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APLICACIONES DE METALURGIA FISICA AL DESARROLLO DE ACEROS

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LECTURE 1

High Strength - Low Alloy Steels

for Structural Purposes

Until about 15 years ago, there were very few developments in the field of High Strength Low Alloy Steels. Mild Steel, the main material, was regarded as possessing fairly simple metallurgical structure, and as such capable of little improvement. The sudden disappearance of all-welded "Liberty" ships during the latter part of the war, and the fact that they broke in two in harbour, altered the whole approach to the subject. Impact fracture behaviour became of major importance, as also did weldability.

The history of the development of High Strength Low Alloy Steels is interesting and shows evidence of the changing criteria on which steels are developed:-

(i) Originally design was based on Tensile Strength, with little cognisance of yield stress, impact strength or weldability. Thus steels contained relatively high carbon contents of the order of 0.3% - e.g.:-

(a) 1907 - Steel for "Mauretania":- 0.27%C, 1.2%Si, 0.72%Mn.

(b) 1932 - Steel for Sidney Harbour Bridge:- 0.30%C, 1.2%Mn, 0.15%Si.

These steels were cheap, carbon being the cheapest alloying addition, and were largely used as rolled with little or no control over the rolling temperatures.

(c) 1934 - BS548:- 0.27%C, 1.5%Mn, 0.25%Si.

(ii) The need to use welding rather than rivetting as a method of joining necessitated a lower carbon content. The strength was maintained by increasing manganese, although no cognisance of the advantage of this in terms of toughness was yet recognised.

(iii) Failure by brittle fracture of welded structures resulted in a recognition that impact (or fracture) toughness was essential, and thus the need for a low impact transition temperature was apparent. Also it became apparent that a high yield strength was more important than a high tensile strength. Thus the carbon content was lowered further, and the manganese was maintained at high levels. The advantages of high Mn/C ratios on impact toughness also was appreciated, and the significance of grain size was at last established.

(iv) Refinement of the grain size by grain refining additions, i.e. Al-N, was the next step, but could only be used in the normalised condition. The result was an increase in yield stress from 15 to 20tsi (225 to 300 MN/m^2), and a lowering of the impact transition temperature to below 0°C.

(v) Further increases in yield stress were achieved by precipitation hardening, still maintaining low carbon and high manganese

contents in fine grained compositions. Nb, V and Ti were used, Nb being the main addition as it allowed an increase in strength in the as rolled condition, which was economically advantageous. But the impact toughness was not good, because the as-rolled grain size was coarse.

(vi) This led to the use of low rolling finishing temperatures, which produced a fine grain size, and maintained some degree of precipitation hardening. The strengths achieved increased to 30-35tsi yield stress (450 - 525 MN/m^2) with impact transition temperatures as low as $-80^{\circ}C$. These controlled rolled, grain refined, precipitation hardening High Strength Low Alloy (HSLA) steels, when grain refined and precipitation hardened by Nb additions, had the added economic advantage that they were balanced, and thus produced a high ingot yield.

(vii) The most recent advance has been to improve the general formability, and particularly try to eliminate a form of welding defect, called "LAMELLAR TEARING". The root problem in this defect is the occurrence of localised planar arrays of non-metallic inclusions. The use of Zr, Ca or Ce additions to eliminate elongated planar arrays of inclusions and thus improve the general ductility, is the most recent development in HSLA steels.

It must not be thought that this process of development was fortuitous or haphazard. It was in fact solidly based on much systematic metallurgical research, and as such can be regarded as a good example of how developments are based upon, and indeed often wait upon, the basic understanding of structure - property relationships, transformations, etc.

The structures of all the steels in this category comprise mainly of ferrite and pearlite. Other HSLA steels can have ferite-bainite, tempered martensite or bainite structures.

Low Carbon Ferrite-Pearlite Steels

The requirements for this type of steel are:-

(i) High Yield Strength
(ii) Low Impact Transition Temperature
(iii) Minimum Cost
(iv) Easy Weldability
(v) Good formability

(a) Structure-Property Relationships

There are two relationships on which the structure-property relationships are based:-

(i) Hall-Petch Equation:- $\sigma_y = \sigma_i + k_y d^{-\frac{1}{2}}$

(ii) Petch Equation:- $\beta T_c = \ln\beta - \ln C - \ln d^{-\frac{1}{2}}$

where:-

σ_y = yield stress, T_c = Impact Transition Temperature,
d = grain size of polygonal ferrite (mean linear intercept).

The equations relating to plain low carbon-manganese steels are:-

1. Yield Stress $(MN/m^2) = 15.44\left[3.5 + 2.1(Mn) + 5.4(Si) + 23(N_f) + 1.13\, d^{-\frac{1}{2}}\right]$

Note:-

(a) Pearlite (i.e. carbon) has no effect in low carbon steels.

(b) Free nitrogen (N_f) has a pronounced effect, but its solubility is limited. Also it has a bad effect on impact properties.

(c) The strengthening effect of grain refinement.

2. Tensile Strength $(MN/m^2) = 15.44[19.1 + 1.8(Mn) + 5.4(Si) + 0.25(Pearlite) + 0.5d^{-\frac{1}{2}}]$

Note:-

(a) Pearlite strengthens

(b) Grain refinement strengthens.

3. Impact Transition Temperature $^{o}C = -19 + 44(Si) + 700(\sqrt{N_f}) + 2.2(Pearlite) - 11.5d^{-\frac{1}{2}}$

Note:-

(a) Pearlite is detrimental

(b) Free nitrogen is very detrimental

(c) Substitutional solutes are detrimental

(d) There is no apparent effect of Manganese - its effect is incorporated in that of grain size.

(e) Grain refinement is very beneficial.

The features to note are:-

(a) Refinement of the polygonal ferrite grain size increases the yield stress and decreases the impact transition temperature.

(b) Pearlite has no effect on the yield stress but increases the tensile strength and is very detrimental on the impact transition temperature.

(c) Solid solution elements increase the yield and tensile strengths, the effect largely depending on the difference in atomic size between the element and iron. These solute elements also are generally detrimental to the impact properties. Their effects on strength are generally small, and it would be expensive and uneconomical to try to use them deliberately, particularly for the case of substitutional solutes.

(d) Interstitial solutes are potent strengtheners, but their solubility is limited, and so they cannot be used to any great extent. Also they are most detrimental to the impact properties.

(b) Strengthening Effects

(i) Grain size - the best effect because it also decreases impact transition temperature. Hence the use of grain refining additions such as Al-N. Such an addition only grain refines in the normalised condition.

(ii) Pearlite - the yield strength depends mainly on the ferrite; hence there is little or no effect of pearlite. Pearlite

however does increase tensile strength by increasing work hardening rate, and it is very detrimental to impact properties.

(iii) Solid solution hardening:- there is a small effect of substitutional solutes, which obey a linear law over the limited range encountered. Interstitial solutes, i.e. N_f, obey a $\sqrt{\text{concentration}}$ law as expected theoretically. Both substitutional and interstitial solutes are detrimental to impact properties, especially the interstitial solutes. Solutes may have other effects such as altering the ferrite pearlite ratio; refining the ferrite grain size by decreasing the transformation temperature on cooling (i.e. Mn); producing precipitation effects (i.e. C and N); withdrawing interstitials from solution (i.e. Al). This latter effect is very beneficial to the impact properties hence excellent impact properties are obtained in Al treated steels.

(iv) Dislocation density:- the flow stress, i.e. yield stress is related to the dislocation density (ρ) by:-

$$\sigma_y = k\sqrt{\rho}$$

In general, decreasing the transformation temperature by either alloying or increasing the cooling rate, both refines the grain size and increases the dislocation density. This increased dislocation density increases yield stress by about $50MN/m^2$. It is not possible to depress the transformation temperature too much, otherwise acicular bainitic structures form which are very detrimental to the impact properties. Thus both Mn and cooling rate are limited, and the faster the cooling rate, the less manganese can be accommodated. Also, interaction of dislocations with interstitial solutes can cause added strengthening, especially if the interstitial content is increased by faster cooling rates. All these effects lead to a decrease in the impact toughness.

(v) Precipitation effects:- markedly increase the strength, but lower the impact resistance. More recent work has combined precipitation hardening elements with grain refinement, i.e. Nb, V or Ti. The effectiveness of these elements depends on their solubility in austenite which controls how much can be dissolved and is thus available for precipitation. Solubility data is available e.g.:-

$$\log_{10}[Nb][C + \tfrac{12}{14}N] = \frac{-6770}{T} + 2.26$$

In the amounts used, i.e. 0.03Nb or 0.10V, there are invariably some undissolved particles at conventional normalising temperatures, which give grain refinement of the austenite and thus, on transformation, a fine ferrite grain size. These particles do not strengthen. On cooling V_4C_3 or Nb(CN) precipitates at the ferrite-austenite interface during the transformation, (interphase precipitation), which produces rows of fine precipitates which strengthen. Due to the higher solubility of V_4C_3 compared with NbC, Vanadium steels can age harden from conventional normalising temperatures such as 950°C, whereas Niobium steels do not because the solubility of NbC at 950°C is too small. Thus on normalising Nb steels are only grain refined, whilst V steels are grain refined and precipitation hardened.

Nb steels can precipitation harden if they are heated to higher austenitising temperatures where more NbC is dissolved, but this also dissolves the grain refining precipitates (or coarsens them) so that the grain refinement is no longer achieved. Thus, whilst the strength is increased the impact properties are very detrimentally affected. Hence Nb steels give precipitation strengthening in the as rolled condition, and later it will be shown how controlled rolling is utilised to maintain a fine ferrite grain size.

The cooling rate also affects the intensity of precipitation strengthening. Fast cooling rates (still maintaining a ferrite-pearlite structure) can prevent precipitation. This is used in controlled cooled strip, the Nb largely being used to prevent grain coarsening on welding. Intermediate cooling rates cause maximum age hardening, whilst slow cooling rates give overageing which, together with the coarser grain size produced by the high transformation temperature, produce low strengths and poor impact properties. If the precipitation has been suppressed, it can be subsequently induced during tempering at $\sim 650^{\circ}C$, which will increase the strength but impair the impact properties. For a steel containing $\sim$0.03%Nb, a maximum increase in yield stress due to NbC precipitation is $\sim 120 MN/m^2$.

The composition of the steel with respect to the ratio Nb/C (or Ti/C, V/C) is also important. The maximum temperature dependence of the solubility of the precipitate occurs at the stoichiometric composition, so that at this composition, the maximum amount of precipitate will be formed. In most structural steels, the ratio Nb/C, Ti/C or V/C is much lower than the stoichiometric ratio, and consequently increasing the metallic alloy addition will increase the strengthening due to precipitation. This explains why the yield stress increases with increasing niobium content and in a Ti treated steel the remarkable strengthening of $300 MN/m^2$ has been observed with a stoichiometric Ti/C ratio and 0.12%C. However this may be associated with very impaired impact properties.

(c) <u>The Design of HSLA Steels</u>

The criteria used are:-

(1) High yield stress and low impact transition temperature. Therefore alloying elements and microstructural parameters which give the least increase in impact transition temperature per unit increase in strength are required.

(2) Good weldability, which is achieved by minimum depression of M_s temperature and low contents of liquitable solutes. Also minimum non-metallic inclusion content is required to prevent lamellar tearing.

(3) Good formability for flat rolled thin sections which required forming into structural members.

(4) Minimum cost.

The change in yield stress and impact transition temperature per weight % of the varying alloying elements is given in the following table:-

Element	Change per 1 wt % alloying element		
	Yield Stress (MN/m^2)	Tensile Strength (MN/m^2)	I.T.T. ^oC
C	∿ +4,600	∿ +6,800	-
N_f	∿ +4,600	∿ +6,800	+700 *
P	+670	+670	+400
Sn	+140	-	+150
Si	+85	+85	+44
Cu	+39	+9	-
Mn	+32	+28	0
Mo	+11	+45	-
Ni	0	+9	-
Cr	-30 ‡	-28 ‡	-
Al	0	0	+75 †

* Not linear

† Al in solid solution only

‡ Negative, possibly due to removal of interstitial solutes

The effects of varying microstructural and compositional parameters on the change in impact transition temperature per 15 MN/m^2 increase in yield stress are as follows:-

Parameter	Change in I.T.T. ^oC per 15 MN/m^2 increase in yield stress	
Pearlite	∝ *	Microstructural
Dislocations	+ 6	
Precipitation	+ 4	
Grain Refinement	- 10	
Phosphorus	+ 53	Compositional
Nitrogen	+ 30	
Tin	+ 17	
Carbon	+ 10	
Silicon	+ 8	
Manganese	- 5	
Aluminium	- 27 †	

* Does not increase yield stress. 20% Pearlite increases I.T.T. by 44 ^oC.

† Large negative factor due to removal of free nitrogen from interstitial solid solution.

The design criterion is for the change in I.T.T. per unit increase in yield strength to have the largest negative value. Consequently

a low carbon, grain refined, high manganese steel is to be preferred. Grain refinement by Al-N additions would give the best impact properties because the Aluminium would remove virtually all the free N as AlN. However there are limitations. For example, too high a Mn content would result in the transformation temperature being so depressed that bainite would form. This would impair both the yield stress (due to internal stresses) and the impact properties. Consequently the manganese is generally limited to ∿1.5%; less manganese being tolerated with higher carbon contents and faster cooling rates, and more with lower carbon contents and slower cooling rates. Also, an aluminium grain refined steel is killed, which makes it economically unattractive due to a low ingot yield and relatively poor surface quality. Grain refinement can be achieved by a cheap (because small) addition of Nb, and this can be used in a balanced steel with economic attractions from the high ingot yield. But grain refinement is only achieved in the normalised condition. However, Nb can give precipitation strengthening, (which is much to be preferred to dislocation strengthening or solid solution strengthening), but only after high solution treatment temperatures, i.e. in the as rolled condition. Consequently a careful control of the rolling finishing temperature is required to ensure both a fine ferrite grain size and the requisite precipitation effect. This technique of CONTROLLED ROLLING will be discussed later. On the other hand, Vanadium could be used to grain refine and produce precipitation strengthening in the conventionally normalised condition.

No development would use the solid solution hardening elements because their effects on strength are small, they are expensive, they increase the I.T.T. too rapidly and they so increase the hardenability that bainite at even martensite would be formed instead of polygonal ferrite at the faster cooling rates or in the smaller section sizes. On the other hand, for specific purposes, copper can be added to increase strength by precipitation, and corrosion resistance, but there are likely to be production problems involving surface quality and ingot break-up.

The criterion for maintaining a high level of weldability is really the M_s temperature. Too low an M_s temperature leads to heat affected zone or weld cracking. An empirical carbon equivalent is frequently used, above which welding may be hazardous. Such an equivalent, (there are many) is typified by:-

$$C.E. = C + \frac{Mn}{6} + \frac{Si}{24} + \frac{Ni+Cu}{15} + \frac{Cr+Mo}{10}$$

This is really a statement of the empirically observed effects of these elements on the depression of the M_s temperature, and a similar carbon equivalent derived from M_s depression data would be:-

$$C.E. = C + \frac{Mn}{16} + \frac{Si}{43} + \frac{Ni+Cr}{28} + \frac{Mo}{22}$$

The relative effectiveness of each element in both relationships is apparent, and again the advantage of low carbon and high manganese stands out.

Finally, a consideration of formability militates against the use of carbon, which lowers both the total ductility and increases the work hardening rate. The question of formability will be considered later in more detail. Another important factor is the non-metallic inclusion content. This should be kept to a minimum, consistent with cost, as inclusions lower the total ductility. In particular, sulphur should be as low as possible, not only to minimise the occurrence of sulphides, but also to prevent liquation

cracking and lamellar tearing during welding. The cost of producing low sulphur contents must be borne in mind.

(d) The Formability of HSLA Steels

Flat rolled strip often requires to be cold formed into structural members. The ability of steel to be formed by a variety of processes depends on:-

(i) The flow stress for a given strain, which governs the forming loads.

(ii) The work hardening rate.

(iii) The maximum uniform ductility prior to necking and plastic instability.

(iv) The total available ductility.

Many of the above parameters can be assessed from true stress - true strain tensile data.

The form of the true stress-true strain curve is seldom described by the classical equation:-

$$\sigma = K\epsilon^n$$

where σ = true stress
and ϵ = true strain

Rather, the relationship follows an equation of the type:-

$$\sigma = a + b\ln\epsilon + c(\epsilon)$$

This conforms with the well known fact that the work hardening rate, $d\sigma/d\epsilon$, decreases with increasing values of ϵ.

For low carbon, ferrite-pearlite structures which are typical of many HSLA steels, the following relationships have been obtained:-

1. $$\sigma_{f_{\epsilon=0.2}} (MN/m^2) = 15.4\left[16 + 29(Mn) + 9(Si) + 60(P) + 11(Sn) + 244(N_f) + 0.27(\text{Pearlite}) + 0.97d^{-\frac{1}{2}}\right]$$

2. $$\left(d\sigma/d\epsilon\right)_{\epsilon=0.2} (MN/m^2) = 15.4\left[25 + 7.2(Si) + 30(P) + 9.9(Sn) + 89(N_f) + 0.09(\%\,\text{Pearlite}) + 1.0d^{-\frac{1}{2}}\right]$$

3. Maximum Uniform Strain, $$\epsilon^* = 0.27 - 0.016(\%\,\text{Pearlite}) - 0.015(Mn) - 0.040(Sn) - 0.040(Si) - 1.1(N_f)$$

4. Total Ductility $$\epsilon_T = 1.3 - 0.020(\%\,\text{Pearlite}) + 0.30(Mn) + 0.20(Si) - 3.4(S) - 4.4(P) + 0.29(Sn) + 0.015d^{-\frac{1}{2}}\right]$$

These equations indicate that high carbon contents, i.e. increasing amounts of pearlite, increase the flow stress and work hardening rate but decrease the ductility. Carbon is therefore undesirable from the point of view of formability. Refinement of the grain size increases the flow stress and work hardening rate by about the same extent. Because ϵ^* is the strain at which $\sigma_f = d\sigma/d\epsilon$, grain size has no effect on ϵ^*, but a refinement of the grain size does improve the total ductility at fracture.

Solid solution hardening elements such as Si, Sn and P, together with interstitially dissolved nitrogen, increase the flow stress and work hardening rate, but have variable effects on the ductility

parameters due to complex interactions involving the flow stress, work hardening rate and fracture stress. The effect of sulphur in decreasing the total ductility reflects the effect of second phase particles of MnS on the total ductility. A similar effect is observed in the case of pearlite, and also oxide inclusions. The effects are not linear as implied by the above equations which cover only a limited range in the variation of the S and C contents. Rather the total ductility decreases exponentially with the increasing volume fraction of second phase particles.

Consequentially it is essential that for good formability, the carbon content (i.e. carbides) and the volume fraction of non-metallic inclusions should be kept to a minimum. Low sulphur contents and clean steel are essential.

In order to achieve a maximum level of strength together with good formability, as for example measured by the extrusion pressure in cold extrusion, a low increase in extrusion pressure for a given increase in yield strength is required. The best strengthening methods which can be used in this situation are a fine grain size and dispersion or precipitation hardening. Carbon is to be avoided, but for a given volume fraction of pearlite, better forming will be achieved by a spheroidising treatment, which in low carbon steels should not greatly lower the yield stress. Clean steel, free from inclusions, is also essential if good ductility and freedom from cracking is required. This latter consideration will be discussed further under the heading of inclusion shape control.

LECTURE 2

A. Methods for producing Improved HSLA Steels

(i) Normalised Steels

Grain refining is essential and Al, V, Nb and Ti are possibilities. Al and V are most effective grain refiners, followed by Nb and lastly Ti. Al produces extra benefits on impact toughness (removes N_f), but implies economic disadvantages of killed steels

Nb additions are used to produce grain refinement, and have the added advantages of being applicable to balanced steels and of producing precipitation strengthening. No precipitation hardening is produced in the normalised condition in Nb steels but only in the as rolled condition or after a high austenitising temperature. The relevance of this with respect to controlled rolling will be discussed later.

V can be used to give grain refinement and precipitation hardening in the normalised condition. The disadvantage is the high cost.

Carbon contents must be low within any confines required by specifications with respect to the YS/TS ratio. Carbon is necessary to increase the tensile strength. With low carbon contents, the ferrite grain size is not refined so markedly, but this can be rectified by the use of higher Mn contents which lower the transformation temperature, and more Mn can be accommodated without bainite formation at the lower carbon contents. The maximum Mn content:-

(a) decreases as the cooling rate increases
(b) decreases with decreasing section thickness
(c) increases with lower carbon content, and with lower residual alloy contents.

Copper can also be used to give an added measure of precipitation strengthening, but there are certain drawbacks.

Whilst Vanadium can be used to grain refine by VN particles, this lowers the amount of vanadium available for precipitation as V_4C_3. Thus a combined addition of Al + V + N grain refines by AlN, removes N to improve further the impact properties, and allows more of the V to be available for precipitation. Certain steels contain higher (V + N) additions to increase the grain refinement and give more precipitation strengthening, resulting in excellent strength and impact properties.

The best normalised HSLA steels can give yield strengths of 450-525 MN/m^2 with impact transition temperatures down to -80^oC.

(ii) As Rolled Steels and Controlled Rolling

Finer grain sizes can be achieved in as rolled steels than in conventionally normalised steels, and the grain size decreases with decreasing rolling finishing temperature. In Nb steels, the precipitation effects can be achieved in the as rolled condition, thus it is necessary to combine this precipitation strengthening with the finest possible grain size. Two factors are important:-

(a) the rate of recrystallisation, which increases with increasing temperature and deformation, but which can be retarded by solutes or precipitates.

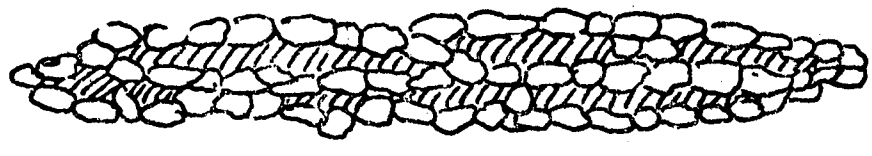
(b) the rate of grain growth, which increases with increasing temperature but which can be retarded by precipitate particles.

In plain C steels, recrystallisation is virtually instantaneous during rolling at temperatures above ~800°C, but occurs increasingly slowly below 800°C, at which temperatures ferrite formation often precedes complete recrystallisation.

Al, V and Ti additions slightly retard recrystallisation, but the precipitate particles markedly inhibit grain growth after recrystallisation. On the other hand, Nb markedly retards recrystallisation and also the Nb(CN) particles inhibit grain growth. Possible reasons for the effectiveness of Nb in retarding recrystallisation are solute drag and precipitation of NbC on sub-boundaries, thus preventing their migration during recrystallisation. Also during rolling, some strain induced precipitation of NbC occurs, which does not cause precipitation strengthening and yet decreases the amount of subsequent precipitation strengthening which can be achieved.

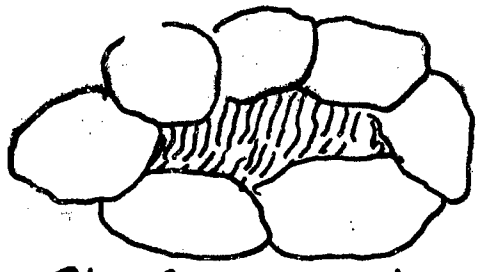
For a very fine ferrite grain size to be produced, it is essential to have a very fine austenite grain size prior to transformation. The correct composition and cooling rate is also essential to achieve as low a transformation temperature as possible within the ferrite-pearlite range. Too fast a cooling rate, or too high a "hardenability", leads to bainite formation, which is accentuated by any coarse un-recrystallised austenite grains present at the end of rolling. Such large un-recrystallised grains, if slowly cooled or present in steels of low "hardenability" give rise to high transformation temperatures, coarse ferrite grains and poor yield strength and impact properties.

Consequently, in controlled rolled steels it is essential to employ the correct amount of deformation and the correct low finishing temperature in order to ensure fine, recrystallised austenite grains. By retarding recrystallisation, Nb could lead to coarse unrecrystallised grains of austenite, with detrimental effects. However, providing the rolling finishing temperature is low, and that large deformations are used, fine ferrite grains will be formed even though the austenite has not recrystallised. This is because very thin elongated austenite grains are produced, and the ferrite nucleated at the grain boundaries remains fine because of impingement:-



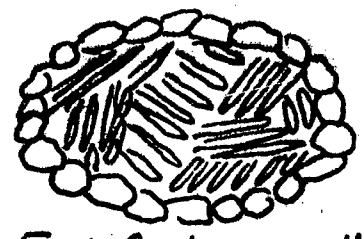
Ferrite also nucleates on deformation sub-structures in the austenite, and possibly on any second phase particles.

But if the deformation is light, the austenite grains are not thin, and either coarse ferrite grains or bainite is the result, with impairment of the properties:-



Slow Cooling or Low "Hardenability"

Coarse Ferrite Grains



Fast Cooling or High "Hardenability"

Fine Ferrite Grains but much Bainite.

Thus heavy deformations and low rolling finishing temperatures are essential. But too low finishing temperatures allow ferrite to be formed during rolling, which is then deformed and incompletely recovered or recrystallised. This greatly impairs the impact properties.

In commercial rolling practices for plain C-Mn non-grain refined steels, the low finishing rolling temperatures of $\sim 850^{\circ}C$ are obtained by interrupting the rolling schedule by one or more holding periods, particularly for the thicker sections. This can lead to recrystallisation and coarse grain sizes which may not undergo sufficient deformation to produce recrystallisation to fine austenite grains during rolling after the interruption. Consequently it is essential that an adequate amount of deformation is applied after the interruption, and at a temperature below $\sim 950^{\circ}C$, in order to produce fine recrystallised austenite grains.

Because of the retardation of recrystallisation in Nb steels, it is also possible to use interrupted rolling to achieve the requisite low finishing temperature, providing the unrecrystallised grains after rolling are sufficiently thin, i.e. they have again received adequate heavy deformation after the rolling interruption. If rolling is interrupted at too high a temperature in Nb steels, recrystallisation to a coarse austenite grain size can occur, and if insufficient deformation is given after the interruption, poor properties will result.

A low finishing temperature can also be achieved by starting with a thicker section such that a greater rolling time and consequently greater cooling is obtained by the time the final section size is reached.

A low initial soaking temperature prior to rolling would also give a low finishing temperature, but this would also lead to less precipitation strengthening as not so much NbC would have been dissolved, and therefore be available for subsequent precipitation.

All these methods have their disadvantages, not least being the increased rolling time associated with either interrupted rolling or with initially thicker material.

