Chapter 1

Introduction

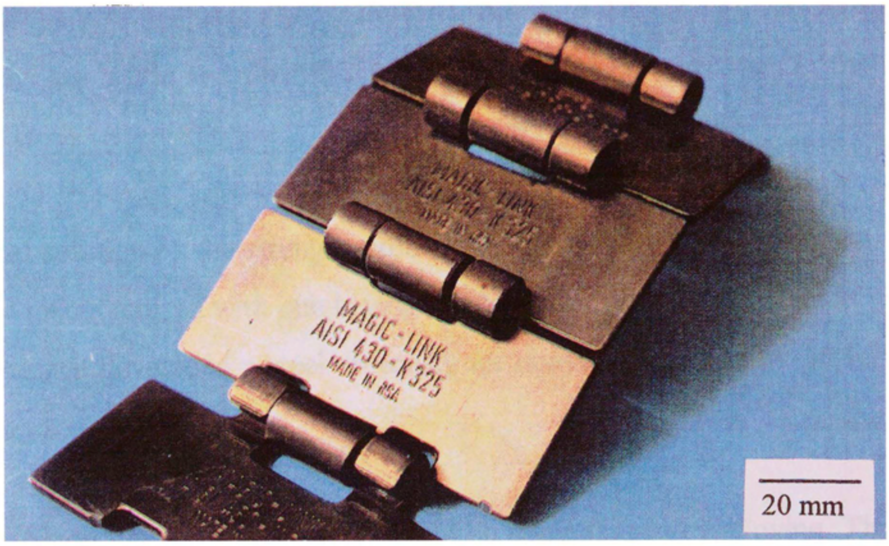

***Figure 1.1:** Slat band chain used as conveyor belt*

In places such as breweries and bottling plants conveyors are used to transport bottles between various stages in the operation. One type of conveyor is slat-band chains, which consist of flat links connected by pins through interlinking holes (figure 1.1). The chains are manufactured by hot rolling a sheet of the material, followed by annealing and then cold rolling it to its final thickness. The links are then formed through a blanking process.

Usually stainless steels are utilised for this application, and in 1990 some 5000 tons of stainless steel, including 2500 tons of the ferritic grade AISI 430, was used in Europe for the manufacture of these transporting lines (Charenton and Baltenneck 1992).

The properties required of a material used as a conveyor are a high tensile strength (ultimate tensile strength 850 to 950 MPa) for abrasion resistance, a high yield strength (0.2% yield strength 750 to 850 MPa) to withstand high tensile loads (for maximum possible conveyor length), good formability (as required for cutting and forming of 3mm thick sheet), together with intergranular and uniform corrosion resistance. These properties coupled with affordability are therefore key issues.

Thus far the steels employed were annealed and cold worked 430 (which is used to the limit of its mechanical properties), and cold worked 201 and 304, which perform satisfactorily, but are expensive. Martensitic stainless steels would be the most economical choice (Thielsch 1951, 1955), but they are brittle and their low formability would be a problem in the manufacturing process.

The traditional solution to the strength problem would be to replace the material from which the chains are manufactured with one having the desired properties. Charenton and Baltenneck (1992) for instance developed a steel especially for conveyors, with a 50-50 ferrite-martensite structure.

As another solution, the existing material could be strengthened by alloying. Though these are sure ways of obtaining the desired effect, they are not always practical, inasmuch as the material is manufactured as a process alloy through mass production, and it may not be economically feasible to produce special batches.

What would be acceptable then, is to find some way to strengthen the material already in use.

Mintek (Council for Minerals Technology) developed the unconventional way of strengthening the 430 by isothermally heating it between 450°C and 500°C after cold working. This temperature range is commonly known as the "475°C Embrittlement Temperature Range", as the effects occur most readily at 475°C. By carefully heat treating the cold worked 430 in this range, it was found that the hardness, yield strength and breaking load could be improved. This made the strength of the locally manufactured chain equal to or even better than any of the imported ones that are available.

The purpose of this study is to elucidate the strengthening mechanism, using type 430 stainless steel containing 16.42% Cr and 0.036% C.

In the manufacturing and treatment process there are several microstructural processes which affect the material properties. Some would cause hardening (or strengthening), while others would have just the opposite effect.

Therefore the following hypothesis was proposed: the mechanisms that could increase the strength of the material are deformation by cold work, strain aging, precipitation of carbides and/or nitrides, precipitation of the Cr-rich phase α'' and the presence of martensite in the structure. The mechanisms that could cause a decrease in strength include recovery and grain growth.

In this study, experiments were designed to establish whether these mechanisms are present and whether their effect can be quantified.

Chapter 2

Literature Survey

2.1. Material

2.1.1. Ferritic stainless steels

Background

Since the second decade of this century the use of stainless steels has been extensive. Austenitic stainless steels especially received much attention because of their excellent mechanical and corrosion properties. However, usage of ferritic stainless steels have been limited because of the comparatively poor toughness demonstrated by the conventional ferritic stainless steels such as Types 430 and 446. A major breakthrough for these steels occurred when it was discovered that by keeping the carbon and nitrogen contents sufficiently low, the toughness and ductility of the ferritic grades could be greatly improved (Sheppard and Richards 1987).

Since the ferritic stainless steels can now be more economically produced, because of improved steel refining practices such as AOD (argon-oxygen decarburisation) and VIM (vacuum induction melting) (Nichol *et al.* 1980), their use has increased considerably. Thus a major advantage of the ferritic stainless steels is their relative low cost.

Ferritic stainless steels are generally straight-chromium types containing from 11 to 30% chromium, with no other major alloying elements, having essentially a single phase bcc (body centred cubic) structure. Some of the grades can be more highly alloyed though.

Chromium is of course the basic alloying element and is added to improve the corrosion resistance of the material. Chromium has the additional effect of leading to either a ferritic or martensitic structure in the steel (Thielsch 1951). The minimum chromium content of stainless steel is about 12.7% while the upper limit of the composition is dictated by the possibility of the formation of the sigma phase. In general the common ferritic stainless steels contain less than 27% Cr (Brooks 1979).

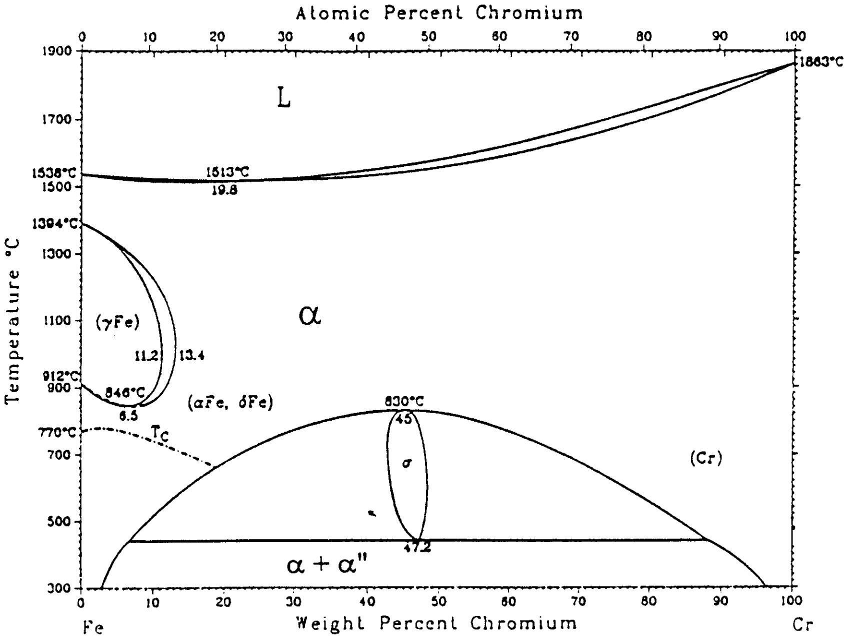

***Figure 2.1**: Iron - chromium phase diagram (Baker 1992)*

In a relatively pure binary solution of iron and chromium the material would be ferritic at most compositions and temperatures (figure 2.1). Because of the alloying elements present in stainless steels a much more complex structure results. With the addition of alloying elements such as C, N and Ni (austenite stabilisers) it is possible to enlarge the austenitic-loop to such an extent that austenite is formed at the customary annealing temperatures. The alloying elements can further retard the ferrite formation sufficiently for the austenite to transform to martensite on cooling (i.e. not having to quench). With alloying it is also possible to stabilise the austenite to such a degree that it is present at room temperature and that the M_s temperature (start of martensite) is below room temperature.

