloys. There is a clear, but relatively small, increase in DBTT as the carbon content increases in specimens annealed at 815 °C. In contrast, the effect of carbon content on the upper shelf energy is significant. Similar tests on 17% Cr alloys containing nitrogen did not, however, show a significant nitrogen effect (Fig. 6).<sup>14</sup> This phenomenon is not unique to ferritic stainless steels but applies to all BCC ferritic steels.<sup>15</sup>

Semchyshen *et al.*<sup>12</sup> showed that if these alloys were heat treated at higher temperatures, a significant nitrogen effect was observed. This is in agreement with observations made by Hochmann as reported in Binder & Spendelow's paper.<sup>11</sup> It may thus be concluded that for relatively low temperature heat treatment nitrogen is less harmful than





**Fig. 5.** Transition curves for Charpy test specimens of a 17% Cr-0.002 to 0.061% C steels.



**Fig. 6.** Transition curves for Charpy test specimens of 17% Cr-0.01 to 0.057% N steels.

carbon. For a high temperature heat treatment, carbon and nitrogen appear to be equally detrimental.

It has also been reported<sup>12</sup> that as the carbon level decreased the debilitating effect of nitrogen become more pronounced and that as the chromium level increases the levels of carbon and nitrogen consistent with good toughness are decreased.<sup>6</sup> The latter is due to a decrease in (C + N) solubility which occurred with increased chromium content.

As shown in Fig. 7, rapid cooling rates enhance the toughness of alloys with total (C + N) in solution, which at low levels can have a favourable effect on toughness. However, as the (C + N) level increases, the effect is reduced and indeed at high (C + N) levels, rapid quenching from temperatures above 1000 °C raised the DBTT.<sup>5,12,16,17</sup>

The increase in the DBTT in high (C + N) alloys following a high temperature anneal has been extensively researched.<sup>5,11,12,17,18</sup> This effect is clearly illustrated in Fig. 8.

Baerlacken *et al.*<sup>5</sup> concluded that this increase in DBTT was connected with the structure and morphology of the carbide precipitates. They also suggested that it was due to the low solubility of carbon in high chromium Fe–Cr alloys. Wright,<sup>6</sup> on the other hand, suggested that the embrittlement was due to dispersed, intragranular precipitation or to actual retention of (C + N) in solution. It is believed that the embrittlement was due to the retention of clustered (C + N) atoms in a grossly supersaturated ferrite matrix, i.e. a true saturation strengthening effect.<sup>6</sup> Alternatively, Demo<sup>17</sup> observed that such quenching embrittlement is associated with fine precipitation on dislocations and presumed low mobile dislocation density. In all cases the effect would be to increase the lattice friction stress and the flow stress.

Plumtree & Gullberg<sup>14</sup> contended that the presence of larger amounts of inhomogeneously distributed precipitates, principally Cr<sub>2</sub>N, at the grain boundaries caused an increase in the DBTT. This effect was demonstrated by increasing the (C + N) content of Fe–15% Cr alloys in the water-quenced condition. They found that the reduction in surface energy in the Cottrell model brought about by these hard second-phase precipitates resulted in a decrease in impact energy.

Demo<sup>17</sup> suggested that although air-cooled alloys with high (C + N) content also contained intergranular precipitates, a metal treated in this manner had much higher impact properties. It was also noted that the air-cooled specimens showed a fibrous shear structure with considerable localised deformation and elongation of the grains. The quenched metals, however, displayed a failure mode that was predominantly intragranular. It was concluded that, in high (C + N) alloys, the precipitation of carbides and nitrides at the grain boundaries did not

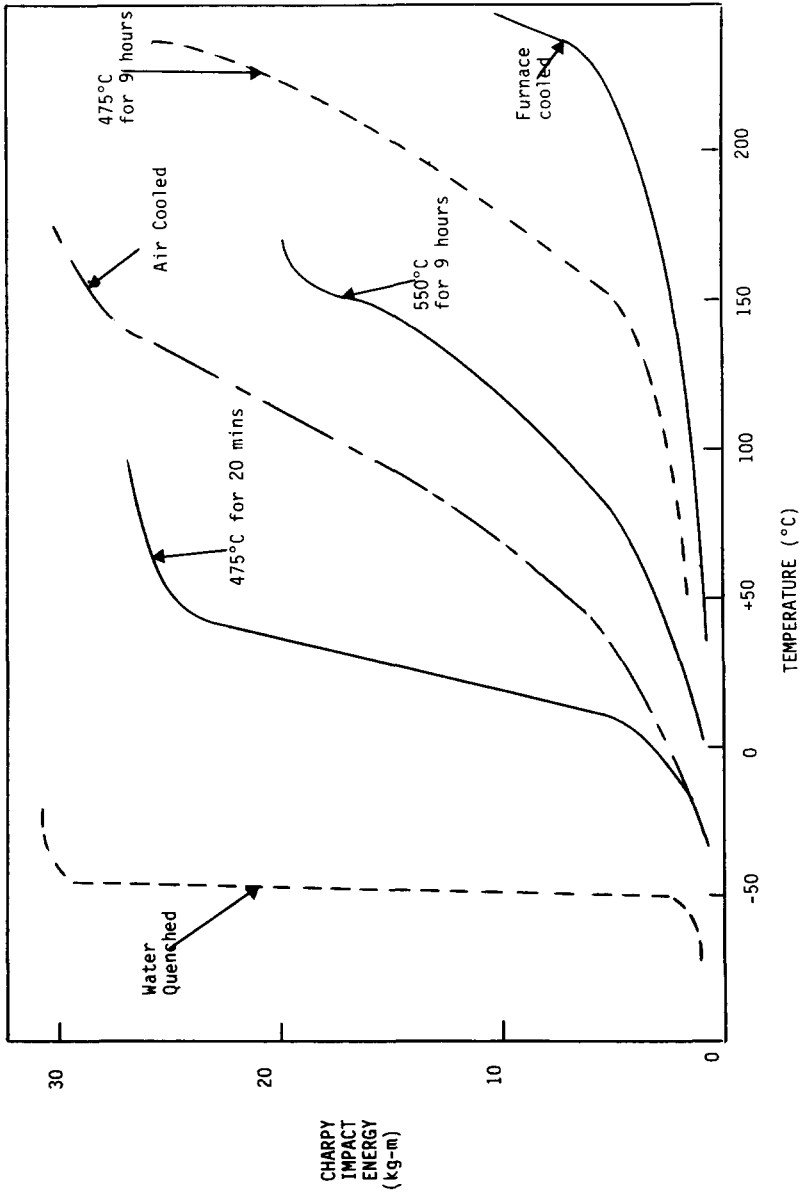


Fig. 7. Impact energy data for a Fe-25% Cr alloy after various isothermal treatments and cooling rates from 850 °C.

