sizes and at low temperature. Assuming that $\tau = \sigma/2$ (i.e. shear stress is at maximum), Equation 2.4 can be written as:

$$\tau = \tau_o + \frac{k_y d^{-1/2}}{2} \qquad ....2.13$$

And finally equations 2.12 and 2.10 can now be restated as:

$$\sigma_y k_y d^{1/2} = k_y^{2} + \sigma_o k_y d^{1/2} > C\gamma_s \qquad ....2.14$$

where C = a constant related to the stress state and average ratio of normal to shear stress on the slip plane.

Although equation 2.14 does not encompass all the practical models of crack initiation, (e.g. nucleation of cleavage cracks at twins or at the boundaries between second phase particles and the matrix of a steel) it nevertheless provides a useful basis for discussing the micro-mechanics of brittle fracture. The equation essentially describes the condition for a brittle-to-ductile transition. When the left hand side of the equation is smaller than the right, a microcrack can form, but cannot grow. Alternatively, if the left hand side of the equation is greater than the right a propagating brittle fracture is produced at a shear stress equal to the yield stress.

Process and compositional variables can directly affect all the factors in this equation[8,9,10,11,20,21,22]. For example:

k_y is related to the number of dislocations that are released into a pile-up when a source is unlocked and is affected by solute distribution and grain boundary precipitation,

d, the grain size, is rather related to the slip band length, since in alloys containing fine precipitates the particle spacing rather than the actual grain size will determine the slip distance,

γ is affected by the presence of flaws in the microstructure (e.g. needle-like precipitates lower γ).

σ_y is related to the state of precipitation (e.g. fine precipitation increases σ_y by precipitation hardening), and

σ_o is a structure sensitive factor (viz. BCC metals show a marked increase in σ_o with a drop in temperature).

In the discussion which follows the various metallurgical variables will be evaluated in terms of their effect on the factors in Equation 2.14.

2.1.4 Embrittling phenomena in ferritic stainless steels

Two recent and comprehensive reviews by Demo and Wright[4,3] have summarised the literature describing the 475°C sigma and high temperature embrittlement of stainless steels. This section draws mainly on their work and references, and merely highlights those points which have particular relevance to this research project.

2.1.4.1 Second phase effects inherent in the Fe-Cr system

(i) 475°C embrittlement

Prolonged exposure of ferritic stainless steels to temperatures in the range 400-500°C results in a drastic loss of ductility. The effect is most pronounced at temperatures of about 475°C.

Details of the changes in mechanical properties related to this phenomenon have been documented by many researchers. Kelly and Stoloff[23], experimenting with an Fe-26Cr alloy, found that exposure to 475°C for 5 hours had the effect of raising the Charpy V-notch transition temperature by at least 500°C. Newell[24] found that prolonged heating of a Fe-27Cr alloy at 475°C resulted in an increase in the tensile strength by 250MPa, an increase in the yield strength by 500MPa and a decrease in the percentage elongation from 35 to 0%. Some of Newell's results are shown in Figure 2.7.

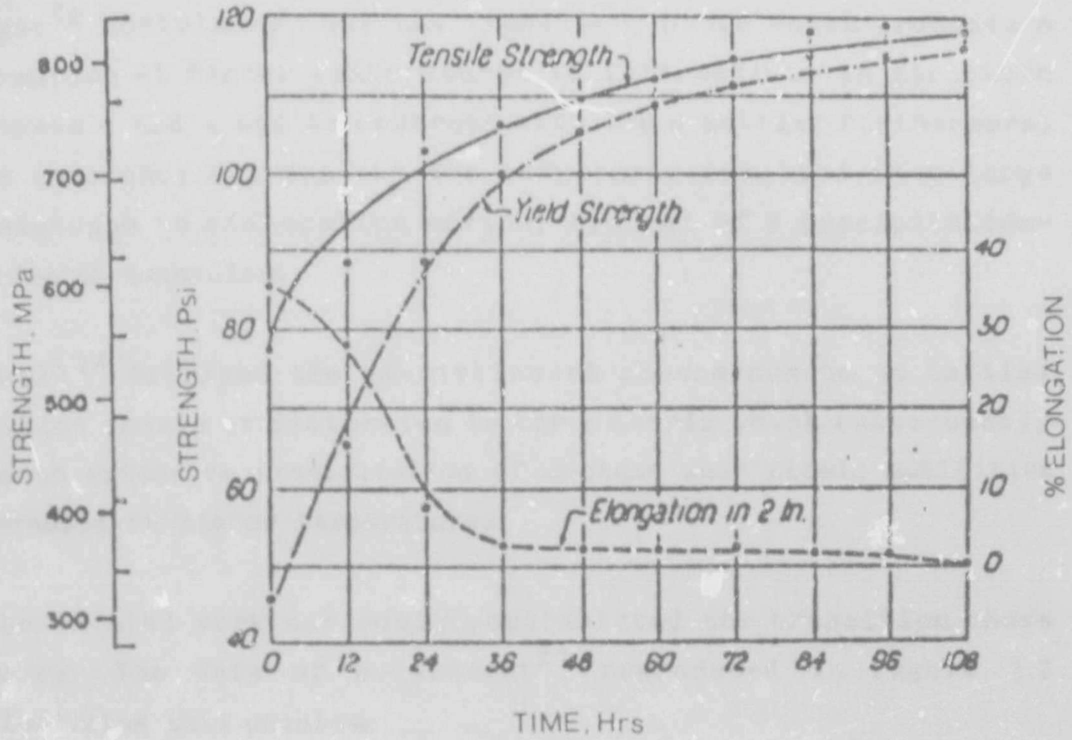


Figure 2.7 The effect of ageing time at 475°C on the room temperature tensile properties of an Fe-27Cr air-melted alloy[24].

Zapffe, Worden and Phebus[25] showed that embrittlement times for notched specimens were shorter than those for unnotched specimens. The results of bend tests on notched specimens of a 26Cr stainless steel indicated embrittlement after only a half hour exposure at 475°C.