Carbon is the principal element which affects the amount of martensite which may be present. In the absence of other carbide formers (such as Ti and Nb), carbon tends to combine with chromium and iron to form the mixed iron-chromium-carbides M_7C_3 and $M_{23}C_6$. At elevated temperatures (up to 540°C), carbon somewhat improves the short time tensile properties and the creep resistance. Above 540°C, however, the carbides tend to coalesce (Thielsch 1951). The carbon content is restricted both to maintain high toughness and ductility and to prevent austenite formation related to the expansion of the gamma loop by carbon (Krauss 1989).

In its tendency to form austenite, nitrogen is almost as effective as carbon. Thus N widens the extent of the gamma loop considerably, particularly the two phase ($\alpha + \gamma$) region (Thielsch 1951). The nitrogen is detrimental to the corrosion resistance and the toughness as it does not stay in solution, but combines with other elements such as Cr. The nitrogen is therefore not added deliberately, but is picked up from the atmosphere during tapping and teeming processes.

Molybdenum is sometimes introduced for improved pitting and crevice corrosion resistance (Redmond and Miska 1982)

Of the standard ferritic steels typically only those with over 18% Cr are truly ferritic, that is, have a bcc delta ferrite structure at all temperatures below the solidus, and thus are not hardenable by a quench-and-temper heat treatment. The remainder form varying amounts of austenite on heating to elevated temperatures; the austenite transforms to martensite on cooling (Truman 1992).

In the absence of carbon and other austenite forming elements, the (austenite + ferrite)-region is very narrow (figure 2.1). With increasing carbon content the fully austenite region widens somewhat and is extended at 0.1%C to about 12.5% Cr. The two phase region is widened considerably more to about 18% Cr. Effects similar to those produced by carbon are produced by other austenite forming elements such as N, Ni and Mn. The ferrite formers, on the other hand, tend to reduce the extent of the gamma loop. These include elements such as Al, Si and Mo (Thielsch 1951).

A pseudo-binary phase diagram was constructed which takes into account the effect of carbon (at a fixed chromium content) on the austenite-loop - figure 2.2. It is indicated by this diagram for instance, that solution treatment at 930°C (for a steel containing 16.4% Cr and 0.05% C, i.e. the one investigated) would result in a three phase structure, namely ferrite, austenite and (Fe,Cr)-carbides (see also section 6.1.1).

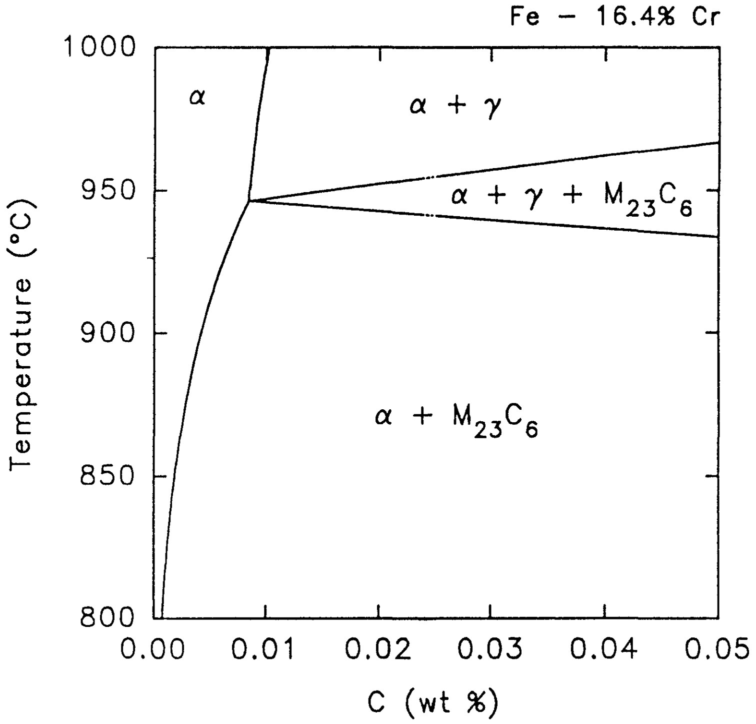

***Figure 2.2**: Pseudo Binary phase diagram at 16,4% Cr (Pistorius and Coetzee 1996)*

In these steels the microstructure-property relationships are important, but by no means simple, because (Truman 1992):

(a) the ferrite commonly contains polygonised sub-grains which influence the yield stress but not the ductile-brittle transition temperature,

(b) the structures often include martensite regions, or tempered martensite, originating from austenite present at the solution treatment temperature. Increasing amounts of austenite cause a progressive grain refinement of the ferrite, due to a second phase pinning effect,

(c) substitutional-interstitial interactions can occur which markedly influence solid solution strengthening,

(d) many interstitial and substitutional solutes have pronounced embrittling effects, increasing the ductile-brittle transition temperature, and

(e) pronounced embrittling effects, produced by precipitation of α" and sigma phase, can occur in certain heat treatment conditions.

In general the mechanical properties of the ferritic grades do not match those of the austenitic steels, but they are being increasingly utilised where the combination of cost and corrosion resistance is the prime selection criterion (Sheppard and Richards 1986).

Ferritic stainless steels are magnetic and can be cold-worked or hot-worked, but they develop their maximum softness, ductility and corrosion resistance in the annealed condition. In this condition the strength of these steels is approximately 50% higher than that of carbon steels, and they are superior to the martensitic stainless steels in corrosion resistance and machinability (M.B. Cortie, personal communication).

In comparison with low-carbon steels, the conventional ferritic stainless steels, such as type 430, exhibit higher yield and tensile strengths, as mentioned, but low elongations; thus they are not as formable as the low-carbon steels. Low levels of sulphur and silicon promote good formability of the ferritic types, because inclusions can act as initiation sites for cracks during forming (Redmond and Miska 1982).

A notable problem with this type of stainless steel is that its impact properties are sensitive to the ferrite grain size. This is a problem in body-centred cubic alloys, and in the ferritic stainless steels the grain size can be controlled only by cold working and annealing. Thus prolonged heating at high temperature will cause grain growth, and hence lower the impact resistance. This can be a problem particularly in welding, where the cast structure or the heat-affected zone may contain large grains which cannot be altered if the fabricated part cannot be cold worked and annealed. To minimise this problem a second phase (e.g. carbides or austenite) may be required at high temperatures to retard grain growth (Brooks 1979).

Generally, toughness in the annealed condition decreases as the chromium content increases. The grain growth and relatively low toughness at low temperatures have limited the use of ferritic stainless steels in structural applications. As a result, ferritics are used for nonstructural applications that require good resistance to corrosion and bright, highly polished finishes.

As a class the ferritics are highly resistant to chloride-induced stress-corrosion-cracking (Redmond and Miska 1982).

An advantage of these steels is that the solubility of carbon and nitrogen at the normal annealing temperature of 800 to 850°C is very low (figure 2.1) so that precipitation and homogenisation are largely completed by such a treatment, and there is no detrimental effect on the corrosion resistance should the steels subsequently be heated for moderate periods at lower temperatures. However, heating to temperatures above 925°C reduces the corrosion resistance and the corrosion is usually intergranular (Truman 1992). At these temperatures the solubility of the carbon is sufficiently high for chromium carbides to be precipitated, on cooling, at the ferrite grain boundaries. Intergranular corrosion results from this precipitation, as it produces local Cr impoverishment (sensitisation) and thus preferential corrosive attack. This problem can be overcome by annealing at 650 to 850°C, which allows Cr diffusion into the depleted regions, or stabilising the steel by additions of Nb or Ti to prevent the precipitation of Chromium carbides (Pickering 1979).

It is commonly believed that these steels cannot be hardened by heat treating, and only moderately so by cold working. This, however, is not invariably true, and carefully controlled heat treatment can give higher hardness and sometimes higher toughness (M.B. Cortie, personal communication).

Embrittlement

Ferritic stainless steels are prone to the following types of embrittlement:

475°C embrittlement

This type of embrittlement will be discussed in detail in section 2.2.4.

Sigma-phase precipitation

Sigma phase is an intermetallic compound of Fe and Cr, with approximately equi-atomic composition. It appears as a hard, highly brittle, nonmagnetic phase exhibiting a tetragonal unit cell in certain chromium steels (Rajkay 1967). The maximum temperature at which this form of embrittlement can occur depends on Cr content; and is approximately 620°C for a 17% Cr steel (Lena and Hawkes 1954), it is also indicated by the Fe-Cr phase diagram (figure 2.1).