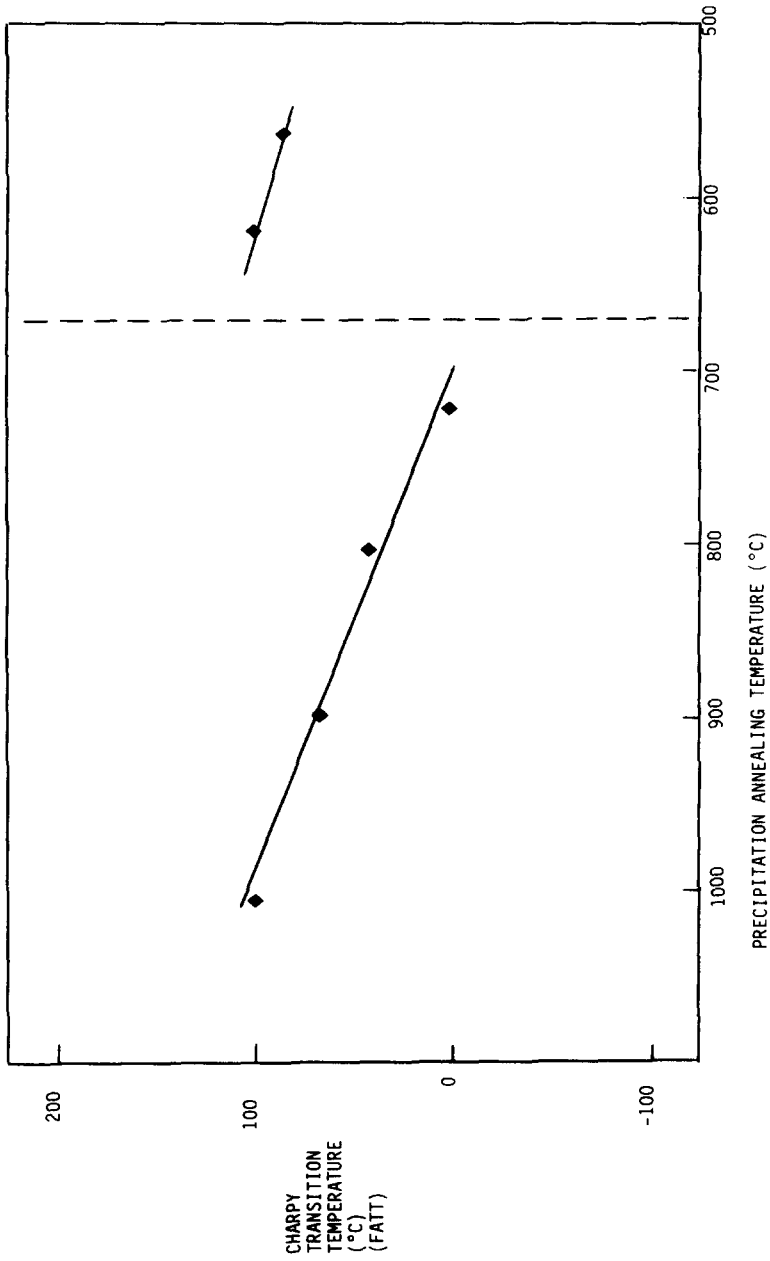


Fig. 8. Effect of precipitation annealing temperature on the Charpy FATT for high interstitial alloys.

grossly affect ductility. Moreover, an embrittled specimen reheated to 850 °C showed restored ductility despite heavy intergranular precipitation. It was proposed, therefore, that the precipitation of carbides and nitrides on dislocations was responsible for the embrittlement.

Two possibilities have been suggested to explain why precipitates form on dislocations during quenching but not during air-cooling, even though both contain intergranular precipitates. Firstly, high supersaturation served as a strong driving force during quenching for rapid precipitation on all high energy surfaces, which include dislocations. During a slow cool, the longer time available to relieve supersaturation may allow for diffusion towards the grain boundary areas where supersaturation is relieved by precipitation on the more preferred high energy surfaces of the grain boundaries. Secondly, dislocation nucleation during the rapid quench occurs simultaneously with the rejection of carbon and nitrogen from solution as the chromium-rich carbides and nitrides precipitate to relieve the supersaturation. With a slower cool, therefore, relief of supersaturation by precipitation on high energy surfaces may have been completed before the dislocations have nucleated.<sup>17</sup>

Semchyshen *et al.*<sup>12</sup> also conducted experiments to investigate the high temperature embrittlement of high interstitial alloys. Figures 9 and 10 show the effect of carbon and nitrogen on alloys heat treated at 1150 °C. These should be compared with Figs 5 and 6 which were heat treated at 815 °C. While very little change was observed after the lower temperature heat treatment, the increase in DBTT in the alloys treated at 1150 °C is quite considerable. It was suggested that the precipitation of chromium carbonitrides, mainly at the grain boundaries, was the principle cause of the observed increases in transition temperatures of alloys quenched from 1150 °C. The lower temperature anneal resulted in much coarser precipitates and these are not as effective in raising the lattice friction or in locking dislocations as are the fine precipitates.

Baerlecken *et al.*,<sup>5</sup> Semchyshen *et al.*,<sup>12</sup> Demo<sup>17</sup> and Plumtree & Gullberg<sup>16</sup> all conclude from their data that the so-called high temperature embrittlement of high chromium ferritic stainless steels is due to precipitation of chromium-rich carbides and nitrides caused by the relief of supersaturation when the alloys are quenched from high temperatures. While Baerlecken *et al.*<sup>5</sup> and Semchyshen *et al.*<sup>12</sup> proposed that embrittlement was due to precipitation at grain boundaries, Plumtree & Gullberg<sup>16</sup> and Demo<sup>17</sup> claimed that the embrittlement results from the formation of fine precipitates on dislocations.

In contrast with the high temperature embrittlement observed in high interstitial alloys, low interstitial alloys experience a substantial increase