The whole aim of controlled rolling therefore, particularly with a Nb steel, is to produce in an economically attractive balanced or semi-killed steel, a very fine ferrite grain size

and yet to maintain a measure of dispersion strengthening by NbC. The Nb in solid solution, and the strain induced NbC precipitates, retard recrystallisation and the strain induced NbC precipitates retard austenite grain growth. These strain induced NbC precipitates do not strengthen, and so detract from the potential dispersion strengthening. Nevertheless a useful measure of NbC precipitation strengthening is achieved.

To summarise, controlled rolling requires that a fine recrystallised austenite or a very heavily deformed austenite is produced in order to give rise to the necessary very fine ferrite grain size. This requires heavy deformations at temperatures below 1000°C, which must be continued until the temperature during rolling is below 900°C. The advantages of a balanced steel, very fine ferrite grain size, and NbC precipitation strengthening, are economically very attractive, particularly when associated with the fact that a given strength level can be achieved with lower C and Mn contents, i.e. lower carbon equivalents, which give better weldability and formability.

(iii) Controlled Cooling

The rate of cooling is important, even in a ferrite-pearlite structure, because it affects the transformation temperatures and thus the ferrite grain size. Recent developments of effective water cooling on rolling mill run-out tables, has allowed strip up to 1cm thick to be produced with a very fine grain size and yield stresses up to 425MN/m^2. To prevent the accelerated cooling producing bainite, or other acicular transformation products, the as rolled austenite grain size must be very fine. The best results are therefore achieved with grain refined steels which have been effectively controlled rolled, and then accelerated cooled. Constraints on the accelerated or controlled cooling process are concerned mainly with the coiling temperature of the strip which:-

(a) must not be so high as to allow ferrite grain growth; Nb prevents grain growth.

(b) must not be so high as to allow any precipitate (which is causing strengthening) to overage; NbC overages less readily than V_4C_3.

(c) must not be so low that the accelerated cooling has produced some bainite.

As has been indicated, the cooling rate controls the intensity of the precipitation strengthening. Also the faster cooling rate can give a slight amount of dislocation strengthening. If the precipitation is suppressed by a rapid cooling rate, the strengthening is virtually all due to the fine ferrite grain size, thus giving the best combination of strength and toughness. Some ageing can then be caused to occur during a tempering treatment.

A controlled cooling treatment can also be used to improve the properties by causing a further refinement of the ferrite grain size in thick sections, either by using a fine water spray or an air blast to lower the transformation temperature. Care must be taken to prevent the surface from forming martensite or bainite.

A controlled cooling treatment is now used fairly widely on

strip mills to produce hot rolled strip with a yield stress of ~425MN/m^2 and good toughness and formability.

(iv) Some Preferred Compositions

The use of modern HSLA steels is widespread in the following typical application:-

Ship plate, structural members (but controlled rolling is difficult to apply to certain sections due to temperature variations), plates, strip, etc.

Preferred steels are:-

(i) Balanced - as rolled C-Mn-Nb (controlled rolled)

(ii) Balanced - normalised C-Mn-Nb; or C-Mn-V for higher strength but at higher cost.

(iii) Killed C-Mn-Al-N - normalised for best impact properties or controlled rolled. This steel is not dispersion strengthened.

(iv) Killed C-Mn-Al-V-N - normalised or controlled rolled for best grain refinement, removal of N_f, and dispersion strengthening.

B. Inclusion Shape Control

A problem in some HSLA steels is a lack of ductility which leads to splitting during bending, lamellar tearing or lack of through thickness ductility in plates during welding, or poor impact toughness in the through thickness direction in plates. It has already been stated that the general ductility decreases exponentially as the volume fraction of second phase particles, particularly non-metallic inclusions, increases. The major detrimental effect is produced when inclusions, particularly sulphides (MnS) are elongated into stringers or tapes during the hot rolling process. This effect is pronounced with very plastic inclusions, and whilst MnS is often affected in this way, oxides can also behave similarly. When the inclusions occur in localised segregates, as for example in the case of type II MnS, the elongated planar arrays very considerably impair the ductility and toughness in transverse or through thickness directions.

A recent method of combatting this problem has been the modification of both sulphides and oxides by additions of Ca, Zr or Cerium (rare earths). This modification, most effective in the case of sulphides, is brought about by the additions decreasing the plasticity of the inclusions with the result that they form rounded globules rather than elongated tapes or planar arrays. The transverse or through thickness ductility and toughness is then greatly improved, as the material does not have an easy plane of fracture.

(a) The effect on ductility

During straining, voids are nucleated around sulphide (and other) inclusions, which grow and link up to give rise to the subsequent ductile fracture. Other inclusions, or even carbides, can crack and thus give rise to void nucleation.

Due to their low stress concentration factors in the transverse direction, globular inclusions show much less rapid void growth than do planar inclusions tested in the transverse direction.

Control over inclusion shape is achieved by:-

(i) Calcium, which can globularise oxides and sulphides. Due to its high vapour pressure, low solubility and great reactivity, its effect is difficult to control during steelmaking.

(ii) Zirconium, which must be added in minimum amounts of (6(%N) + %S) as it combines with both nitrogen and sulphur. The Zr can enter the MnS and decrease its plasticity, or more often replaces MnS by a virtually non-deformable zirconium sulphide.Zirconium cannot be used as a sulphide modifying agent in steels which owe their properties to high nitrogen contents, in which case cerium additions are used. However Zr can be used with Nb treated steels.

(iii) Cerium, which is very expensive, and requires a minimum Ce/S ratio of 1.5 for complete sulphide modification. Its recovery can be erratic.

Whilst Ce and Zr have been used mainly to produce sulphide shape control, calcium is more frequently used for oxide inclusion shape control. The major effect of these additions is to increase the transverse, or through thickness ductility, to values much more comparable with those in the longitudinal direction.

(b) The effect on toughness

Inclusions markedly decrease the impact (Charpy) shelf energy values, which are the ductile energy values occurring above the impact transition temperature. This is particularly marked inthe transverse testing direction, i.e. through the thickness of plates. The use of inclusion shape control has been shown almost to double the transverse shelf energy impact value, and the ratio of longitudinal to transverse shelf energy approaches unity. There is evidence that this ratio more nearly approaches unity as the addition of Zr or cerium (rare earths) increases, and the amounts required are similar to those needed for optimum effects on ductility.

The effect of inclusions on the impact transition temperature is by no means so clear cut. Various effects have been reported, but as cracked carbides can initiate cleavage cracks and increase the impact transition temperature, there is some reason to suspect that inclusions may crack and produce a similar result. Experimental evidence on sulphides suggests that in both longitudinal and transverse directions, an increase in the MnS volume fraction first increases the impact transition temperature (ITT) and then causes it to decrease at higher MnS volume fractions. This may be due to firstly an increase in the number of crack initiating sites, followed by an increase in the number of crack arresting or crack dividing sulphide stringers as the volume fraction of MnS increases. The effect is particularly evident in longitudinal tests when the crack has to propagate across many inclusion fibres. Recent evidence indicates that, by eliminating these inclusion fibres, inclusion shape control by Zr can raise the ITT by $\sim 50^{\circ}C$, i.e. by removing the crack arresting characteristic. There is also evidence that if Zr contents much greater than 6(%N) + (%S) are used, the excess Zr forms ZrC and $Zr_4C_2S_2$, which embrittle the steel and decrease

the impact shelf energy. Whilst being beneficial to impact shelf energy when carefully controlled, there is some doubt as to the beneficial effect of inclusion shape control on the ITT.

(c) Quenched and Tempered low alloy steels

It has been realised that by rapidly quenching low carbon, high manganese, plain carbon steels, an acicular ferrite structure can be achieved which gives rise to very attractive properties. These structures should not be confused with tempered higher carbon martensites, as will be shown later. Grain refining, by the usual additions or by controlled rolling, coupled with dispersion strengthening by Nb or V can also be employed, and the quenching often prevents precipitation which then can be induced to occur by a tempering treatment. Quenching from the controlled rolling temperature produces the best combination of strength and toughness. The lower the finishing rolling temperature, the better are the properties due to the finer prior austenite grain size which gives rise to a very fine acircular ferrite grain size, and because of the defect structure introduced by the deformation, which is not all annealed out. This latter is very effective, strength-wise, when the final rolling occurs at temperatures where the austenite-ferrite transformation takes place in very low carbon steels, but the impact properties may be impaired.

The carbon contents of these steels may be reduced very considerably without the strength being impaired, because the acicular ferrite has a high strength by virtue of its very fine grain size and high dislocation density, coupled with good impact toughness. In some recently developed steels, carbon contents as low as 0.04% are used with high manganese contents to increase the "hardenability" so that the acicular ferrite is produced even on air cooling after controlled rolling.

Acicular ferrite is different from martensite, the latter owing most of its strength to carbon in solution. Acicular ferrite owes its properties to a very fine ferrite grain size and a high concentration of mobile dislocations which give rise to good toughness and ductility, though rather lower strength than martensite. In fact these acicular ferrites may be regarded as very similar to very low carbon bainite, as will be seen later. Also, precipitation of, for example, NbC by tempering strengthens low carbon acicular ferrite but reduces its toughness; precipitation of carbon from solution in martensite by tempering decreases the strength but usually increases the toughness. Thus the metallurgy and design philosophy of these steels should not be compared with the standard quenched and tempered low alloy engineering steels.

Optimum properties for this type of steel, controlled rolled and quenched and tempered at $\sim 600^{\circ}C$, range upwards to $850 MN/m^2$. They invariably contain Nb or V, which not only promotes and maintains the fine prior austenite grain size so necessary to achieve the fine grained accular ferrite, but also allows some precipitation strengthening during tempering. Hence the need for relatively high tempering temperatures to produce the precipitation of NbC or V_4C_3. Whilst the yield strengths are much higher than those obtainable in ferrite-pearlite structures, as the yield strength increases from 550 to $825 MN/m^2$ the ITT increases from $\sim -100^{\circ}C$ to above room temperature. Thus the strength which can be achieved is limited by the toughness requirements. At the lower level of strength, the combination of properties is rather similar to those in the highest strength ferrite-pearlite steels.

The major drawbacks to these steels would seem to be economic:-

(i) They require expensive plant for quenching such product forms as plate

(ii) They require a tempering treatment

(iii) The alloy content required is usually rather higher than for the ferrite-pearlite steels in order to achieve the required hardenability, particularly as the carbon contents are usually lower. Thus the material may be more expensive.

In an attempt to overcome some of the economic disadvantages associated with the quenching treatment, steels have been developed with a composition which enables the acicular ferrite structure to be produced by air cooling after controlled rolling. These steels, containing ~0.04%C, require even more alloy additions to achieve the "hardenability" necessary for the thicker sections. Two typical examples are:-

(a) 0.04%C, 1.7%Mn, 0.25%Mo, 0.25%Cu, 0.21%Ni, 0.06%Nb.

(b) 0.03%C, 2.5 to 3.4%Mn, 0.05/0.10%Nb.

The structures and properties of such steels are very similar to, in fact virtually an extension of, those of bainitie steels which will be discussed later, but they employ considerably lower carbon contents.

LECTURE 3

Medium - High Carbon Ferrite - Pearlite Steels

Steels which have predominantly pearlite structures are widely used for such purposes as rails, wheels, tyres, axles, etc in railway engineering, and for drill rods, reinforcing bar, and rod for drawing into high tensile wire. The increased pearlite content plays a useful role in increasing the tensile strength and imparting a measure of wear resistance, but at the expense of a deleterious effect on the impact toughness and overall ductility. Traditionally these steels have not been required to possess a large measure of toughness, but recent failures have highlighted the need for improved toughness. This could be achieved by lowering the carbon content, but only at the expense of introducing ferrite into the structure with a resulting loss of strength and wear resistance. Consequently, systematic investigations into the factors controlling the strength and toughness have led to a more complete understanding of the way in which the properties may be optimised.

(a) The Yield and Tensile Strength

The following relationships are applicable to steels comprising the whole range of pearlite contents up to eutectoid compositions.

1. Yield Stress (MN/m^2): $$15.4\left\{f_\alpha^{\frac{1}{3}}\left[2.3+3.8(Mn)+1.13d^{-\frac{1}{2}}\right]+\left(1-f_\alpha^{\frac{1}{3}}\right)\left[11.6+0.25S_o^{-\frac{1}{2}}\right]+4.1(Si)+27.6\sqrt{(N)}.\right\}$$

2. Tensile Strength (MN/m^2) = $$15.4\left\{f_\alpha^{\frac{1}{3}}\left[16+74.2\sqrt{(N)}+1.18d^{-\frac{1}{2}}\right]+\left(1-f_\alpha^{\frac{1}{3}}\right)\left[46.7+0.23S_o^{-\frac{1}{2}}\right]+6.3(Si)\right\}$$

where f_α = volume fraction of ferrite

d = grain diameter (mean linear intercept) of ferrite

and S_o = interlamellar spacing of pearlite in mm.

The functions $f_\alpha^{\frac{1}{3}}$ and $\left(1-f_\alpha^{\frac{1}{3}}\right)$ represent the ferrite and pearlite contents, and the index of 1/3 is required because the yield and tensile strengths vary non-linearly with pearlite content. At low pearlite content the amount of pearlite does not influence the strength, as shown in similar equations for low carbon steels described earlier. As the pearlite content increases up to 100%, its effect on the strength become increasingly predominant.

The yield stress depends on the ferrite grain size, but this gives a smaller contribution to the strength as the pearlite content increases. As the eutectoid composition is approached, the pearlite influences the strength more intensively, and the effect of the pearlite interlamellar spacing is clearly apparent. Considering the more complex analysis required to describe the strength, the various regression coefficients are remarkably similar to those derived for low carbon steels. The equation for the tensile strength shows very similar features.

These structure-property relationships were applicable to steels which had been normalised from temperatures up to 1100°C, and were found to hold irrespective of whether the steels had been treated with the grain refining additions Al-N, Nb or Ti. This was because the solubility of NbC or TiC in these high carbon steels was so small

that little or no Nb or Ti was dissolved in the austenite, and thus there was no precipitation produced on transformation. For example, less than 0.01%Nb can dissolve in 0.45%C austenite at 1250°C. An exception was observed in the case of vanadiun grain refined steels, because of the increased solubility of V_4C_3. However the precipitation strengthening was only of the order of 30-50MN/m^2; about half that obtained in low carbon steels. This is due to the higher carbon content decreasing the solubility of V_4C_3, and also due to the grain refinement by VN which causes a high transformation temperature and allows the precipitated V_4C_3 to average. It is interesting to note that in the case of the yield stress, the Mn influences only the ferrite contribution to the strength, whereas the nitrogen and silicon affect the strength by virtue of their solid solution strengthening of both ferrite and pearlite. In the case of the tensile strength, Mn in solid solution has no effect whilst the effect of nitrogen is limited to the ferrite in the structure.

(b) The Impact Toughness

The temperature at which an impact value of 27J is obtained, I°C, is given by the equation:-

$$I^{\circ}C = f_\alpha\left[-46 - 11.5\alpha^{-\frac{1}{2}}\right] + \left(1-f_\alpha\right)\left(-335 + 5.6\,S_o^{-\frac{1}{2}} - 13.3\,p^{-\frac{1}{2}} + 3.48\times10^{6}t\right) + 48.7\,(Si) + 762\,\sqrt{(N_f)}.$$

where the symbols are the same as those used previously and:-

p = pearlite colony size in mm
t = pearlite cementite plate thickness in mm
N_f = free interstitially dissolved nitrogen

Again the similarity in the regression coefficients with those observed for low carbon steels is apparent. It is clear that grain refinement, low silicon contents and a low free nitrogen content should be used for optimum impact properties. The detrimental effect of solid solution strengthening is again evident. Just as a refined ferrite grain size is beneficial to the toughness, so is a small pearlite colony size; pearlite colony boundaries acting to impede crack propagation.

The morphology of the pearlite has complex effects however, in that a decrease in the interlamellar spacing is detrimental to the impact properties, but the simultaneously observed decrease in the pearlite cementite plate thickness is beneficial. There is thus a balance between a decrease in the interlamellar spacing adversely affecting impact resistance, probably through its effect in increasing the strength, and the simultaneous decrease in carbide plate thickness which improves the impact resistance, because the thinner carbide plates can bend rather than crack and so initiate a cleavage failure. Frequently these two opposing effects cancel one another, so there is no overall effect of the pearlite morphology, but either effect can predominate causing either an improvement or deterioration in the impact properties with decreasing interlamellar spacing. The effects are further complicated by any changes which occur in the pearlite colony size.

Because S_o and t have opposite effects on the impact resistance, there will be an optimum interlamellar spacing for the best impact toughness. It is also clear that the dilution of the pearlite will be important, because increasing the carbon content of the pearlite will either decrease the value of S_o or increase t, both of which will impair the impact properties. The pearlite dilution factor is defined as:-

where f_p = volume fraction of pearlite in the structure.

D will be unity for a fully pearlitic steel of eutectoid composition, but will be greater than unity for a fully pearlitic hypo-eutectoid steel such as can be produced by low transformation temperatures approaching the nose of the pearlite C curve. It can be shown that the optimum interlamellar spacing for the best impact properties is related to the dilution factor by:-

$$S_{opt} = 6.7 \times 10^{-6} (D - 0.12)^{\frac{2}{3}}$$

This optimum interlamellar spacing increases as D increases, and the impact toughness also increases (I^oC decreases) as D increases. Thus a low carbon dilute pearlite is conducive to good impact resistance. This of course is for a fully pearlitic structure, and it can be concluded that increasing the pearlite content for a given carbon content will be beneficial to toughness. However,the precise effect will also depend on the balancing of the effects of the ferrite and pearlite caused by a decrease in the ferrite content, especially if the toughness of the ferrite is very high, i.e. it has a very fine grain size. If this latter was the case, increasing pearlite dilution could be detrimental to impact resistance. Some of these complex interrelationships can lead to certain steels having impact properties which are independent of the morphology of either ferrite or pearlite. However, with the higher pearlite contents, the pearlite morphology plays a more dominant role.

It is also important to consider the effect of transformation temperature, as controlled by alloy content, cooling rate and prior austenite grain size, on the impact properties. In general it can be concluded that lowering the transformation temperature is detrimental because of its major effect in decreasing S_o, but some depression of the transformation temperature is essential to cause refinement of the ferrite grain size, and the pearlite colony size.

For an optimum combination of strength and toughness in these predominantly pearlite steels, there should be:-

(i) a minimum carbon content consistent with the strength requirements.

(ii) a minimum of solid solution hardening by Si, N etc., although Si can be useful to promote wear resistance in lower carbon materials. The nitrogen is useful in providing grain refining precipitates, i.e. VN, but the nitrogen in solid solution should be kept to a minimum.

(iii) increased manganese because it is beneficial in lowering the transformation temperature and causing refinement of the ferrite grain size and pearlite colony size, but this can produce variable effects on the toughness through the interactions between pearlite dilution, S_o and t. In general however the effects of Manganese are self cancelling and often have no effect on the impact resistance.

(iv) Grain refinement to produce a fine ferrite grain size and pearlite colony size. Vanadium is a preferred addition as it can produce slight precipitation strengthening even in these

high carbon steels, which can also be achieved in the normalised condition.

(v) A normalising treatment to give the required grain refinement, either with or without grain refining additions.

It can also be shown that controlled rolling can produce similar benefits to normalising by virtue of its grain refining effect, but in controlled rolled steels there is likely to be rather more free nitrogen, even though the steel is grain refined by Al or V additions. Also, in sections such as rails, the control of the temperature during controlled rolling is difficult due to very great local variations in the section size. This can lead to roll wear and difficulties in the preservation of accurate dimensions.

(c) General Ductility Effects

Increasing the volume fraction of pearlite markedly decreases the maximum uniform strain and the total strain at fracture. It also increases the flow stress and the work hardening rate. These effects are all detrimental in terms of the ductility of the steels.

Decreasing the interlamellar spacing of the pearlite causes both the flow stress and the work hardening rate to increase. These effects are self cancelling and do not affect the maximum uniform strain. However, a fine interlamellar spacing is beneficial with regard to the total ductility. The reason for this is that the carbide lamellar are also fine and can bend or deform, whilst coarser carbide lamellar crack and initiate ductile (or brittle) fracture. This is the reason why a very fine pearlite, which is produced by patenting treatments applied to wire rods, is capable of more deformation during wire drawing than a softer annealed structure in which the carbide lamellar are coarse. Thus a greater total ductility is observed with a fine pearlite interlamellar spacing because of the delayed fracture and cavitation as ductile fracture is approached.

The general ductility of fully pearlitic steels can be considerably improved by a spheroidising treatment. This produces a decrease in the flow stress by increasing the ferrite free path as the lamellar carbides are spheroidised. Thus the effect of spheroidisation is beneficial not only on the maximum uniform strain, but also on the total ductility. There are also mechanistic effects operative, because whilst the cracking of lamellar and spheroidal carbides are both stress dependent, and hence considerable strain is possible before ductile fracture is nucleated, the strains required to crack lamellar pearlite are smaller than those required to crack spheroidal carbides. This is due to the higher flow stress in the pearlitic carbide (lamellar). Once a pearlite carbide lamella cracks, the strain is transmitted to adjacent lamellae so that rows of cracks occur. These coalesce and give rise to sharp cracks across the pearlite which cause large stress concentrations. These cracks grow rapidly and fracture occurs at overall lower ductility than for spheroidised carbides.

(d) The Development of Fracture Tough Steels

The development of a fracture tough rail steel is a recent example of how the principles described can be utilised. Many rail failures, which may lead to derailments, occur by brittle cleavage fracture from an initial fatigue or quench (braking) crack, or other small defect. In order to minimise the tendency for this to occur, it is necessary to ensure that the steel shows freedom from brittle fracture down to -15°C. At the same time it is necessary to

maintain an adequate level of tensile strength and wear resistance.

Current rail steels contain ∿1% Mn with 0.40/0.50%C in the high nitrogen Bessemer steels or with 0.50/0.60%C in Open Hearth steels. These compositions give 27J impact value temperatures approaching +100°C, and impact values of only 7J at 20°C. They are "as rolled".

The current steels can be improved by either controlled rolling or normalising, but not sufficiently to meet the required properties, despite considerable refinement of the grain size which is produced. Consequently a lower carbon, higher manganese base is used, namely 0.35%C, 1.5%Mn which leads to more dilute pearlite and hence better impact resistance. In the controlled rolled condition the impact criterion of 27J at -15°C are met, but the strength is slightly below the required levels of TS = 680MN/m² and 0.2%PS = 450MN/m². Further grain refinement can be achieved by using aluminium or vanadium grain refined steels in the normalised condition. This added grain refinement allows all the required properties to be met, but in view of the high cost of vanadium, a normalised Al grain refined composition is preferred. The wear resistance however is slightly inferior to that of the currently used steels, due to the lower carbon content and the rather greater volume fraction of pearlite. However, in the normalised aluminium grain refined steels, it is possible to enhance the wear resistance by an addition of 1%Si, which is cheap, and which can be tolerated despite its adverse effect on impact resistance because of the very excellent impact properties of the normalised Al grain refined steels. Slightly higher strengths at somewhat higher costs could be obtained by controlled rolled or normalised steels, grain refined by vanadium.

As in all developments, the cost of an improvement in properties has to be assessed. The developments described will undoubtedly be more expensive than currently used steels because:-

(1) They are slightly more highly alloyed, i.e. Mn + Si, but this will be marginal.

(2) They must be normalised or controlled rolled which implies a further heat treatment or a lower mill output. In addition any capital costs of a suitable normalising furnace have to be considered.

(3) They will be "killed", i.e. will be piped and thus have a lower ingot yield than previously used acid Bessemer steels which, because of their higher nitrogen content, are "balanced" and have a high ingot yield.

(4) The grain refining additions, particularly vanadium (0.01%) will increase the base steel cost.

In assessing the feasibility of such a development replacing current steels, the increased cost will have to be compared with an intangible assurance of safety.

LECTURE 4

Low Carbon Bainitic Steels

We have already seen that there is a limit to strength, with adequate impact resistance, for ferrite-pearlite structures. In order to achieve higher strengths, quenched and tempered structures may be necessary, but at some economic disadvantage. Already we have seen that certain compositions have been developed, which can employ the more economical air cooling after controlled rolling or normalising, in order to achieve the acicular ferrite structure and the requisite properties. These latter developments can be regarded as extensions of the low carbon bainitic steels to very low carbon contents.

The Development of the low carbon bainitic steels was designed, using a 0.10/0.15%C base composition, to attempt to produce a steel with proof stress values which could extend upwards from 450 MN/m^2 to some 800 MN/m^2 in a weldabable composition with adequate impact resistance. Moreover it was intended that such properties should be attained in the as rolled or normalised condition, and preferably without resort to tempering. Not all these features were possible, as will be apparent.

(a) The requirements for bainitic steels

It is fairly well known that the lower strength bainitic structures for a given steel are often equal to or even slightly lower in strength than the lowest temperature transformation products in the ferrite-pearlite range. Bainites form at temperatures between the ferrite-pearlite reactions and the martensite reaction. Consequently it should be possible to produce in bainite of a given composition, a range of strengths ranging between the highest strength in the ferrite-pearlite structures, and the strength of martensite.

The requirements and aims for the development of a low carbon bainitic steel are:-

(i) to produce the bainitic structure by air cooling, thus eliminating the economic disadvantages of quenching and subsequent tempering. Air cooling would also prevent quench cracking and minimise distortion during heat treatment.

(ii) to use a low carbon content, and a low carbon equivalent, in order to obtain good weldability and formability, although the latter would tend to be restricted to bending rather than the more severe cold forming processes.

(iii) to provide a range of tensile strengths from 600 MN/m^2 to 1200 MN/m^2 with proof or yield stresses varying from 450 MN/m^2 to 900 MN/m^2.

(iv) to obtain the above properties in the air cooled condition either directly after rolling or by the use of a simple normalising treatment, it also being appreciated that tempering might be required at the highest strength levels.