There has been some controversy concerning the cause for the increase in strength and hardness and reduction in ductility at 475°C. The early theory of minor impurity precipitation proved untenable when alloying additions and prior heat treatment did not improve resistance to embrittlement[4]. Many early investigators[4] believed that 475°C embrittlement was related to the formation of σ-phase and it was reported that while no changes in lattice parameters were observed, atomic disturbances and grain boundary widening did occur. Heger[26] and Newell[24] formalised this theory. It was suggested that a chromium-iron alloy, heated in the embrittling range, underwent the reaction

$$\alpha\text{-phase} \longrightarrow \text{transition phase} \longrightarrow \sigma\text{-phase}$$

Heger[26] postulated that the transitory phase which precedes σ formation at higher temperatures is intermediate in structure between α and σ and is coherent with the α matrix. Furthermore, the coherency between the two structures resulted in a large resistance to dislocation motion, typical of a precipitation-hardening mechanism.

Newell[24] ascribed the embrittlement phenomenon to an initial lattice change or distortion in the α matrix which subsequently led to extensive precipitation of σ-phase when atomic mobilities increased at higher temperatures.

Experimental work seriously contradicted the transition phase theory. The data of Houdremont[27] reproduced in Figure 2.8 illustrates this problem.

In the narrow temperature range of 550-600°C alloys containing 17 and 28,4% Cr did not show any signs of hardening whereas significant hardening did occur in the 400-500°C and 600-900°C temperature ranges. Thus it is apparent that although 475°C embrittlement is inherent in the Fe-Cr system, it is not related to σ-phase formation.

Subsequently, two new hypotheses emerged[4]. The first attributed the 475°C embrittlement to atomic ordering, and the second postulated that it is a consequence of the precipitation of a Cr-rich BCC phase, α', which forms due to the presence of a miscibility gap in the Fe-Cr system. Despite numerous attempts, a superlattice has not yet been observed in Fe-Cr alloys and consequently the second hypothesis has been more widely accepted.

Williams and Paxton[28] were the first to explicitly propose the existence of a miscibility gap below the σ-forming region in the equilibrium diagram. The results of their work are shown in Figure 2.9.

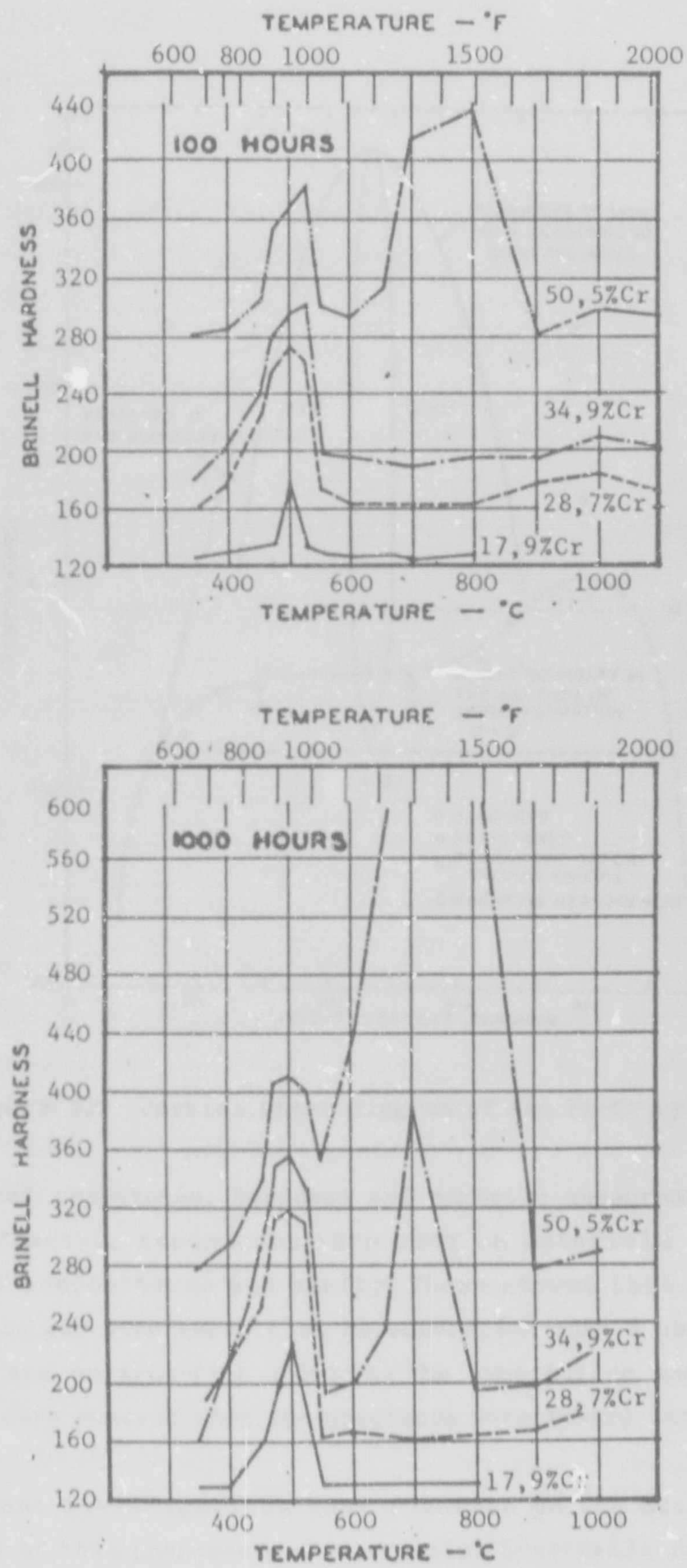


Figure 2.8 Effects of temperature and ageing time on the hardness increase caused by 475°C brittleness and sigma precipitation in several chromium-iron alloys[27].