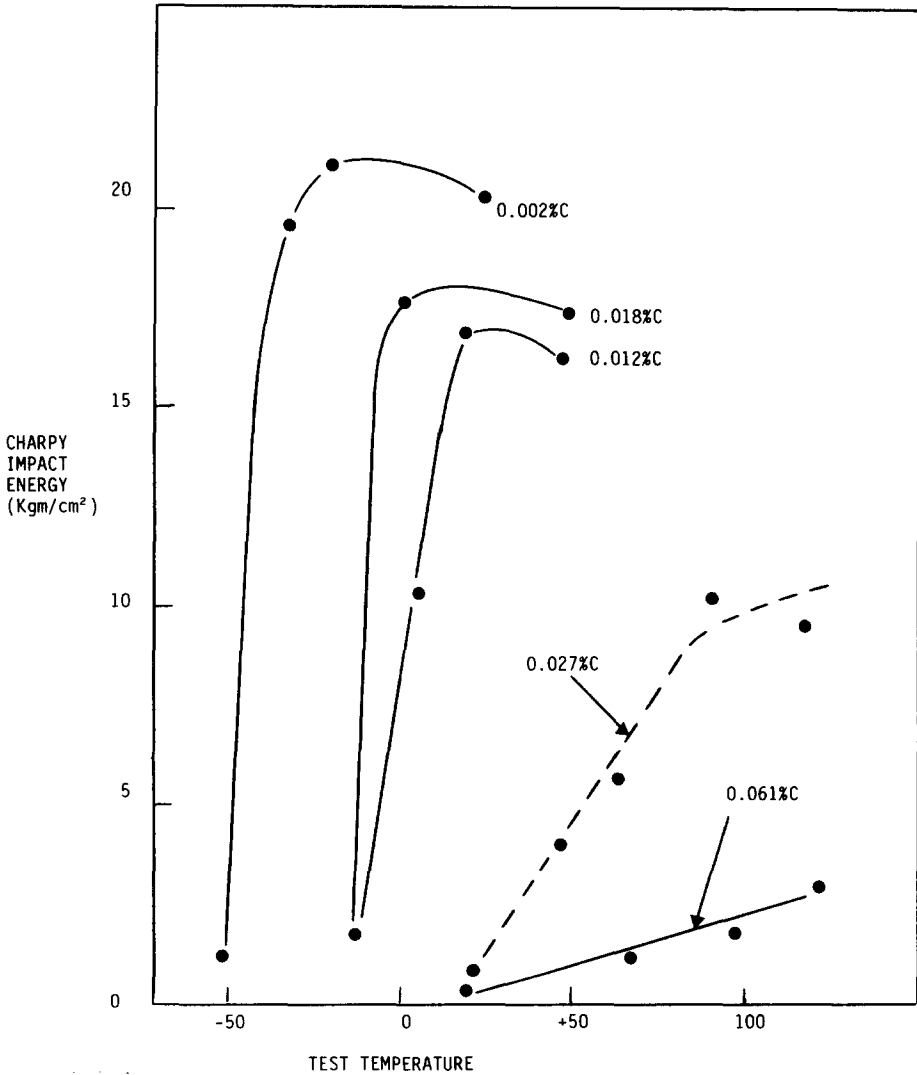


Fig. 9. Charpy impact transition curves for 17% Cr-0.002 to 0.061% C steels.

in toughness when quenched from high temperatures (Fig. 11).<sup>18</sup> In low interstitial alloys, carbide and nitride precipitation was entirely suppressed and all the carbon and nitrogen was retained in solution.<sup>14</sup>

The DBTT increases considerably when carbide and nitride precipitation was induced through isothermal annealing at low or intermediate temperatures or slow cooling. The grain boundary precipitates formed during slow cooling provide strong barriers to slip propagation across grain boundaries and hence cause crack initiation sites and serve to increase  $k_y$  and decrease  $\gamma$  in the Cottrell model.<sup>6,8,14,16,18</sup> McMahon

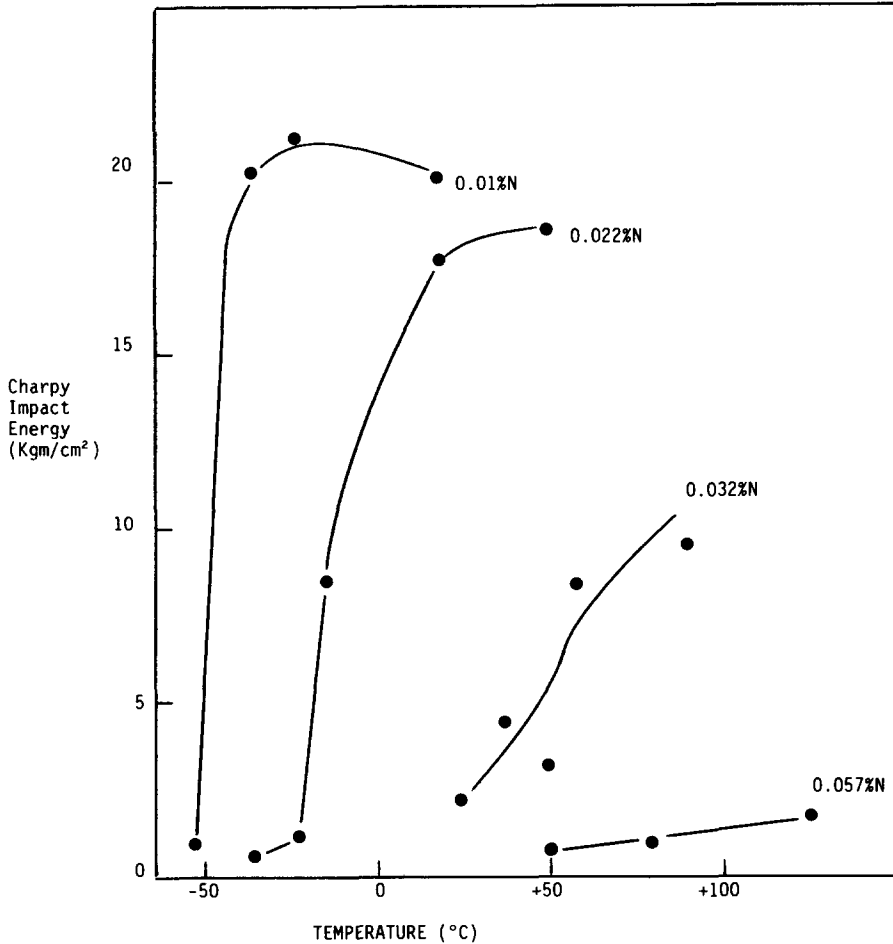


Fig. 10. Charpy impact transition curves for 17% Cr-0.01 to 0.057% N steels.

& Cohen<sup>19</sup> have shown that such grain boundary precipitates can act as starting points or initiation sites for fracture, thus causing a marked increase in DBTT. Pollard<sup>9</sup> contended that the low tensile ductility at room temperature of large-grained Fe-26% Cr ferritic stainless steels was caused by the formation of grain boundary carbonitrides, which began to precipitate at around 900 °C.

It is quite clear that the embrittlement experienced by ferritic stainless steels is dependent on the precipitation of carbides ( $Cr_{23}C_6$ ), nitrides ( $Cr_2N$ ) and carbonitrides. Carbide precipitation generally occurred above 850 °C while nitride precipitation occurred at much lower temperatures.