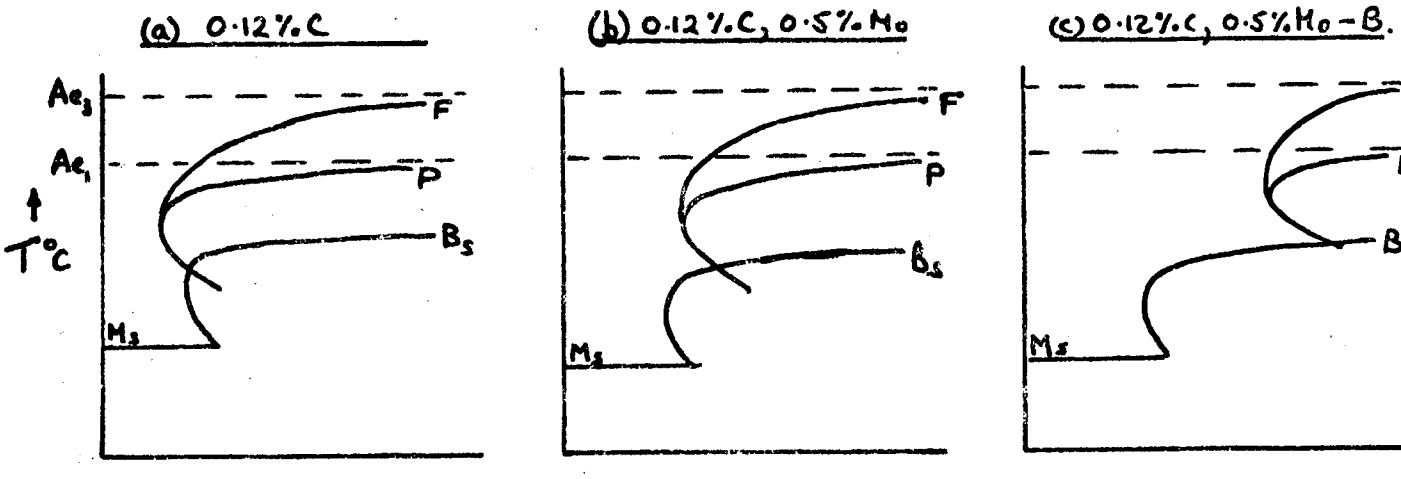
(v) to obtain the above properties with a minimum of variation over as wide a range of section size, (i.e. cooling rate) as possible, and yet not form martensite by becoming air hardening in the smaller section sizes (i.e. at the faster cooling rates). This requires a flat top to the Bainite Transformation "C" curve and the highest possible bainitic hardenability coupled with the lowest possible martensite hardenability.

(vi) to obtain the maximum impact properties consistent with the strength. Hence the low carbon content.

(b) The development of bainitic steels

The starting point was a low carbon weldable steel containing 0.10/0.15%C. However it is not possible in plain carbon steels for bainite to be produced during continuous cooling because the ferrite-pearlite reactions are much faster than the bainite reaction. Thus air cooling (i.e. normalising) simply results in a ferrite-pearlite structure. However it was known that several low alloyed low carbon steels, particularly a 0.10/0.15%C, 0.5%Mo steel, produced a structure of polygonal ferrite and bainite after normalising because the molybdenium retarded the ferrite reaction sufficiently for the bainite "C" curve just to be intersected during a continuous cooling treatment.

The problem was therefore to ensure that the separation, in terms of temperature, between the ferrite and bainite transformation "C" curves, was maintained, and to retard very greatly the polygonal ferrite transformation without any retardation of the bainite reaction itself.



Schematic T.T.T Curves, showing 0% transformation curves.

It was known that an addition of 0.002% boron could improve the hardenability of the steel, mainly by retarding the polygonal ferrite transformation which was nucleated at the austenite grain boundaries. This boron had little effect on the rate of the bainite reaction, but did retard the polygonal ferrite reaction, and produced just the type of transformation characteristics which were required. During continuous cooling, bainite formed over a wide range of cooling rates, and moreover the Bainite "C" curve had a flat top so that the transformation temperature was constant over a wide range of cooling rates. This led to the result that the strengths were constant over a wide range of section sizes, and there was little variation in strength across fairly large air cooled sections.

In the manufacture of boron steels, it is essential that the boron is in solution in the austenite, because it owes its action to the fact that it segregates to the austenite grain boundaries at which the polygonal ferrite nucleates. Boron present as oxide or nitride is useless, and therefore the steels must be Al-killed and often are treated with Ti additions to prevent BN from forming and decreasing the amount of Boron in solution. These bainitic steels therefore are killed, grain refined steels. There is also an optimum boron content, above which the retardation of the polygonal ferrite transformation becomes variable and less pronounced. This is because the boron produces Fe_2B or $M_{23}(CB)_6$

precipitates at the austenite grain boundaries when the optimum boron content is exceeded. These precipitates can nucleate for polygonal ferrite formation. This optimum boron content decreases as the austenite grain size increases.

So effective was the boron addition to the low carbon -½%Mo steel, that fully bainitic structures were obtained from ¼" dia to >20" dia aircooled round bars. The maximum rate of transformation occurred at ~650°C, so that the structure formed was low carbon upper bainite, and the transformation temperature was so constant with variation in cooling rate that decreasing cooling rates from 450°C to 6°C/minute (½" dia to 25" dia air cooled) only caused the proof stress to decrease from 500MN/m² to 450MN/m².

It can be seen that the proof stress is as high as that obtained in many fine grained ferrite-pearlite structures, and it was much higher than the yield stress of 230-300MN/m² obtained in the low carbon-molybdenum steel in the absence of boron.

(c) The development of higher strength Bainitic Steels

It seemed reasonable to believe that, as the temperature at which the bainitic structure was formed was dependent on the B_s (or more directly the B_{50}) temperature, if the B_s could be depressed whilst maintaining a low carbon content, a weldable steel of higher strength could be produced. The B_s, like the M_s, is depressed by most alloying elements, and Steven and Haynes showed:-

(a) $B_s{}^{\circ}C = 830 - 270(\%C) - 90(\%Mn) - 37(\%Ni) - 70(\%Cr) - 83(\%Mo)$

(b) $B_{50} = B_s - 60^{\circ}C$

(c) $B_f = B_s - 120^{\circ}C$

It was found that additions of C, Mn, Cr, Mo, W, Ni, Cu, V and Ti all were capable of lowering the transformation temperature and producing higher strength bainitic structures. By this means, alloying the low carbon ½%Mo-B base steel produced a range of strengths of:-

Tensile Strength:- 530-1200MN/m²

0.2% Proof Stress:- 450-980MN/m²

These strength levels were all obtained in the air cooled condition after austenitising at 900/950°C, and could be achieved over a wide range of cooling rates or section sizes, with very little variation. At the same time, the temperature for the completion of transformation did not become so low that the weldability was impaired, i.e. transformation was always complete above the 290°C limit defined by Cottrell as that below which heat affected zone cracking might be anticipated. The reason for this was that martensite was not formed in the structures, which in all cases were low carbon bainite. With decreasing transformation temperature, the structures became finer and more acicular, and below a transformation temperature of about 550°C the structure changed from predominantly upper bainite to predominantly lower bainite.

Over the whole range of transformation temperatures observed, from 650°C down to 450°C, there was a linear increase in the strength as the 50% transformation temperature decreased, providing the carbon content was restricted to the range 0.05/0.20% and that the depression of the transformation temperature was brought about by metallic alloying additions. It was also found that the tensile strength could be related to the composition by an empirical equation of the type:-

$$T.S.(MN/m^2) = 15.4\left[16 + 125(\%C) + 15(\%Mn + \%Cu) + 12(\%Mo) + 6(\%W) + 8(\%Ni) + 4(\%Cu) + 25(\%V + \%Ti)\right]$$

The reason for this type of relationship is that the strength is linearly related to the transformation temperature, which is linearly related to the B_s (or B_{50}) temperatures, which in turn is linearly related to the chemical composition, i.e. the alloy content. Consequently there is a linear relationship between tensile strength and alloy content.

(d) The choice of alloying additions

This is governed by the combination of properties required, and also by economics. The primary requisites are weldability, formability and good impact properties. For good welding, a maximum carbon equivalent may be required, in which case alloying elements which are required to achieve a high level of strength may require to be compensated by a slight decrease in the carbon content.

The important mechanical properties are strength, ductility and impact resistance. The ductility is largely dependent on the level of strength irrespective of the alloying elements used, whilst the impact resistance depends on a complex of interactions involving strength, transformation temperature, austenite grain size, tempering treatment and composition. This will be discussed later, but for the best impact properties it would be necessary to start with a high level of strength produced by a depression of the transformation temperature by Nickel, with the carbon kept to a minimum. This would require a large amount of nickel, because it has a relatively small effect in depressing the B_s temperature, and for all but the most special applications the cost would be quite uneconomical. Such a high strength structure would require to be tempered, incurring further costs.

Onthe basis of simple alloying costs, Mn and Cr are the most acceptable elements and in fact are used in the higher strength bainitic steels. A sound metallurgical principle is to develop maximum strength without impairing weldability. This requires that the additions made should give maximum depression of the B_s temperature for a minimum depression of the M_s temperature, which will prevent heat affected zone cracking during welding. Thus the ratio, Depression of B_s : Depression of M_s, per wt % alloy addition, should be a maximum.

Element	Ratio $\frac{\text{Depression } B_s/\text{wt \%}}{\text{Depression } M_s/\text{wt \%}}$
Carbon	0.57
Manganese	2.72
Chromium	4.11
Nickel	2.18
Molybdemum	3.19

Carbon is obviously undesirable, even though it is cheap; thus increased strength is not achieved by increasing the carbon content - it would also be disastrous to the impact resistance.

On the basis of the above table, Cr, Mo and Mn are the obvious choices. Of these, ½% Mo must be present to achieve the bainitic structure by control of the transformation diagram. Because Mo is expensive, there is no incentive to use more. Consequently the preferred elements to produce high strength are Mn and Cr, both of which are relatively inexpensive. These elements are in fact used in two commercial compositions:-

(a) 0.12%C, 0.5%Mo-B + 1%Mn + 1%Cr

(b) 0.12%C, 0.5%Mo-B + 1½%Mn + 2%Cr

Of these, the second more highly alloyed composition gives a tensile strength of 1100-1200MN/m^2 with a 0.2% Proof Stress of 900MN/m^2 in the air-cooled condition.

(e) General Mechanical Properties

The tensile strength increases linearly as the transformation temperature decreases, as has already been shown, and it is observed that the proof stress increases linearly with increasing tensile strength according to:-

$$0{\cdot}2\%\ P.S\,(MN/m^2) = 0{\cdot}67 + 0{\cdot}55\ T.S\,(MN/m^2).$$

However, as the tensile strength increases, the ratio of 0.2%PS:TS decreases from ∿0.70/0.75 at TS = 450MN/m^2 to ∿0.65 at TS = 1200MN/m^2. This is due to internal stresses caused by the lower transformation temperatures required to produce the higher strengths. Relief of such stresses by tempering at 400°C does not cause any change in the tensile strength, but causes the ratio 0.2%PS:TS to increase to 0.75/0.80 irrespective of the initial tensile strength.

The tensile ductility of these low carbon bainitic structures is closely related to their strength, both the % Elongation and the % Reduction of Area decreasing as the strength increases, and the ductility values generally lie within a band defined by similar relationships obtained for tempered martensitic structures. There seems to be no systematic effect of alloy addition on the tensile ductility. The results, particularly for % Elongation, lie in a fairly narrow band so that a knowledge of the composition would enable the tensile strength to be calculated and the tensile ductility then to be estimated.

The impact properties are influenced by many factors, and before discussing them it is necessary to consider the bainitic microstructure and the strengthening mechanisms which are operative.

(f) The Microstructure of Bainite and the Strengthening Mechanisms Involved

Bainite is a transformation product which occurs at temperatures between the lower part of the ferrite (or pearlite) reaction and the M_s temperature. It is a shear transformation, the first formed nucleus generally being considered to be ferrite. This is true in lower carbon steels but may be questionable at higher carbon contents. The growth of the shear transformation product is diffusion controlled. There are two clearly defined forms of bainite, distinguished both morphologically and by the orientation relationship between the ferrite and the carbide. In the lower carbon steels the carbide is Fe_3C, but in higher carbon steels at low transformation temperatures there is some evidence that ε-carbide may form.

(i) Upper Bainite

The ferrite forms by shear as plates or laths, which co-operatively nucleate side-by-side in packets. It occurs at temperatures above 350°C in steels containing >0.6%C, but at somewhat higher temperatures in lower carbon steels, i.e. the temperature above which predominantly upper bainite forms seems to depend on the carbon content. At the temperatures at which it forms, carbon is sufficiently mobile to diffuse in the austenite in front of the growing bainite ferrite. Thus carbon enriched austenite is entrapped between the bainitic ferrite laths. This carbon enriched austenite can be retained, can form high carbon martensite or can form Fe_3C between the ferrite laths depending upon the composition, degree of carbon enrichment, rate of cooling or transformation temperature. If the structure contains retained austenite or martensite it may be termed granular bainite. The general structure comprises carbide films or elongated particles lying between the bainitic ferrite laths, i.e. at the lath boundaries. This

carbide has an orientation relationship with the ferrite derived from the mutual individual relationships between the ferrite and the austenite and the carbide (Fe_3C) and the austenite. The activation energy for the transformation is that for carbon diffusion in austenite. The lower the transformation temperature, the finer are the bainitic ferrite laths and the smaller and more numerous are the carbides at the lath boundaries. The higher the carbon content, the finer are the bainitic ferrite laths and the more numerous and continuous are the carbide films between the ferrite laths, so that the structure takes on a pearlitic aspect.

(ii) Lower Bainite

Forming at lower transformation temperatures, the initial ferrite plates are supersaturated with carbon, because carbon cannot so readily diffuse away from the growing ferrite. To maintain the driving force for the reaction, the carbon must precipitate within the bainitic ferrite laths, which do not form so readily as side-by-side nucleated bainitic ferrite packets. Thus the carbide precipitates as small plates within the ferrite laths, at a characteristic angle of $\sim 55^\circ$ to the long axis of the lath. This Fe_3C has an orientation relationship with the ferrite in which it precipitates. The activation energy for the process is that for carbon diffusion in ferrite. The lower the transformation temperature or the higher the carbon content, the finer are the bainitic ferrite laths, and the finer and more numerous are the carbide particles.

In both upper and lower bainite, the boundaries between the bainitic ferrite laths within a packet are low angle boundaries, which are obstacles for dislocation movement but not for crack propagation. The boundaries between packets, or the prior austenite grain boundaries, are high angle boundaries which impede crack propagation.

(iii) Strengthening Mechanisms

The strengthening mechanisms which are operative in bainite are:-

1. A fine ferrite grain size, i.e. lath size, which gives the usual Petch relationship with strength. The length of lath depends on the austenite grain or patch size. The width of laths decreases with decreasing transformation temperature, as also does the overall bainitic ferrite grain size.

2. The dislocation density, which increases as the transformation temperature decreases. These dislocations are due to the transformation strains, but also the more numerous the carbides the greater is the dislocation density.

3. The carbide dispersion which is increasingly effective with increasing carbon content and with decreasing transformation temperature.

4. The carbon dissolved in the bainitic ferrite, which increases with decreasing transformation temperature. This causes solid solution strengthening, and strengthening by interaction with dislocations.

It can be seen that all these strengthening mechanisms increase in intensity as the transformation temperature decreases, but at present it is not possible theoretically to explain the linear increase in strength with decreasing transformation temperature.

A recent analysis shows that:-

$$0{\cdot}2\%\ P.S\ (MN/m^2) = 15{\cdot}4\left[-12{\cdot}6 + 1{\cdot}13 d^{-\frac{1}{2}} + 0{\cdot}98 n^{\frac{1}{4}}\right]$$

where d = bainitic lath size (mean linear intercept) in mm
n = number of carbides per mm^2 intersecting a plane section.

This equation only applies for relatively finely dispersed carbides, and carbide dispersion only becomes significant as a strengthening mechanism if the carbide spacing is less than that of the bainitic ferrite lath grain size. Thus in low carbon upper bainite, the strength is virtually completely controlled by the bainitic ferrite lath size. Only in the lower bainites, and in certain cases in higher carbon upper bainite, is there a significant contribution from carbide dispersion strengthening. In upper bainite the dislocation strengthening is incorporated in the grain size effect, as the dislocations largely form the bainitic ferrite lath boundaries, but in lower bainite dislocation strengthening tends to be incorporated into the carbide dispersion affect.

Kelly has attempted to break down the contributions from the individual strengthening mechanisms in lower bainites. Whilst an overall equation relating microstructure to proof stress was not described, it was shown that reasonable values of austenite grain size, dislocation density and carbide interparticle spacing can account in general terms for the strengths observed. By manipulating his various relationships, an equation of the following type is obtained:-

$$0{\cdot}2\%\,P.S\,(MN/m^2) = 9{\cdot}8\,(60 + 1{\cdot}25\,\mu b\, n^{\frac{1}{2}} + 1{\cdot}2\times10^{-4}\sqrt{\rho})$$

where n = number of carbides per mm^2 on a planar section
μ = shear modulus
b = burgers vector
ρ = dislocation density in lines per mm^2

The constant (60) incorporates an austenite grain size term, but there is no term for the bainitic ferrite grain size, probably because the carbide interparticle spacing is much smaller than the bainitic ferrite grain size and thus eliminates the latter as a major strength controlling mechanism.

On the other hand, Smith and Heheman produce an equation:-

$$0{\cdot}2\%\,P.S\,(MN/m^2) = 650 + 12{\cdot}3\times10^{2}\,\bar{\omega}^{-1} + 41\times10^{-3}\,\lambda^{-1}$$

where $\bar{\omega}$ is the average bainitic plate width
and λ is the average planar interparticle carbide spacing, both being measured in mm.

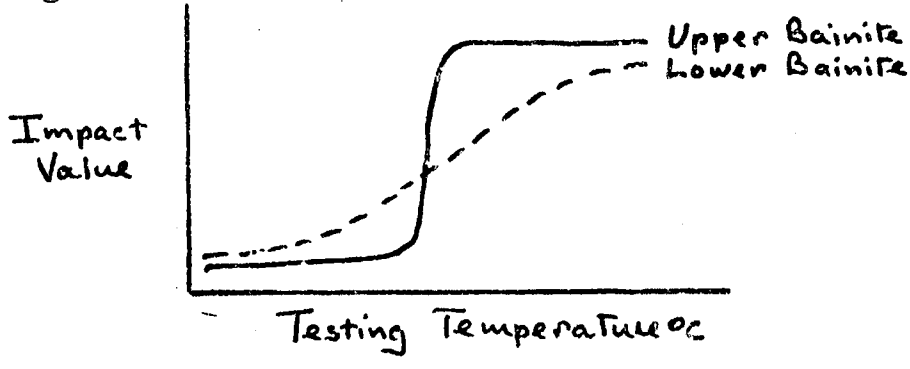
It will be observed that this latter equation does not follow the $d^{-\frac{1}{2}}$ relationship, nor does it include the dislocation density.

LECTURE 5

(a) The Impact Properties of Bainite

Much confusion has existed concerning the relative merits of bainite and tempered martensite from the point of view of impact toughness. This has been largely due to an inadequate basis for comparison, often a lower carbon bainite being claimed to be superior in toughness to a similar strength tempered martensite which was invariably of higher carbon content. When equivalent carbon contents are compared, there is some evidence that isothermally transformed high carbon bainites are superior to tempered martensite. The reason for this might be concerned with the freedom from quench cracking in the bainite compared with the tempered martensite.

However, there is no doubt at all that, in low carbon steels, upper bainite has inferior impact resistance compared with lower bainite. As the strength of low carbon bainite increases, the impact transition temperature increases, as expected. At a tensile strength of $\sim 900 MN/m^2$, the transformation temperature being $\sim 550^{\circ}C$, the structure of 0.10/0.15%C bainite changes from the upper to the lower form, and there is an abrupt decrease in the I.T.T. With increasing strength in the lower bainite structure, the Impact Transition Temperature again increases. Thus, for a comparable strength, upper bainite has lower impact toughness than lower bainite, and this behaviour is observed in bainites of many different compositions, although the actual level of Impact Transition Temperature varies with composition, i.e. Ni gives generally lower Impact Transition Temperature values. Also, the change from upper to lower bainite is accompanied by a change in the shape of the impact transition curve from an upright type to one with a much wider and less distinct transition range.



The reasons for this behaviour are:-

(a) in upper bainite, the large carbides or high carbon martensite areas crack, and once initiated the cleavage crack is not obstructed by the low angle bainite ferrite boundaries, but only by the higher angle "packet" boundaries or prior austenite boundaries. Thus the crack propagates rapidly.

(b) in lower bainite, the smaller carbides do not crack and thus there is no easy brittle failure initiation. Once a cleavage crack is initiated however, the propagation is obstructed by the many carbides and increased dislocation density. Thus, although the cracks initiate at higher temperatures because of the higher strength, they do not propagate so easily. In fact they frequently are arrested and have to be re-initiated; hence the extended impact transition temperature region, and the very sloping transition curve. Due to the form of the curves, there are temperatures at which lower bainites have higher impact values than lower strength upper bainites.

These features have consequences upon the design of bainitic steels. Upper

bainites can only be improved in impact resistance by refining the prior austenite grain-size, which will lower the Impact Transition Temperature. The steel is already grain refined by the (Al + Ti) addition, and so resort must be made to controlled rolling to lower the finishing temperature and refine the prior austenite grain size. This can only be achieved in the lower strength steels, because such a fine austenite grain size is required in the higher strength upper bainites that a sufficiently low rolling finishing temperature cannot be achieved. Tempering cannot be used in upper bainite because no softening (and hence benefit on the Impact Transition Temperature) is achieved until very high tempering temperatures, when ferrite grain growth occurs which still further impairs the impact properties.

In lower bainites, because of their good initial impact resistance, a reduction of the strength by tempering will produce a lowering of the Impact Transition Temperature, the beneficial dispersion of carbides is still being maintained. Thus tempering a high strength lower bainite progressively lowers the Impact Transition Temperature. At the highest tempering temperatures however, ferrite grain growth occurs which increases the Impact Transition Temperature. A band of results is thus obtained for Impact Transition Temperature against the tempered strength, the lowest Impact Transition Temperature values in the band being obtained with expensive nickel steels. The optimum combination of strength and toughness is an Impact Transition Temperature of -40°C at a 0.2%PS value of 530MN/m^2.

(b) Methods of Improving Bainitic Steels, and their Applications

(i) Very low normalising temperatures and rapid austenitising rates. This gives the best impact properties, and high strength.

(ii) Very low finishing rolling temperatures, as in thin strip. Finishing rolling as low as 600°C has given excellent impact resistance and high strength in upper bainitic structures.

(iii) Ausforming, but the effect is smaller as the transformation temperature increases, due to self annealing effects.

(iv) Precipitation hardening in the air cooled condition. Nb can be used but the strength increase is small at the high strength levels involved i.e. 75MN/m^2, and therefore only gives a marginal improvement. Copper additions can give 150MN/m^2 increase in yield stress, which is appreciable, and can be made to occur in the air cooled condition without a separate ageing treatment if 3%Cu is added.

(v) Bainitic steels can be used in the quenched and tempered condition, but only with detriment to their economic attraction. Nevertheless such material would not be so susceptible to loss of properties if slack-quenched, and would give more uniform properties across thicker sections.

Various alternative low carbon bainitic steels have been developed:-

(i) 0.10/0.15%C, 1%W-B, which is more expensive than ½%Mo-B steel.

(ii) Semi-bainitic steels using combinations of Cr + Mo, without Boron. These produce ferrite and bainite structures. To obtain the best properties they are quenched and tempered, giving good Impact toughness.

(iii) Ni-Mo-B steels with only ¼%Mo. These have excellent impact properties, but are expensive.

(iv) Very low carbon (0.02%) 3%Ni, 2%Mo steels grain refined by Nb or (Al+N). These steels give strengths of the same order of magnitude as the

½%Mo-B higher strength bainitic steels, but because of their very low carbon content and high nickel content, they show excellent impact properties. However, with such high Ni and Mo contents they are extremely expensive.

(v) The "Fama" steels containing 0.03%C with 2.5-3.5%Mn, and 0.05-0.10%Nb As might be expected, these steels show excellent strength, but require to be quenched to achieve the best impact properties.

(vi) Recently developed 0.03%C, 1.7%Mn, 0.25%Mo, 0.06%Nb steels for gas and oil pipe lines, containing also 0.2%Ni + 0.2%Cu, to acquire the necessary hardenability and depression of the transformation temperature. These are used in the controlled rolled condition, and employ inclusion shape control, but currently it is doubtful whether they will take over from the controlled rolled fine grained ferrite-pearlite steels for pipe-lines, due to their extra cost. Even the low carbon content increases the cost considerably.

Applications for low carbon bainitic steels include pressure vessels, boilers, cranes and lifting equipment, pipes for gas and oil transportation, earth moving vehicles, structural members of light weight bridges, mine supports, fans, strong structural components in aircraft engineering, engine mounts, plates for heavy engineering applications etc. .

(c) High Carbon Bainitic Steels

Weldability requirements have limited the carbon content of all the previous steels considered, and this also limits the strength to little more than 1150MN/m^2 unless precipitation hardening is used, because this is the tensile strength of 0.10/0.15%C martensite. For applications where weldability is not essential, higher carbon can be used, and higher strengths are possible. The objective in the development of higher carbon bainitic steels is to lower the B_s temperature even further so as to obtain lower transformation temperatures and higher strengths, and to produce bainite over a wide range of cooling rates without the formation of martensite, which in these higher carbon steels could give quench cracking and inferior impact resistance due to mixed bainite-martensite structures.

The increased strengths obtainable are due to:-

(i) Increased carbide dispersion strengthening.

(ii) Further refinement of the bainitic ferrite grain size.

(iii) Increased dislocation density due to the lower transformation temperatures.

(iv) Increased interstitial carbon content due to lower the transformation temperatures.

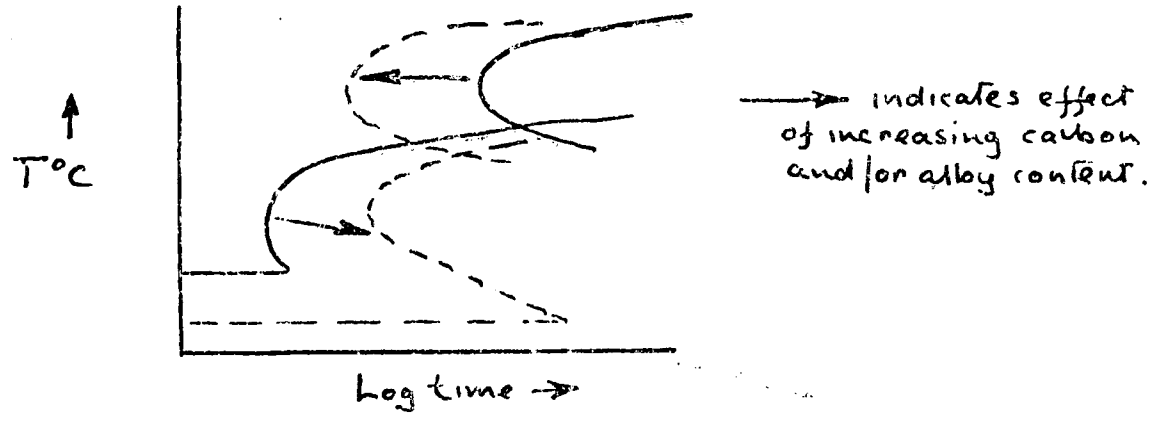
The base compositions used for these developments were the high strength low carbon steels, containing up to 1% Cr with 1½%Mn + ½%Mo-B, with carbon additions of up to 1.0%. It must be appreciated that as the carbon content increases to the entectoid composition, the effect of boron on the hardenability decreases to zero, and so at the highest carbon content, boron has little value.