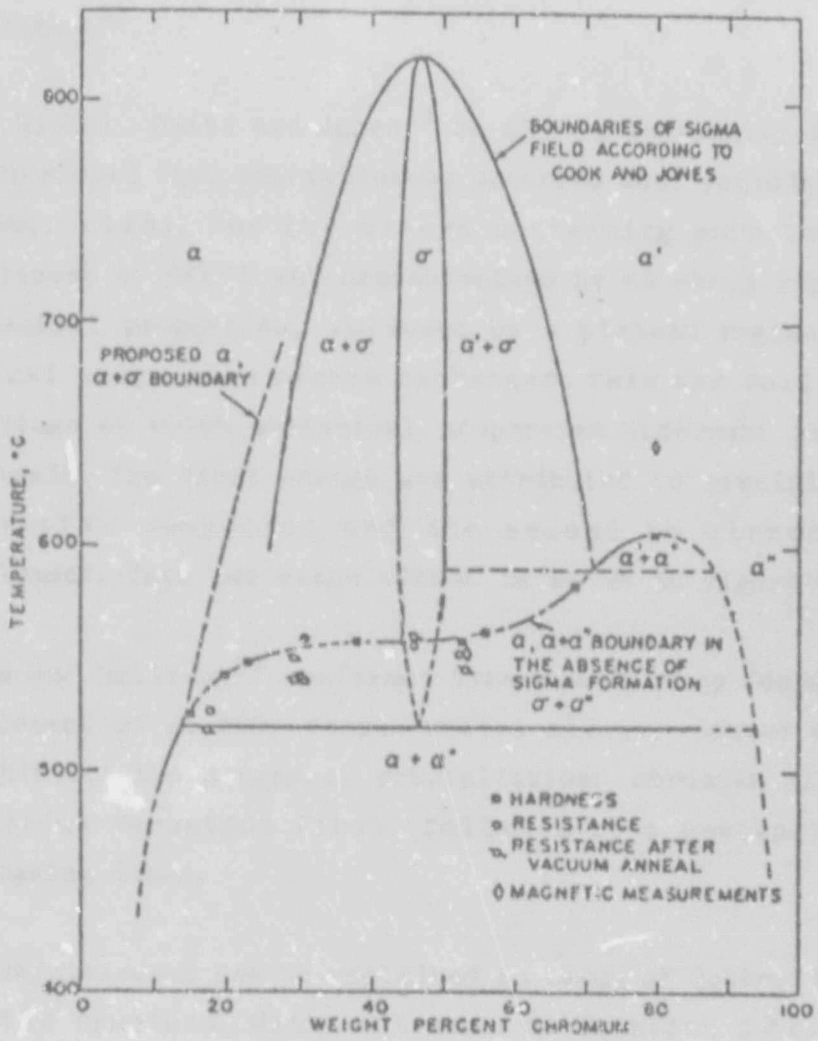


Figure 2.9 Partial phase diagram of the Fe-Cr system[28]

Electrical resistance, hardness and magnetic measurements, and X-ray diffraction techniques were used on materials with a wide range of compositions and purity. These showed that alloys aged within the gap were embrittled by separation into a chromium rich-ferrite and an iron-rich ferrite. The embrittling and separation effects were removed when the specimens were heated above 550°C[28].

Subsequent investigations have focussed on the mechanisms and kinetics of this phenomenon. For example, Courtnall, Pickering and Grobner[29,30,31] have shown that interstitials such as carbon and nitrogen, and to a lesser extent additions of molybdenum, niobium and titanium, accelerate this embrittlement. It has also been found that increasing chromium content also increases the rate of embrittlement[32].

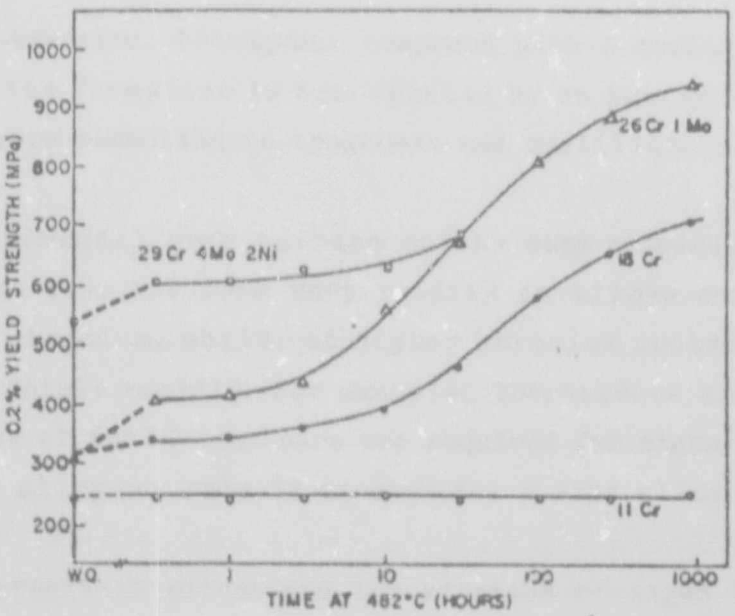
Work by Nichol, Datta and Aggen[32] on alloys containing 11, 18, 26 and 29%Cr showed that embrittlement occurred most rapidly at 482 °C in a 29%Cr alloy. For the alloys containing more than 11%Cr, embrittlement at 482 °C was characterised by an early rapid change in mechanical properties, followed by a plateau region in which mechanical properties remain unchanged. This was followed by a second stage at which mechanical properties underwent significant change again. The first change was attributed to precipitation of interstitial compounds and the second to classic 475 °C embrittlement. This two stage effect is shown in Figure 2.10.

Plumtree and Gullberg[33] confirmed this result. They found that the embrittlement of Fe-25Cr vacuum-melted alloys, heated at 475 °C, also exhibited two stages of precipitation: chromium nitride and carbonitride formation first, followed by α precipitation at longer ageing times.