Grubb & Wright<sup>18</sup> report that carbide precipitation should be

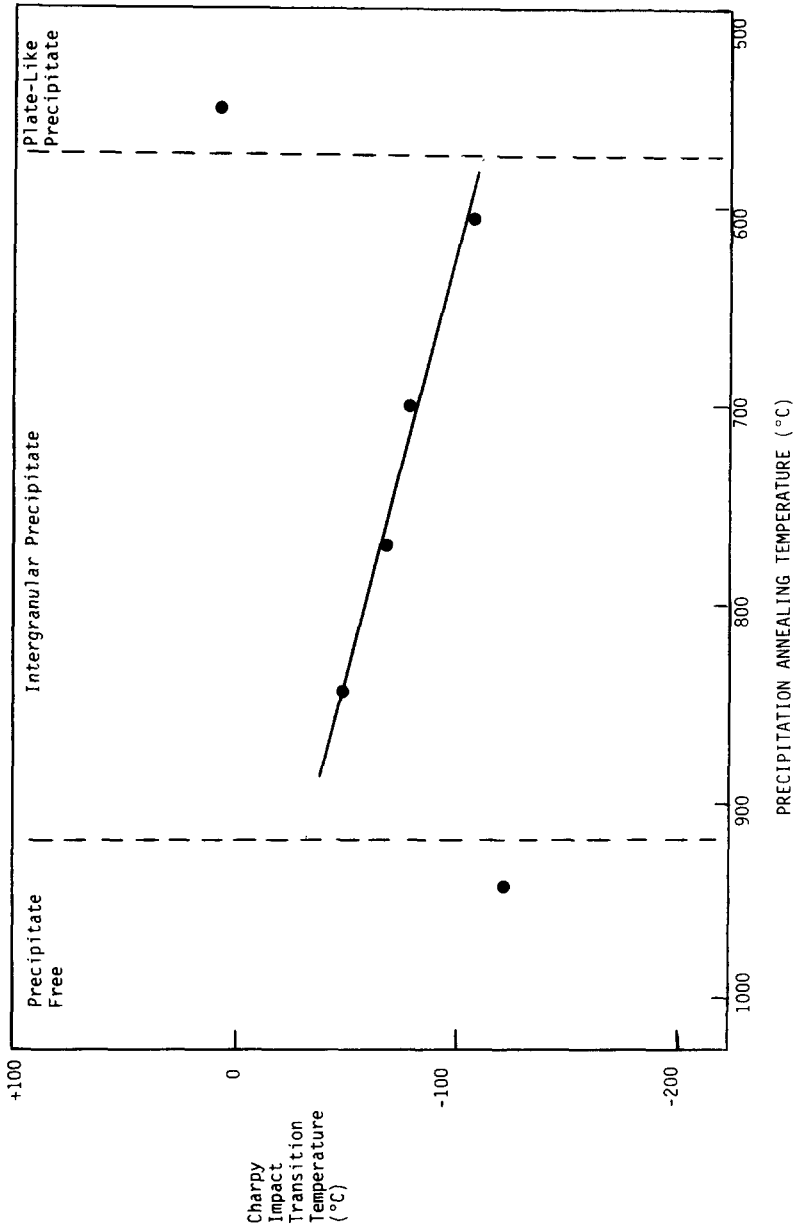


Fig. 11. Effect of precipitation annealing temperature on the Charpy impact transition temperature for low interstitial alloys.



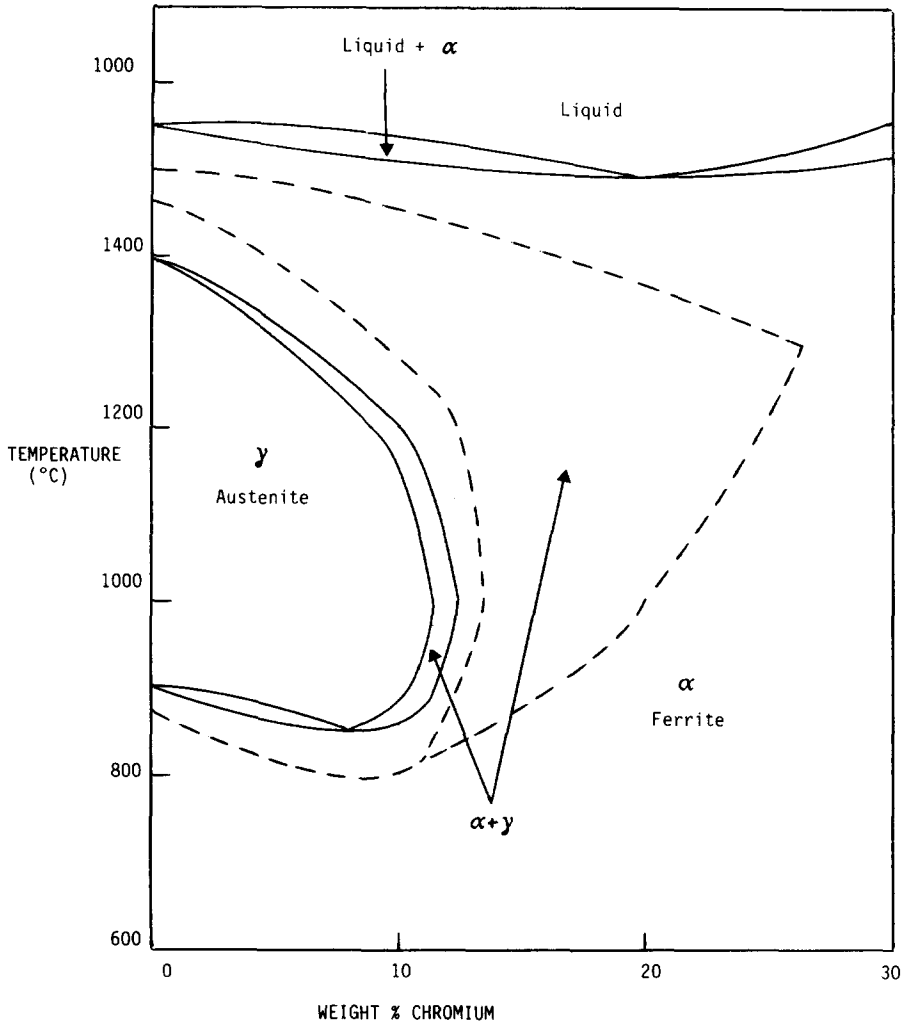
essentially completed by the 870 °C anneal, while nitride precipitation may not be completed by the 500 °C anneal. The precipitation of carbides, nitrides and carbonitrides is ultimately dependent on the carbon and nitrogen content of the steels. In high interstitial alloys both (C + N) in solution and (C + N) precipitates contributed to embrittlement, while in low interstitial alloys only (C + N) precipitation caused severe embrittlement.

Relatively little is known about the effects of oxygen and oxides on ferritic stainless steel toughness properties, particularly in the low oxygen range (<100 ppm) which can be commonly achieved with electric furnace practice and other modern melting techniques. While oxygen might intuitively be expected to have the same effect on toughness as carbon and nitrogen, most previous studies have tended to ignore oxygen effects. Nevertheless, where oxygen has been considered, contradicting results have been observed. Wright<sup>6</sup> and Allen *et al.*<sup>20</sup> have reported that an increase in oxygen content from 90 to 535 ppm has essentially no effect on the DBTT of wrought ferritic stainless steel, while it has been shown<sup>21,22</sup> that the impact energy of Fe–40% Cr can be increased significantly by decreasing the oxygen content.