In most alloys the rate of sigma formation is very slow (10^3-10^4 hours for a 18% Cr steel (Folkhard 1984, p.130)), but cold work has been shown to enhance the formation. It deteriorates both notch toughness and corrosion resistance (Rajkay1967, Mashimo *et al.* 1985).

High temperature embrittlement

This phenomenon seems to be structure-dependent, as it appears in the completely ferritic matrix (usually at temperatures higher than 1150°C) as soon as the carbides are in solution; and is apparently caused by the failure or inability of the carbides to reprecipitate during the cooling process (Rajkay1967).

It is accompanied by severe grain growth, although a large grain size alone will not account for the embrittlement: it appears that the severity of the high temperature embrittlement depends on carbide solution and not on grain growth (Thielsh 1951). The solution of carbides not only promotes subsequent grain growth, but the carbon in the matrix that is obtained in this way is not uniformly distributed in the ferrite lattice. The carbon is grouped in atomic clusters, as suggested by the segregation or coherent state theory. These carbon clusters cause the embrittlement (Demo 1971).

The embrittlement is especially pronounced with high cooling rates but the detrimental effects can be removed by annealing between 730°C and 790°C. This will, however, not reduce the excessive grain size. The detrimental effects can be prevented by retention of some austenite at carbon-solution temperatures, or by stabilisation of the carbides (Thielsch 1951 and 1955, Rajkay 1967, Demo 1971).

2.1.2. Type 430 Ferritic Stainless Steel

Type 430 has about 17% Cr and is a general-purpose grade. It has good drawing properties due to its low rate of work hardening, as well as good ductility and corrosion resistance to atmospheric conditions. It is used frequently for automotive trim, nitric acid tanks, annealing baskets and other such applications in which weldability is not a requirement. It is also used increasingly for domestic sinks, kitchen utensils and cutlery.

The composition range of 430 ferritic stainless steel is given in Table 1 (Redmond and Miska 1982):

Table 2.1: *Composition of type 430*

Element	C	Mn	Si	Cr	P	S
Weight%	0.1*	1*	1*	16 - 18	0.04*	0.03*

* maximum values

The specific composition of the material studied in this investigation will be given in Chapter 3.

2.2. Strengthening Mechanisms

The two main ways to strengthen ferritic stainless steels are cold work, and solution treatment and aging. These are discussed in more detail.

2.2.1. Cold Work

When a metal is plastically deformed at temperatures that are low relative to its melting point, it is said to be cold worked. The temperature defining the upper limit cannot be expressed exactly, for it varies with composition as well as the rate and amount of deformation (Reed-Hill 1992).

Cold work distorts the grains and causes a persisting deformation of the crystalline structure of the metal (increase in dislocation density), as recrystallisation does not occur simultaneously with the plastic deformation (unlike hot working). The stress needed to continue the process of cold working increases with increasing degree of deformation (work hardening), as is illustrated in the true stress - true strain curve (figure 2.3).

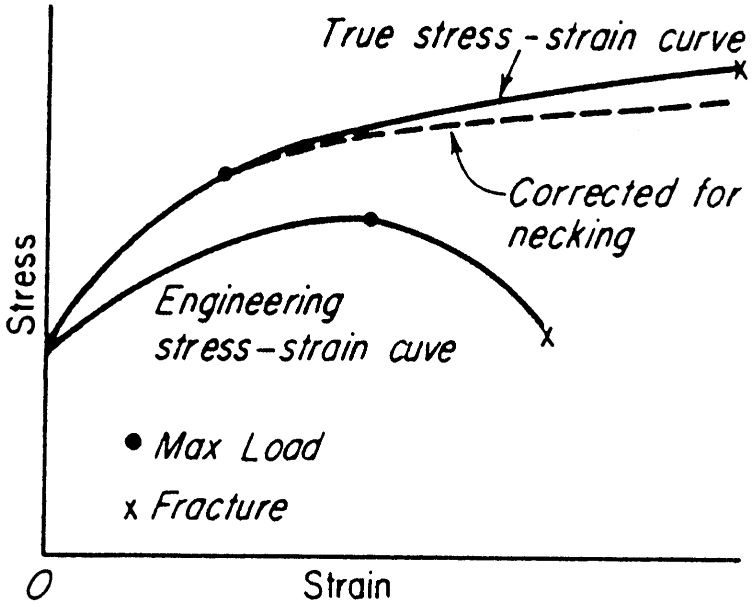

***Figure 2.3**: True stress-true strain curve (Dieter 1988, p.285)*

All the properties of the metal that are dependent on the lattice structure are affected by this plastic deformation. Tensile strength, yield strength and hardness, as well as electrical resistance, increase after cold work. Ductility is lowered by the increase in the number of dislocations. Certain planes in the crystal structure become severely distorted (Dieter 1988, pp. 229-231).

Every metal shows a certain amount of elongation before it breaks. During cold work some of this elongation is consumed, reducing the available ductility. In general, heat treatment after cold work produces recovery or recrystallisation and a subsequent lowering in hardness, with restoration of ductility.

Most of the energy expended in cold work is converted to heat, but a finite fraction is stored in the metal as strain energy associated with the various lattice defects created by the deformation. The amount of energy retained depends on the deformation process and a number of other variables, such as composition of the metal and rate and temperature of deformation.

The fraction of the energy that remains in the metal can be up to as much as 10% (Reed-Hill 1992, pp. 227-228).

It had been shown that the stored energy increases with increasing deformation, but at a decreasing rate, so that the fraction of the total energy stored decreases with increasing deformation. The amount of stored energy can be greatly increased by increasing the severity of the deformation (as mentioned), lowering the deformation temperature and by changing the pure metal to an alloy.

The increase in internal energy, particularly at the grain boundaries, renders the material more susceptible to intergranular corrosion; stress corrosion cracking can occur due to residual stresses.

Cold working, as said before, greatly increases the number of dislocations in a metal. Since each dislocation represents a crystal defect with an associated lattice strain, increasing the dislocation density increases the strain energy of the metal.

2.2.2. Solution Treatment and Aging

Solution treatment and aging can be used as a strengthening procedure in an alloy where the solubility of the alloying element increases significantly with increasing temperature. The solubility of carbon in 430 is a case in point - figure 2.2.

In the most simplistic approach, if an alloy is solution treated, i.e. reheated to the single phase region, all excess of the second phase will be dissolved and the structure will be a homogeneous solid solution. If the alloy is then rapidly cooled (quenched) to room temperature, a supersaturated solution results with the excess elemants which form the second phase trapped in solution. This is an unstable state and the excess solute will tend to come out of solution.

The rate of precipitation, when a solution treated alloy is aged, varies with temperature (figure 2.4).

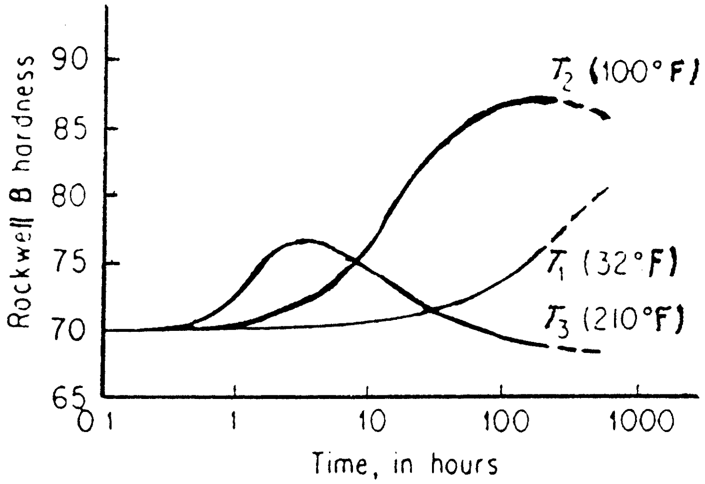

***Figure 2.4**: The influence of temperature on precipitation (Avner 1992)*

At low temperatures (represented by T_1) the diffusion rate is so low that no appreciable precipitation occurs. At high temperatures (T_3) hardening occurs quickly, due to rapid diffusion, but softening effects are also accelerated, resulting in a lower maximum hardness. The optimum temperature is where maximum hardening occurs within a reasonable length of time.