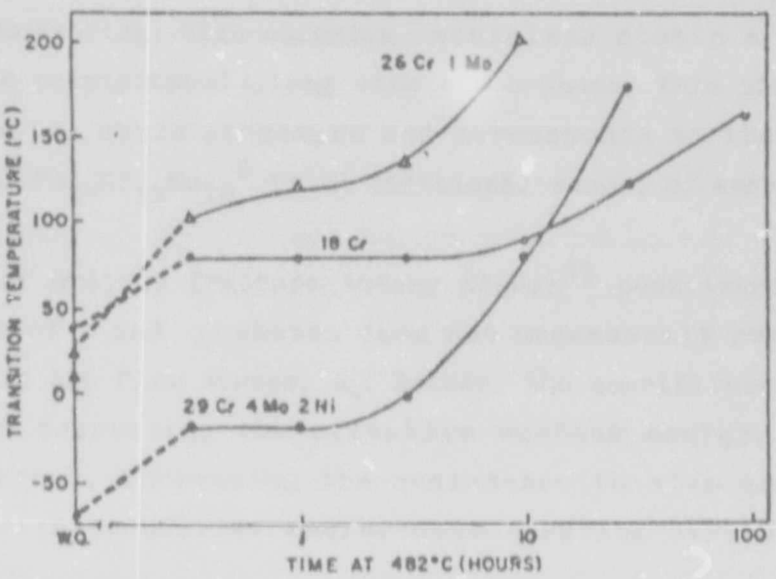
475 °C embrittlement can be explained in terms of Cottrell's theory of brittle fracture. With reference to Equation 2.14, Wright[8] suggested that the lattice friction stress, σ_o, is the principal variable affected by α precipitation. The precipitates lock dislocations and impede dislocation motion. The net effect is a large increase in σ_o.

(ii) Sigma phase embrittlement

Chromium stainless steels, including austenitics, may be embrittled by the precipitation of σ-phase in the range 500-900 °C. Pure σ forms at chromium contents between 42 and 50% while duplex structures containing both α and σ phases form in alloys with as little as 20 and as much as 70% chromium[4]. Although Chevenard[34] and Bain and Griffiths[35] suspected the existence of an intermetallic phase at 50%Cr in the Fe-Cr system as early as 1927, sigma was not positively identified until 1936[4]. Sigma phase is a



(a)



(b)

Figure 2.10 (a) Yield strength vs time at 482 °C. (b) Fracture appearance transition temperature (FATT) vs ageing time at 482°C[32].

hard non-magnetic, tetragonal compound with a nominal composition of FeCr. Its formation is accompanied by an increase in hardness and a severe reduction in toughness and ductility.

The experimental work carried out by many researchers indicates that sigma does not form very readily in alloys containing less than 20% chromium, while, at higher chromium contents formation proceeds fairly rapidly. For example, Shortsleeve and Nicholson[36] found that at 600°C ten hours was required for sigma precipitation in a 26Cr alloy but only 15 minutes for a 35Cr alloy.

In many practical situations the kinetics of sigma formation are even more rapid. For example, cold work which is necessary for grain size refinement, is known to increase the precipitation rate significantly. Alloying elements such as Mo, Ni, Mn and Si also affect the kinetics. They shift the σ-phase region to lower chromium contents and stabilise it such that longer holding times and higher temperatures are required for dissolution. In molybdenum-bearing, high-chromium stainless steels a chi-phase (χ) may be precipitated along with the σ-phase. This phase, which has a complex cubic structure and corresponds to the chemical formula of $Fe_{36}Cr_{12}Mo_{10}$[8] is an additional source of embrittlement.

In terms of brittle fracture theory Nichol[32] postulated that the formation of σ and χ phases does not necessarily result in an increase in the flow stress, σ_y. Rather, the embrittlement has the effect of decreasing the effective surface energy, γ, of an initial crack, increasing the resistance to slip propagation across grain boundaries and/or concentrating stresses in the matrix.

2.1.5 The role of interstitials in embrittlement

2.1.5.1 Interstitial precipitates: carbides, nitrides and oxides

The detrimental effects of carbon, nitrogen and oxygen [illegible]e toughness of ferritic stainless steels is well established. In 1951,[4] in a laboratory experiment, it was shown that vacuum-melted Fe-Cr alloys were ductile at room temperature if their interstitial impurity content did not exceed 0,003%C and 0,010%N. By 1970, industrial methods capable of purifying steels of interstitials had been developed and the production of low-interstitial stainless steels became commercially viable. Today, modern melting techniques such as vacuum oxygen decarburisation (VOD) and argon-oxygen decarbonisation (AOD), are well known and widely used. Fe-Cr stainless steels of enhanced purity and toughness are now produced and used in industries in the USA, West Germany, Japan and Sweden[4,38,39].

Prior to 1950, the reduced toughness of plain chromium steels with high chromium contents was associated with their high chromium content per se. It was generally considered that as the chromium content of a steel increased, its toughness decreased. In 1950, Joseph Hoffman[8,37] first described the astonishing increase in the toughness of high chromium steels which could be achieved when the interstitial element content was kept to a minimum.

Hoffman cited carbon, nitrogen and oxygen as the principal impurities contributing to low toughness in 25% chromium ferritic steels. The range of interstitial levels in his vacuum-melted alloys were carbon less than 0,003%: nitrogen 0,003 to 0,012%: and oxygen 0,002-0,006%. The interstitial content of any alloy,air or vacuum melted, also depended on the crucible used (alumina, beryllium or magnesia). Some of the data related to the use of different crucibles are shown in Table 2.1.

Table 2.1 The effect of crucible type on interstitial content[37].

Metal melted under vacuum	Carbon %	Nitrogen %	Oxygen %
Alumina crucible	0,002-0,003	0,005-0,008	0,002-0,003
Beryllia crucible	0,002-0,003	0,002-0,003	0,001-0,002
Magnesia crucible	<0,002	0,006	0,012

The vacuum-melted alloys had impact strengths ranging from 23kg/m/cm^2 to 34kg/m/cm^2 (225 - 330J), whereas the impact strengths of the air-melted alloys were much lower, less than 1kg/m/cm^2 (10J). When 0,03 to 0,04% carbon was added to the vacuum-melted alloys, it was found that the toughness advantage over the alloys melted in air was eliminated.