With a 0.5%Mo-B base composition, fully bainitic structures are obtained in the austenitised and air cooled condition with up to 0.8%/1.0%C. The maximum strength with 0.8%C, is about 1300MN/m^2 tensile strength, which can be achieved in air cooled section sizes from ½" to 12" diameter.

This is a more restricted range of section sizes than is possible with low carbon bainitic structures, and the reason for this will be discussed later. Little change of strength occurs on tempering up to 500°C, but there is a progressive loss of strength on tempering further to 650/700°C.

In the ½%Mo-B steels, the transformation temperature is still high in the bainitic range at ~550°C, but lower transformation temperatures and higher strengths can be achieved by increasing the Mn or Cr contents to 1%-1½%. Tensile strengths of >1500MN/m^2 can then be achieved in 0.6%C steels, the transformation temperature being depressed to 450°C. Due to the lower carbon content compared with the ½%Mo steels, those Cr-Mn-Mo-B steels form bainite over a wider range of section sizes, i.e. up to 25" diameter air cooled. If the austenitising temperature is increased to dissolve all the carbides, even higher strengths of 1750MN/m^2 can be obtained. The higher the tensile strength, the lower is the proof ratio, being only 0.65 at 1550MN/m^2 tensile strength. As in the case of the low carbon bainitic steels, tempering at 400/500°C increases the proof ratio to 0.80/0.85 and proof stress values of 1100MN/m^2 are obtained. Up to about a tensile strength of 1050MN/m^2, the tensile elongation is superior to that in martensite tempered to an equal strength, but at higher strengths the elongation is inferior to that of tempered martensite. At all strength levels, the reduction of area values are lower than those for equivalent strengths in tempered martensite. These effects probably are due to the higher carbon contents of the bainitic structures compared with those of the tempered martensitic steels. This is also reflected by the impact properties which are relatively poor for the bainitic steels, although they can be improved somewhat by tempering, albeit at the expense of some loss of strength.

Major limitations to the application of higher carbon bainitic steels are produced by the fact that, with both increasing carbon and alloy contents the bainite reaction is considerably retarded. Martensite thus forms at slower rates of cooling, i.e. the martensitic hardenability is increased. Also at the higher carbon contents, the steels are hyper-eutectoid, which together with the lack of an effect of boron, causes the pearlite reaction actually to be accelerated.



The result is a limitation of the range of rates of cooling over which bainite can form during continuous cooling, because martensite forms at ever slower cooling rates and pearlite at ever faster cooling rates. An example of this is shown by the fact that in a 1.0%C, 1%Cr, ½%Mo-B steel, bainite will only form in air cooled sections of 2 to 5 inches diameter. Air cooled bars less than 2 inches diameter form martensite and greater than 5 inches diameter form pearlite. Such a steel has a very limited range of use.

The design of the steels with respect to the choice of alloying elements is thus very important. What is required is an alloying element which greatly depresses B_s but which does not markedly retard the bainite

reaction at higher carbon contents. This would give the lowest transformation temperature, i.e. the highest strength, and also allow a minimum carbon content to be used so that the ductility and impact properties would be optimised. Also bainites would form over a wide range of cooling rates, particularly if the steel was not hyper-eutectoid, so that the pearlite reaction was retarded rather than accelerated. Mn and Cr are the cheapest, and virtually the most effective elements for depressing the B_s temperature. Little is known quantitatively about the effect of alloying elements in retarding the bainite reaction, particularly at high carbon contents, but from general hardenability effects coupled with cheapness, manganese would be expected to be preferred to chromium. Obviously carbon should be kept to a minimum consistent with the strength level required, as it markedly retards the bainite reaction and particularly lowers the Ms temperature, thus running the risk of quench cracking. In addition high carbon lowers impact toughness and ductility. Finally, the higher the tensile strength of the bainite, the lower the proof ratio, but this can be increased by tempering, which also can improve both toughness and ductility.

Applications for these steels are likely to be in large section sizes where they would be in competition with quenched and tempered martensitic steels. Being air cooled, they would be free from distortion and quench cracking, nor would they require elaborate and expensive quenching equipment. In a large section size, a quenched and tempered steel would require much more alloying additions to achieve the necessary hardenability (martensitic), because the bainite reaction together with the ferrite-pearlite reactions would need to be greatly retarded. Undoubtedly the bainitic steel would be cheaper as it would be much less alloyed, but the bainitic steel would contain higher carbon contents. Thus, where welding and high fracture toughness are less essential, high carbon bainitic steels can possess economic advantages, and particularly would be useful in wear resistant applications.

Some typical applications are large die blocks, mandrel bars, back-up rolls and high strength statically loaded machine parts. In addition potential uses could include drill rods, very high strength reinforcing bars, and wear resisting wheels and tyres. However, it must be appreciated that their uses are likely to be much more restricted than those of the low carbon bainitic steels.

LECTURE 6

Ultra High Strength Steels

Ultra high strength steels usually are considered to have 0.2% Proof stress values greater than 1400MN/m^2. The major uses are in applications such as aircraft undercarriages, high strength bolts and fasteners, certain types of pressure vessel, rocket motor cases, missile bodies, springs, high speed rotors, bearings and shafts, machine parts and in any weight saving application where a high strength:weight ratio is essential. The impetus for their development arose from aero-space and aircraft requirements, initially, in response to the development of the highest strength aluminium alloys which however could not match steels with respect to elastic modulus, impact resistance and elevated temperature properties.

The major requirements for this type of steel are:-

(i) the requisite strength
(ii) adequate ductility
(iii) impact resistance and toughness
(iv) fatigue strength
(v) some measure of weldability, particularly in sheet for rocket motors and missile casings.

Apart from the metallurgical principles on which their design is based, and which will be considered later, the adequate fatigue strength and ductility are best guaranteed by freedom from non-metallic inclusions. These play an increasing role as the strength exceeds 1200MN/m^2, because the material then becomes increasingly notch sensitive and any stress raisers are particularly detrimental. There is therefore an increasing tendency to use ultra-pure materials and vacuum melting in the production of these steels, both of which greatly add to the cost. For good weldability, purity is essential, particularly freedom from sulphur and phosphorus. The higher the carbon content, the greater the welding problems, so hydrogen must be kept to an absolute minimum. Hydrogen embrittlement is a particular problem, and electro-plating to give corrosion resistance has resulted in delayed brittle failure of aircraft undercarriages.

The strength of a martensitic steel depends mainly on the carbon content, and is relatively little affected by metallic alloying elements provided the steel is fully martensitic and untempered. Metallic alloying elements cause very slight solid solution hardening, but can slightly increase the hardness by depressing the M_s, causing less auto-tempering, and thus allowing the carbon content to exert its full hardening in the martensite.

The major strengthening therefore must generally be by carbon, except in the marageing or precipitation hardening steels, but the carbon should be as low as possible, consistent with the strength requirement, because:-

(i) there is a need for some degree of weldability, particularly in sheet
(ii) there is a need to maintain the ductility and toughness as high as possible
(iii) the higher the carbon, the lower the M_s and the more likely there is for quench cracking to occur
(iv) the decrease of hardness during tempering is more rapid with higher carbon contents, and so the tempering treatment would be more difficult to control.

Because quenched martensite is brittle a tempering treatment is required. The alloying elements are therefore selected to provide both adequate hardenability for the section size to be treated, and the requisite level of tempering resistance.

There are two main methods by which ultra-high strengths can be achieved in conventionally heat treated steels:-

(a) by using low tempering temperatures up to 350°C
(b) by using a secondary hardening reaction and tempering at temperatures in the range 550°-650°C.

The latter method has the advantage that the strength can be maintained to higher service temperatures, but has the economic disadvantage of requiring a more highly alloyed steel.

Other methods of inducing ultra high strengths, which will be considered, are:-

(i) thermo-mechanical treatments
(ii) rapid austenitising treatments
(iii) cold working or strain ageing of martensite
(iv) cold drawing pearlite
(v) age hardening very low carbon martensites, i.e. the Marageing Steels.

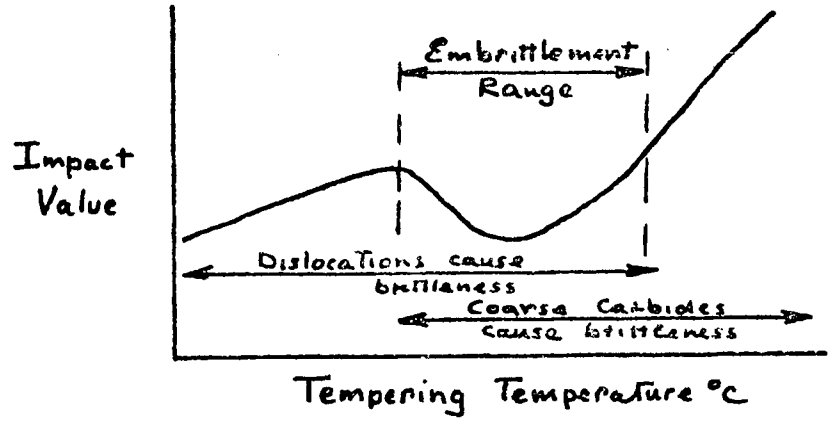
(a) Steels tempered at low temperatures

To obtain tensile strengths of 1500-2100MN/m², carbon contents of 0.3/0.4% are needed even when tempering is carried out at ∿200°C. This carbon content is therefore the minimum which can be used. The tempering temperature should be as high as possible so as to restore as much ductility and toughness, consistent with the strength requirements. In unalloyed 0.3/0.4%C martensite, it should be possible to temper at 300/350°C and still maintain a tensile strength higher than 1500MN/m². However the higher tempering temperatures in this range cannot be used because there is a decrease in the impact resistance when martensite steels are tempered at 250°/300°C. If tempering temperatures lower than 250°C are used to avoid this embrittlement, the general ductility will be very poor due to insufficient tempering of the martensite. If tempering is carried out above 350°C in order to achieve adequate impact resistance and ductility, the strength requirements are no longer obtained.

Several mechanisms have been suggested to explain the embrittlement which occurs in martensites tempered at 250/300°C:-

(i) the formation of cementite films at martensite plate boundaries.
(ii) ferrite films associated with cementite films at martensite plate boundaries. It is a well known phenomena that thin ferrite networks in a strong tempered martensite matrix, lead to marked embrittlement.
(iii) impurity elements, in particular embrittling elements such as Sn and P which raise the impact transition temperature and also induce intergranular embrittlement.
(iv) embrittlement produced by coarsening carbides whilst the dislocation density and matrix strength remains high. The embrittlement thus occurs at a temperature high enough to cause the martensite plate boundary carbides to coarsen and become sites at which cracking may initiate, but where the temperature is not high enough to anneal out the dislocation and so the matrix is still hard and has not recovered sufficient tough-

ness to impede the propagation of a cleavage or other brittle crack.



It is clear that if the tempering resistance can be increased by the use of alloying elements which retard carbide formation, then it should be possible to temper at temperatures above 300°C, thus avoiding the embrittlement region but still obtaining the requisite strength level because of the increased tempering resistance introduced by the alloying. An element which can produce this effect is silicon which markedly retards tempering at temperatures above 200°C. Other elements, for example, Al or P, also behave similarly, as do the stronger carbide formers, W and V. The choice of a suitable combination of alloying elements will require that:-

(i) the correct level of hardenability is obtained.
(ii) there is the required degree of retardation of tempering at temperatures above 300°C.
(iii) the M_s should not be depressed too much, otherwise quench cracking may occur. As low a carbon content as possible is advisable from this point of view, consistent with meeting the strength requirements.
(iv) the steel shall be as cheap as possible.

On the basis of these requirements, the ratio of the retardation of tempering per weight per cent alloy addition to the depression of the M_s per weight per cent alloy addition, should be a maximum. Appropriate data is:-

Element	Retardation of tempering per weight per cent (HV)	Depression of M_s per weight per cent (°C)	Ratio. $\frac{\text{Retardation of Tempering}}{\text{Depression of } M_s}$
Carbon	-40*	474	-12
Manganese	8	33	0.24
Silicon	20	11	1.8
Chromium	0	17	0
Nickel	8	17	0.48
Tungsten	10	11	0.9
Molybdenum	17	21	0.8
Vanadium	30	?	>1
Cobalt	8	Small Rise	>8

* Note that carbon accelerates tempering

It can be concluded that:-

(i) Carbon is detrimental and should be as low as possible consistent with the strength level required. About 0.3/0.4%C is necessary.
(ii) Cr contents should be limited, although about 1% may be necessary for the required hardenability.
(iii) Additions of Si and Co are very effective and beneficial.
(iv) Of the elements Mo, W and V, Mo is preferred to W on a cost basis, and Mo is also preferred to V because it does not require such high austenitising temperatures to dissolve the carbides prior to quenching. A high austenitising temperature would produce a coarse austenite grain size and much impaired impact properties.

Several high Silicon steels have been developed such as:-

(i) Modified SAE 4330 or 4340, 0.30/0.40%C, 0.7/0.9%Mn, 1.8%Ni, 0.85%Cr, 0.20/0.40%Mo with up to 1½%Si.
(ii) Various higher silicon, 0.3/0.4%C, Ni-Cr-Mo or Cr-Mo-V steels containing up to 2½%Si.
(iii) SAE 4137 + Co containing 0.4%C, 1%Si, 1%Cr, 1%Co, 0.25%Mo, 0.15%V. Note the presence of both 1%Si and 1%Co.

All these steels give 0.2% proof stress values of 1550-1700MN/m^2 when tempered above 300°C, i.e. above the toughness minimum. It should also be noted that two other types of alloy have been developed:-

(a) a high carbon-high cobalt steel was developed in USA, but does not seem to have been extensively used commercially.
(b) a 0.35%C, 2.25%Si, 1%Mo, 0.2%V, 2%Cu steel was developed in an attempt to minimise the transformation strains during martensite formation, and thus to minimise distortion and the tendency for quench cracking. The Copper not only improves hardenability, but can also give some added precipitation hardening after ageing at ∿450-500°C. This steel however is not widely used.

(b) Secondary Hardened Steels Tempered at 550-650°C

A carbon content of 0.30/0.40% is still required in order to produce proof stress values of more than 1550MN/m^2. If a higher tempering temperature is required so that the properties can be maintained at higher service temperatures, the problem is to increase the tempering resistance so that the requisite properties are achieved after tempering in the range 550°-650°C. This means that a secondary hardening reaction must be used, involving the precipitation of alloy carbides during tempering.

Primarily it is required to assess the chromium content which will give the required hardenability, in the appropriate section sizes, and the necessary corrosion and oxidation resistance at the service temperatures. Also the effect of Cr on the tempering resistance must be considered. It can be shown that 6%Cr can impart reasonable tempering resistance, without causing secondary hardening, but more than 6%Cr gives little added advantage on tempering at 550°C and above. A well known 5%Cr steel is used as a hot work die steel, and this can be employed as a base composition, although we shall see later how the Cr content can be reduced with advantage. The carbide precipitated in 0.3/0.4%C, 5%Cr steels is Cr_7C_3. This steel shows retarded tempering but no true secondary hardening, and Cr_7C_3 overages rapidly. The maximum retardation of tempering occurs at about 500°C but chromium is less effective as the tempering temperature increases to 700°C.

Secondary hardening by Mo and V additions markedly increases the tempering resistance. More than 1%Mo is needed to give the necessary secondary hardening, but little extra benefit is gained by more than 3%Mo. An optimum economic addition is about 2/2½%Mo, secondary hardening being due

to Mo_2C precipitation, which is formed in 5%Cr steels in preference to Cr_7C_3 due to the strong carbide forming tendency of Mo.

The use of ½%V can also produce adequate secondary hardening, V_4C_3 being formed. The addition of ½%V to a 2%Mo steel is not sufficient to form V_4C_3; the V dissolving in the Mo_2C and stabilising this carbide so that it forms at higher temperatures and overages less rapidly. This increases the tempering resistance. V_4C_3 would begin to form with additions of greater than ½%V, but only if the vanadium-rich carbide was completely dissolved by the use of high austenitising temperatures. This would lead to austenite grain growth and a loss of ductility and impact resistance. Thus vanadium additions are limited to ∿½%.

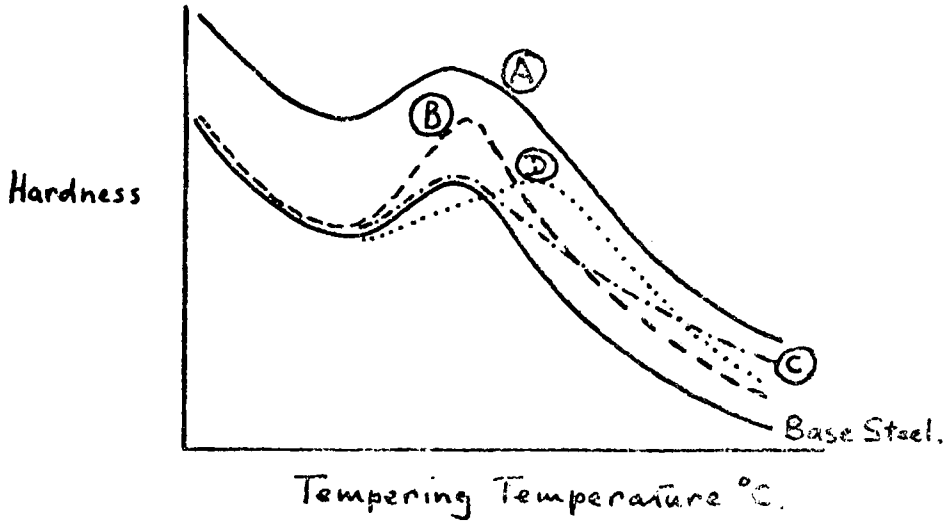
These steels, which contain Cr, Mo and V, have sufficient hardenability for all conceivable applications; in fact they are somewhat over-alloyed with respect to hardenability but require the alloying additions to promote the required tempering resistance. They are therefore expensive. Two typical examples of such steels are:-

Analysis (wt%)						Tempered 600°C 1h		
C	Mn	Si	Cr	Mo	V	U.T.S.	0.2%PS	%El
0.30	0.60	0.35	3.00	2.00	0.50	1750MN/m²	1320MN/m²	19
0.40	0.60	0.35	5.00	2.00	0.50	2000 " "	1560 " "	13

The criteria used in deciding the carbide forming elements are:-

(i) the increasing carbide forming tendency Cr→Mo→V.
(ii) the increasing resistance to carbide growth and overageing, $Cr_7C_3 \rightarrow Mo_2C \rightarrow V_4C_3$.
(iii) the temperature at which maximum retardation of softening occurs during tempering, or at which secondary hardening occurs, namely Cr_7C_3 (500°C); Mo_2C (575°C); V_4C_3 (600/625°C).

Certain general principles governing the intensity of secondary hardening can be employed to improve the properties still further. It can be seen that improved tempering resistance, and thus higher strength at a given tempering temperature (or the use of a higher tempering temperature to achieve a given strength and thereby a better ductility) can be produced by raising the whole level of the tempering curve (A), increasing the intensity of secondary hardening (B), decreasing the rate of overageing of the secondary hardening carbide (C), or by increasing the temperature of secondary hardening (D).



Increasing the whole level of the curve (A) could be achieved simply by increasing the carbon content, but this would drastically reduce the toughness and ductility, to say nothing of weldability, as well as tending to increase the rate of overageing. Carbon cannot therefore be used. Other substitutional solutes are also ruled out due to the very large and expensive additions required for any appreciable effect. However the intensity of secondary hardening can be increased by increasing the mis-match between precipitate and matrix. Whilst this tends to causemore rapid overageing the nett effect is beneficial, so that a higher strength after tempering is achieved. Increased mismatch is produced by:-

(i) increasing the lattice parameter of the carbide precipitate.
(ii) decreasing the lattice parameter of the matrix.

The carbide, Mo_2C, can dissolve both Cr and V. Cr, being a smaller atom than Mo, reduces the lattice parameter of Mo_2C, but V increases it. Chromium therefore tends to decrease the intensity of secondary hardening and moreover causes the Mo_2C to be less stable, i.e. to give maximum secondary hardening at lower tempering temperatures and also to accelerate overageing. Cr is therefore not desirable, but between 1% and 2% is required for the necessary hardenability and in this amount does not greatly impair the tempered hardness. More than 2%Cr is detrimental. On the other hand, V increases the lattice parameter of Mo_2C and stabilises the carbide. The result is a greater intensity of secondary hardening which occurs at higher tempering temperatures. Thus the tempering resistance is increased by vanadium, which therefore is beneficial. However, too much vanadium cannot be used due to its low solubility and the need for high austenitising temperatures, and so the vanadium must be limited to $\sim\frac{1}{2}$%.

Many elements increase the lattice parameter of the matrix ferrite, but silicon is one of the few elements which decrease it. It has the added advantage of cheapness. Silicon thus increases the intensity of secondary hardening, but also causes overageing to be more rapid and the maximum hardness to occur at rather lower tempering temperatures. The overall effect is however beneficial, giving a higher hardness after tempering at 550-650°C. An addition of 1%Si is therefore useful, and cheap. Too much silicon will however tend to make overageing too rapid for easy control, and so about 0.75%Si is about the optimum.

Using the above concepts, a steel has been developed containing 0.4%C, 0.75%Si, 1.5%Cr, 2%Mo, $\frac{1}{2}$%V, which gives a tensile strength of 1800MN/m^2 after tempering at 600°C, and 1560MN/m^2 after tempering at 650°C. This steel has the added advantage that the improved tempering resistance allows the use of marginally lower carbon contents, which together with the lower Chromium content give a lower M_S and less tendency for quench cracking. The hardenability is quite sufficient for most purposes.

As might be expected, these steels which are tempered at temperatures of 600/650°C, maintain their strength up to service temperatures of 500/550°C. However if the steels are tempered at the temperatures of maximum secondary hardening, in order to give the maximum strength, this is accompanied by a minimum in the impact resistance. Consequently the steels are always tempered to produce slight overageing, which whilst giving slightly lower strength produces much improved impact resistance, i.e. a better combination of properties.

It has already been indicated that the tendency for hydrogen embrittlement, and their sensitivity to impurity elements [illegible] the ultra high strength steels often being vacuum melted, albeit [illegible] increased cost. However, vacuum melting has the added advantage of

lowering the inclusion content, which gives much improved fatigue resistance. Steels with tensile strengths above 1550MN/m^2 tend to become increasingly notch sensitive, particularly with respect to fatigue resistance. Up to tensile strengths of about 1550MN/m^2 the fatigue ratio remains constant at about 0.5, but decreases to 0.4 with higher tensile strengths. Thus the effect of inclusions, which act as notches or stress raisers, can be very marked in these steels and it may well be that steels of 1860MN/m^2 tensile strength will have equal or even worse fatigue limits compared with steels of 1550MN/m^2 tensile strength. An example of this effect of inclusions impairing fatigue resistance is the development of special deoxidation techniques to produce clean steels of the 1%C-Cr type for roller bearings. A very good correlation has been obtained between the fatigue life and inclusion content in such steels.

LECTURE 7

(a) Thermo-Mechanical Treatments

(i) Low Temperature Thermo-Mechanical Treatment (LTMT)

This is basically "Ausforming" - in which the metastable austenite is deformed below Ae_1, after austenitising at conventional temperatures. Quenching is carried out directly after the deformation, followed by tempering of the martensite. The requirements for such a process are that there is an adequate metastable austenite bay in which deformation can be carried out, that the period of induction is sufficiently long for the deformation to be effected, and that the transformations are not accelerated very greatly by the deformation. The steel must obviously have adequate hardenability for the section sizes involved.

The quenching of the deformed metastable austenite occurs before any recrystallisation has taken place, and even recovery may only be partial due to the low temperatures at which the deformation occurs. The main drawbacks to the process are:-

(1) Deformations tend to be restricted because high loads are involved. Some control difficulties are experienced with regard to dimensions.

(2) General control of the process, i.e. preventing transformation during the deformation, is difficult.

(3) The process cannot be applied to carbon or very low alloy steels because of inadequate periods of induction.

(4) The process is expensive, special processing being required which prevents normal utilisation of plant, or even the installation of special plant.

The usual deformation temperatures are in the range 450-600°C, and in order to obtain significant strengthening, >70% reduction is necessary. It is found that:-

(1) The strength increases linearly with increasing reduction, at a rate of about $6MN/m^2$ per percent.

(2) The strength increases with increasing carbon content, but it is probable that the actual increase in strength due to ausforming is largely independent of carbon content.

(3) The ductility decreases as the carbon content increases.

(4) The strength tends to increase more or less linearly as the ausforming temperature decreases.

The choice of alloying elements is dictated by the need to obtain sufficient metastability of the austenite for the deformation to be accomplished. Silicon is reported to be beneficial as it inhibits recovery, as also does molybdenum, whilst nickel improves the impact strength. Chromium is reported to be detrimental to the response to ausforming. The prior austenitising temperature should be just sufficient to dissolve the carbides. Because higher strengths are obtained in ausformed steels, a slightly lower carbon content can be accommodated which gives rise to better ductility and toughness and less tendency for quench cracking.

It is often claimed that ausformed steels have superior toughness and ductility compared with conventionally treated steels. There seems some confusion concerning this effect, but it appears that when a strict comparison is made at the same carbon and strength levels, ausformed steels containing less than 0.45%C have poorer ductility than conventionally treated steels. The reverse seems to be the case for steels containing more than 0.45%C. Without doubt, very high strength levels, approaching 300MN/m^2 tensile strength can be achieved by ausforming:-

Carbon Content	Yield Stress MN/m^2			
	0.30%	0.40%	0.50%	0.60%
Conventionally Treated	1700	1900	2080	2280
Ausformed 91% @ 540°C	2080	2320	2620	2880

Ausformed steels are also able to hold their strength rather better than conventionally treated steels even at the highest tempering temperatures, but at high tempering temperatures the strengths of ausformed and conventionally treated steels do tend to approach one another. Ausforming can also be applied to bainitic steels, providing the deformation is applied above the B_s temperature. The strengthening achieved is less when the bainitic transformation occurs at high temperatures compared with low temperatures, due to some annealing out of dislocations from the deformed austenite, thus giving a lower dislocation density in the bainite.