Honda & Taga<sup>23</sup> have found that oxygen in BCC metals promoted the occurrence of intergranular fracture while carbon counteracted this tendency. They found that when the carbon content reached a certain level, no intergranular fracture occurred, even at high oxygen levels. The critical carbon level was thus independent of the oxygen level. However, the critical oxygen content did depend on the carbon content.

The effects of carbon and nitrogen on the toughness properties became greatly reduced at chromium levels in the 17% Cr range and lower. Some benefit was still achieved from (C + N) control,<sup>12</sup> but in this range it became more important to eliminate martensite. Chromium is a ferrite-stabilising element and therefore, as the chromium level is increased, the tendency to form martensite is reduced. However, carbon and nitrogen are powerful austenite stabilisers and high levels of (C + N) can push the austenite–ferrite boundary far towards higher chromium contents (Fig. 12).<sup>24</sup>

Thus at low chromium levels, weld heat-affected zones, hot-rolled banded structures and some annealed stock may contain some untempered martensite. The presence of this martensite leads to an increase in the DBTT. This effect is most likely due to strain concentration included in the soft ferrite adjacent to the hard martensite.<sup>6</sup> The addition of ferrite-stabilising elements (e.g. silicon, titanium, molybdenum, aluminium) aid in the prevention of martensite formation, as do annealing and tempering treatments.



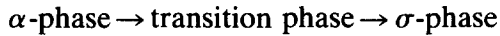
**Fig. 12.** Iron–chromium equilibrium phase diagram for alloys containing less than 0.01% carbon or nitrogen —, and alloys containing 0.1 to 0.2% carbon or nitrogen - - -.

#### 4.2 Embrittlement at 475 °C

When iron–chromium alloys are aged in the 400–500 °C temperature range the room temperature ductility and impact strength decrease sharply while the tensile strength and hardness increase markedly. However, this increase in tensile strength is of no practical significance because of the extreme brittleness of the alloy.

The cause of this behaviour was unexplained for a long time but it

was believed that this phenomenon was connected with the tendency to form sigma-phase. It was suggested that ageing was the result of the formation of a transition lattice prior to the formation of equilibrium sigma-phase<sup>25</sup> and that at higher temperatures an iron–chromium alloy heated in the embrittling range undergoes the following reaction:<sup>10,26</sup>

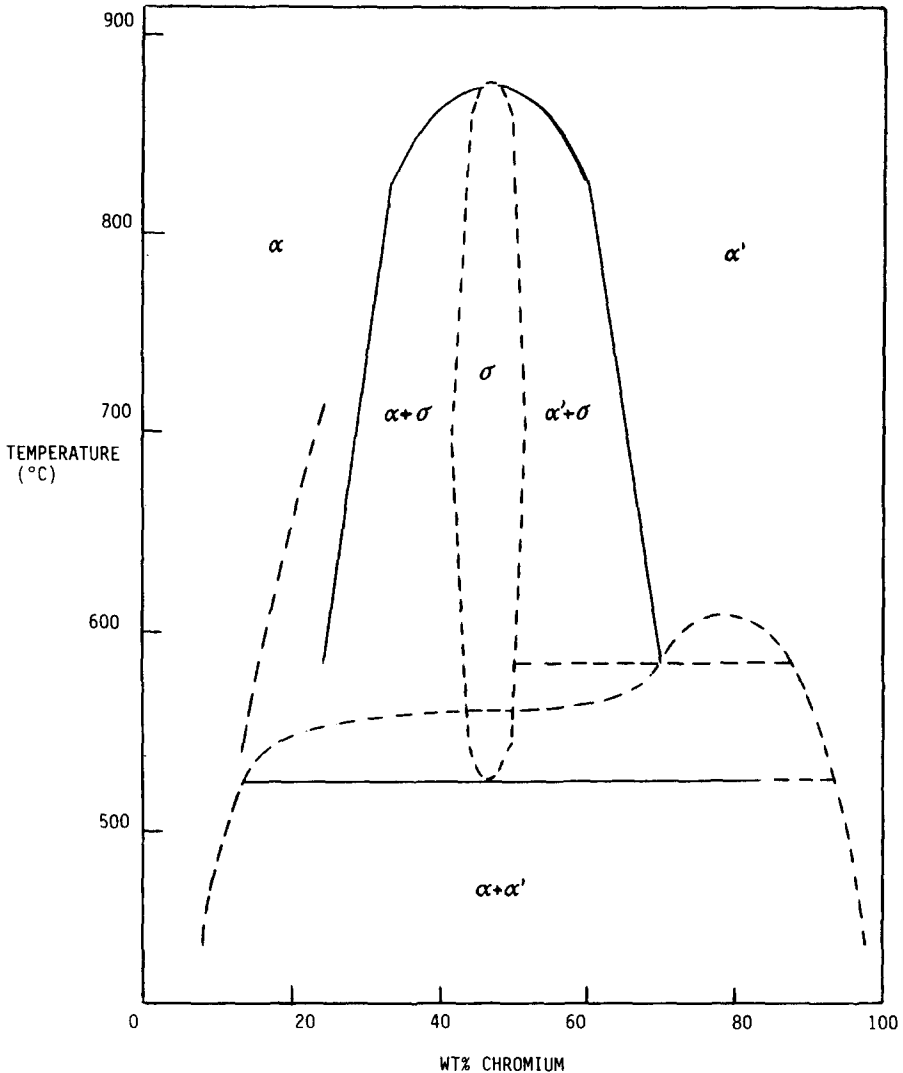


It was proposed that this reaction was incomplete at lower temperatures and that the transitory phase that precedes sigma formation at higher temperatures caused 475 °C embrittlement.<sup>27</sup> It was believed that this transition phase was coherent with the matrix alpha-phase. The presence of this coherency between the two different structures caused large resistance to dislocation motion typical of a precipitation hardening mechanism.<sup>27</sup>

This theory was later shown to be incorrect. The occurrence of 475 °C embrittlement is a result of the formation of a coherent precipitate due to the presence of a miscibility gap in the iron–chromium system below approximately 550 °C, in a chromium range where sigma can form at higher temperatures. Williams & Paxton<sup>25</sup> were among the first investigators to verify this miscibility gap in the absence of sigma. The extent of this miscibility gap is shown in Fig. 13. Alloys aged within the gap would separate into chromium-rich ferrite ( $\alpha'$ ) and iron-rich ferrite ( $\alpha$ ). Reversion to the unaged condition occurs when the metal is heated above 550 °C. It was found that at 520 °C sigma decomposed eutectoidally into two immiscible solid solutions:  $\alpha'$  and  $\alpha$ . This was confirmed by Solomon & Levinson<sup>28</sup> and Chandra & Schwartz<sup>29</sup> using Mossbauer effect spectroscopy.