In the early theory of the aging process, it was thought that the excess phase comes out of solution as fine submicroscopic particles, many of which form on the slip planes. These particles were thought to have a keying action, thereby interfering with movement along planes of ready slip, thus increasing strength and hardness. Subsequent studies showed that the strengthening of a heat treatable alloy by aging is not due merely to the presence of the observable precipitate, but also to both the uniform distribution of a finely dispersed submicroscopic precipitate and the distortion of the lattice structure by those particles before they reach a visible size.

The coherent lattice theory is widely accepted as one mechanism by which these second phase particles harden the matrix: after solution treatment and quenching the alloy is, as mentioned before, in a supersaturated condition, with the solute atoms distributed at random in the lattice structure (figure 2.5a).

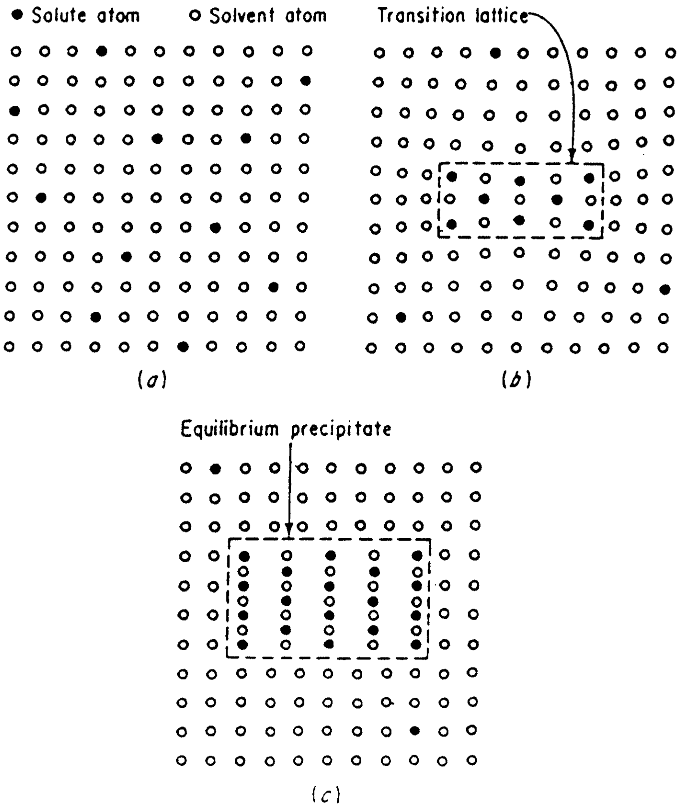

Figure 2.5: Schematic diagram of a lattice structure consisting of two elements (Avner 1992) (a) solution treated, (b) aged to form coherent precipitate and (c) overaged to form equilibrium precipitate

During an incubation period, the excess solute atoms tend to migrate to certain crystallographic panes, forming clusters or embryos of the precipitate. With aging, these clusters form an intermediate crystal structure or transitional lattice, maintaining coherency with the lattice structure of the matrix.

In most cases the excess phase will have different lattice parameters from those of the solvent, and as a result of the atom matching (coherency), there will be considerable distortion of the matrix (figure 2.5b). This distortion extends over a larger volume than would be the case if the excess phase were a discrete particle. It is this distortion that interferes with the movement of dislocations and accounts for the rapid increase in hardness and strength during the aging process.

Eventually, the equilibrium excess phase is formed with its own lattice structure (figure 2.5c). This causes a loss in coherency with the matrix and accordingly less long distance distortion.

The material properties are not only affected by the aging temperature, but also by the time held at temperature. Figure 2.6 gives a schematic illustration of the effect that aging time has on the most important mechanical properties.

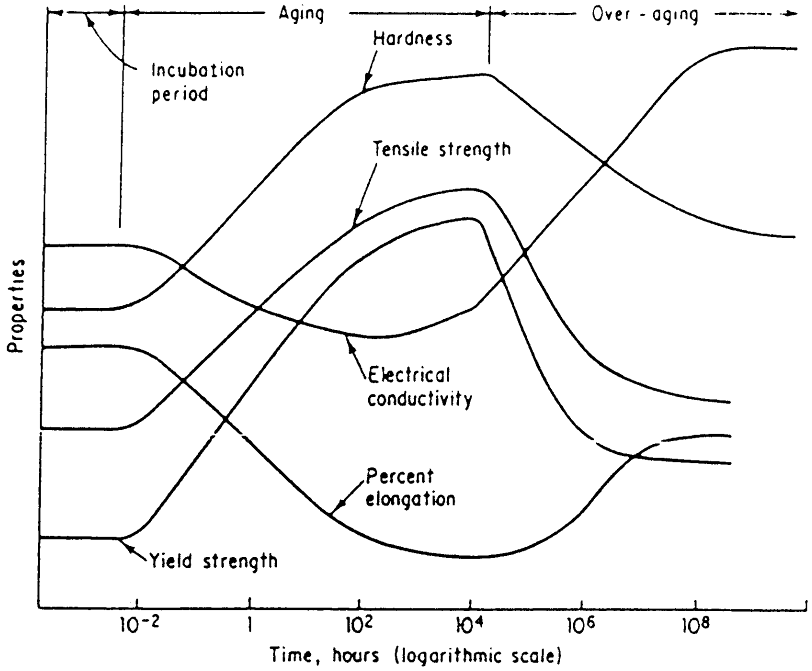

***Figure 2.6.**: Effect of aging time on mechanical properties (Avner 1992)*

2.2.3. Fine Particles

It was mentioned in the previous section that fine coherent particles can cause strengthening by producing local strain fields in the matrix and their influence on dislocation movement. Coherent and noncoherent particles can further induce strengthening through *their* effect on dislocation motion.

Coherent precipitates can act as particles through which dislocations can pass, but only at stress levels much above that required to move dislocations through the matrix phase. The dislocation-particle interactions cause an increase in strength.

Noncoherent precipitates can also be strong impenetrable particles where an increase in strength is obtained by the shear stress required to bow a dislocation line between two particles - the Orowan mechanism. As dislocations pass around the particles, dislocation loops are left around each particle, leaving the original dislocations free to move on. The dislocation loops exert a back stress on dislocation sources which must be overcome for additional slip to take place. This results in an increase in shear stress (Dieter 1988, pp 215-219).

This strengthening mechanism is typical of hard particles, such as carbides, and the strengthening effect of these particles becomes greater as the size of the particles decreases.

2.2.4. 475°C Embrittlement

Another, unconventional way to strengthen a material is to embrittle it. In most cases embrittlement operates on the same principle as the classic precipitation hardening where dislocation motion is impeded or arrested - causing an increase in strength. As mentioned before, ferritic stainless steels are prone to four main types of embrittlement, one of which - 475°C embrittlement - was used in the strengthening treatment applied to the original chains.

Background

Early work showed that when Fe-Cr alloys containing between 13 and 90% Cr are held in or slowly cooled through the temperature range 800-400°C hardening accompanied by embrittling occurs. In this, two distinct reactions are involved: the formation of the hard and brittle sigma phase (at high temperatures) and the Cr-rich precipitate known as α'' in the lower temperature regions (Newell 1946, Blackburn and Nutting 1964).

This latter type of embrittlement was noted after the steels have been exposed to temperatures between 371°C and 550°C. The embrittlement can occur during manufacturing of the steels, with handling of primary or intermediate product forms such as ingots, slabs and hot-rolled coils, or during fabrication of finished products where welding is necessary (Plumtree and Gullberg 1976, Nichol *et al.* 1980).

As this embrittlement affects the mechanical properties, it is usually thought of as detrimental and thus worthwhile avoiding.

Proposed Theories

At first several theories were advanced to account for the embrittlement observed with aging at the lower temperatures. These include the precipitation of minor phases such as carbides, nitrides, oxides (Blackburn and Nutting 1964) and phosphates (Lena and Hawkes 1954) and the formation of a series of super-lattices (ordering) based on Fe_3Cr and FeCr (Williams and Paxton 1957; Marcinkowski *et al.* 1964).

Theories of this kind, however, have difficulties accounting for the influence of alloying elements on the embrittlement, for the fact that a minimum Cr content is necessary for embrittlement, as well as that the intensity of embrittlement increases with Cr content. Grobner (1973) demonstrated through the construction of a free energy diagram of the iron-chromium system at 482°C that ordering processes cannot be responsible for this phenomenon; the free energy diagram contains the local maximum which is typical of alloys which exhibit immiscibility.