The strengthening effects in ausformed steels are now believed to be due mainly to:-

(1) Very fine martensite plate sizes; deformation of the austenite inhibits the growth of the martensite plates. This is a relatively slight effect.

(2) Fine carbides which are induced to form in the austenite by the deformation, and which pin dislocations. Thus the austenite is able to recover less readily and shows greater strain hardening which is retained in the transformation product. Thus steels which precipitate carbides give greater response to ausforming:-

% Carbon	0.30	0.40	0.50	0.60
% increase in Yield Stress	22%	22%	26%	27%

In the higher carbon steels, these fine carbide precipitates lower the carbon in solution in the martensite, give less tetragonality, and probably contribute to the better ductilities in the higher carbon steels.

(3) A high dislocation density retained in the transformed product due to the increased dislocation density in the strained austenite prior to transformation.

Previous suggestions that strain induced carbide precipitation, preferred orientation effects and depression of the M_s were responsible for strengthening, are now believed to be of minor importance.

Applications of ausformed steels include springs for trucks and cars, torsion bars, cold heading punches, various tools, dies, rocket motor cases, armour plate, rifle and mortar barrels, high strength fasteners, etc. The usage has not been great due to the processing costs involved and the processing control difficulties. Also, restricted steel compositions only can be used for optimum effects, and plant loads are very high. The wear on rolls and extrusion dies is also great, and there is considerable difficulty in the final machining of ausformed components. The machining problem may be overcome by "cryoforming" in which the steel composition is so adjusted that the M_s is below room temperature. The austenite can then be deformed at or above room temperature, providing the M_d is not too high, the components machined at room temperature and then hardened by refrigeration followed by tempering. The problems, apart from the higher cost of the more highly alloyed material, are associated with the multiple processing involved, and dimensional instability and distortion during and after the transformation.

(ii) High Temperature Thermo-Mechanical Treatment (HTMT)

High temperature thermo-mechanical treatments are an extension of conventional rolling or hot deformation to lower than conventional finishing temperatures. They are in fact a controlled rolling treatment followed by quenching directly from the rolling finishing temperature, tempering then being carried out. The hot working is not usually carried down to below the Ae_3 temperature, and the main advantage is to cause considerable refinement of the prior austenite grain size. This is accelerated if elements such as Nb, Mo or Si are present, which retard recrystallisation.

The strength increases with increasing amounts of deformation, which should be 25-30% reduction in a single pass to achieve recrystallisation, and with decreasing deformation temperature. In fact there is no reason why the properties should not be continuous with those produced by ausforming:-

Finishing Temperature	0.2%P.S.	T.S.	%El
Conventional Rolling	2000MN/m²	2510MN/m²	-
750°C	2110 "	2570 "	4.0
730°C	2130 "	2590 "	4.0
680°C	2130 "	2610 "	4.8
650°C	2170 "	2630 "	5.0
Ausformed	2280 "	2880 "	3.0

The above properties are achieved with a constant reduction in a 0.6%C, 1.4%Si, 0.6%Mo, 0.2%V steel.

It is suggested thatthe HTMT process can be quite effective if the steel is allowed to recrystallise between each pass, provided the 25/30% reduction is achieved during the final pass. This indicates that this reduction is necessary in order to obtain recrystallisation to a fine grained austenite. Whilst a certain amount of strengthening is due to the smaller martensite plates brought about by the finer prior austenite grain size, there is also likely to be incomplete annealing out of dislocations as the finishing temperature is lowered, and these are inherited by the transofmration product. In fact Russian workers, who have been very active in this field, claim that if some short delay is allowed prior to quenching, extra recovery occurs which leads to the

development of higher ductilities, although at rather lower strength levels.

Very little work has been done on the effect of alloy composition, but again Russian workers indicate that secondary hardening steels containing Mo, V and Nb give the best response, and that in particular the strengths are maintained at higher service temperatures. The reason for this may be the precipitation of strain induced alloy carbides during the lower temperature deformation. It is also claimed that improved fatigue resistance can be obtained by the HTMT process, but there are some doubts whether this is the case when large deformations are used.

The major advantage of HTMT processing, compared with ausforming, is that there are no restrictions imposed by the transformation characteristics, because in general the deformation is carried out in the stable austensite range. This is not always the case however, as HTMT processes can be carried out as low as 650°C. The process is not very widely used, the major investigations having been conducted in the USSR. Service trials using HTMT processing for tools and dies have indicated useful increases in service life compared with conventionally treated steels.

(b) Rapid Austenitising Treatments

The advantage of a small prior austenite grain size is due to the small martensite plate size produced during transformation. This produces not only increased strength, but also improved ductility and toughness.

A method of refining the prior austenite grain size considerably is to use a very rapid heating rate to the austenitising temperature, coupled with very short holding times just above the Ac_3 temperature. A short flash superheat is then used to dissolve the carbides, but is insufficient to coarsen the austenite grain size.

The proof stress is increased by such treatments by about 10%, as a result of grain refinement of the martensite and by an increased dislocation density produced during quenching. The reason for the latter effect is not clear, but tempering at temperatures below 200°C is insufficient to anneal out these dislocations and poor impact properties are produced. Higher tempering temperatures do anneal out the dislocations, and the properties are then controlled mainly by the very fine martensite (or tempered martensite) plate size. Thus the impact properties are improved by rapid heat treatments when tempering temperatures above 400°C are used. The effect is however, relatively small. There is also evidence that rapid heat treatment prior to ausforming, whilst giving only slight increases in strength compared with conventional austenitising prior to ausforming, does produce quite substantial increases in toughness. This is in large measure due to the increased grain refinement produced by the rapid austenitising process.

The use of rapid austenitising treatments in order to produce marked improvements in the strength and toughness of ultra high strength steels has largely been confined to laboratory studies. There are considerable control problems, and capital plant would be required for commercial heat treatment practice. Also there are limitations imposed on the section size of components which could be heat treated in this way, due to the thermal constants of steel, unless the properties are only required in a thin surface layer (i.e. induction hardening).

(c) Other methods of treating Ultra-High Strength Martensite Steels

Various rather special methods have been investigated for increasing the strength of martensite or tempered martensite, with a view to producing extremely high strengths. None of the following have apparently yet found commercial application, not only because of the processing

difficulties encountered, but also because of the rather restricted sizes or section shapes which may be processed.

(i) Cold Working

Cold working of martensite by cold drawing can give very high strengths, but even with tempered martensitic structures the drawing reductions are limited to about 10%. Wear on the dies is of course a major problem, as also is the difficulty of obtaining uniform properties across all but the smallest section sizes. Using a 0.40%C-Ni-Cr-Mo, SAE 4340, steel, tempered to give a proof stress of 1660MN/m^2, the following properties can be achieved after cold drawing:-

% Reduction during cold drawing	0.2 P.S. MN/m^2	T.S. MN/m^2	%El	%R of A
0	1660	2110	9.0	35.3
3	2370	2540	5.5	31.5
6	2560	2730	4.5	25.5
9	2670	2750	2.0	10.5

It can be seen that a mere 10% reduction increases the proof stress by over 60%, but only at the expense of a considerable decrease in ductility. The sizes in which such properties have been produced are about 12mm diameter.

(ii) Strain Ageing

By cold drawing martensite or tempered martensite at temperatures of 100-300°C, strain ageing effects can be produced which result in very high strength levels, but this process has not proceeded beyond laboratory studies.

(d) Structure - Property Relationships in Tempered Martensite

Many workers have identified the strengthening mechanisms which contribute to the high strength of martensite. These include:-

(i) Carbon in solid solution.
(ii) A high dislocation density, particularly in lath martensite.
(iii) Precipitation of zones or actual carbide particles, the latter being the case in tempered structures.
(iv) Restriction of the dislocation free path by twin boundaries in internally twinned high carbon martensite.
(v) Interaction between carbon atoms and dislocations.
(vi) The fine martensite plate or lath size.

Whilst attempts have been made to quantify the contributions from each of the various mechanisms to the overall strength of martensite, and tempered martensite, relatively little progress has been made in relating the properties to microstructural parameters in the same way that ferrite-pearlite, and to a less extent bainite structures have been treated.

In tempered martensitic structures, recent attempts to relate the flow or 0.2% Proof stress to measurable microstructional parameters have led to the following types of equation being used with some success:-

(i) flow stress (MN/m^2) = $16.3 \times 10^3 \ (\rho^{\frac{1}{2}} + \lambda^{-1} + 1.1w^{\frac{1}{3}})$
where ρ = dislocation density, lines/cm^2
λ = inter-precipitate spacing, A°
w = weight % carbon in solution

It can be seen that the grain size does not enter into the relationship, because this is controlled by the interparticle spacing, i.e. the precipitates pin the tempered martensitic ferrite grain boundaries, and in fact λ is the controlling parameter as it is invariably less than the mean linear intercept of the grain size.

(ii) 0.2% P.S. $(MN/m^2) = 343 + 9.8\left[\left(\frac{k_1}{\lambda} \cdot \ell_n \frac{\lambda}{2b}\right) + k_2 \rho^{\frac{1}{2}}\right]$

Again the strength depends on λ^{-1} and $\rho^{\frac{1}{2}}$, b being the Burgers Vector of the dislocations.

(iii) 0.2% P.S. $(MN/m^2) = 550 + 1.23 \times 10^{-1} w^{-1} + 4.1 \times 10^{-2} \lambda^{-1}$
where w is the martensite plate size.

(e) Cold Drawn Pearlitic Steels

A very common method of producing ultra high strengths of considerably more than 1600MN/m^2 tensile strength is by cold drawing eutectoid carbon steel into wires. Many thousands of tons of such material is produced each year for such applications as high strength wire rope, springs, pre-stressed concrete wire etc.

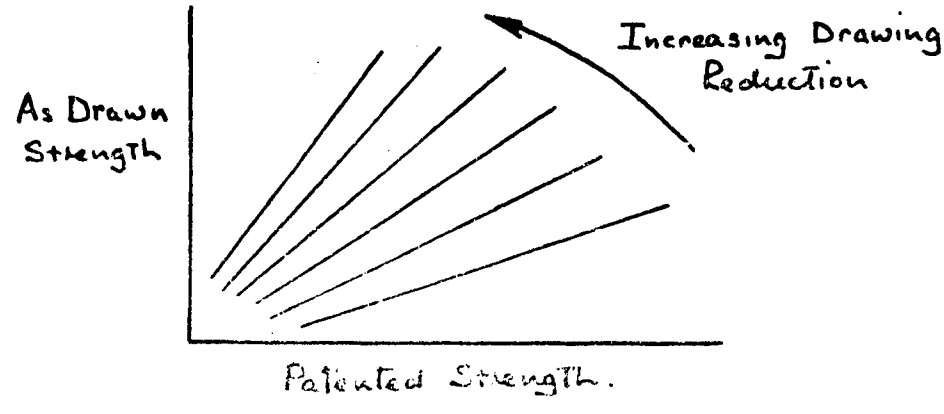
The strengths available by this process depend on the initial strength prior to drawing, and on the wire drawing reduction. The initial microstructure must be capable of being drawn readily without fracture, and therefore must be patented to give the finest interlamellar spacing of the pearlite. This allows the pearlitic carbide plates to be very thin and to bend during wire drawing, rather than to break and thus initiate failure. A minimum pearlite spacing of the order of 1000A$^{\circ}$ is achieved during lead patenting. A further advantage of the use of the finest pearlite interlammellar spacing is that the strength prior to drawing is high and thus less drawing reduction is required to achieve a given level of tensile strength. Also, the higher the initial strength, the greater is the work hardening rate, due to the smaller interlamellar spacing, so that this contributes to a lower wire drawing reduction in order to achieve a given strength level.

During wire drawing, the ferrite first work hardens and then the pearlitic carbide deforms by two processes:-

(i) initially pearlitic carbide lamellae allign themselves parallel to the direction of drawing, and often show kinking where slip bands cross them.

(ii) later the pearlitic carbide lamellae may deform and also become closer together as the ferrite slips out from between them. This gives a much increased work hardening rate.

The general relationships between the drawn tensile strength and patented tensile strength for varying reductions are shown schematically:-



The actual tensile strength which can be achieved increases with decreasing final wire size. For example about 98% reduction to produce 0.15mm dia wire can give a tensile strength of 3000MN/m^2, but this reduction could not be achieved to produce 5mm dia. wire because the starting size would require to be too great and the drawing forces would be unacceptably high. Consequently the limiting strength in 5mm dia. wire would be about 1650MN/m^2. The maximum strengths achievable appear to be of the order of 4600MN/m^2 in specially produced 0.08mm dia. wire in eutectoid steel. The alignment of the carbide lamellar in such material probably result in some fibre strengthening. The ductilities are very low, usually much less than 2% elongation. Also, the drawn tensile strength increases with increasing rate of wire drawing. Thus the larger number of dies used to produce a given reduction, the lower is the tensile strength.

In wire which has been heavily cold drawn to a high tensile strength, the proof stress is quite low, giving a proof ratio of 0.7/0.8. Ageing at room temperature gives an increase in the proof stress, but the effect is not too predictable. Secondary heat treatments, or stress relieving at 100^o - 450^{o}C are used to give more predictable movements in both proof stress and tensile strength, which increases the usable elastic range. For example, stress relief at 200^{o}C in a 0.8%C, 0.37mm dia. wire causes a strain ageing effect which raises the tensile strength from 1700MN/m^2 to 1850MN/m^2 but the proof stress increases from 1150MN/m^2 to 1700MN/m^2, albeit at the expense of a decrease in ductility. Due to these strain ageing effects, wire must be kept reasonably cool during drawing. A process has been developed in which the steel is drawn at temperatures of about 300^{o}C, called stabilising, which increases both proof and tensile strength at the expense of ductility.

(f) Marageing Steels

An alternative method of producing ultra-high strength with much improved ductility, and particularly toughness, is the development of the Marageing Steels. The concept uses high purity, vacuum melted, very low carbon steels, which are highly alloyed with nickel. This gives the steel the ability to transform to a very low carbon martensite, even at very slow cooling rates. The very low carbon content, high purity and high nickel content produce excellent impact resistance and fracture toughness, which also is a result of the fine grain or lath size of the martensite. This martensite contains a high dislocation density, but in general the martensite is relatively weak, with typical properties.

0.2 P.S.	T.S.	El%	R of A%	H.V.
650-800MN/m^2	950-1050MN/m^2	17-19	70-75	290-320

The strength of this low carbon martensite then is increased by age hardening with intermetallic compounds, the most usual additions being cobalt and molybdenum with a little titanium and aluminium, or higher titanium and aluminium additions alone. Three main types of Marageing steel have been developed:-

(i) 18%Ni Steels

These steels are predominantly Fe-18%Ni alloys which are age hardened by large amounts of Mo and Co with minor amounts of Ti and Al. Three alloys have been developed of this type to give yield or proof stresses of 1350, 1650 and 1950MN/m^2. Typical compositions are given in the following table, and all contain a very low impurity content, are single or double vacuum melted and contain additions of 0.003%B, 0.02%Zr and 0.05%Ca to scavenge impurities and help improve hot workability. The steels are inherently fine grained.

Nominal Yield Stress MN/m^2	Analysis wt. %									
	C	Mn	Si	S	P	Ni	Co	Mo	Al	Ti
1350	<0.03	<0.10	<0.10	<0.01	<0.01	17-19	8 -9	3 -3½	0.10	0.20
1650	<0.03	<0.10	<0.10	<0.01	<0.01	17-19	7 -8½	4.6-5.1	0.15	0.40
1950	<0.03	<0.10	<0.10	<0.01	<0.01	17-19	8½-9½	4.7-5.2	0.15	0.60

Note the low impurity contents and the fact that as the strength increases, so does the Mo and Ti contents. The precipitation hardening phase is predominantly Ni_3Mo (ortho-rhombic) which forms as small plates, but some Ni_3Ti is also precipitated. In the heavily overaged condition, Fe_2Mo has been reported. The role of cobalt is to intensify the precipitation hardening due to Ni_3Mo, but Molybdenum is the major age hardening addition. All the alloy additions, with the exception of Cobalt, depress the M_s temperature. A particularly useful function of the cobalt is to raise the M_s temperature and thus keep the M_f of the alloy above room temperature, so that it is fully transformed. Solution treatment temperatures are 850/870°C, followed by air cooling or water quenching, and ageing is carried out at 480°C for 3h. The ageing temperature or time can be adjusted to produce a range of strengths, but too high an ageing temperature results in re-austenitisation, the austenite often being so stable as to be retained as such because it is sufficiently alloyed for its M_s to be below room temperature. Should higher strengths be required, it is possible to cold work the initial low carbon martensite by about 50% reduction prior to ageing. Typical properties are:-

Nominal Strength	0.2 P.S. MN/m^2	T.S. MN/m^2	%El	%R of A	Impact value at 20°C-J
1350MN/m^2	1290-1430	1350-1500	14-16	65-70	81-149
1650 "	1650-1850	1730-1900	10-12	48-52	24-35
1950 "	1950-2080	2040-2100	12	60	14-27

The impact properties are excellent at the high tensile strengths produced, and in fact the alloys notch strengthen so that the ratio of notched tensile strength:tensile strength is in the range 1.35-1.65. Cold working 50% prior to ageing can increase the yield or proof stresses to 1700, 2000 and 2100MN/m^2 for the three nominal strengths discussed.

(ii) 20%Ni Steels

The base analysis is similar in terms of impurity levels to the 18%Ni-Mo-Co alloys, but the Ni is increased to 20%. Instead of Mo + Co additions, precipitation hardening is produced by about 1.5%Ti, 0.25%Al and 0.5%Nb. The M_s temperature is rather lower than for the 18%Ni steel, but the alloy is substantially transformed after solution treatment and cooling to room temperature; should transformation be incomplete, it may be completed by refrigeration at -78°C or by cold working, which raises the M_s temperature. Ageing is then carried out at 480°C for 3h, either with or without refrigeration, which has little effect on the strength because the alloy is largely transformed prior to refrigeration. Increased strength is produced if the alloy is cold worked prior to ageing. The precipitates responsible for the age hardening are $Ni_3(AlTi)$ and Ni_3Nb. Typical properties are:-

	S.T, 820°C + 480°C-3h	S.T, 820°C C.W So Vo + 480°C-3h
Tensile Strength MN/m²	1750	1880
Yield Stress MN/m²	1700	1850
%El	11	12
%R of A	45	57
Impact value at 20°C-J	20-27	-

This alloy has never been widely accepted commercially, as is very expensive

(iii) 25%Ni Steels

This 25%Ni base steel contains about 1.5%Ti, 0.25%Al and/or 0.5%Nb. The M_s temperature is below or very close to room temperature, and it is largely austenitic after solution treatment. Prior to age hardening it is necessary to transform the alloy to martensite, and two treatments have been used. These treatments, designed to transform the austenite to martensite, are:-

(1) Ausageing

The austenite is aged at 700°C to precipitate $Ni_3(AlTi)$ and/or Ni_3Nb. This lowers the solute content of the austenite, thereby increasing the M_s temperature so that on subsequently cooling to room temperature the alloy transforms predominantly to martensitic. Full transformation can be ensured by subsequent refrigeration at -78°C prior to the age hardening treatment at 480°C for 3h. The ausageing at 700°C will age harden the austenite, by the formation of γ' $Ni_3(Al\ Ti)$, but this γ' will lose coherency as the austenite transforms to martensite. However less Ti + Al will be available for subsequent age hardening of the martensite and thus the strength is lower as shown in the properties given later.

(2) Cold Work and Refrigeration

The austenite must be cold worked at least 25% reduction in order to raise the $M_s - M_f$ range sufficiently for full transformation to occur at -78°C. A lower refrigeration temperature of -196°C is optional. This cold work and refrigeration treatment allows the full intensity of precipitation hardening to be developed from the alloy additions, thus the strengths achieved are higher than in the ausaged condition.

This alloy is very expensive to make, process and heat treat, and has been little used commercially. Typical properties are:-

	S.T + Ausage at 700°C Refrigerate -78°C Age 480°C-3h	S.T + CW 60% Refrigerate -78°C Age 480°C-3h
Tensile Strength MN/m²	1850	2000
Yield Stress MN/m²	1730	1950
%El	12	13
%R of A	53	58

(iv) Alternative Marageing Steels

In view of the high cost of the marageing steels, attempts have been made to produce cheaper versions based on:-

(a) Alternative base compositions in which the Nickel is partially or wholly replaced by Mn, Co or Cr.

(b) Alternative and cheaper age hardening additions to the normal Co-Mo combination.

Whilst alternative and cheaper base compositions can be found, which give similar strength levels to the Fe-Ni base alloy, this is only at the expense of a marked decrease in ductility, and especially in toughness. In fact the toughness may sometimes be inferior to that of conventional ultra high strength steels. Also suitable alternative precipitation hardening additions can also be found which will give equivalent strengths to the Co-Mo combination. Strong age hardening is produced by Al-Ti, Ti or Be; moderage age hardening by Al, Nb, Mn, Si, Ta, V and W; weak age hardening by Cu, Co and Zr. Of these the cheaper additions are Al, Al-Ti, Si and Cu, but the strengths can only be achieved at the expense of loss of toughness. Particularly interesting are the precipitation effects observed with Si and Be additions. The precipitates are body centred cubic, and due to a very small misfit with the α-Fe matrix, occur as small coherent spherical particles which resist growth. NiBe is an example of this type of precipitate, being capable of imparting high strengths. The amount of Be required is small (0.2%) but the cost is high.

The 18%-25%Ni marageing steels are not corrosion resistant, which tends to limit their use. Consequently alloys have been developed in which Cr partially replaces some of the Nickel. Two typical alloys are:-

(i) 0.02%C, 10%Ni, 10%Cr, 2%Mo, 0.3%Al, 0.2%Ti.
This alloy is not heavily age hardened and only achieves yield strengths of 1170-1400MN/m^2, but does have impact values comparable with those of 18%Ni-Co-Mo steels at similar strength levels.

(ii) 0.02%C, 7%Ni, 10%Cr, 10%Co, 5.5%Mo.
This alloy is considerably more highly alloyed and expensive, but shows marked age hardening which gives yield strengths of the order of 1500-1600MN/m^2.

Both alloys have very much improved corrosion resistance, and the higher Cr content changes the precipitating phase in the second steel from Ni_3Mo to the Cr-Co-Mo compound, R phase, which is similar to the phase precipitating in 12%Cr-Co-Mo steels which will be discussed later.

(v) General Properties and Applications

Generally, alternative marageing steel compositions do not lead to properties which are superior to the standard 18%Cr-5Mo-Co composition. The general properties of this composition over a range of strengths are:-

Tensile Strength MN/m^2	0.2% P.S MN/m^2	Impact Value at 20°C J
770	620	190
920	790	136
1080	950	108
1230	1130	68
1540	1460	27
1850	1800	20
2000	1950	15

The cost of the marageing steels is high, not only because of the cost of the alloying elements involved, but also because of the high purity materials required to ensure the best fracture toughness and the need to single or double vacuum melt. In addition, the multiple processing, i.e. heat treatments, required in some of the alloys, further increase the cost.

The 18%Ni-5%Mo-8%Co alloy is the only alloy which has achieved commercial application to any significant extent. It possesses very much superior toughness compared with conventional quenched and tempered steels, having at least a 450MN/m^2 advantage in yield strength for the same impact transition temperature. At the same yield strength, the room temperature impact values may be two or three times as high as those of conventional ultra high strength steels. This is not surprising in view of the very low carbon, high purity, high Ni, vacuum melted, compositions.

The major uses are for ultra-high strength, light weight structures where toughness is essential and cost no major limitation. Typical applications have been in light weight military bridges, rocket casings, highly stressed jigs and fixtures, extrusion rams and dies, special high duty gears and shafts, die casting moulds, indexing plates on automatic tools, holders for dies and light weight high strength fasteners. As with all ultra-high strength steels, machining is a problem, but no more so than with conventional quenched and tempered steels.

LECTURE 8

Stainless Steels

(a) Introduction

The first and most important property of the high chromium stainless steels is their corrosion resistance. Without this essential property, these steels would find little commercial use as their general level of mechanical properties and forming characteristics can be equalled or exceeded by many other types of steel at much lower cost.

Above 12%Cr also provides a considerable measure of oxidation resistance. Thus the stainless steels are also used for high temperature creep resisting or heat resisting applications, the temperature of application increasing with increasing chromium content. For creep resisting applications, the steels must be suitably alloyed to produce the required creep strength.

The important factors which must be considered in the design of the various types of stainless steel are:-

(i) the corrosion and oxidation resistance in the operating environment.

(ii) the mechanical and physical properties.

(iii) the fabrication characteristics from the point of view of both hot and cold working.

(iv) welding, as many of the stainless steels require to be readily weldable, and welding must not impair either the corrosion resistance, creep resistance or general mechanical properties.

(v) cost, particularly in relation to the prime material cost compared with maintenance, fabrication and installation costs. Also, as these steels are frequently employed in critical components, the complex series of costs incurred when such a component fails must also be considered.

There are many different stainless steels, and the main types which will be considered are:-

(i) Martensitic steels containing 12-17%Cr and 0.1%-1.0%C. These are often alloyed to produce the required tempering resistance and strength. They are austenitic at temperatures of 950-1000°C but transform to martensite on cooling. They have high hardenability, and are martensitic air hardenable even in large section sizes. This can lead to difficulty in softening for machining and fabrication, particularly as they are frequently alloyed to produce a high degree of tempering resistance. The steels are usually tempered to produce useful combinations of strength, ductility and toughness, and may also be precipitation hardened.

(ii) Controlled Transformation Stainless Steels, which contain rather higher Cr contents in the range 14-17%, together with some nickel. These are austenite at the solution treatment temperature, but have M_s temperatures which can be adjusted by various thermal and mechanical treatments so that they can be either metastable austenite or martensite at room temperature. In many respects they are the Stainless Steel analogues of the 25%Ni marageing steels, and were developed rather earlier. The transformation to martensite then requires the steels to be tempered, during which an age hardening

reaction can be introduced.