It was observed that the interstitials were deleterious to the toughness of the alloys under different conditions. When a steel was heat-treated at 900 °C for 30 minutes and quenched in water, nitrogen contents of 0,045 to 0,055% did not cause embrittlement. In contrast, following heat treatment at 1200 °C, the same alloy had a very low impact toughness.

Carbon additions showed a similar effect. When grain size was taken into account, only 0,023%C was required to decrease the toughness properties significantly after annealling at 1200 °C.

Oxygen was found to reduce notch-impact values after treatments at both 1200 °C or 900 °C.

Finally, hydrogen also seemed to have a deleterious effect equivalent to that of any of the other elements when carbon and nitrogen levels were at a few thousandths of a percent. Hoffman's results concerning hydrogen effects are, however, widely scattered due to control problems[37].

In a definitive work, Binder and Spendelow[37] studied the influence of carbon and nitrogen on the mechanical properties of a series of annealed, vacuum-melted and air-melted chromium steels with chromium contents ranging from 0,3 to 55%. It was found that for reasonable values of impact resistance, the requirements for low carbon and nitrogen become more stringent as the chromium content was increased. This concept is illustrated in Figure 2.11. It should be noted that the tolerance of a 40Cr alloy for carbon and nitrogen is less than 0,02% (i.e. less than 200ppm).

In this work it was assumed that carbon and nitrogen were equivalent with respect to their effects on toughness. This assumption was tested by preparing scatter plots, based on room temperature toughness measurements, in which the carbon and nitrogen contents of the steels tested appear as coordinates. One such plot for 24 to 26% Cr steels is shown in Figure 2.12. Because a straight line with a slope of 45° can be drawn to separate zones of high and low toughness, they concluded that their assumption was reasonable.

Binder and Spendelow did not find oxygen particularly detrimental to the toughness of their alloys. In addition Hoffman's experiments related to oxygen contents were repeated, but neither quenching from 900°C or 1200°C affected the toughness of their 25%Cr alloys. The oxygen contents of these alloys ranged from 0,016 to 0,12%. It was concluded that the discrepancy between these results and those of Hoffman could be related to the mode of occurrence of oxygen rather than the total oxygen content.

The 1950's and 1960's produced a large volume of work confirming the basic thesis of Hoffman, and Binder and Spendelow that low interstitial contents lead to good toughness properties in ferritic stainless steels. Some of the researchers examined the metallography of their alloys more closely and tried to relate the solution and precipitation behaviour of the interstitials to heat treatment procedures and the toughness properties of the alloys.

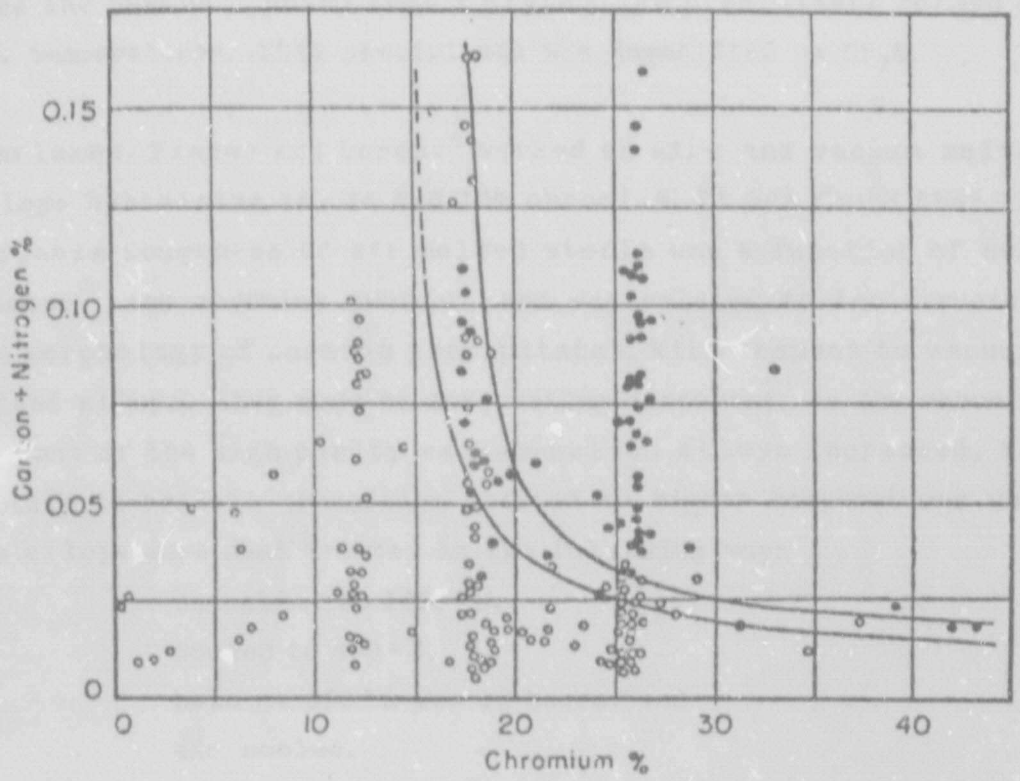


Figure 2.11 Influence of carbon and nitrogen on the toughness of chromium-iron alloys. Open circles - high impact strength alloys: solid circles - low impact strength alloys[37].