The formation of a transition phase prior to the formation of equilibrium sigma phase was also suggested as a possible explanation for the embrittlement (Williams and Paxton 1957). Several factors have, however prevented the complete acceptance of this theory. Foremost is that the embrittlement can be removed by reheating for short periods above 600°C, which in the higher Cr steels, is well within the stable sigma region. No sigma has ever been observed after one of these curing treatments, nor has any sigma been found as a result of embrittlement at 475°C. In addition, the simple precipitation of the sigma phase cannot explain the time-temperature relationship for reactions between 350°C and 750°C. Lena and Hawkes (1954) proposed a schematic time-temperature dependence diagram for the formation of σ and 475°C embrittlement (figure 2.7), which indicate these to be quite separate processes.

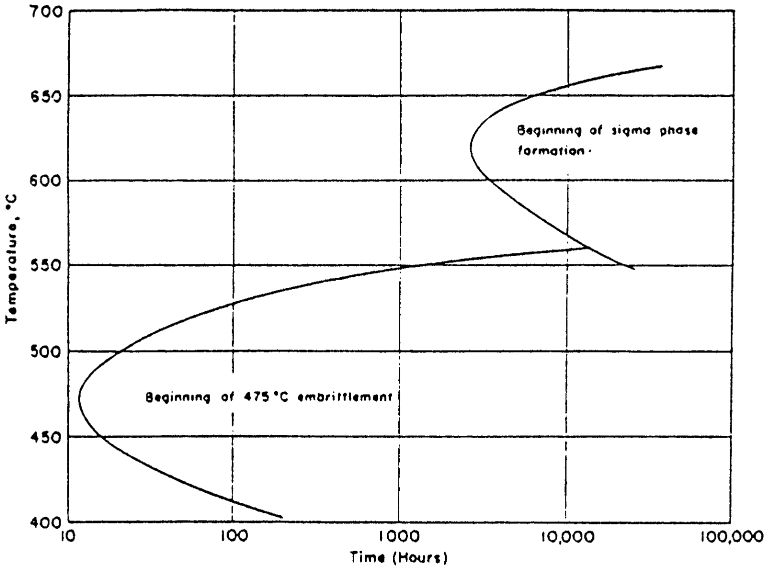

Figure 2.7: Schematic time-temperature dependence diagram for the formation of sigma phase and 475 °C embrittlement (arbitrary alloy) (Lena and Hawkes 1954)

The most widely accepted theory for the 475°C embrittlement is the one first proposed by Williams and Paxton (1957), namely the precipitation of a coherent Cr-rich phase, α". It is an aging or precipitation hardening phenomenon, where precipitation occurs because of a miscibility gap in the Fe-Cr system.

Stages in the embrittlement process

It was found that the 475°C embrittlement was actually a two stage process. Hardness and strength increase rapidly in the early stages of aging was observed, followed by a plateau region and then a relatively large increment after long periods of aging (Plumtree and Gullberg 1976, Nichol *et al.* 1980, Golovin *et al.* 1992).

The initial increase (at short aging times) is ascribed to the precipitation of Cr-rich carbides and nitrides at and near grain boundaries and at inclusions and dislocations. The precipitates were identified as $M_{23}C_6$ and Cr_2N (Blackburn and Nutting 1964, Marcinkowski *et al.* 1964, Lagneborg 1967).

The influence of α" precipitation seems to come into effect only after longer periods of aging (several hours, even days), and it is believed that the rate of α" formation is much lower than the precipitation of carbides and nitrides, because the interstitial atoms have relatively high diffusivities (Chun and Polonis 1992, Golovin *et al.* 1992). This argument assumes that the formation of α" is governed by the growth rate of the particles, whereas it may well be that the nucleation rate is the determining factor.

Interstitial elements

The two most important interstitial elements are carbon and nitrogen. Both form interstitial solid solutions in ferrite and the atomic radii and weights of the two are nearly the same (Binder and Spendelow 1950).

Carbon solubility is considerably lower than that of nitrogen at temperatures below 982°C and is approximately 0.004% at 900°C, where the kinetics of carbide formation are so rapid that it is impossible to prevent completely carbon precipitation, even by water quenching (Pollard 1974).

Carbon has three hardening effects: a straining effect in solid solution, dispersion hardening by precipitation of carbides (Orowan mechanism) and an increase in nucleation of α" because of the mechanical straining effects of the precipitated carbides (Tisinai and Samans 1957).

It was demonstrated that for good room temperature toughness, ductility and impact strength, as well as resistance to intergranular corrosion, the interstitial content must be reduced with increasing Cr content - for an 18% Cr steel of high toughness the maximum interstitial content, which still allows acceptable toughness, is approximately 0.055% (Binder and Spendelow 1951, Grobner 1973, Aggen *et. al.* 1978, Chun and Polonis 1992).

The interstitials have a two-fold effect on 475°C embrittlement: as precipitates they cause strengthening, and they influence the precipitation of the α". Precipitates of carbon and nitrogen below 500°C appear to consist of little more than clusters of C and N on the {100} planes of the ferrite (Cortie 1995). These precipitates or clusters are surrounded by intense strain fields, and exert a hardening and embrittling effect on the microstructure. There are some controversy as to the precise effect the interstitials have on α" formation. Some investigators reported an enhancement in precipitation, because of the local strain fields surrounding the carbide and nitride precipitates; while others reported significant retardment in the development of α" formation (Cortie 1995).

α" precipitate

Precipitation

Convincing proof was found for the existence of a region in the Fe-Cr system where the iron and chromium atoms are not randomly distributed on the bcc crystal lattice, but separate and cluster (Krause 1989). This necessitated a modification to the central portion of the FeCr phase diagram - figure 2.8 - to include the miscibility gap.

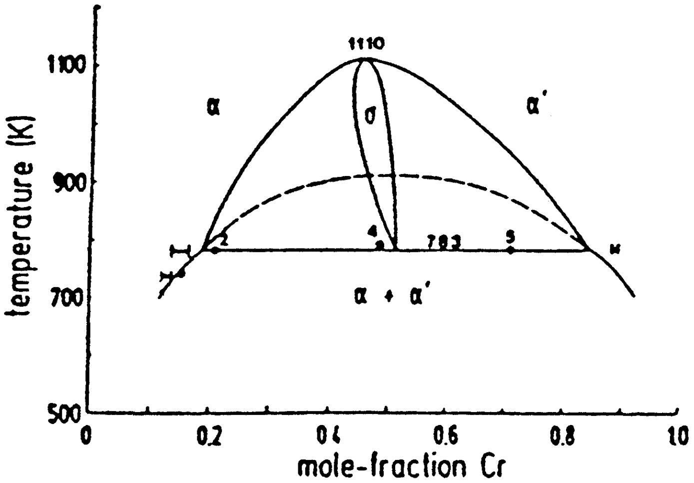

***Figure 2.8**: Thermodynamic assessment of the Fe-Cr system (Dubiel and Inden 1987)*

This region is formed due to the thermodynamic qualities of the Fe-Cr system rather than to basic structural distinctions. Consideration of the thermodynamic properties of regular solutions with positive heats of mixing leads to the conclusion that in such a system a critical temperature must exist above which the components are completely miscible, and below which the system consists of a mixture of two solutions, one rich in component A and the other in component B - in this case Fe and Cr (Grobner 1973, Trindade and Vilar 1991).

The phase diagram proposed by Williams indicates that in alloys with 14 to 18% Cr, formation of the α" phase can be expected at temperatures up to about 516°C and that it can be completely redissolved at temperatures higher than this. The lower temperature limit of this embrittlement is evidently determined by the kinetics of the α" formation. The kinetics are those of two partially parallel processes: that of nucleation, and growth of the nuclei. That is to say the nucleation process of new α" centres continues while growth of the initial nuclei occurs.

Chemical and/or magnetic energies are considered to be responsible for this miscibility gap rather than strain energy or valency effects. The miscibility gap is connected by an eutectoid reaction to the region where sigma phase is stable and the eutectoid temperature for the decomposition of α into the Fe- and Cr-rich regions lies within the interval 500°C to 532°C (Williams and Paxton 1957, Dubiel and Inden 1987).

The miscibility gap contains what is known as a spinodal. The spinodal is the locus of points for which the second derivative of free energy (G) with composition (c) equals zero. In the region where the mechanism of nucleation and growth prevails, $d^2G/dc^2 > 0$ and the resultant activation energy restricts decomposition to nuclei of a critical size and a composition very near the equilibrium values given by the miscibility gap solubility boundaries. Below the spinodal $d^2G/dc^2 < 0$ (i.e. no internal stability) and no activation energy for growth exists, so the decomposition is governed by diffusion alone and can start spontaneously without any nucleation event (Miller 1961, Lagneborg 1967, Chandra and Schwartz 1971, Porter and Easterling 1992).