(iii) Ferritic steels containing 15-30%Cr with very low carbon, no nickel and often some Mo, Nb or Ti. These are highly corrosion resistant, show little or no transformation and, being fully ferritic, are reasonable formable. Despite certain drawbacks, they can in some circumstances replace the more expensive austenitic stainless steels.

(iv) Austenitic Steels, which contain 18-25%Cr with 8-20%Ni and low carbon contents. These steels often contain additions of Mo, Nb or Ti, and are predominantly austenitic at all temperatures, although if the ferrite forming elements are high, some delta ferrite may be present at high temperatures. The austenite may have varying degrees of stability, being transformed by cold work at room temperature in some compositions, whilst other compositions are stable down to -196°C and are not transformed even by the most severe deformation.

(b) Low Carbon Martensitic 12%Cr Stainless Steels

(i) Constitution

Above about 12½%Cr suffices to close the loop in the Fe-Cr system, but the loop is extended by carbon and other austenite forming elements such as nickel, reaching about 18%Cr at 0.6%C. As the steels are primarily used as stainless high strength structural steels, it is necessary that they are weldable, formable and have good impact toughness. Hence the carbon content is kept to about 0.1%C, and it can be seen from the Fe-Cr phase diagram that at 0.1%C the 12%Cr steel is borderline for forming delta ferrite at about 1050°C.

In order to develop the maximum strength, the steel should compromise 100% austenite at the solution treatment temperature of 1050°C, i.e. be fully martensitic after air cooling, because any delta ferrite detracts from the strength which can be achieved. However the strength of 0.1%C martensite is limited to about 1300MN/m tensile strength, and as the steel must be tempered it is necessary to alloy to increase the tempering resistance and thereby achieve the highest level of strength which is possible. The most effective alloying additions, as will be shown later, are the ferrite formers such as Mo and V. These will however tend to produce delta ferrite in the structure at 1050°C, and thus lower the strength obtainable. Therefore it is necessary to balance the constitution by additions of austenite forming elements such as Ni, Co, Mn or Cu. In this way a fully austenitic structure is achieved at 1050°C which results in a fully martensitic structure prior to tempering. In order to assess the constitutional balance the amount of delta ferrite introduced by unit weight per cent of alloying addition requires to be known. For 0.1%C, 12%Cr steels, this data is as follows:-

Element	Change in delta ferrite % per wt % alloying addition
N	-220
C	-210
Ni	-20
Co	-7
Cu	-7
Mn	-6
Si	+6
Mo	+5
Cr	+14
V	+18
Al	+54

The effect of elements such as Ti and Nb are difficult to assess as they are not only ferrite formers, but also combine with and remove the austenite formers C and N from solution. Approximate values for their ferrite forming effects are +12% and +14% delta ferrite respectively per wt % Nb and Ti.

The cheapest austenite forming addition would be carbon, but this is unacceptable as a higher carbon content would decrease the toughness and weldability, and require higher solution treatment temperatures to dissolve the carbides, with a consequent coarser austenite grain size and low toughness. Nickel is the most potent austenite former after carbon and nitrogen, and despite its cost suffers from fewer disadvantages than some of the other austenite forming elements; also less is required for a given balance to be achieved. As will be seen later, the use of nickel is also limited.

(ii) Transformation Effects

The M_s temperature of 0.1%C, 12%Cr steels is about 300°C, with the M_f temperature in the range 100-150°C. Any alloying to improve the tempering resistance and balance the constitution, with the exception of expensive cobalt, will further depress the M_s-M_f range so that there will be a tendency for retained austenite to be produced which will lead to:-

(i) possible distortion effects as it transforms;

(ii) lower strengths prior to tempering;

(iii) the formation of untempered martensite after the tempering treatment, because carbide precipitation will have raised the martensite range of the retained austenite to above room temperature.

Thus the alloy additions must be controlled in order to ensure that the M_s temperature is not below room temperature. Typical effects of various alloying elements in depressing the M_s temperature are:-

Element	Depression of M_s°C per wt %
C	-474
Mn	-33
Ni	-17
Cr	-17
Mo	-21
W	-11
Si	-11

Obviously, carbon is to be avoided, as also is Manganese, but Nickel can be used as it is very effective in lowering the delta ferrite content without depressing the M_s temperature too much. In fact a good criterion for a suitable element is for the ratio, decrease in delta ferrite per wt %:decrease in M_s temperature per wt % to be a maximum. Ni obviously fulfills this criterion.

However, Ni will decrease the Ac_1 temperature and thus limit the upper temperature at which tempering can be carried out without re-austenitisation (and either retained austenite or untempered martensite) occurring. As will be shown later, it is necessary to temper at as high a temperature as possible to achieve the best toughness and ductility for a given strength level, (hence the need to increase the tempering resistance), and also to give the best resistance to stress corrosion cracking. The effect of alloying elements in raising or lowering the Ac_1 temperature are as follows:-

Element	Change of Ac_1 °C per wt %
Ni	-30
Mn	-25
Co	-5
Si	+25
Al	+30
Mo	+25
V	+50

It can be seen that no more than 3%Ni can be accommodated if the steels are to be capable of being tempered at 650°C, and if reaustenitisation must not occur below 700°C, 2%Ni is the limit. In this respect it is fortunate that the elements which impart tempering resistance, Mo and V, increase the Ac_1 and thus offset the effect of nickel.

(iii) Tempering Resistance

The tempering of an unalloyed 0.1%C-12%Cr steel shows a marked retardation of softening up to tempering temperatures of the order of 500°C, followed by pronounced softening. The retardation of softening, rather than a pronounced secondary hardening, is produced by the formation of small precipitates of Cr_7C_3, but also there is some M_2X phase which likewise occurs as fine precipitates and has a close packed hexagonal structure based presumably on $Cr_2(CN)$. The presence of nitrogen causes M_2X to increase at the expense of Cr_7C_3, and the presence of Mo and V also accentuate M_2X formation with the result that true secondary hardening is produced. In the overaged condition, $M_{23}C_6$ forms progressively larger particles as the M_2X is replaced by the more stable carbide. Mo and V stabilise the M_2X, making its replacement by $M_{23}C_6$ less rapid so that the tempering resistance is increased. The principles employed are analogous to those already described for the secondary hardening ultra-high strength steels, and molybdenum is preferred to vanadium as an alloying addition to increase the tempering resistance. The M_2X formed in 12%Cr-Mo-V steels is of the type $(Cr.Mo.V)_2(CN)$. Molybdenum is also a less effective ferrite former than vanadium, and hence requires to be offset by less nickel. This is advantageous because nickel accelerates overageing and lowers the tempering resistance.

(iv) The design of high strength low carbon 12%Cr Steels

The design criteria for these high strength structural stainless steels can be summarised as follows, in that they require:-

1. A maximum tempering resistance.

2. The absence of delta ferrite.

3. An M_f temperature above room temperature.

4. An Ac_1 temperature as high as possible.

The reasons for these criteria have already been outlined. The uses of such steels are in petro-chemical and chemical plant construction, gas turbine engines, electrical generation plant, turbine blades, compressors and discs, and in a variety of aircraft structural and engine applications.

The combination of properties for these exacting applications is critical; toughness and ductility are a prime requisite together with the maximum strength possible. Accepting that the carbon, for obvious reasons, must be kept to 0.1%, and that the steel should be as cheap as possible, i.e. contain a minimum of the expensive alloying elements Ni, Mo and V, it is useful to consider the variation in properties which can be obtained by tempering at various temperatures.

From the general tempering curves it is clear that high strengths can be achieved by tempering at temperatures below 400°C, although the ductility and toughness might not be very great. Tempering at the temperature for maximum secondary hardening could produce rather higher strength, but as in secondary hardening ultra-high strength steels, the impact values are then a minimum and in addition the proof stress is very low due to the internal stresses associated with the secondary hardening. Tempering to the overaged condition restores the proof stress to a high level, and also causes a marked increase in the impact toughness, and in order to combat stress corrosion in many of the applications envisaged, the higher the tempering temperature the better. There are thus very good reasons for requiring the optimum tempering resistance. Consequently, these steels can be tempered either at low temperatures of $\sim$ 300°C to give the highest strength, but lower toughness and resistance to stress corrosion, or at higher temperatures of the order of 600/650°C to produce good toughness at lower strength, but the optimum stress corrosion resistance.

The principles on which the design of these low carbon 12%Cr steels are based demand a careful balancing of the composition, and this tends to impose certain limitations on the composition variables which can be used. An optimum composition which has been developed is:-

0.1%C, 12%Cr, 2%Ni, 1½%Mo, 0.3%V.

This is solution treated at 1050°C and tempered either at 300°C or 650°C for 1 h. If improved impact properties are required, at the expense of some loss of strength, a 0.1%C, 12%Cr, 1½%Ni, 1½%Mo steel can be used. Note that less nickel is required in this steel due to the absence of vanadium. Typical properties of these steels are:-

Steel	0.1%C, 12%Cr, 2%Ni 1½%Mo, 0.3%V		0.1%C, 12%Cr, 1½%Ni 1½%Mo	
Tempering Temperature	300°C - 1h	650°C - 1h	300°C - 1h	650°C - 1h
Tensile Strength MN/m^2	1310 - 1390	925 - 1000	1250 - 1330	770 - 850
0.2%P.S. MN/m^2	940 - 1040	740 - 820	925 - 1000	570 - 650
% Elong.	16 - 20	17 - 21	18 - 22	21 - 24
Impact Value at 20°C J	40 minimum	68 minimum	68 minimum	108 minimum

(c) The development of higher strengths in low carbon 12%Cr Steels

Various methods are available:-

(i) The Intensification of Secondary Hardening

The intensity of the secondary hardening reaction, and causing it to occur at higher tempering temperatures, will increase the tempering resistance and thus the strength for any given tempering treatment. Such an intensification of secondary hardening by increasing the amount of M_2X precipitation can be achieved by slightly increasing the carbon content, and by increasing the nitrogen content. The use of increased carbon is obviously limited, as also is the use of nitrogen due to solubility considerations which can lead to porosity in the ingots. Nevertheless some improvement can be made, and after tempering at 650°C - 1h the 0.2%P.S is given by:-

$$0.2\%P.S.\ MN/m^2 = 710 + 770\ (C + 2N)$$

0.2%P.S. values of 900MN/m² can be achieved in 0.15%C, 0.05%N_2 steels, but at the expense of a lower impact value of 41J, at 20°C.

It is also possible to apply the same principles for increasing the secondary hardening intensity as are used in secondary hardening ultra-high strength steels, i.e. by increasing the lattice parameter of the M_2X and decreasing the lattice parameter of the matrix. This can be done by increasing the Mo + V to the limit, adding 1%Si and balancing the constitution and transformation characteristics by Ni, N_2 and Co. Cobalt is particularly useful as it does not depress the Ac_1 temperature and actually raises the M_s temperature. Some Nb can be used to increase the stability of the M_2X and refine the prior austenite grain size, which improves the ductility and toughness, or rather does not allow them to deteriorate so markedly as the increase in strength might indicate. An alloy of composition:- 0.12%C, 1.2%Si, 12%Cr, 2%Ni, 3%Mo, 0.35%V, 0.4%Nb, 4%Co and 0.05%N_2 will give the following properties after tempering at 650°C-1h:-

Tensile strength:-	1350MN/m²
0.2% Proof Stress:-	1100MN/m²
% Elongation:-	18%
% R of A:-	44%
Impact Value at 20°C:-	8.J

The Co also gives slight solid solution hardening.

(ii) The Introduction of Precipitation Hardening Reactions

Various precipitation hardening additions can be used to increase the strength, although with an accompanying decrease in impact resistance. Some typical age hardening additions are Copper, which precipitates copper and at 3% to 4% Cu can increase the proof stress by a maximum of 75-150MN/m², or Aluminium and/or Titanium when accompanied by somewhat increased nickel contents. There are problems with such compositions, because whilst age hardening can be made to occur by the precipitation of Cu, NiTi or NiAl, the maximum effect usually occurs on tempering at ~500°C which is too low for good toughness. Therefore higher tempering or ageing temperatures result in marked overageing and loss of strength. However, the main difficulty is to maintain the constitutional balance and the correct transformation characteristics. Consequently such steels are not widely used in commercial practice.

However, by increasing the Mo content and balancing the ferrite forming tendency with Co, which does not depress the M_s temperature, precipitation

reactions can be made to occur at higher temperatures, thus allowing tempering temperatures of 600/650°C to be used. With increasing Mo and Co contents, the whole level of the tempering curve is raised and the normal secondary hardening by M_2X is gradually replaced by the precipitation of an intermetallic compound based on the Mo-Cr-Co phase, R.phase. This intermetallic precipitation occurs in the presence of more than 4%Mo and the maximum hardness occurs on tempering at 600/650°C, compared with 500/550°C for M_2X. This type of precipitation does not depend on the carbon content, which can be lowered to 0.03/0.04% in order to maintain the ductility and toughness at the much higher strength levels achieved. A disadvantage with this type of reaction is that overageing tends to produce large particles of Fe_2Mo (Laves phase) or chi phase (a molybdenum variant of sigma phase); these cause embrittlement. However, an analogous age hardening reaction can be produced by substituting W for Mo, but rather more W than Mo is required. The advantage of W is that it is less liable to form large intermetallic compounds during overageing, and thus gives better impact properties at tensile strengths up to 1400MN/m² than does molybdenum.

Steels can thus be achieved with the correctly balanced constitution, M_S and Ac_1 temperatures, each capable of very high strength levels, based on Mo-Co and on Mo-W additions. The compositions and properties after tempering at 650°C for 1h are as follows:-

Analysis wt %						Properties			
C	Cr	Mo	Co	N	W	TS(MN/m²)	0.2PS(MN/m²)	% El	J at 20°C
0.04	12.2	6.3	10.0	0.05	-	1800	1300	10	14
0.10	12.0	-	5	0.03	6	1450	1100	15	20

It can be seen that the Co-Mo steel gives the higher strength, but a greater strength can be achieved in the Co-W steel by increasing both the W and Co contents. Two commercial steels of this type have been developed, employing rather higher Co contents and lower Mo contents:-

AFC 77:- 0.16%C, 14%Cr, 5%Mo, 13%Co
AFC 260:- 0.08%C, 15%Cr, 4½%Mo, 13%Co, 2Ni

AFC 260 has better impact resistance than AFC 77, and even better impact properties can be achieved by employing grain refinement by Nb, and by producing retained austenite after the appropriate tempering treatment. Such steels are, of course, very expensive.

Other, and less important methods of increasing the strength of low carbon 12%Cr steels are by:-

1. Ausforming.

2. Double tempering, which allows further precipitation to occur at lower tempering temperatures than the initial tempering temperatures. This can often increase the proof stress by ~150MN/m², and the treatment is usually employed to steels which precipitate M_2X. The impact strength however is markedly reduced.

(d) Higher Carbon 12%Cr steels

Increasing the carbon content of 12%Cr steels increases the strength, and as this means there will be more carbides present, there will be a need for high austenitising temperatures and a tendency for lower impact properties.

The weldability and toughness will obviously be impaired by the higher carbon content. Such alloys are used for steam and oil refinery pumps and valves. The well known cutlery stainless contains 0.3%C-12%Cr, and is tempered to a hardness of about 400HV. This steel may also be used for gears, stainless bearings, needle valves and for general components for elevated temperature use. However, the higher carbon content results in the precipitation of $Cr_{23}C_6$ at the prior austenite grain on heating at 550°C and above. This can cause localised Cr impoverishment and a loss of corrosion resistance which leads to pitting corrosion, well seen in stainless knives with brazed handles.

A further increase in carbon to 0.6/0.7% produces a marked increase in hardness and such steels are widely used as stainless razor blades, not because of their stainless characteristics but because they have sufficient tempering resistance to allow the coatings which are used to be cured without the blades losing hardness or cutting ability. Even higher carbon contents of 1% can be used, but this removes so much chromium as carbide that the chromium content has to be increased to 16/17% to restore adequate corrosion resistance. These steels are hardened and tempered to 600/700HV, for use as stainless ball bearings for high temperatures, stainless surgical implements, scalpels, coal hammers etc. These alloys then overlap further with increasing carbon contents up to 2% into the field of tool steels.

(e) Higher Chromium Steels

Should greater corrosion resistance be required, for example in marine atmospheres or seawater environments, the Cr content may be increased to 16/17%. This will introduce delta ferrite into the microstructure and to keep the steel fully transformable it will be necessary to balance the constitution by nickel; 2% being a common addition. More Nickel cannot be used as the M_s temperature is then so depressed that some austenite is retained at room temperature. Such austenite, which can be in very large amounts, may be transformed by various means as in the Controlled Transformation Steels, which contain $\sim$4%Ni, and modifications of such steels have led to the development of the TRIP, (transformation induced plasticity) steels, both of which will be discussed later.

LECTURE 9

Controlled Transformation Stainless Steels

(a) Introduction

The original demand which gave rise to the development of the controlled transformation steels was the requirement of the aircraft industry for a steel of high strength which could operate at temperatures above 200°C in the skin of high speed aircraft. Such a steel had to be capable of easy fabrication and welding, and yet maintain its strength in the welded condition and at temperatures as high as 400°C. In order to have a strength:weight ratio equivalent to the highest strength aluminium alloys, it would require a minimum tensile strength of 1100MN/m^2. Such strengths could be achieved in 12%Cr transformable steels, which were difficult to fabricate in the heat treated condition, and even more difficult to heat treat after fabrication to complex shapes in the softened condition. On the other hand, cold worked austenitic or ferritic steels could produce the required strength, but would suffer from varying strength when fabricated, and would lose strength after welding or on prolonged service at 400°C.

What was required, therefore, was a steel which would be soft and ductile when in sheet form, and which could then be hardened uniformly after fabrication. This could be obtained by an age hardening austenitic steel, but the strengths achievable were not quite high enough, and they often required very high solution treatment temperatures, besides being very expensive. Attention was thus turned to an austenitic structure capable of being transformed to martensite after fabrication by a fairly low temperature heat treatment which would not cause distortion in a complex component. The steel must then be capable of being strengthened further by a low temperature precipitation hardening treatment of the martensite.

(b) The basis for the design of Controlled Transformation Stainless Steels

The basic requirements are:-

(i) A steel which has an austenitic structure after solution treatment and air cooling from temperatures not exceeding 1050°C.

(ii) An M_s temperature sufficiently below room temperature that transformation does not occur to any major extent during fabrication, but not so low that it is impossible to transform the austenite to martensite by relatively simple treatments.

(iii) Sufficient tempering resistance to maintain the strength to temperatures of $\sim$400°C.

(iv) The ability to introduce precipitation hardening at relatively low temperatures of less than 500°C.

(v) A low carbon content for maximum formability and resistance to corrosion by weld decay. If possible the composition should be capable of accepting the addition of some Ti or Nb to minimise weld decay.

(vi) Sufficient chromium to give adequate corrosion resistance.

(vii) As low a cost as possible.

These design requirements are very severe.

(c) The development of Controlled Transformation Stainless Steels

The need for low carbon contents and 16-19%Cr means that in order to produce a structure substantially free from delta ferrite at the solution treatment temperature of 1050°C, considerable amounts of the austenitising elements Ni, Co, Mn, Cu are required. The M_s temperature is already low because of the high chromium content, and it is essential that the austenite forming elements should not depress the M_s temperature too far below room temperature. In addition, the elements which provide tempering resistance, i.e. Mo, V etc., also depress the M_s temperature, and they are ferrite formers which thus require a balancing addition of austenite formers. The problem of producing a balanced constitution with very little delta ferrite, and a suitably controlled M_s temperature requires careful control of the composition. It is essential to know how the various alloying elements affect the amount of delta ferrite, and how they affect the M_s temperature. This data is for 17%Cr-4%Ni base steels:-

Element	Change in % delta ferrite per wt %	Change in M_s °C per wt %
Nitrogen	-200	-450
Carbon	-180	-450
Nickel	-10	-20
Cobalt	-6	+10?
Copper	-3	-35
Manganese	-1	-30
Tungsten	+8	-36
Silicon	+8	-50
Molybdenum	+11	-45
Chromium	+15	-20
Vanadium	+19	-46
Aluminium	+38	-53

As carbon and nitrogen cannot be used for obvious reasons, to balance the constitution with respect to delta ferrite, nickel must be used as it is the next most effective austenite former. But nickel is expensive, and is by no means the most effective depresser of the M_s temperature. Thus if Ni alone was used to adjust the M_s temperature, too much would be required, with an excessive cost. Thus a cheap element such as Manganese is used to control and adjust the M_s-M_f temperature range.

Various combinations of alloying additions can be used to achieve the correctly balanced constitution and the appropriate M_s temperature, but within any one composition the analysis control is very critical in order to achieve the controlled transformation characteristics. Consequently, the steels are difficult to manufacture, and expensive not only due to the alloys used but also because due economic consideration has to be taken of the possibility of producing misfit casts.

In order to provide the correct tempering resistance, so that proof stress values of $>1100MN/m^2$ and tensile strengths $>1250MN/m^2$ can be achieved after tempering at 400-450°C, the steels are alloyed with molybdenum or vanadium. Precipitation hardening reactions are then added by means of alloying further with Co + Mo, Cu, Al or Ti. All these elements complicate the constitution and M_s control, resulting in a very difficult alloy design problem.

A number of typical compositions which have been developed to give Controlled Transformation behaviour, together with varying amounts of ageing, are:-

Alloy	Analysis wt %										
	C	Mn	Si	Cr	Ni	Mo	V	Cu	Co	Al	Ti
Armco 17.4P.H.(a)	0.04	0.5	0.2	16.5	3.5	-	-	3.5	-	-	-
(b)	0.10	0.5	0.2	17.0	4.0	-	-	2.0	-	-	-
A.M.350	0.10	0.5	0.2	17.0	4.2	2.75	-	-	-	-	-
U.S.S. (a)	0.10	3.0	0.2	17.0	4.0	-	-	-	-	-	-
U.S.S. (b)	0.10	0.5	0.2	16.0	6.0	-	1.0				
U.S.S.Stainless.W	0.07	0.5	0.2	17.0	7.0	-	-	-	-	0.2	0.7
Armo 17-7 P.H.	0.07	0.5	0.2	17.0	7.0	-	-	-	-	1.1	-
Armco 15-7 P.H.	0.07	0.5	0.2	15.0	7.0	2.5	-	-	-	1.2	-
F.V. 520	0.07	2.0	1.0	16.0	5.0	2.0	-	-	-	-	0.5
S.F. 80T	0.07	2.0	0.2	17.0	3.5	2.0	-	1.2	2.0	-	-

A number of variations of composition around the basic analyses of FV 520 and SF 80T have been developed.

(d) Methods of Achieving Transformation

It is necessary to transform the austenite to form the low carbon martensite structure with a proof stress of $\sim$ 1100MN/m^2, which is subsequently tempered or age hardened. There are two main methods:-

(i) Refrigeration

The M_s-M_f range is of the order of 100-140°C, and if the M_s temperatures just below room temperature, the M_f will be at -80 to -120°C. A readily obtained sub-zero temperature is -78°C, and refrigeration at this temperature will cause substantially complete transformation in many cases. Refrigeration at -196°C is more difficult and expensive to carry out, but does ensure complete transformation. Transformation by refrigeration allows the full carbon content of the austenitic to be available to cause strengthening in the martensite. Consequently a steel transformed by refrigeration gives the highest strength level.

(ii) Primary Tempering at 700°C

Tempering the austenite at 700°C allows quite extensive precipitation of $M_{23}C_6$ carbide to occur. This withdraws Cr and C from the austenite, and in so doing raises the M_s temperature so that on subsequent cooling to room temperature from the primary tempering temperature, the steel is substantially transformed to martensite. By lowering the carbon content of the austenite, and therefore of the martensite formed from it, the strengths achieved are somewhat lower than those obtained by refrigeration treatments.

The $M_{23}C_6$ carbides form mainly at the austenite grain boundaries, but if delta ferrite is present in the microstructure the delta ferrite-austenite interfaces are very effective nuclei for precipitation of the carbide, as high chromium ferrite is in contact with high carbon austenite. Consequently the rate of precipitation of $M_{23}C_6$ is faster, and the primary tempering process is more effective in promoting transformation. In steels which are to be transformed by primary tempering at $\sim$ 700°C, therefore, it is advisable to design the steel so as to contain about 10% delta ferrite in as finely divided form as possible, as this will facilitate carbide precipitation and thus transformation of the austenite.

(iii) Cold Work

Cold work can markedly increase the M_s temperature, and thus the austenite can be transformed by cold working. This process however is not normally

used as it cannot be relied upon to produce uniform transformation in a structure which has been fabricated by cold working. It can however be applied to flat sheet or wire, and because the deformation is inherited by the martensite, very high strength levels can be achieved. For example, a steel containing 0.1%C, 17%Cr, 4%Ni, 3%Mn after more or less fully transforming by 40% reduction had a 0.2% Proof Stress of 1700MN/m^2 (110 tsi). An interesting application of transformation by cold work will be discussed in the development of the TRIP steels.

(e) The Effect of Austenitising Temperature

It has been shown that the simultaneous control of both the constitution and the M_s temperature poses a difficult metallurgical problem. However, this control problem can be somewhat alleviated by varying the austenitising or solution treatment temperature to produce some measure of control over the M_s temperature. By lowering the solution treatment temperature, not all the $M_{23}C_6$ carbides are dissolved, and the lower the solution treatment temperature the more carbide is left out of solution. This $M_{23}C_6$ carbide, being chromium rich, causes a lower Cr and C content in the austenite which therefore has a higher M_s temperature. The lower the solution treatment temperature, therefore, the higher the M_s temperature. Thus varying the solution treatment temperature can be used as a measure of control over the transformation characteristics, but it should be realised that the lower the solution treatment temperature the lower will be the strength developed even when transformation is achieved by refrigeration.

So critical can the effect of composition be on the M_s temperature, that in manufacturing controlled transformation stainless steels it is found that the correct solution treatment temperature to obtain the appropriate M_s temperature varies from cast to cast, and may have to be determined individually for each cast. This can lead to varying properties from cast to cast. For this reason, many steels no longer try to apply the controlled transformation principles and are produced simply as fully transformable, high chromium, high strength stainless steels.

(f) The effect of Secondary Tempering and/or Ageing

In order to improve the ductility, and also to produce a high proof stress and proof ratio, the martensite produced by the transformation of the austenite must be tempered. Such tempering should be at as high a temperature as possible so as to restore as much ductility as possible to the structure, and thus elements such as Mo and V, which retard tempering, are used. If, as is the case, the steels must maintain their properties to about 400°C, then tempering must be carried out at 400°C or above. The upper limit of temperature at which tempering can be carried out is, however, much reduced by the presence of the high Ni and Mn contents, both of which lower the Ac_1 temperature (by $\sim$ 25/30°C per wt %). As there is often 6-7% (Ni + Mn) present, the Ac_1 temperature may be as low as 500°C, and consequently it is often not possible to temper at above 500°C without re-austenitisation occurring. Usually the steels are tempered at 400/450°C, and it is fortunate that in martensite, many of the age hardening reactions occur at about this temperature range.