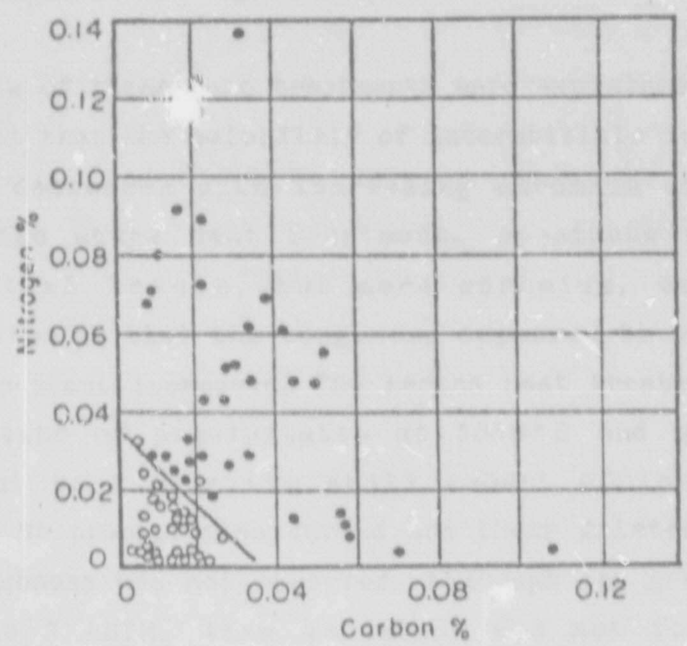


Figure 2.12 Effect of carbon and nitrogen on the toughness of 24 to 26% chromium-iron alloys. Open circles - high impact strength alloys: solid circles - low impact strength alloys[37].

Lena and Hawkes[40] noted that a plate-like precipitate formed at low temperatures. This precipitate was identified as Cr_2N.

Baerlaken, Fisher and Lorenz[6] worked on air- and vacuum-melted alloys containing 16, 20 and 30% chromium. It was found that the variable toughness of air melted steels was a function of heat treatment and chromium content, and was related to the structure and morphology of carbide precipitates. With respect to vacuum-melted alloys, they made an interesting discovery. As the chromium content of the high purity vacuum-melted alloys increased, the ductile-to-brittle transition shifted to higher temperatures when the alloys were heat treated in the following way:

annealled at 1050°C,
cooled to 800°C,
held at 800°C for 25 hours, and
air cooled.

However, when the same vacuum-melted alloys were reheated to 1050°C for 30 minutes and water quenched, excellent low temperature impact values were obtained for all the alloys. These results are shown in Figure 2.13.

The effects of these heat treatments were explained with reference to the fact that the solubility of interstitials in ferrite solid solution decreases with increasing chromium content. In the initial two stage heat treatment, specimens with the same interstitial levels, but more chromium, contained more precipitates so that the toughness appeared to decrease as the chromium content increased. The second heat treatment, involving the solution of precipitates at 1050°C and quenching, was sufficient to retain the small amount of interstitials in solution. No precipitates formed and their deleterious effect on notch toughness was not observed. Although the grain size varied from 1 to 3 ASTM, this variation was not found to affect toughness.

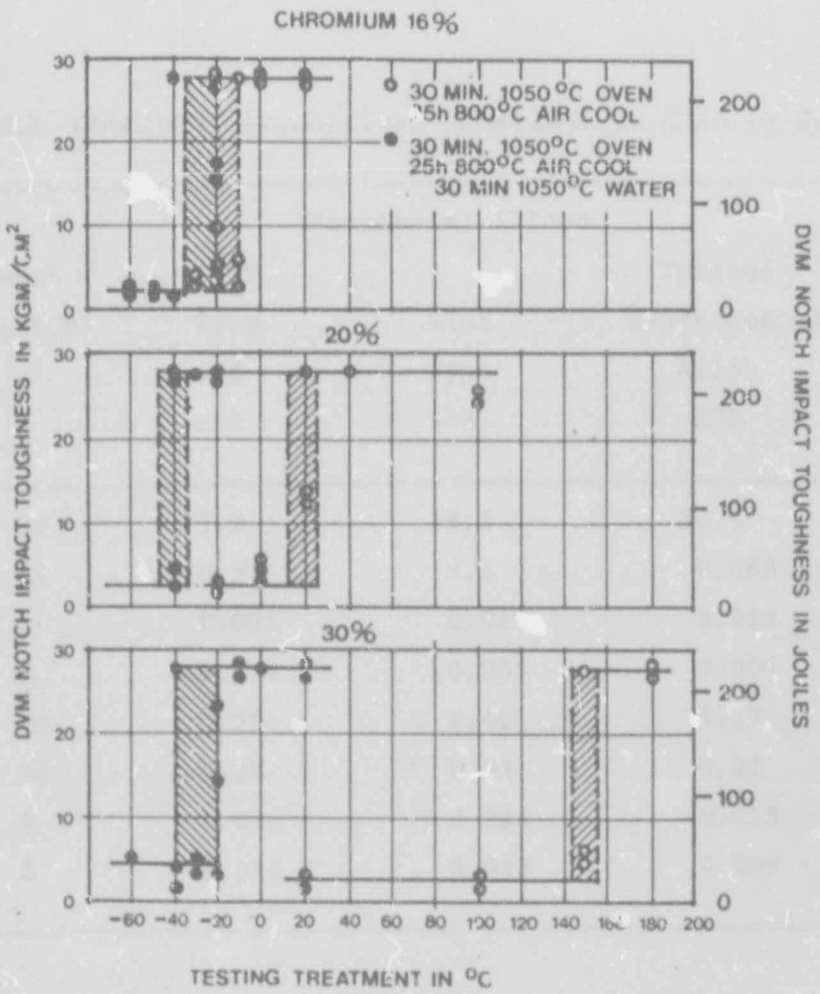


Figure 2.13 Effect of heat treatment on the position of the sharp drop of the notch impact toughness-temperature curve of vacuum-melted chromium steels with 16 to 30% chromium[6].

More recent research up to the present time has built on the work of Baerlaken et al[6]. The effects of heat treatment on interstitial behaviour at various concentrations has continued to be studied, and techniques such as transmission electron microscopy (TEM) and detailed studies of the fracture mechanisms have been utilised in an effort to understand and control the variables which affect the toughness of the new ferritic stainless steels.

Demo[41] has published a study on the effect of thermal treatments on the ductility (tensile elongation) of high and low interstitial purity alloys containing 18 and 26% Cr. The composition of the alloys are shown in Table 2.2.