In this way two mechanisms, depending on alloy composition and aging temperature, exist by which α" is formed: nucleation and growth and spinodal decomposition.

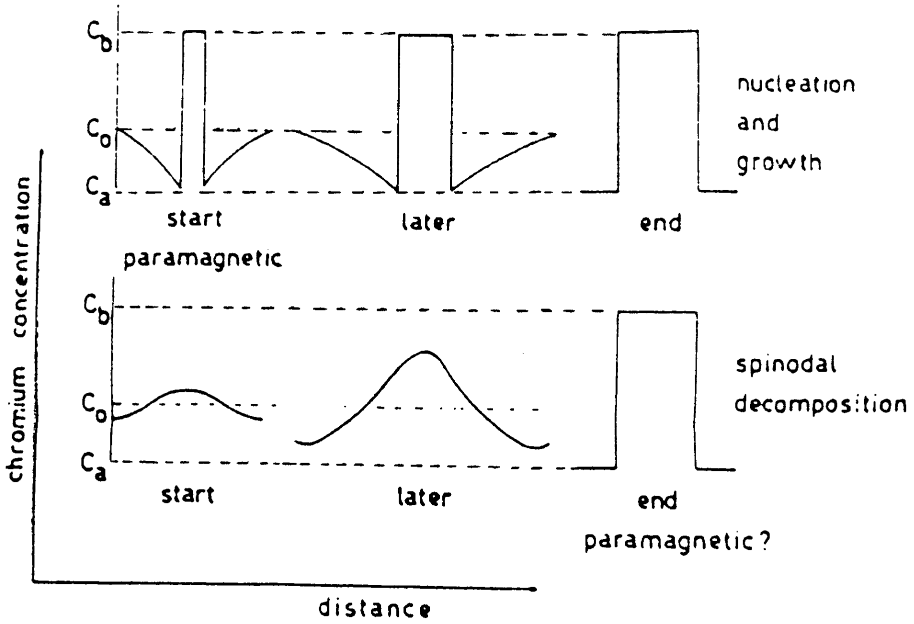

***Figure 2.9**: Schematic evaluation of concentration profiles to illustrate the difference between the spinodal mechanism and nucleation and growth (De Nys and Gielen 1971)*

In the nucleation and growth process, the solid solution separates into two phases, one of which, the chromium-rich, must be paramagnetic from the very beginning of the process, since it has the final composition right from the start - see figure 2.9.

Spinodal decomposition, on the other hand, produces fine clusters of iron and chromium without well defined interfaces and with fine-scale concentration gradient. It is proposed that in this decomposition mechanism, the Cr-rich region should become paramagnetic only at the end of the decomposition, because the chromium regions form slowly and the Cr concentration in these regions increases slowly with time - figure 2.9 (De Nys and Gielen 1971).

Spinodal decomposition is favoured by high Cr contents and low aging temperatures (Nichol *et al.* 1980). An alloy with less than 24% Cr - as the one investigated in this study - is expected to lie outside the spinodal and hence decompose via nucleation and growth processes (Chandra and Schwartz 1971, De Nys and Gielen 1971, Grobner 1973).

Size and detection of the α" precipitate

No apparent changes in microstructure (as revealed by optical microscopy and X-ray diffraction analysis) accompany the embrittlement, except for an initial widening of the grain boundaries, which may indicate an increased rate of attack by etchants (Fisher *et al.* 1953, Blackburn and Nutting 1964, Grobner 1973, Aggen *et al.* 1978, Nichol *et al.* 1980).

The precipitates have been detected through transmission electron microscopy and though the orientation of the foils is critical - primarily because of the similarity in scattering factors and atomic volumes of the Fe and Cr atoms (Lagneborg 1967) - the precipitates could be detected because they were mostly defined by regions of contrast adjacent to them. These regions have been interpreted as regions of coherency strain induced in the matrix lattice by differences in atomic size of the zone constituents or differences in lattice parameter of the precipitate phases.

The α" precipitates were revealed to consist of a simple bcc phase of approximately 200Å in size (after 10 000 to 34 000 hours at 475°C), with a lattice parameter of 2.878Å - only 0.2% larger than the matrix. This corresponds to an Fe-Cr alloy with 70 - 90% Cr. This phase is not ferromagnetic (Fisher *et al.* 1953, Grobner 1973).

As the volume fraction of the precipitates increases their morphology changes from isolated, roughly spherical to a continuous interconnected network as predicted from percolation theory. The volume fraction might be increased either by increasing the solute content or by changes in the aging temperature and shape of the miscibility gap at a constant solute content (Miller 1961). It has also been shown that in the iron-chromium system, a plate-like morphology (as opposed to spherical) would be expected to lead to a somewhat lower strain energy (Blackburn and Nutting 1964, Lagneborg 1967). A decrease in the coherency strains will lower the activation energy for nucleation and will consequently enhance the rate of nucleation. Hence, it seems likely that discs, which produce a minimum coherency strain, will form outside the spinodal where the decomposition must be initiated by nucleation.

It is thought that a slow process like coalescence may determine the growth rate, also at fairly short times, which offers an explanation for the lack of significant changes in the particle sizes during the first 1000 hours of aging. The reasons for the very slow coalescence is the low surface energy between the precipitate and the matrix, and the low diffusion rate at 475°C (Lagneborg 1967).

Rate at which embrittlement occurs

It was found that the time of most rapid embrittlement coincided with the beginning of the formation of zones enriched in Cr and also that the rate and intensity of the embrittlement increase with increasing Cr and interstitial content. This may be related to carbide and nitride precipitation acting as competing or supplementary reactions to that of the α" precipitation (Lena and Hawkes 1954, Tisinai and Samans 1957, Grobner 1973, Aggen *et al.* 1978, Nichol *et al.* 1980, Golovin *et al.* 1992).

There is evidence that lattice straining increases the rate of nucleation of α" (Tisinai and Samans 1957) and that the rate of *growth* of the α" precipitate during extended periods of aging at 475°C is very low, as the sizes stay virtually the same between 10 000 and 34 000 hours of aging (Fisher *et al.* 1953).

Mechanical properties

It was found that the formation of α" phase causes significant changes in the mechanical properties of the steels.

Hardness increases markedly when aged at 475°C, but stays virtually constant with aging at 550°C. For the first few hundred hours at 475°C the increase in hardness is rapid. After that the hardness still increases, but at a much lower rate. Eventually (at 10 000 to 34 000 hours of aging) no further changes are apparent (Lagneborg 1967, Fisher *et al.* 1953). Also, higher hardness (and yield strength) can be obtained for samples quenched from 850°C in water, rather than cooled in the furnace, before aging; in the former, a uniform distribution of α" is responsible for the hardness increase whereas on furnace cooling, the hardening is mainly due to the heterogeneous precipitation of relatively large chromium nitrides (or carbonitrides) at the grain boundaries (Plumtree and Gullberg 1976).

Thus the changes in the physical and mechanical properties can be summarised as follows: the hardness, yield stress and Curie temperature increase while the electrical resistiwity, impact resistance and corrosion resistance decrease.

Mechanism by which strengthening is obtained

The fact that iron and chromium have almost the same diffusion coefficient and because their lattice parameters, both bcc, are almost identical (iron = 2.86005Å and Cr = 2.8786Å), make the determination of the way by which strengthening is obtained difficult (De Nys and Gielen 1971).

Both the matrix and precipitate (α'') are under essentially isotropic stresses and are strained to a common lattice parameter, that of the unaged material. Strengthening is caused by the interaction of the particles and matrix with the hydrostatic stresses around edge dislocations. It is proposed that both the matrix and the particles are hydrostatically stressed and that the particles are unable to withstand great shearing forces in that they are continuous with the matrix and the slip planes are undistorted. The coherency also increases the hardness due to internal strains (Fisher *et al.* 1953, Williams and Paxton 1957).

Through an increase in the Peierls friction stress the presence of the small spherical α'' precipitates could strengthen Fe-Cr alloys. A large friction stress arises as dislocations move through high-chromium ferrite. It was found that, for a 47.8% Cr alloy, in the case of slip, lattice friction within the Cr-rich α'' phase and the chemical energy associated with the interface between the two phases contribute about 60% of the total strength. The contributions of coherency strains and modulus differences are thought to contribute the remaining 40%, but are difficult to evaluate because of the uncertainties regarding the flexibility of the dislocation line (Marcinkowski *et al.* 1964).