Fisher *et al.*,<sup>30</sup> using electron microscopy, confirmed that the 475 °C embrittlement was accompanied by the precipitation of a very fine chromium-rich BCC phase with a lattice parameter close to that of the matrix. This phase ( $\alpha'$ ) was about 200 Å in diameter and contained up to 80% chromium. Nichol *et al.*<sup>31</sup> observed that the early stages of embrittlement were accompanied by wave-like contrast striations of chromium atoms clustering on the (100) planes and that upon embrittlement the deformation mode undergoes a change. Research carried out by Grobner<sup>32</sup> and Jacobsson *et al.*<sup>33</sup> revealed that the mechanism of embrittlement was connected with the locking of dislocations by the  $\alpha'$ -phase, and the growth of the particles causes only very little additional decrease in toughness in the chromium alloys investigated, implying that the nucleation rate determines the ageing time necessary for embrittlement.

Plumtree & Gullberg<sup>14</sup> also proposed that 475 °C embrittlement was



**Fig. 13.** Partial phase diagram of the Fe-Cr system.

associated with the presence of very fine  $\alpha'$  particles, which cause the friction stress to increase, therefore increasing the probability for crack initiation.

Unlike hardness, which after a short interval of incubation increases gradually with ageing time, toughness drops abruptly after a certain period of ageing.<sup>14,32</sup> It can thus be concluded that a definite time period is associated with the development of an embrittled structure. This time period depends on the composition and temperature of ageing.

Plumtree & Gullberg<sup>14</sup> and Williams & Paxton<sup>25</sup> also noticed that no over-ageing occurred and that hardness increased continually. Williams & Paxton<sup>25</sup> and Grobner & Steigerwald<sup>34</sup> explain this by proposing (on the basis of considerations of driving force and diffusion) that particle growth is slow. When particles reach a size of 100 Å, the driving force (interfacial energy) will be very small compared with the initial driving force. Distances of diffusion are now larger than those during precipitation and the ratio of the rate of particle growth to the rate of precipitation is therefore small.

Nichol *et al.*<sup>31</sup> found that 475 °C embrittlement was enhanced by increasing the chromium content, while Grobner<sup>32</sup> and Courtnall & Pickering<sup>35</sup> observed that it was also enhanced by the addition of interstitial elements. Grobner,<sup>32</sup> however, believes that the addition of stabilizers (e.g. Ti and Nb) slow down the ageing process, while Courtnall & Pickering<sup>35</sup> report that these also increase the rate of  $\alpha'$  precipitation. Grobner & Steigerwald<sup>34</sup> report that cold work had no significant effect on the kinetics of 475 °C embrittlement.

### **4.3 Sigma-phase embrittlement**

Very high chromium content ferritic stainless steels may be embrittled by the precipitation of sigma-phase in the 500–900 °C temperature range.<sup>6,27</sup> The range of alpha-phase stability for the binary iron–chromium system can be clearly seen on the phase diagram (Fig. 1). Pure sigma forms between 42 and 50% chromium, while a duplex structure of both sigma and alpha has been found to form in alloys with as little as 20% and as much as 70% chromium when they are exposed to the critical temperature range.

Sigma-phase is an intermetallic compound with an approximate composition, FeCr. It is hard, brittle and non-magnetic, and has a tetragonal unit cell. Elements like Mo, Si, Ni and Mn shift the sigma-forming range to lower chromium contents. Although the phase generally forms very sluggishly, cold-work enhanced the precipitation rate considerably, and, in very high chromium content alloys sigma-phase has been found in the air-cooled as-cast structure.<sup>36</sup>

The temperature range of rapid sigma formation coincides with the normal temperatures used for annealing ferritic stainless steels, and consequently highly alloyed ferritic stainless steels must be annealed in the 1050 °C range and rapidly cooled through the critical range to avoid sigma-phase embrittlement. Fortunately, sigma-phase developed in an alloy may be redissolved with relatively short holding times at a temperature above 800 °C.

## 5 GRAIN SIZE

Although the effect of grain size on the toughness properties of ferritic stainless steels is well documented it is not always clearly understood. It has been proven that the DBTT tended to increase with increased grain size (Fig. 14).<sup>12,16,36-39</sup> Ohashi *et al.*<sup>40</sup> believe that while the grain size affected the DBTT, the upper shelf energy of ferritic stainless steels is independent of grain size. They report that the effect of grain size was noticeable in V-notched materials, but slight in specimens with brittle weld cracks. Therefore, coarse grains tended to promote crack initiation, even in blunt-notched specimens, and thus the grain size effect contributed mainly to resistance to initiation of brittle fracture and only slightly to crack propagation. Plumtree & Gullberg (39) have shown that the DBTT increased linearly with  $d$  and that the DBTT of lower purity alloys tended to be less affected by grain size changes.<sup>16</sup>

However, it is difficult to produce fine grain sizes in ferritic stainless steels because of the desirability to anneal above the sigma solvus line,<sup>41,42</sup> and the differences between large grain sizes normally developed have been shown by several researchers to have no significant effect on the DBTT.<sup>5,41,43</sup> Mintz *et al.*<sup>37</sup> proposed that this variability was due to the difficulty in isolating the grain size from other variables (such as carbide thickness) that affect the impact properties. Although fast cooling may result in a finer grain size, it can be accompanied by an

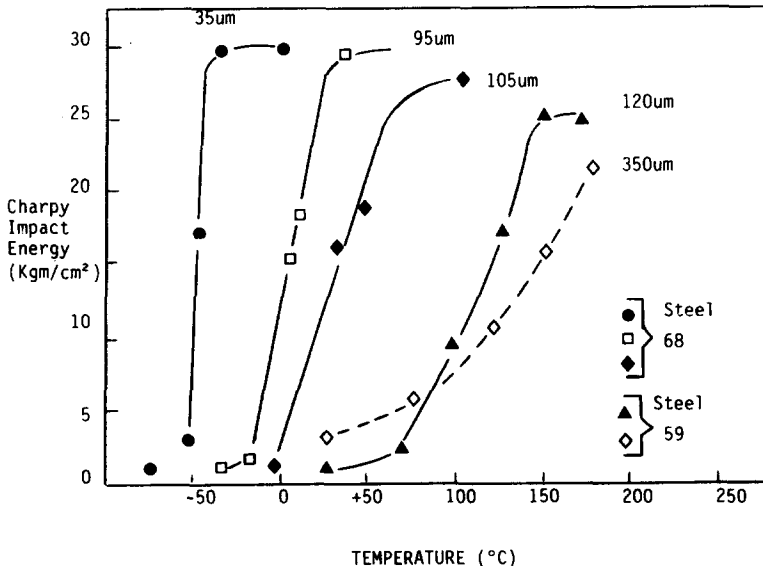


Fig. 14. Impact energy transition curves for two steels at various grain sizes.

increase in hardness in the ferrite matrix, which may offset any improvement in toughness from grain refinement. A coarse grain size from slow cooling resulted in coarse carbides which can also decrease toughness. Therefore, it is possible that the apparent absence of a grain size effect on impact behaviour is due to the obscuring effect of other variables.