The required retardation of tempering which is brought about by Mo, and also by V, is due to the precipitation of M_2X, as in the 12%Cr steels already discussed. The addition of Co may intensify this M_2X precipitation, but usually it is not possible to accommodate the higher Mo contents needed to produce intermetallic age hardening by the Mo-Co-Cr compound, R phase, due to difficulties in controlling the constitution and the M_s temperature.

Age hardening by additions of 1% or 2% Cu are widely used, giving increases of strength when tempered (i.e. aged) at 450/500°C of about 150 MN/m^2. The precipitating phase is metallic copper. Age hardening can also be produced by Al additions, usually about 1%, and occur at 400°C to 500°C. This age hardening is perhaps slightly more effective than that due to copper. The age hardening precipitate is small spherical particles of Ni Al, which are coherent with the b.c.c. matrix and of very similar lattice parameter. An analogous age hardening by b.c.c. Ni Ti in titanium bearing steels also occurs.

(g) Some Typical Properties and Uses

The transformation must be substantially complete in order to achieve the highest strength, and in particular if more than about 10% of retained austenite is present after the transformation treatment, the proof stress and proof ratio tends to be low. This might be due to:-

(i) the retained austenite itself, or

(ii) the secondary tempering treatment precipitating carbides and so destabilising the retained austenite that it transforms to martensite on cooling to room temperature.

Also, in order to achieve the maximum strength no delta ferrite should be present, but as already indicated, in some steels about 10% delta ferrite may be necessary to promote transformation by primary tempering.

Some typical properties are:-

Composition	Heat Treatment	T.S (MN/m^2)	0.2PS MN/m^2	% El
0.1C, 17Cr, 4Ni, 3Mn (Showing effect of cold working)	925°C, T450-3h 925°C, C.W.20%, T450-3h 925°C, C.W.40%, T450-3h	950 1340 1700	620 1300 1670	10 5 3.5
0.1%C, 17Cr, 4Ni, 3Mn	950°C, 700-2h, 450-2h 925°C, -78°C, 400°C-1h	1280 1440	1110 1200	15 19
0.1C, 17½Cr, 3Ni, 3Mn, 2Cu	1050, 700-2h, 400-24h 975, -78, 400-24h	1120 1500	940 1260	5 11
0.1C, 17½Cr, 4Ni, 3Mn, 1Al	950, -78, 450-4h	1450	1260	13
0.1C, 17Cr, 4Ni, 2Mo, 2Co	1000, -78, 450-6h	1340	1150	23
0.06C, 16½Cr, 2Mn, 5Ni, 1½Mo, 2Co, 1Al	1050, 700-2h, 450-4h 950, -78, 450-4h	1430 1520	1270 1240	3 21
0.07C, 17½Cr, 3Ni, 2Mn, 2Mo, 2Co, 1Cu	1050, 700-2h, 450-4h 950, -78, 450-4h	1250 1360	1110 1240	10 20

It can be seen that these typical properties illustrate that refrigeration generally produces greater strength than transformation by primary tempering. Primary tempering also invariably produces lower ductility due to the embrittling effect of carbides precipitated at the prior austenite grain boundaries.

Much of the application of controlled Transformation Stainless steels has been in the aerospace industries, for such applications as the skins

of supersonic aircraft, and rocket casings. Other uses involve light weight high strength components for use in corrosive environments, such as filters (wire mesh), or moving parts in weaving machines. However the general use has not been great, despite the very high strengths which can be achieved, due to the major difficulties in the control of composition needed to ensure the correct constitution and transformation characteristics. Consequently, many of the basic compositions have been modified so as to be used as fully transformed, age hardening 17%Cr steels, without any use being made of the controlled transformation behaviour. They then extend the uses of the 12%Cr, high strength structural steels to more corrosive environments.

LECTURE 10

Ferritic Stainless Steels

The ferritic stainless steels, whilst not being classed as high strength steels, nevertheless form an increasingly important groups of materials. They particularly are presenting an ever increasing challenge to the established austenitic stainless steels in areas where the highest corrosion resistance is not required, and despite certain drawbacks such as lower corrosion resistance, less formability and brittleness in impact at low temperatures, they have the very considerable advantage over the austenitic stainless steels of cheapness.

(a) General Characteristics and Compositions

The Chromium contents range from 11-25%, but more generally from 17-25%, and the steels are essentially free from nickel. Fe-Cr alloys of this composition would be entirely ferritic up to their melting points, i.e. show no transformation to austenite. In the presence of 0.1%C, the 17%Cr steels consist of ferrite with a little austenite at temperatures of about 1000°C. The amount of austenite depends critically on the carbon and nitrogen contents, but also on the relative amounts of austenite and ferrite forming elements. As the steel is heated, the amount of austenite first increases, and then decreases at the highest temperatures as the allcy passes through the edge of the gamma loop. At temperatures above about 1150°C, the 17%Cr steels usually become completely ferritic. On cooling, however, the austenite often precipitates as a network at the ferrite grain boundaries and as laths in a Widmanstatten structure within the grains. This has considerable relevance to the welding of these alloys. Any austenite present at the solution treatment temperature, or formed during cooling, transforms to martensite on cooling to room temperature. This martensite can then be tempered by annealing at temperatures up to $\sim$780°C, at which austenite reforms. The tempering of the martensite produces ferrite and carbide. At the higher Cr contents and higher temperatures $Cr_{23}C_6$ is the stable carbide, but Cr_7C_3 tends to form at lower temperatures and lower Cr contents. Whilst it would appear from the equilibrium diagram, that sigma phase would only form at Cr contents $>$35%, in commercial steels this embrittling intermetallic compound based on FeCr can form at considerably lower Cr contents, and another form of embrittlement can occur due to the formation of a chromium-rich solid solution.

At chromium contents $>$20%, commercial steels are fully ferritic, but a 17%Cr steel containing very low carbon and nitrogen will also be fully ferritic especially if it contains additions of Mo, Ti or Nb. Many 17/18%Cr ferritic stainless steels contain such additions and hence show no allotropic transformation.

There are a number of standard ferritic steels, the AISI 400 series, which contain varying additions. Of these additions,

(i) Mo is a strong ferrite former, as are Si and Al.

(ii) C and N are austenite formers, as also to a less extent is Mn. The major austenite forming element, Ni, is virtually absent from these steels.

(iii) Nb and Ti are strong ferrite formers, and also remove carbon and nitrogen from solution as insoluble carbides and nitrides. This further stabilises the ferrite.

Some typical standard, and proprietary compositions are as follows:

Designation	Analysis wt %							
	C	Si	Mn	Cr	Mo	Nb	Ti	Al
AISI 430	0.06	0.40	0.40	17.0	-	-	-	-
AISI 430 Ti	0.07	0.25	0.40	17.0	-	-	0.50	-
AISI 430 Nb	0.05	0.25	0.40	17.0	-	0.50	-	-
AISI 434	0.05	0.25	0.40	17.0	0.90	-	-	-
AISI 436	0.05	0.25	0.40	17.0	0.90	0.50	-	-
AISI 442*	0.08	0.25	0.40	21.0	-	-	-	-
AISI 446*	0.08	0.25	0.40	25.0	-	-	-	-
Sichromal 10*	0.10	1.00	0.40	18.0	-	-	-	1.0
18SR*	0.05	1.00	0.50	18.0	-	-	-	2.0
HWT*	0.07	0.40	0.40	18.25	-	-	0.85	-
18/2	0.02	0.40	0.40	18.0	2.0	-	-	-
E-Brite 26-1	0.02	-	-	26.0	1.0	-	-	-

* These higher Cr alloys, containing also high Si, Al or Ti, are heat resisting grades.

Mo is added to increase the corrosion resistance, whilst Nb and Ti are added to stabilise the steel against intergranuled corrosion by lowering the (C + N) dissolved in the steel. Also this will tend to improve the ductility and impact resistance, the latter making the steels more useful for the manufacture of chemical vessels. Modern steelmaking techniques for these ferrite stainless steels are designed to produce very low interstitial contents, i.e. C and N, by the use of argon-oxygen or even electron beam refining. Until recently, the higher chromium steels were used exclusively for heat resisting purposes.

(b) The Processing of Ferritic Stainless Steels

Whilst many processing variations are used, the following is a general summary of the major processing routes which are used:-

(i) The steels are melted in electric arc furnaces, often with argon-oxygen blowing to lower the (C + N) contents. Basic oxygen furnaces are also being used, which keeps the nitrogen low. However, tapping and teeming in air allows pick-up of nitrogen, particularly due to the high Cr content. The general interstitial levels obtained are:-

	C%	N%	C+N%
Basic Electric Arc	0.05	0.03	0.08
Argon-Oxygen	0.01/0.02	0.02	0.04
Electron Beam	0.002	0.008	0.01

(ii) The ingots are coarse grained and brittle, and must not be subjected to thermal shock. Rolling to slab starts at 1220/1330°C and finishes about 1050°C, followed by air cooling. 17%Cr steels are notoriously soft and easily marked during rolling, hence the slabs are ground, slowly reheated to 1000-1100°C and rolled to hot band, finishing at 950/1000°C or even lower. The hot rolled coils are annealed, usually in batches, edge trimmed and pickled in HF/HNO_3 acids.

(iii) Cold rolling to intermediate gauges is followed by surface grinding and bright annealing at 820/860°C. Conventional annealing is followed by descaling in electrolytic HNO_3 baths. Final cold reduction is often done on a Zendzimir mill followed by bright annealing at

820/860°C, using a final planish or pinch pass. The sheet is then ready for subsequent forming.

(c) Mechanical Properties and Structure-Property Relationships

The yield stress of ferritic stainless steel is greater than that of austenitic stainless steel, being 310-460MN/m² compared with 230MN/m² for austenitic steels. Ferritic steels however work harden much less rapidly than do the austenitic steels, but the tensile ductility and especially the impact resistance of ferritic stainless steels are lower than for austenitic steels. High chromium ferrite is notoriously brittle, and exhibits a ductile-brittle transition.

The structure-property relationships are complex and not yet fully understood or quantified. These factors are important:

(i) Grain Size

Refinement of the ferrite grain size increases the yield and tensile strengths according to the Petch relationship, i.e. the strength is a linear function of $d^{-\frac{1}{2}}$. However, the measured ferrite macro-grain size may not be the controlling one, because high chromium ferrite grains contain many sub grains which themselves influence the strength. Consequently the yield and tensile strength depends on the sub-grain size, but because the sub-grain boundaries do not impede the propagation of cleavage cracks the impact properties depend on the coarse, more readily observed macro-grain size.

As already stated, ferritic stainless steels show a brittle-ductile transition, the impact-transition temperature being considerably higher than that for mild steel due to the embrittling effect of chromium dissolved in ferrite. As the grain size decreases, so the impact transition temperature decreases, and the rather coarse grain sizes in these steels due to their non-transformable nature, is a major problem.

(ii) Solid Solution Effects

Solid solution hardening effects in fully ferritic stainless steels are similar to those in low carbon steels, but when there is some austenite (martensite) in the structure the effects also depend on the nature of the alloying element. Austenite forming elements increase the strength rapidly by increasing the amount of austenite, which transforms to martensite. Ferrite forming elements however first decrease the strength by decreasing the amount of austenite, and only when the structure is wholly ferrite does normal solid solution hardening become apparent. The interstitial solutes appear to increase the strength linearly, and nitrogen is more effective than carbon because it is more readily soluble. Both interstitial and substitutional solutes decrease the ductility and increase the impact transition temperature, the interstitial solutes being particularly detrimental to the impact properties.

(iii) Martensite

Increasing amounts of austenite, which have transformed to martensite, cause a linear increase in tensile strength. Increasing amounts of martensite however first lower the yield stress, due to internal stresses, but more than 15/20% martensite then causes the proof or yield stress to increase. However, increasing amounts of austenite at the solution treatment or annealing temperature also cause a refinement of the ferrite grain size. This grain refinement complicates the strengthening effects and also tends to offset the detrimental effects of martensite on the impact properties. The effects of martensite on the tensile ductility are complex.

(d) Embrittlement Effects

Chromium rich ferrite is naturally brittle, but in addition, 17-25%Cr steels suffer from 485°C embrittlement when heated to temperatures of this order. This embrittlement lowers the general ductility and markedly impairs the impact properties. 485°C embrittlement is due to the precipitation of zones of Cr-rich ferrite, which cause some precipitation strengthening.

Also, the higher Cr ferritic steels may form sigma phase (FeCr), which markedly embrittles the alloy. Sigma can form in commercial steels not containing chromium contents in the sigma phase field of the equilibrium diagram, due to Mo and Ti also forming phases of the sigma type, and accentuating sigma formation. Austenitic stainless steels also form sigma phase, but do not suffer from 485°C embrittlement.

(e) Welding

Welding is generally considered to be a major problem because:-

(i) The absence of a phase transformation allows very coarse grains to develop in the weld and heat affected zone. This causes brittleness.

(ii) If the steel passes through the edge of the gamma loop on heating, the ferrite grains grow at temperatures above the gamma loop. On subsequent cooling a coarse Widmanstatten structure of austenite forms, the austenite then transforming to martensite. This results in very marked embrittlement.

Post weld annealing can alleviate the martensite embrittlement by tempering, but cannot refine the ferrite grain size. Post weld annealing can however precipitate carbides which may both harden and embrittle. The ferrite grain size can be prevented from growing during welding by Nb or Ti additions which produce undissolved carbo-nitrides. However, post weld annealing of Nb or Ti steels may precipitate NbC or TiC, again causing hardening and embrittlement, although Ti seems less detrimental than Nb in this respect.

Generally, because the weld is very coarse grained and brittle, an austenitic filler metal is used. If a post weld heat treatment is used, the filler must be stabilised to prevent intergranular carbide precipitation. Thin sheet of ferritic stainless steel can be autogenously welded, but the grain size is again coarse. Nitrogen in the shielding gas is reported to refine the weld metal grain size by the formation of nitrides.

Although welding is not easy, the ferritic stainless steels can be adequately welded using the appropriate precautions. A problem when using austenitic filler metal is that the different coefficients of expansion of ferrite and austenite can lead to distortion and thermal fatigue during thermal cycling.

(f) Formability

Ferritic stainless steels can be formed by most methods, but are not so formable as the austenitic stainless steels due to their higher initial strength and lower general ductility. In such applications as kitchen sinks, domestic catering equipment, etc., the designs must have shallower depths of draw and more generous radii than for austenitic steels.

Their low work hardening rate makes them suitable for deformations which emphasise metal flow, and in this they are similar to mild steel. They are readily coined, embossed, cold headed, cold forged, roll formed and spun. Austenitic steels, on the other hand, are better than ferritic steels where

stretch forming is required.

Being ferritic, the steels exhibit stretcher strains during drawing or stretching, unless skin passed after final annealing. A more serious problem is ROPING which produces markings not unlike stretcher strains. However rope markings are not due to a yield phenomenon, but due to a crystallographic textural effect, the rope marks being parallel to the rolling direction and thus differentiated from stretcher strains. The unfavourable texture producing roping is developed during hot working, which must be carefully controlled. The main methods of minimising roping involve:-

(i) Low soaking temperatures and heavy deformation schedules. This places restrictions on plant, but is the cheapest remedy.

(ii) Alloying to promote austenite formation so as to accelerate recrystallisation and obtain a random texture. The formation of martensite, and the general hardness then become a problem, and the material must be annealed very thoroughly. This all adds to the costs especially if Ni is used to promote austenite formation.

(iii) Nb additions to produce Nb(CN), thus promoting recrystallisation and a random texture of fine grain size. About 1%Nb is required and is thus expensive.

(iv) The use of powder metallurgy processes, which are costly and involve the installation of special plant.

Despite the drawbacks compared with austenitic steels, ferritic stainless steels can be formed adequately, but require rather more simple designs.

(g) Corrosion

Under the most severe corrosive conditions ferritic stainless steels are less corrosion resistant than austenitic stainless steels. For many applications under atmospheric or mild domestic corrosion conditions, the 17%Cr steels are however perfectly adequate, and are much more economic than austenitic stainless steels. The corrosion resistance increases markedly with increasing Cr content, and with increasing Mo which is particularly beneficial with respect to pitting corrosion in chloride environments. In general, 17%Cr steels will suffer little corrosive attack under atmospheric conditions, but regular washing is needed especially in marine atmospheres. The main form of corrosion is tarnishing.

The ferritic stainless steels are susceptible to intergranular corrosion, for example in the heat affected zone of a weld. This is due to the precipitation of Cr carbides at the ferrite grain boundaries, which produces local Cr impoverishment and thus preferential corrosive attack. The phenomenon is analogous to that occurring in austenitic steels, but whereas austenitic steels are sensitised on heating at 650°/700°C, the ferritic steels only sensitise on heating to above 900°C. At these higher temperatures, the solubility of C and N in the high Cr ferrite is sufficiently high that on cooling chromium carbides are precipitated at the ferrite grain boundaries. The problem can be overcome by annealing at 650°/850°C which allows Cr diffusion into the Cr-impoverished regions, or by stabilising the steel by additions of Nb or Ti. These combine with the carbon and nitrogen to form insoluble carbides and nitrides and so prevent chromium carbide precipitation. Ti however is not a very effective addition to prevent intergranular corrosion in oxidising acids, because TiC and TiN are vigorously attacked, and often occur at the ferrite grain boundaries.

In contrast to austenitic stainless steels, one of the major advantages of

ferritic stainless steels is their resistance to and in fact virtual immunity from chloride induced transgranular stress corrosion cracking. This would make them very suitable for certain chemical vessels were it not for their poor impact toughness and welding characteristics, because it is well known that the presence of a grain boundary network of martensite, such as occurs in the heat affected zone of a weld, leads to stress corrosion cracking through the martensite. Also, the presence of Cr carbides at the ferrite grain boundaries can lead to a form of stress induced intergranular corrosion, which can give severe cracking in ferritic stainless steels.

(h) Developments and Current Status of Ferritic Stainless Steels

The main requirement in ferritic stainless steels is for improved toughness, ductility, corrosion resistance and weldability. Considerable progress towards meeting these requirements can be achieved by lowering the interstitial solute contents, i.e. (C + N). This is the main aim of current developments, where total interstitial levels of 0.01/0.03% are being aimed for. However, the lower the interstitial content, the lower is the strength due to a loss of interstitial solid solution strengthening and also due to a coarser grain size brought about by the absence of grain boundary pinning particles. Thus it is necessary to refine the grain size, particularly as the impact transition temperature is very dependent on the ferrite grain size. In fact, the benefits brought about by a decrease in the interstitial content can be completely offset by the coarse grain size which can result, and the lack of interstitial solutes means that it is difficult to produce the particles of Ti(CN) or Nb(CN) to give grain refinement when Ti or Nb additions are made. The possibility of using a controlled rolling treatment is currently being investigated.

Another advantage produced by decreasing the interstitial solute content is less tendency for intergranular corrosion. Also there is reported to be less tendency for 485°C embrittlement because there is less (C + N) to interact with Cr and thus produce Cr-rich zones. Finally lower interstitial contents lead to less pitting corrosion, and in this respect the addition of Mo and extra Cr is beneficial. Thus current developments include low interstitial 18Cr-2Mo and 26Cr-1Mo steels. In addition, non-metallic inclusions and impurities in the steel impair the corrosion resistance. Hence some current developments make use of very expensive electron beam refining techniques, although such techniques are likely to be restricted due to economic limitations.

There has been little emphasis on the development of high strength levels in the fully ferritic stainless steels. This is probably because the steels have mainly been used for forming and corrosion resistant applications, and because they have not had the impact toughness which would be required in a structural application in which higher strengths would be required. This situation may be altered by the current developments which are designed to increase the toughness by reducing the interstitial content and refining the grain size. In view of the importance of the sub-grain size on strength, it is doubtful whether grain refinement will produce other than a minor strength increase, but the improved impact properties may allow the use of more powerful strengthening mechanisms. A considerable amount of work has been done to investigate precipitation hardening in fully ferritic high chromium steels and very considerable increments in hardness can be achieved by various age hardening reactions, particularly those involving inter-metallic compounds. Some typical age hardening systems involve the additions of Co-Mo, P, Ni-Al, Ni-Ti, or Ni-Al-Ti. It is probable that the precipitates based on the formation of b.c.c. phases such as NiTi, NiAl or Ni(AlTi) will prove

to be most suitable, as very high hardness values can be achieved. Unfortunately the ductilities and toughness are very poor. The steels seem able to accommodate the 4%Ni necessary to produce the appropriate precipitates, even when they contain as little as 17%Cr, due to the very great ferrite forming potential of the 1-3% Al or Ti which is required. The reason for the very high strengths which can be developed is that the b.c.c. precipitate has a very similar lattice parameter to the b.c.c. ferrite matrix, and has thus little misfit and so forms small spherical coherent zones and precipitates which are very slow to grow. Also, the volume fraction of precipitate is large. So far these developments of high strength in ferritic stainless steels have been solely confined to laboratory investigations.

The current status of ferritic stainless steels is that their corrosion resistance is adequate in any but the most severely corrosive environments. In domestic, atmospheric and catering type environments, they would be very adequate replacements for the austenitic stainless steels, besides being considerably cheaper. Currently they are used in some kitchenware applications such as washing machine tubs, sinks, and drainers, holloware etc.

These steels do not currently possess the toughness for pressure vessel applications, particularly for cryogenic use. They are more than adequate however for automobile trim, stainless bumpers, and domestic and architectural trim. A fully ferritic 12%Cr-Ti steel which is quite weldable, is used for transport container frameworks and is sufficiently ductile to be used for coinage. The 17%Cr steels are used for nitrogen fixation vessels and certain chemical vessels not subject to high stress. Alloying with 1%Mo increases the corrosion resistance almost up to that of austenitic steels in all but the most severe corrosive conditions. However, for applications involving forming the greatest problem is the roping phenomenon in the ferritic stainless steels, although methods now seem to be available for minimising this. A major advantage of the steels is their virtual freedom from stress corrosion cracking compared with the austenitic stainless steels, although this may be offset to some extent by their less overall corrosion resistance.

LECTURE 11

Austenitic Stainless Steels I

(a) The Constitution of Austenitic Steels

The addition of Ni to 18%Cr steels enlarges very considerably the gamma loop. Increasing nickel has two main effects on the constitution and microstructure:-

(i) it increases the amount of austenite present at the solution treatment temperature, but at low nickel contents of ~5%, this austenite may transform wholly or partially to martensite.

(ii) it decreases the M_s temperature, so that with about 8%Ni the M_s temperature is just below room temperature, and stable austenite is retained after cooling from the solution treatment temperature to room temperature.

An 18%Cr, 8%Ni steel is borderline with respect to a fully austenitic structure, and may contain a little delta ferrite. In a carbon-free steel, about 12%Ni is required to produce a fully austenitic structure at solution treatment temperatures of about 1050°C. However because carbon is a powerful austenite forming element, in the presence of 0.1%C an 18Cr-8Ni alloy is fully austenitic above about 900°C, although the M_s temperature is only just below room temperature so that the austenite would transform partially to martensite either during a refrigeration treatment or during cold working. The interaction between Cr and Ni in promoting the formation of stable austenite in 0.1%C steels, after cooling from a typical solution treatment temperature of 1050/1100°C, is therefore of the utmost importance. Some of the main effects are:-

(i) at low Cr contents, Cr acts as an austenite stabiliser by expanding the gamma phase field up to the minimum in the gamma loop.

(ii) at about 18%Cr, a minimum nickel content is required to promote a fully austenitic structure which is stable at room temperature.

(iii) with more than 18%Cr, the ferrite forming tendencies of Cr begin to assert themselves and require increasing amounts of Ni to eliminate delta ferrite and produce a fully austenitic structure, although the austenite itself is increasingly stable with respect to martensite formation.

A final point with respect to the constitution is concerned with carbon, which results in the formation of $Cr_{23}C_6$ carbide at temperatures below about 800/850°C. This can have marked effects on the corrosion properties.

(b) The Processing of Austenitic Stainless Steels

The main uses of austenitic Stainless Steels are in the form of flat rolled products, i.e. plate and strip or sheet. Plate is usually produced hot rolled, with perhaps a softening treatment produced by solution treatment at 1050°C. Strip and sheet products involve cold rolling treatments.

(i) Plate

The ingots are rolled to slab, and the slab then rolled to plate. The plate may then be solution treated and descaled. Alternatively, to achieve specific properties, the plate may be controlled rolled to temperatures below 900°C and even as low as 700°C. Such "controlled rolled" materials are not softened, but a certain amount of stress relief can be allowed if the steel is alloyed with Nb or Ti to retard or inhibit

recrystallisation.

(ii) Strip and Sheet

Strip and sheet material is usually hot rolled to coiled hot band, surface ground, cold rolled, annealed and descaled (or controlled atmosphere annealed).

The strip or sheet is then cold rolled to size. It may then be supplied with varying degrees of cold working, giving a range of strength values, or it can be supplied:-

(1) bright annealed for forming applications

(2) cold rolled, softened by a rapid solution treatment at 1050°C, and descaled; this also is used for forming applications

(3) bright polished for applications requiring slight forming or for decorative trim.

A consideration of processing would be incomplete without considering the hot working of austenitic stainless steels. It is a common feature that whilst fully austenitic structures are readily hot workable, the presence of delta ferrite markedly impairs the hot workability. This delta ferrite is formed during solidification, the amount depending on the composition and temperature at which any subsequent reheating has occurred.

It seems that ~5% delta ferrite at room temperature, which corresponds to very much larger amounts at the hot working temperature, is particularly detrimental to hot workability, and there is evidence which indicates that a maximum γ/α interfacial area is the cause of this.

Some steels which contain Ti or Nb may also exhibit strain induced precipitation of TiC or NbC during hot working, which leads to strengthening and low ductility. This may lead to cracking, especially with very slow strain rates during hot deformation, by pressing, spinning or dishing. Also, Nb containing steels often contain NbC eutectics which can liquate if the hot working temperature is too high, and thus lead to cracking.