Chemical strengthening arises as a dislocation cuts through the Cr-rich precipitates, creating an interface between the particle and the matrix which consist of unlike Fe-Cr bonds. The creation of these bonds requires an expenditure of energy and thus impedes the motion of the dislocation.

The effects of differences in lattice parameter and elastic modulus (of the Cr-rich zones and the matrix) are thought to be greater for slip than for twinning, and because of this the shear stress for slip increases rapidly with aging time until it surpasses that for twin propagation. As embrittlement proceeds, twinning becomes an increasingly important mode of deformation at room temperature (Blackburn and Nutting 1964; Marcinkowski *et al.* 1964; Aggen *et al.* 1978).

It seems that the embrittlement of pure Fe-Cr alloys requires the presence of lattice strains, which increases the energy level of the homogeneous α and provides energy for the decomposition to α and α''. Although stresses are necessary for extensive embrittlement in short times, the amount of stress required does not have to be large. The straining necessary for embrittlement can be achieved by external deformation or by the precipitation of a second phase such as carbides and nitrides (Lena and Hawkes 1954).

The presence of antiferromagnetism is believed to result in an additional strengthening mechanism very similar to that for ordered precipitates (atomic ordering) (Williams 1958).

Overaging

As the embrittlement is an age-hardening phenomenon it should exhibit overaging, but this is not observed experimentally, even after thousands of hours of exposure (Fisher *et al.* 1953, Marcinkowski *et al.* 1964).

This unique feature of Fe-Cr alloys not to produce overaging is thought to be due mainly to slow coalescence. The coalescence is slow because of low surface energy between the precipitates and matrix, and the low diffusion rate at 475°C (Lagneborg 1967).

Recovery

The embrittlement can be removed by re-annealing. With heating above 550°C complete resolution of the particles and reversion to the unaged condition can be attained.

Considerable growth of the carbide and nitride phases might however occur at this temperature (Blackburn and Nutting 1964, Marcinkowski *et al.* 1964, Brooks 1979).

Effect of alloying elements on embrittlement

It was found that the rate of the embrittlement increases with increasing Cr content and appears to decrease with increasing purity (i.e. decrease in mainly C and N content). Although the phase diagram predicts that 475°C embrittlement could occur in steels with as low as 10% Cr, effects are rarely noted unless the Cr content exceeds 13% (Heger 1951; Nichol *et al.* 1980).

The extent of changes in physical characteristics during embrittlement depends on Cr concentration and time at temperature, higher alloy content and longer time both promoting more rapid and extensive changes. The temperature of most pronounced embrittlement decreases with declining Cr content (Binder and Spendelow 1950, Fisher *et al.* 1953, Rajkay 1967).

Carbon increases the effects of the embrittlement as hardness was seen to increase and elongation decrease with increasing C.

Titanium accelerates the embrittlement phenomenon, as it forms carbides and thus prevents the forming of chromium-carbides. In this way more Cr is left to take part in the embrittling process (Heger 1951; Grobner 1973; Nichol *et al.* 1980).

Niobium accelerates the embrittling in the same way as titanium (Heger 1951; Nichol *et al.* 1980).

Molybdenum has a negligible effect at low Cr contents, but significantly increases embrittlement as the amount of Cr is increased (Heger 1951; Grobner 1973; Nichol *et al.* 1980).

Manganese (up to 3%) lowers the effect of the 475°C embrittlement, perhaps by promoting the formation of austenite, while the embrittling is confined to ferrite (Heger 1951).

Si, P, Al and N also intensify the embrittlement (Heger 1951, Trindade and Vilar 1991).

Addition of nickel enhances the spinodal decomposition kinetics and hence the rate of embrittlement (Nichol *et al.* 1980, Trindade and Vilar 1991) at low amounts, while at higher concentrations austenite begins to form and hence embrittlement is decreased (Heger 1951).

Vanadium decreases rather than increases the 475°C embrittlement, as it slightly lowers the rate of embrittlement, although it increases the hardness if added in amounts up to approximately 1%. Because the atomic diameter of the vanadium atom is larger than that of iron or chromium, the dissolution of V would cause higher coherency stresses and thus a greater increase in hardness during aging (Koutaniemi *et al.* 1974).

Effect of cold work on embrittlement

Although it had been reported that deformation before aging does not have an effect (Williams and Paxton 1957, Lagneborg 1967), it was demonstrated that a small degree of deformation can cause a decided increase in the amount of hardening produced by subsequent heat treatment at 475°C. This effect is usually attributed to increased nucleation because of strain (Lena and Hawks 1954, Tisinai and Samans 1957). Severely cold worked alloys seem to be more susceptible to 475°C embrittlement than annealed or tempered grades (Thielsh 1951).

It was also found that cold work before aging promotes the formation of sigma phase (Fisher *et. al.* 1953).

Effect of aging at 475°C and cooling rate from annealing temperature on corrosion properties

It seems that no deterioration in corrosion resistance with the aging at 475°C, is to be expected, and that effects on corrosion resistance appear to occur more slowly and have less significance than the effects on mechanical properties (Aggen *et al.* 1978).

Sensitisation might be a problem, though it can be largely reduced by low interstitial contents (Grobner 1973, Plumtree and Gullberg 1976, Aggen *et al.* 1978). The interstitial content would have to be less than 0.002% to be effective, however, and this is not commercially viable yet.

2.3. Microstructure

Two further aspects may have an influence on the properties of the material, they are grain size and the presence of martensite in the microstructure.

2.3.1. Grain size

Rates of grain growth in ferritic stainless steels become appreciable only when temperatures are reached at which the structure is fully ferritic (i.e. contains no austenite or martensite) (Rajkay 1967). Hence it is not expected that grain size and growth would have an effect in the present study.

2.3.2. Martensitic-ferritic stainless steels

Ning *et al.* (1991) found that the strengthening of 17% Cr - 2%Ni steels is mainly caused by the presence of martensite in the microstructure (after austenitising at temperature in the range 950-1150°C, oil quench and tempering at 300 - 650°C. These steels are also susceptible to 475°C embrittlement where the ferrite (but not the martensite) is affected (Anzai *et al.* 1988)

Chapter 3

Material and Experimental Procedure

In the previous two chapters the practical and theoretical background of this work was outlined. This chapter provides a description of the experimental procedures which were followed to investigate the possible strengthening mechanisms.

3.1. Material

The material examined in the investigation - Type 430 ferritic stainless steel - was tested in the form of links of the actual slat-band chain as well as 8mm hot-rolled sheet. The sheet material was used to investigate the effects of cold rolling and aging such as may be used during the chain manufacturing process.

3.1.1. Slat band chain

The chain links are manufactured from continuously annealed and cold rolled 430 stainless steel. The composition of the material (as determined through Spark spectroscopy analysis) is as follows:

Table 3.1: *Composition of the slat band chain*

Element	Cr	C	N	Ni	P	S	Mn	Si	Mo
Weight%	16.0	0.05	0.012	0.15	0.024	0.003	0.61	0.77	0.032

3.1.2. Sheet material

The 430 sheet in the received form was 8mm thick, hot-rolled, batch annealed and pickled. The composition of this sheet is given in table 3.2.

***Table 3.2:** Composition of sheet material (provided by Columbus Stainless)*

Element	Cr	C	N	Ni	P	S	Mn	Si	Mo	Co
Weight%	16.42	0.036	0.033	0.13	0.025	0.004	0.57	0.63	0.02	0.02

3.2. General Experimental Procedure

The following is a simplified flow chart of the steps followed in the preparation of samples and the investigation itself.