## 6 THERMOMECHANICAL PROCESSING

As has been mentioned in the previous section, toughness of ferritic stainless steel is dependent on grain size, and grain size can be refined by thermomechanical processing. However, thermomechanical processing also affects precipitation of carbides, nitrides and sigma-phase.<sup>40</sup> In this section four methods of thermomechanical processing will be considered, viz. cold-working, hot-working, controlled rolling and heat treatment.

### 6.1 Cold-working

Cold-working does raise the DBTT, but the effect is not consistent, nor is it very great.<sup>6,44</sup> Differences in cold-working temperatures and the extent of preferred grain orientation make the effects more difficult to study and analyse. It is known, however, that cold-working increased the flow stress.

The general effect of cold-work seems to be that of a DBTT increase of 1–2 °C percent rolling reduction.<sup>6</sup> Cold-work may complicate other forms of embrittlement, the acceleration of sigma-phase formation being the most significant.

### 6.2 Hot-working

Ferritic stainless steels can be easily hot-worked. However, grain refinement during the hot-working process does not occur readily and the structure of the metal after hot-working can be quite coarse.<sup>22,24,32</sup> It has been found<sup>22</sup> that even after heat treatment, Fe–40% Cr had a coarse grain size of ASTM Number 2–3.

Hot-working may also accelerate the precipitation of sigma-phase. It is thus imperative not to work in the temperature range of stable sigma precipitation. After hot-working, the metal is usually quenched through the 900–500 °C temperature range to prevent sigma forming. Care must also be exercised when working high interstitial alloys. Working at high temperatures and quenching can lead to high temperature embrittlement, as described earlier.

### 6.3 Controlled rolling

Controlled rolling involves the refinement of the grains by a recrystallisation process during rolling. This is achieved by decreasing the finishing temperature and increasing the reduction per pass. It is, however, essential to employ the correct amount of deformation and the correct low finishing temperature to ensure fine grains. In ferritic stainless steels the application of controlled rolling is limited by the precipitation of brittle sigma-phase below 750 °C which prevents the use of a low finishing temperature. In stabilised stainless steels, Ti and Nb retard recrystallisation but the precipitate particles markedly inhibit grain growth after recrystallisation.<sup>45</sup>

### 6.4 Heat treatment

Typical commercial heat treating practice involves annealing at 850 °C. However, as has been stated before, this temperature falls inside the range of stable  $\alpha$ -precipitation. Therefore high chromium content ferritic stainless steels are normally annealed outside this range at 1050 °C. The anneal is followed by rapid cooling through the critical temperature range to prevent  $\alpha$ -precipitation during cooling.

It has been reported<sup>22</sup> that the temperature of annealing had a significant effect on toughness, even when annealed above 900 °C. It was found that the higher the annealing temperature, the lower the room temperature toughness. This phenomenon was ascribed to the precipitation of increasingly fine precipitate which locked the dislocations.

Annealing at high temperatures can also cause grain growth and this, too, induces a decrease in toughness. However, by keeping (C + N) levels very low, concern about grain size-related DBTT increases can be prevented.

With a total (C + N) content below approximately 500 ppm, quenching generally produces optimum toughness by preventing sigma precipitation as well as carbide and nitride precipitation. With higher



(C + N) levels, nothing is gained by quenching and if a high temperature anneal is used, rapid quenching can cause embrittlement by severe carbide and nitride precipitation. This rapid cooling embrittlement can be reduced substantially by the addition of carbide and nitride stabilisers.<sup>12</sup>

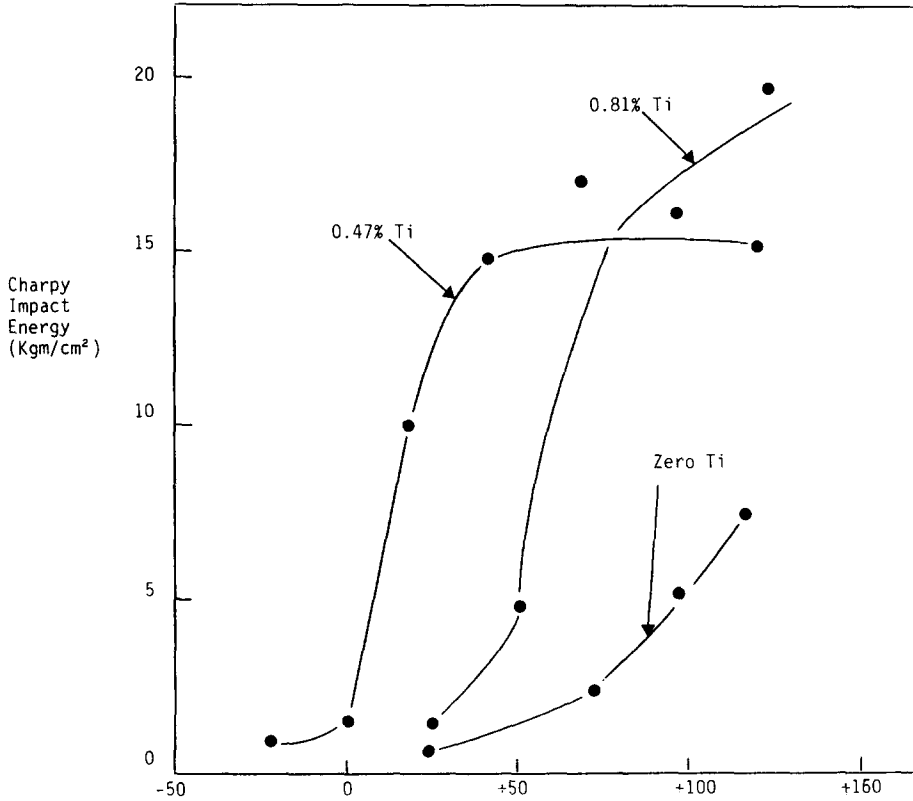
## 7 STABILISED FERRITIC STAINLESS STEELS AND REM ADDITIONS

The embrittling effect of interstitials may be controlled by the addition of stabilising elements. Such elements include titanium, niobium, zirconium and tantalum. These elements are strong carbide and nitride formers and these are more stable than the chromium carbides and chromium nitrides. Therefore with small amounts of these stabilisers, the interstitial elements are effectively tied up as stable carbides and nitrides such that their effective level in solid solution is reduced.<sup>9,27</sup> Furthermore, stabilising elements tend to refine the grain size, thus promoting a tougher alloy.<sup>42</sup> Consequently, stabilised alloys at relatively high levels of carbon and nitrogen act similarly to the very low interstitial alloys.