Table 2.2 Chemical compositions of alloys studied by Demo[41].

Element (weight %)	Commercial Alloys: AISI Type 446 SA2	AISI Type 304	Typical Experimental Alloy E72
Cr	27,2	18,4	26,0
Ni	0,35	9,1	0,062
C	0,095	0,057	0,014
N	0,077	0,035	0,004
Mn	0,59	1,46	1,37
Si	0,28	0,43	0,92
P	0,016	0,025	0,015
S	0,013	0,013	0,009

The AISI Type 446 stainless steel which contained a high level of interstitials, showed a loss of ductility when heated to 1100°C and water quenched. The same alloy, when cooled more slowly from the high temperature exposure (i.e. air- or furnace-cooled) proved very ductile. The embrittled 446 alloy also showed excellent ductility after a second heat annealing treatment at 850°C. However, the ductility of the low interstitial alloy, E72 was not affected by heat treatment. These results together with those for AISI Type 304 are shown in Table 2.3.

Examination of the fracture surfaces showed that both the brittle water-quenched and the ductile air-cooled specimens exhibited intergranular fracture. Some localised deformation and elongation of a few grains was observed in the air-cooled specimens and the ductile slowly-cooled specimens showed failure in fibrous shear.

Since grain boundary precipitates were present in all the samples, it was concluded that grain boundary precipitates did not play a significant role in determining ductility. Thin film electron

Table 2.3 Effect of thermal treatments on the ductility of stainless alloys[41].

	Elongation (in 25,4mm) for the Indicated Stainless Steels After Heat Treatment		
Condition	AISA Type 446	High Purity[a] E72, 26Cr	AISI Type 304
Annealed	25	30	78
30 min, 1100°C, water quench	2	30	84
30 min, 1100°C, air cool	27	32	85
30 min, 1100°C, slow cool[b] to 850°C water quench	33	30	-
30 min, 1100°C, water quench + 30 min, 850°C, water quench	27	29	-
120 min, 677°C, air cool[c]	-	-	84

[a] 0,014% carbon, 0,004% nitrogen.
[b] Cooled in furnace at 2,5 °C/min.
[c] A heat treatment known to cause sensitisation in AISI Type 304.

microscopy revealed that unlike the air- and slow-cooled specimens, the brittle, water-quenched specimen had precipitates on nearly all the dislocations. It was proposed therefore that the precipitation of carbides and nitrides on dislocations within a grain, and not the precipitates at the grain boundaries, was responsible for the severe loss in ductility when the alloys were heated to high temperatures. The fine precipitates immobilised the dislocations and diminished the ability of a steel to deform.

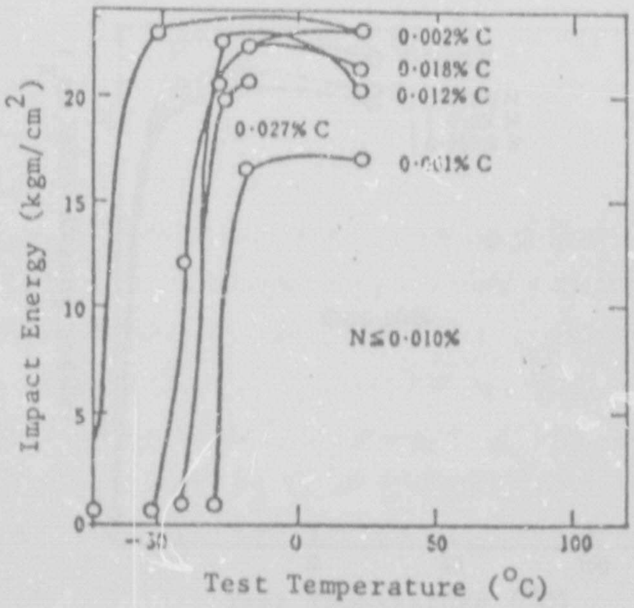
Semcheyshen, Bond and Dundas[42], in a subsequent study, determined the ductile-to-brittle-transition-temperatures for a series of ferritic stainless steels containing 14 to 28%Cr and various amounts of carbon, nitrogen, molybdenum and titanium. It was verified that the DBTT increased with increasing chromium content and a detailed investigation was carried out on the effects of varying carbon and nitrogen content in 17%Cr alloys.

Figures 2.14 (a and b) show the effect of carbon content on the impact energy absorbed by specimens of a 17%Cr alloy with nitrogen contents of up to 0,010%. The results shown in Figure 2.14a represent specimens which were annealed for 1 hour at 815°C and water quenched. In this case the increase in DBTT corresponding to increasing carbon content is small. When the same series of alloys was tested after heat treatment at 1150°C, the deleterious effect of carbon on impact properties was greatly accentuated (Figure 2.14b).

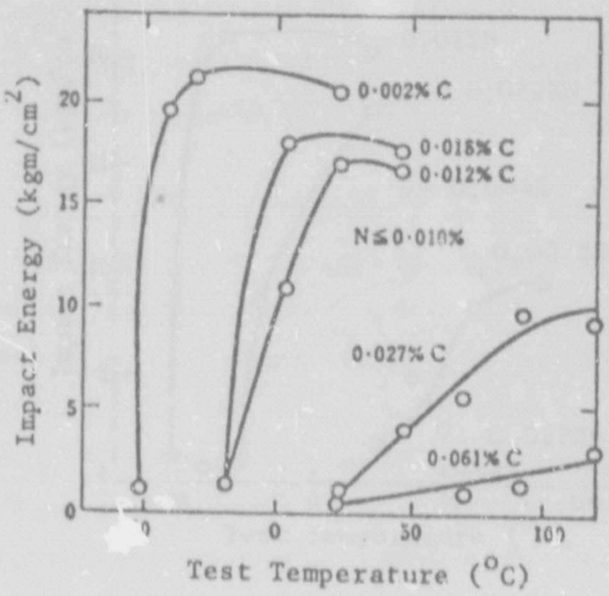
Tests on alloys with nitrogen at varying levels (with carbon less than or equal to 0,04%) showed a similar trend (Figure 2.15, a and b).