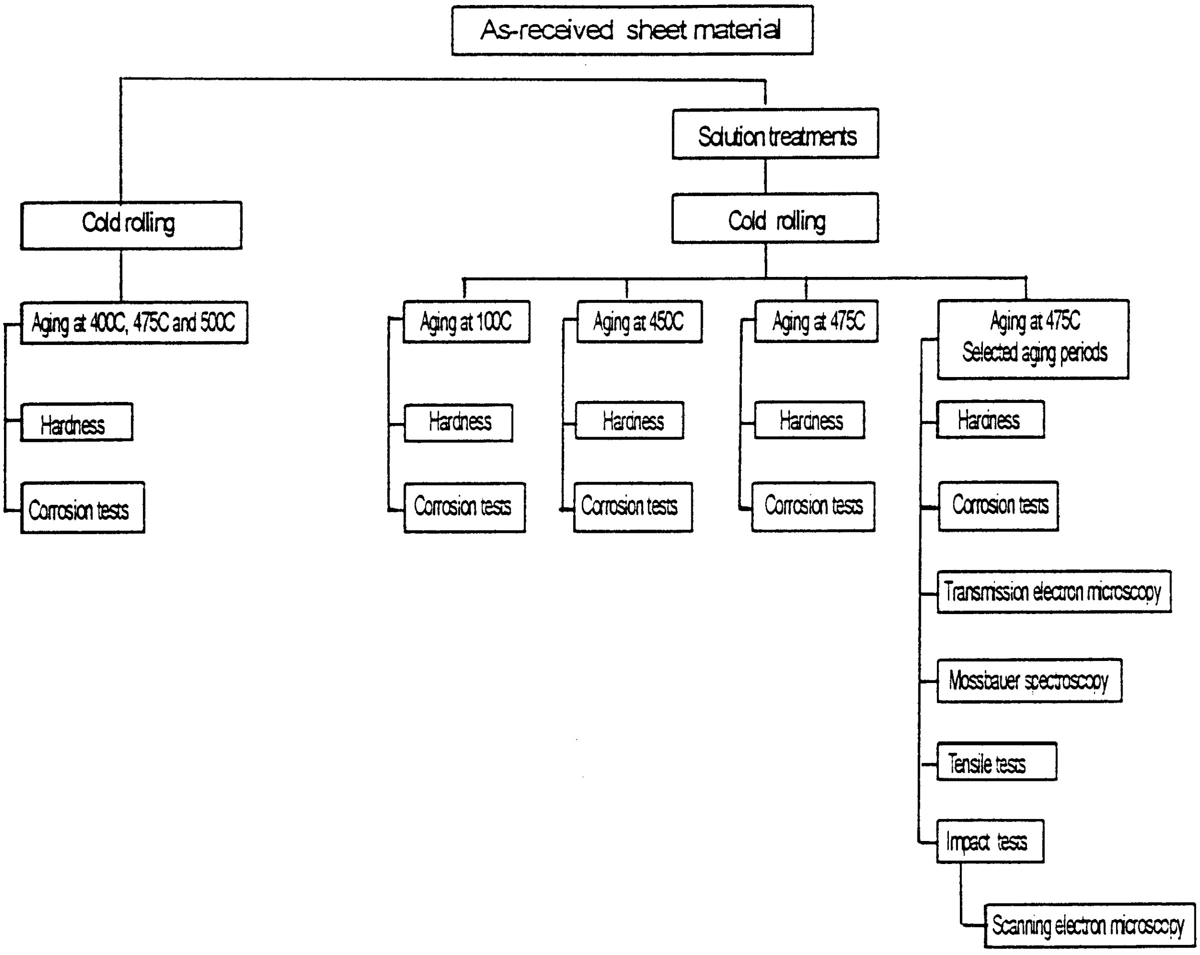

***Figure 3.1**: Flowsheet of experimental procedure*

The investigation was performed along two parallel paths. In the first the as-received sheet material was cold rolled before aging, while in the second, solution heat treatments were performed prior to cold rolling and aging. Table 3.3 describes the experimental procedure in detail:

***Table 3.3**: Aging treatments and testing procedures on the 8mm hot-rolled sheet.*

Solution treatment (°C) before cold rolling	920		930	none			800-1200	930	990	880 and 930	880 and 930
Reduction in area during cold rolling	0	38%	38%	38%			0	38%	38%	38%	38%
Aging temperature (°C) after cold rolling	475	475	100	400	475	500		475	475	475	450
Aging times (h)	0-260	0-260	0-14	0-48	0-260	0-260		0-260	0-260	0-2072	0-520
Vickers hardness tests (20 kg load) performed on	all	all	all	all	all	all	all	all	all	all	all
Potensiodynamic corrosion tests in 0.5M H_2SO_4 performed on	all	all	all	all	all	all	all	all	all	all	
Potensiostatic corrosion tests at 0V in 0.5M H_2SO_4 performed on									0h and 16h		
Pitting corrosion tests in 3.56% NaCl performed on				0h and 260h							
TEM (100 keV) performed on										0;0.13;32; 260h	
Mössbauer spectroscopy performed on										0;0.13;32; 260;2072h	
Impact tests performed on										0;0.13;32h	
Tensile tests performed on										0;0.13;32; 277h	
SEM performed on										0;0.13;32h	
Described in section	4.1.2	4.1.2	4.3.2	5.1	5.1	5.1	6.1.1	6.2.2	6.2.2	6.3.1;6.4.1 6.4.2;7.1; 7.2	6.3.2

Cold rolling was done at ambient temperature, in the original rolling direction. In all instances the area was reduced by 38% (8mm down to 5mm), since it was found that for type 430 ferritic stainless steel, 40% cold work produces a yield and tensile strength corresponding to the minimum levels required for conveyor applications (Charenton and Baltenneck 1992).

Aging treatments were mostly performed in a lead bath because of its good thermal stability, but some samples were solution treated and aged with the aid of a weld simulator. The simulator works on the principle of a current passing through the sample, which will cause it to heat up because of internal resistance. By using a controller at a certain EMF setting (which corresponds to the desired temperature) the sample could be held at temperature for any length time, after which it rapidly cools to room temperature. For temperature control a Pt -

Pt13%Rh thermocouple was spot welded onto the sample. The welding simulator was used for short-term heat treatments where changes in the lead bath temperature could have affected the aging behaviour.

Hardness values were determined by using a Vickers diamond pyramid indentor, each value being the mean of twenty measurements. The specimens were ground to a 1200 grit finish before hardness testing, which used a load of 20 kg.

The corrosion resistance was established by potentiodynamic testing in a 0.5M H_2SO_4 solution at room temperature. A scanning rate of 2 mV/s was used and a 123mm^2 area was exposed to the solution. Pitting corrosion tests were performed according to ASTM standard G61-78 (1979) in a 3.56% NaCl solution.

The dimensions of the samples used to determine tensile and impact strengths are shown in figure 3.2:

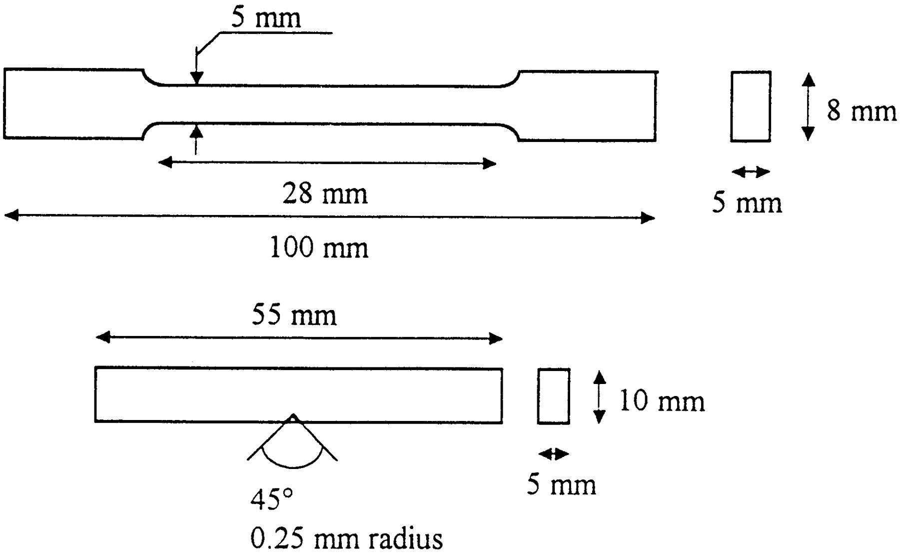

***Figure 3.2**: Dimensions of tensile and impact samples*

The impact fracture surfaces were analysed with the aid of a scanning electron microscope.

Transmission electron microscopy studies were performed in a 100 keV microscope. The foils were prepared longitudinal to the rolling direction.

Mössbauer studies (using a cobalt source) were performed. Tests ran for two days.

All the mechanical tests were performed at room temperature.

3.3. Handling of material and sample selection

The sheet material was received as a 8mm thick sheet of 1×2m in size. Solidification effects such as segregation are probably present in the sheet. To minimise bias from such inhomogeneity, the sheet was cut into 140 smaller pieces (170×70×8 mm) and allocated randomly to three groups. Specimens were then procured as needed, sampling from one group until it is depleted. Thus it was assured that samples would be extracted randomly and from different positions in the sheet.