The effects of stabilising additions to the impact properties in comparison to the impact properties of low interstitial alloys have been extensively studied and described by Semchyshen *et al.*<sup>12</sup> and Wright.<sup>6</sup> Semchyshen *et al.* found that titanium carbonitrides and, to a lesser extent, niobium carbonitrides were less harmful to the toughness of ferritic stainless steels than chromium carbonitrides. Titanium and niobium are both effective in retarding the increase in transition temperature, with titanium appearing to be more effective than niobium (see Figs 15 and 16). The amount of stabiliser added is critical, since above a certain level they will cause the toughness to decrease.<sup>46,47</sup>

Several studies have been conducted on the effects of rare earth metal (REM) additions on not only the toughness of stainless steels but also the toughness of pure chromium and chromium-base alloys. Research on the latter has been carried out principally in the USSR.<sup>48-51</sup> These researchers have found that alloying with REM is particularly effective as a means of purifying and refining chromium and stainless steel.<sup>49,52-54</sup> Alloying with REM also increases the plasticity and workability of chromium.<sup>50</sup> It is thus possible to lower the processing temperature and to increase the reduction per pass during hot-working.

As with stabilisers, however, an optimum exists in the amount of REM to be added (usually 0.4–0.7% by weight). Researchers have

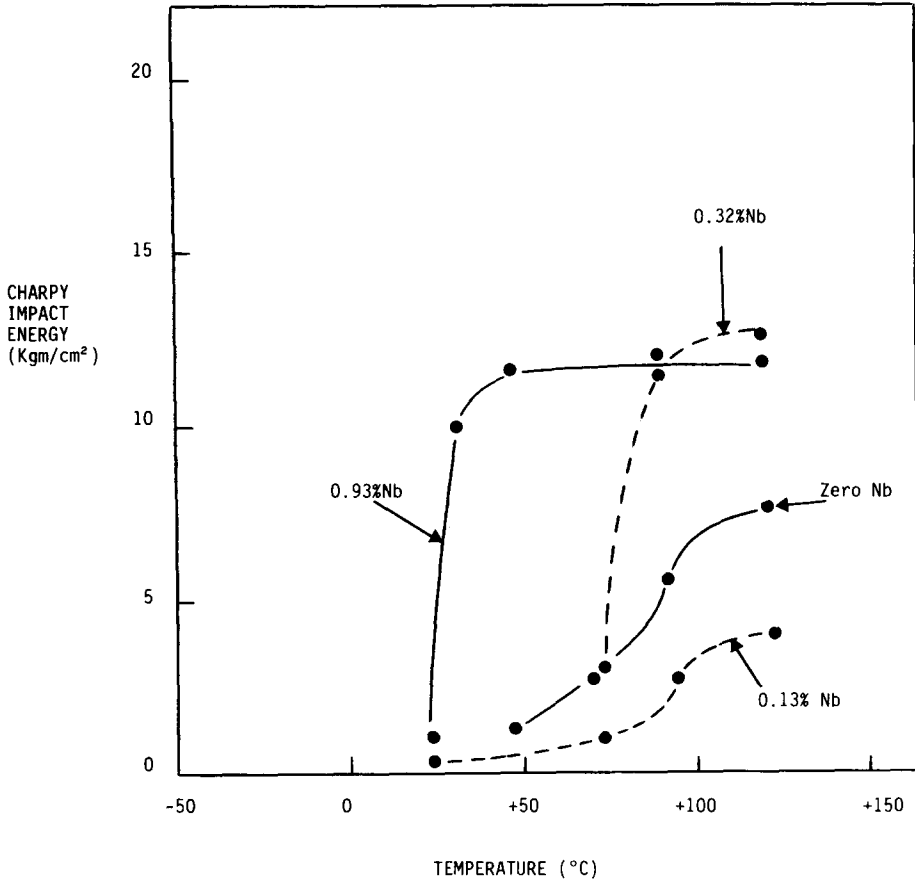


**Fig. 15.** Charpy transition curves for a 18% Cr-2% Mo ferritic stainless steel at various titanium additions.

found that REM additions in this range produce minimum DBTTs in both as-cast and work-hardened chromium alloys.<sup>49,50,52,55</sup>

## 8 SUMMARY

It has been clearly demonstrated that the presence of second phases, viz. carbides, nitrides and oxides, as well as the formation of very fine particles and sigma-phase can significantly influence the toughness properties of a range of ferritic stainless steels. In the case of carbides and nitrides it has been established that at relatively low temperature heat treatments additions of nitrogen are less harmful than carbon additions; however, at high temperature heat treatments both appear to be equally detrimental. In high carbon and/or nitrogen (C + N) alloys the toughness is decreased by a high temperature annealing treatment



**Fig. 16.** Charpy impact transition curves for a 18% Cr-2% Ferritic stainless steel at various niobium additions.

which increased the lattice friction stress and the flow stress as a result of the precipitation of carbides and nitrides on dislocations.

In contrast with the high temperature embrittlement observed in the high (C + N) alloys, low interstitial alloys experienced a significant increase in the toughness properties when quenched from high temperatures; this is the result of the suppression of carbide and nitride precipitates. It is evident that the embrittlement experienced by ferritic stainless steels is dependent upon the degree of precipitation of carbides, Cr<sub>23</sub>C<sub>6</sub>, nitrides, Cr<sub>2</sub>N, and carbonitrides. Carbide precipitation generally occurred above 850 °C while nitride precipitation could take place at much lower temperatures. The effects of carbon and nitrogen on the toughness properties are significantly decreased at chromium levels below 17%. The influence of oxygen and oxides on the

toughness of ferritic stainless steels is somewhat contradictory inasmuch that one study observed that an increase in oxygen level exhibited little effect on toughness while another independent study recorded the beneficial effects of decreasing the oxygen level on the impact toughness properties.

When iron–chromium alloys are aged in the temperature range 400–550 °C the impact toughness dramatically dropped in value. This phenomena is known as 475 °C embrittlement and is the result of the precipitation of fine chromium-rich ferrite, i.e.  $\alpha'$ . Extremely high chromium containing ferritic stainless steels can also undergo marked embrittlement as a result of the precipitation of sigma ( $\sigma$ )-phase in the temprature range 500–900 °C.

The influence of the structural parameter or grain size on the toughness properties of ferritic stainless steels is, although well documented, not always understood. This is the result of other factors that mask or obscure the true grain size effects.

Thermomechanical processing can significantly affect the toughness properties through their influence on grain size control and the precipitation of carbides, nitrides and the sigma-phase.

Finally, the embrittling effects of interstitial elements can be controlled through the small additions of stabilising elements such as titanium, niobium, tantalum and zirconium, which preferentially form more stable carbides and nitrides than their chromium counterparts. However, strict control of the actual additions is required, usually 0.4–0.7% by weight, as excessive amounts of stabilisers are detrimental to toughness considerations.

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