Examination of the microstructure and further heat treatment trials revealed that alloys containing only 0,01% carbon and/or 0,02% nitrogen contained grain boundary precipitates, while alloys of higher purity remained free of precipitates after quenching from above 925°C. X-ray diffraction and TEM diffraction analyses showed the precipitates were a mixture of $Mo_{23}C_6$ and Cr_2N.

Semcheyshen et al[42] postulated, in contrast to Demo[41], that embrittlement at high temperature was associated with the formation of grain boundary precipitates. However, the presence of untempered martensite in alloys which contain large amounts of



(a)



(b)

Figure 2.14 Transition curves for 1/4 - size Charpy specimens of a 17%Cr ferritic stainless steel with varying C contents. a) 815°C for 1 hour and water quenched, b) 815°C and 1150°C for 1 hour and water quenched[42].

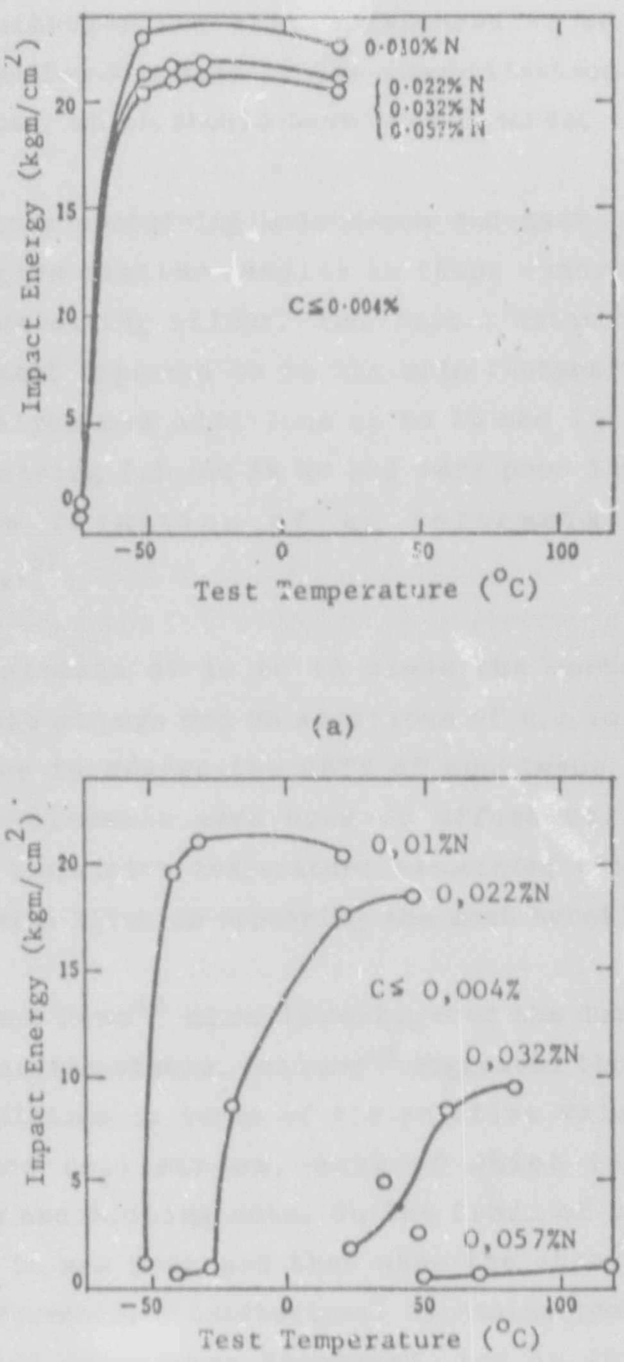


Figure 2.15 Transition curves for 1/4 - size Charpy specimens of a 17% chromium ferritic stainless steel with varying N contents. a) 815°C for 1 hour and water quenched. b) 815°C and 1150°C for 1 hour and water quenched[42].

carbon and nitrogen was also considered to be a contributing factor. No mention was made of the immobilisation of dislocations by precipitates, which should have been observed using TEM.

Tests on alloys containing molybdenum and heat treated at 815 °C and 1150 °C gave similar results to those observed for the non-molybdenum containing alloys, i.e. heat treatment and carbon and nitrogen content appeared to be the main factors which determined the DBTT. Molybdenum additions up to 2% had little effect, but alloys containing 3,5 and 5% Mo had very poor impact resistance due to the formation of an intermetallic compound $(Fe_{36}Cr_{12}Mo_{78})$[52].

Titanium additions of 10 to 12 times the carbon and nitrogen content of the alloys and Nb additions of 0,1 to 0,9% either had no effect, or increased the DBTT of specimens heat treated at 815 °C. Both elements were however effective in reducing the increase in transition temperature associated with heat treatment at 1150 °C, with titanium appearing the most beneficial.

Pollard[43] and Demo[44] also investigated the ductility of welded ferritic stainless steels. Pollard[43] suggested that weld ductility could be explained in terms of the relative values of yield (σ_y) and fracture (σ_f) stress, each of which is a function of composition and cooling rate. On the basis of tensile tests on weld metal it was proposed that when the chromium level of an alloy was increased, substitutional hardening took place. Thus, σ_y was increased and σ_f was decreased, and in this way the weld ductility was reduced. The effect of carbon and nitrogen depended on whether or not they were in solution. In solution they reduced the dislocation mobility and σ_y increased, while σ_f decreased. Precipitated carbon and nitrogen reduced σ_y and their effect on σ_f depended on the precipitate morphology. Pollard also demonstrated that the ductility of welded 26Cr and 35Cr stainless steels could be improved by Ti, Zr or Nb additions. The amount of Ti, Zr and Nb required, however, should be carefully assessed as they could also promote embrittlement when added in excess.