(c) Structure - Property Relationships

Excellent correlations have been obtained between compositional and microstructural parameters and the tensile strength and proof stress values. The equations which have been derived to predict the strength are:-

$$0.2\%\ \text{Proof Stress (MN/m}^2) = 15.4\{4.4 + 23(C) + 1.3(Si) + 0.24(Cr) + 0.94(Mo) + 1.2(V) + 0.29(W) + 2.6(Nb) + 1.7(Ti) + 0.82(Al) + 32(N) + 0.16(\delta\text{-ferrite}) + 0.46d^{-\frac{1}{2}}\}$$

$$\text{Tensile Strength (MN/m}^2) = 15.4\{29 + 35(C) + 55(N) + 2.4(Si) + 0.11(Ni) + 1.2(Mo) + 5.0(Nb) + 3.0(Ti) + 1.2(Al) + 0.14(\delta\text{-ferrite}) + 0.82t^{-\frac{1}{2}}\}$$

where δ-ferrite = % delta ferrite
d = mean linear intercept of grain diameter (mm)
t = twin spacing (mm)

A similar type of relationship for the reduction of area in a tensile test is much less successful in explaining the variation in this property, as the effects of alloying elements are not linear, as will be shewn later. However, the relationship obtained was:-

$$\% \text{ R of A} = 77 + 0.81(\text{Si}) + 0.94(\text{Mn}) + 1.3(\text{Cu}) + 1.6(\text{Al}) - 0.20(\text{Ni}) - 6.6(\text{Nb}) + 0.99t^{-\frac{1}{2}} - 1.0d^{-\frac{1}{2}}$$

The points of interest are as follows:-

(i) The twin spacing does not affect the proof stress. This is because the stacking fault energy, which controls the work hardening rate, has little or no effect because work hardening does not have any great influence at the low strains at which the proof stress is measured.

(ii) The twin spacing is much more important than the grain size in affecting the tensile strength, because the effect of stacking fault energy on the work hardening rate, and hence on the tensile strength, is quite significant.

(iii) Increasing the grain size decreases the proof stress value.

(iv) Delta ferrite increases the proof stress and tensile strength values by a dispersion strengthening effect. The ferrite has a higher yield stress than the austenite, and a recent analysis of the effects of delta ferrite indicates that it is due to strain concentration in the softer austenite phase which thus work hardens to a strain greater than the nominal 0.2%, and therefore gives a higher proof stress value. In the case of the tensile strength, about 80% of the strenghening due to delta ferrite is due to partitioning of C and N to the austenite, thereby increasing the work hardening rate.

(v) The interstitial solutes C and N have the greatest solid solution strengthening effects, followed by the ferrite forming substitutional solutes, whilst the austenite forming substitutional solutes have very little solid solution strengthening effect. The solid solution strengthening effects also reflect the atomic diameter of the solute relative to that of iron.

The effect of martensite formation in metastable austenite is also important, mainly because of its effect on the ductility, as will be shown later. However martensite also influences the strength. There are two modes of occurrence of the martensite, namely that which is already present prior to straining, and that which is produced during the straining in a tensile test. The following effects are observed:-

(i) Up to 35% martensite present prior to straining does not materially affect the 0.2% Proof Stress due to the internal stressed produced. In fact, up to 20% martensite prior to straining may actually lower the 0.2% Proof Stress.

(ii) Due to the low strains involved at the proof stress, very little martensite forms during straining to this strain level, and thus it has little effect on the proof stress.

(iii) More than 35% martensite prior to straining means that the martensite becomes the load bearing phase, and the 0.2% Proof Stress then increases with increasing martensite content prior to straining.

(iv) The effect of martensite on the tensile strength is complex. In steels which contain martensite prior to testing, there may or may not be more martensite formed during straining, depending on the stability of the austenite. The tensile strength of such steels increases linearly with increasing amounts of martensite prior to straining, according to an equation:-

$$\text{Tensile Stress (MN/m}^2\text{)} = 15.4\{T_c + 12 + 0.82(\%M)\}$$

where T_c is the tensile strength calculated from the previously described regression equation, and %M is the percentage of martensite prior to tensile testing.

This equation can be re-written:

$$\delta Y \text{ (MN/m}^2\text{)} = 185 + 9.84\ (\%M)$$

where δY is the difference between the observed and calculated tensile strengths. The intercept of 185MN/m^2 at 0% prior martensite in these relatively unstable steels, probably represents the strengthening produced by martensite which is formed during straining up to the maximum uniform strain, i.e. the strain at which the tensile strength is measured.

(d) Cold Working and Cold Formability

Many applications of austenitic stainless steels involve cold working by either stretch forming or deep drawing. For improved stretch forming it is necessary to have a high maximum uniform strain, whilst for deep drawing softness, the correct textures and 'r' values are important. Much development work has been concentrated on improving the stretch forming characteristics, because stable and well softened austenitic steels generally have good deep drawing properties.

The maximum uniform elongation in a tensile test, a high value of which is very beneficial to good stretch forming properties, is defined as the strain at which the flow stress and the work hardening rate are numerically equal. Thus increasing the work hardening rate relative to the flow stress will increase the maximum uniform elongation and thus will also improve the stretch formability. In considering the cold formability of austenitic steels, two types of steel must be considered:-

(i) Stable Austenitic steels which do not transform to martensite during straining.

(ii) Unstable Austenitic steels which transform to martensite during straining.

(i) Stable Steels

In a stable austenitic steel which does not form martensite during straining, the M_s temperature has not been raised sufficiently for the M_d temperature to be at or above the temperature of straining, usually room temperature. In such a steel the value of the work hardening rate decreases continually as the strain increases, and the steel usually contains fairly high concentrations of Ni, Mn, C, N_2 etc, all of which markedly depress the M_s temperature as also do other elements such as Cr, Mo etc. The M_s is generally considered to be depressed linearly with increasing alloying element content.

For the best cold formability in a stable steel, there should be a low proof stress and a low work hardening rate so that the steel does not harden appreciably and the forming loads are low. The work hardening rate depends on the stacking fault energy, lowering the stacking fault energy increasing the work hardening rate. The stacking fault energy is decreased by such elements as Cr, C, N, Mo, Co and Si, whilst it is increased by Ni and Cu. Thus in a stable austenitic steel, as high a stacking fault energy as possible is required in order to keep the forming loads low, and allow maximum deformation for a given forming load. But it is also necessary to consider how a high stacking fault energy and a low work hardening rate would affect ductility. In general, a decrease in the

work hardening rate will lower the maximum uniform ductility and be detrimental to the stretch forming characteristics unless there is a corresponding decrease in the level of the flow stress. This latter effect can be achieved by lowering the initial proof stress value by:-

(1) a coarse grain size

(2) using alloying elements which increase the stacking fault energy but have as small a solid solution strengthening as possible.

On the other hand the total ductility at fracture will depend on the level of the flow stress relative to the fracture stress. A coarse grain size and a high work hardening rate will again be beneficial as the flow stress will be low and thus the total ductility at fracture will be high, assuming that the fracture stress is constant.

Hence for a stable austenitic steel to be capable of the optimum formability, the following acquirements are needed:-

(1) the grain size should be coarse, i.e. the steel should be well annealed

(2) there should be a low work hardening rate, i.e. a high stacking fault energy. This can be achieved by high Ni or Cu contents, and by keeping N_2 and C to a minimum.

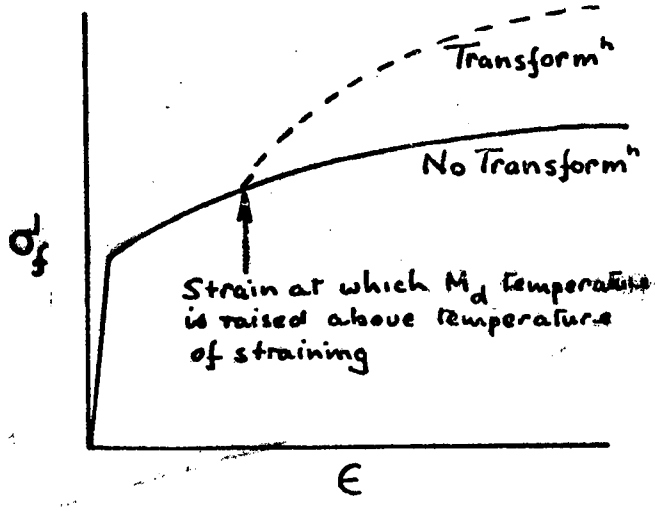
(3) solid solution hardening should be at a minimum

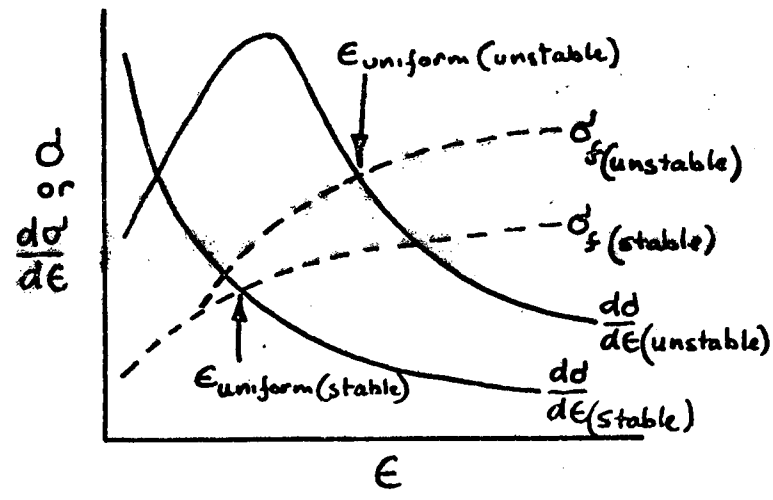
(4) low flow stress levels are required.

High Ni contents are not economic, and it is perhaps not surprising that recent stable steels developed for good formability contain high Mn + Cu contents replacing some of the nickel. In normal austenitic steels, replacement of Ni by Mn doesnot greatly alter the stacking fault energy, and in fact slightly lowers the work hardening rate. In the Mn replacement stainless steels however, a high nitrogen is used to assist the Mn in replacing larger amounts of Ni, and this nitrogen markedly increases the flow stress and work hardening rate, so giving less general formability than in the Cr-Ni austenitic stainless steels. It must also be appreciated that the crystallographic texture is important in controlling the deep drawing and pressing characteristics of stable austenitic stainless steels.

(ii) Unstable steels which form Martensite during Straining

When the M_d temperature is high enough for martensite to form during straining, this produces a transformation strain which augments the applied strain. The result is a low work hardening rate compared with a stable steel. As more martensite is formed during continued straining, and because this martensite is strong, the flow stress rapidly increases as the martensite itself starts to participate in the deformation. This produces an increase in the work hardening rate to a level much above that for a stable steel at the same strain. The high work hardening produced by the martensite being deformed, more than counterbalances the transformation induced strain, i.e. the transformation plasticity. The effects are shown in the following diagram.





Therefore a steel which forms martensite as soon as strain is applied has an initial work hardening rate below that of a stable steel, but the work hardening rapidly increases to a maximum as more martensite is formed, and then decreases as the formation of strain induced martensite ceases. It can be seen that the maximum uniform strain for an unstable steel is considerably greater than that for a stable steel because of the higher work hardening rate at intermediate strain values. This greatly improves the stretch forming characteristics.

It can also be appreciated that any given alloying element will not have a unique effect, as its effect will depend on the stability of the base steel into which it is introduced. For example, in a steel with the M_s temperature above room temperature, the presence of martensite prior to straining will give high flow stress values and low uniform elongations. Adding alloying elements will depress the M_s temperature so that martensite only forms during straining, in which case the uniform ductility will be increased. More alloying addition will cause the steel to be completely stable, with a low work hardening rate, and the uniform ductility will then decrease. Thus with increasing alloying addition there will be a maximum uniform strain value at some critical alloy content, the critical alloy content and the value of the maximum in the uniform strain depending on the base composition of the steel. This effect is observed for many alloying additions.

It is clear therefore, that the strain inducement of martensite must occur at an appropriate stage in the deformation cycle in order to obtain the highest value of the uniform strain and thus optimum stretch formability. This means that there will be an optimum M_d temperature, i.e. an optimum combination of alloying contents for maximum stretch formability. It is possible to optimise these variables so that the composition of a steel with maximum uniform strain values, and therefore optimum stretch-formability, can be predicted. It is found that the higher the (C+N) and chromium equivalent compositions, the less nickel is required for the optimum composition. This confirms the well known observation that it is the leaner nickel steels which generally have the better stretch formability.

It will be appreciated that once the amount of alloying addition has been reached which effectively inhibits the formation of martensite during straining, further alloying additions will have no effect through the mechanism of transformation induced plasticity, although they can have effects through the stacking fault energy and work hardening rate.

What is needed therefore in an unstable austenitic stainless steel for optimum formability is:-

(1) No martensite to be present prior to straining, as this would increase the flow stress level relative to the work hardening rate and decrease the uniform strain value.

(2) An optimum amount of martensite to be formed at a critical stage in the straining process, so that a high work hardening rate gives rise to a high uniform strain value.

(3) A coarse grain size, i.e. a well annealed steel to give a low flow stress value.

(4) No delta ferrite, because delta ferrite increases the flow stress value and lowers the value of the uniform elongation. Delta ferrite also increases the work hardening rate and decreases the total ductility.

There is also some evidence that there is an optimum alloy content for a maximum total ductility, possibly due to:-

(1) Strain induced martensite not contributing to void growth during ductile fracture.

(2) Strain induced martensite being most intense at the surfaces of the voids and thus preventing them from growing, thereby retarding the process of ductile fracture.

(e) Embrittlement Effects

Unlike ferritic stainless steels, the austenitic stainless steels do not suffer from 485°C embrittlement. On heating at 700°C-950°C, however, the austenitic stainless steels can form the brittle intermetallic compound, sigma phase. The tendency to form sigma phase increases with increasing Cr content, and elements such as Mo, Ti and Si accentuate its formation. The precipitation of sigma phase lowers both the ductility and toughness, and is particularly troublesome after long time high temperature treatments, either in service or during testing. Sigma phase is not particularly detrimental whilst the steel is hot, but does cause embrittlement when the steel is cold.

Fortunately sigma phase forms very slowly from a fully austenitic structure, but if delta ferrite is present, this rapidly transforms to sigma phase and austenite. This is due to the delta being richer in Cr than the austenite. Also, all ferrite formers partition to the delta ferrite, and many accentuate sigma formation. For heat resisting applications, the manganese is often increased to eliminate delta ferrite, especially as heat resisting steels frequently contain added silicon to promote heat resistance, and silicon also tends to produce delta ferrite in the structure.

(f) Welding and Weld Decay

Asutenitic steels can generally be readily welded; no hard structures occur in the heat affected zone. A number of detrimental effects can however occur:-

(i) During welding, parts of the heat affected zone are heated in the range in which $Cr_{23}C_6$ precipitates at the austenite grain boundaries. This locally lowers the Cr content, so that preferential corrosive attack occurs in the Cr impoverished zone around the grain boundaries. This is the well known phenomenon of weld decay, i.e. intergranular corrosion. A number of remedial measures can be taken:-

(1) After welding, a full solution treatment at 1050°C can be applied This has economic drawbacks, and the necessary furnace capacity may not be available. Also the welded structure may distort or oxidise.

(2) After welding, annealing may be carried out at about 900°C to allow Cr to diffuse back into the impoverished zone. This is sometimes called a "healing" treatment to differentiate it from the sensitisation heat treatment which produces the $Cr_{23}C_6$ precipitate and Cr improverished region.

(3) The steel may be "stabilised" by alloying with Ti or Nb, which combine with the carbon to form TiC or NbC. This lowers the carbon in solution, so that $Cr_{23}C_6$ is not precipitated or is precipitated only very slowly due to the decreased supersaturation. Stabilisation is not effective if the steel is solution treated at too high temperatures prior to welding, because the TiC/NbC dissolves and thus allows enough carbon to be in solution for $Cr_{23}C_6$ to precipitate in the heat affected zone. Also, because Ti and Nb combine with nitrogen, sufficient must be added to combine with both the carbon and the nitrogen; usually Ti = 5 x (C+N) and Nb = 10 x (C+N); often the stoichiometric ratio is exceeded in order to guarantee a sufficient degree of stabilisation.

(4) Because stabilisation is rarely entirely effective, a modern trend is to produce steels with very low carbon contents of 0.03% maximum. This means that the carbon content is very close to or even below the solubility limit of $Cr_{23}C_6$ at 550-750°C, at which temperatures the $Cr_{23}C_6$ precipitates. Thus $Cr_{23}C_6$ precipitation, and intergranular corrosion, are prevented.

(5) In the absence of efficient stabilisation, a low heat input during welding may be used to minimise the time for which the heat affected zone is in the sensitisation temperature range, and to decrease the width of that sensitised region.

(ii) A fully austenitic weld metal can produce hot cracking, called crater cracking, because of the stresses set up during the contraction which accompanies solidification of the weld. This can be overcome by ensuring that the weld metal contains a little delta ferrite, i.e. it solidifies by means of a peritectic reaction which minimises the contraction stresses and prevents hot cracking.

(iii) Various forms of liquation cracking can occur in both the weld metal and heat affected zone close to the weld metal, if low melting point phases are present, such as borides.

(iv) In stabilised steels, especially those containing Nb, the high temperatures in the heat affected zone can dissolve some NbC (or TiC) despite the short times involved. Subsequent precipitation of the NbC (or TiC) can occur during a post weld stress relieving treatment, and this causes strengthening. This can lead to a form of low ductility creep rupture cracking, because some stress induced precipitation occurs due to the plastic deformation which occurs during stress relief. This can be overcome by stress relieving at higher temperatures at which the NbC overages and does not strengthen, i.e. ~950°C. Alternatively a full solution treatment may be used, but this is often not feasible or economical.

(g) Corrosion and Stress Corrosion

(i) Corrosion

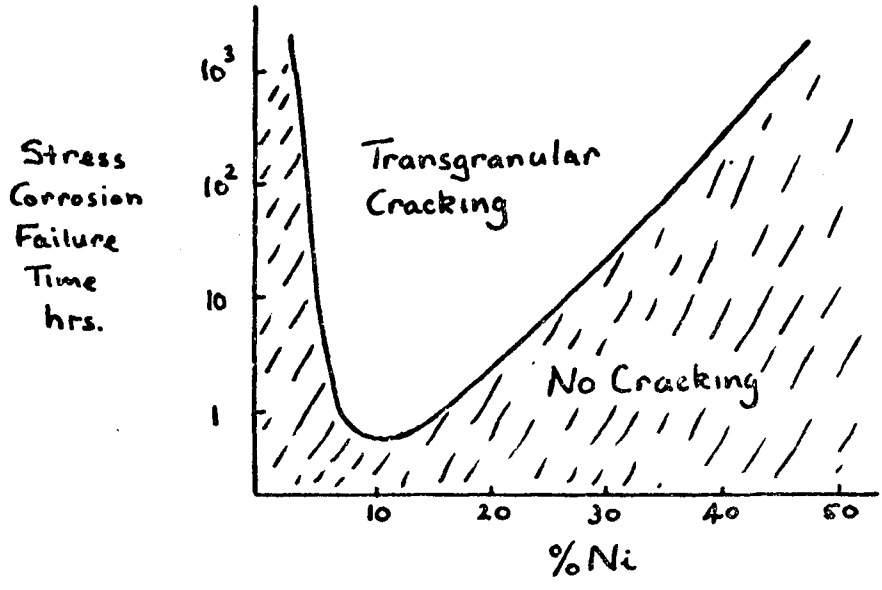
Austenitic stainless steels are very corrosion resistant in a wide range of corrosive media. Particularly, they have excellent atmospheric corrosion resistance, but the chloride in marine environments does slightly lower this corrosion resistance. The Ni content improves their

resistance to many organic acids and to H_2SO_4. In HNO_3 they passivate, as they do in oxidising media generally.

It is in chloride environments that the corrosion resistance is most impaired, the Cl^- ion penetrating the passive film and giving rise to pitting corrosion. Mo is very beneficial in improving corrosion resistance in chloride environments, and in minimising pitting corrosion. In general, the higher the Cr content, the better is the overall corrosion resistance, and Mo also improves corrosion resistance in H_2SO_4, but it does introduce delta ferrite into the microstructure.

(ii) Stress Corrosion Cracking

This phenomenon results in cracking which occurs under a static load with little or no deformation, in a corrosive environment. In austenitic stainless steels it is most pronounced in hot chloride solutions, and takes the form of transgranular cracking. It is said to be made worse by a low stacking fault energy which produces planar dislocation arrays. The prevalence of stress corrosion cracking is very dependent upon the Ni content, being virtually absent in low Ni ferritic or martensitic steels, at its worst in 8-10%Ni austenitic steels, and markedly reduced in high nickel austenitic alloys, i.e. > 30 %Ni.



The only method of avoiding stress corrosion cracking is to prevent the stressed material coming into contact with hot chloride or other aggressive solutions. Minor compositional changes produce little effect, but high Ni and high Si contents give some advantage, but are very costly and give rise to poor hot workability.

Even though an alloy may have considerable resistance to stress corrosion cracking, it may still suffer from stress assisted intergranular corrosion in which the corrosion is associated with Cr denudation around grain boundary precipitates, or with the $Cr_{23}C_6$ precipitate itself. It occurs even in the "healed" condition, the carbide being attacked. Low interstitial contents are reported to be beneficial.

The classical chloride induced stress corrosion cracking does not occur in ferritic stainless steels, and so it is not surprising that the presence of delta ferrite considerably improves the resistance of austenitic steels to stress corrosion. A very fine delta ferrite disperson is very beneficial, and microduplex steels have been developed to achieve this, i.e. 25Cr-6Ni-Ti. Such micro-duplex steels do however lose their stress corrosion resistance when welded, as the heat affected zone loses its micro-duplex character and

develops a widmanstatten structure. The presence of delta ferrite does improve the strength, however.

LECTURE 12

Austenitic Stainless Steels II

(a) The Compositions and Applications of Standard Austenitic Stainless Steels

Standard austenitic stainless steels contain a range of Cr and Ni contents. An increase in either Cr or Ni contents induce stability against the formation of martensite, whilst the relative proportions of Cr and Ni influence the constitution with respect to delta-ferrite formation. Some standard steels are given in the following table:-

AISI type Composition	301	302	304	310	316	321	347	201	202
C%	0.15 max	0.08	0.08	0.25	0.08	0.08	0.08	0.15 max	0.15 max
Mn%	-	-	-	-	-	-	-	5.5/7.5	7.5/10.0
Cr%	16/18	17/19	18/20	24/26	16/18	17/19	17/19	16/18	17/19
Ni%	6/8	8/10	8/12	19/22	10/14	9/12	9/13	3.5/5.5	4.0/6.0
Mo%	-	-	-	-	2/3	-	-	-	-
Ti%	-	-	-	-	-	5 x C	-	-	-
Nb%	-	-	-	-	-	-	10 x C	-	-
N_2%	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.25max	0.25 max
Properties Solution Treated									
Tensile Strength MN/m^2	571	541	541	571	571	541	556	806	741
0.2% Proof Stress MN/m^2	247	247	247	247	247	247	247	386	371
% Elongation	50	50	50	50	50	50	50	48	50
	Standard 300 series of Cr-Ni Steels							Low Ni 200 Series, Mn + N_2 replacing some Nickel	

It should be noted that types 304 and 316 are often made with a very low carbon content of 0.03% maximum, and are then designated 304L and 316L. Also, the tensile strength and proof stress values can vary depending on the form of the product; the values quoted are typical of solution treated material.

Of the chromium-nickel steels, types 301 to 310, the stability with respect to martensite formation increases from 301 to 310. Type 316 contains 2-3%Mo for improved corrosion resistance in chlorides and in H_2SO_4, and for improved resistance to pitting corrosion. Mo also leads to improved high temperature properties, hence this steel is used for creep resistance. The Ni is increased to compensate for the ferrite forming tendency of Mo. Types 321 and 347 are stabilised against $Cr_{23}C_6$ precipitation, weld decay and intergranular corrosion, by additions of Ti and Nb respectively. These strong carbide formers also cause precipitation of TiC and NbC which imparts creep resistance. Hence, they also are used as creep resisting steels, particularly Type 347. Again a higher Ni is used to compensate for the ferrite forming tendency of Ti and Nb, and also to compensate for the removal of the austenite forming elements C and N.

The 200 series of steels contain lower Ni, which is compensated by the addition of the austenite forming elements Mn and N_2, together with a little higher carbon content where necessary. These alloys were developed to conserve Ni in times of the recurrent shortages of the strategic metals. They also are less expensive.

Austenitic stainless steels which are free from delta ferrite and are stable with respect to martensite formation, are non-magnetic. They have low proof stress values of the order of 230MN/m^2 in the solution treated condition, which are much lower than those for ferritic stainless steels. It should be noted that the low Ni (200 series) steels have higher proof stress values and tensile strengths than the 300 series, due particularly to the solid solution strengthening imparted by the high Nitrogen content. The austenitic steels, however, work harden rapidly, and the rate of work hardening increases with decreasing stacking fault energy and with decreasing stability with respect to martensite formation. In this they are very different from the ferritic stainless steels. The austenitic stainless steels do not exhibit a ductile-brittle transition.

Due to their high ductility, especially at low temperatures, their all-round corrosion resistance, oxidation resistance and creep strength, they are used over a wider temperature range than almost any other material, i.e. -196°C to +800°C. As they are readily fabricated by forming and welding besides being readily machined, their versatility is outstanding; but their main drawback is their high cost largely due to the presence of nickel. Nevertheless, the uses of austenitic stainless steels are widespread, as indicated by the following summary:-

1. The Chemical Industry - plates and tubes, cladding, pressure and chemical reaction vessels, valves and pumps.

2. Power Plant - mainly as tubes for superheater and condenser systems.

3. Fertiliser Production - manufacturing plant for nitrates, phosphates, ammonia and urea. 316 is used for very corrosive conditions, 304L, 321 and 347 for less corrosive conditions.

4. The Brewing and Dairy Industries - beer vats, tanks, barrels, and appropriate piping. Milk coolers and storage tanks.

5. Architecture and Building - window frames, door panels, architectural panels and curtain walling, roofing, sanitary applications, water tubing, masonry bolts and stays.

6. Transport - exhaust systems, silencers, anti-pollution devices, bumpers (fenders), wheel hubs, trim, containers, coach panelling, windscreen wipers etc.

7. The Aircraft Industry - wide ranging applications from engines to airframes. Missile components and aircraft and missile skins.

8. Cryogenics - storage and transportation of liquid gases, including ethylene, methane, natural gas and air gases. Both marine and land tankers.

9. The Laundry and Catering Industries - domestic and commercial washing machines, driers, tumblers, etc. Commercial and domestic refrigerators, cooking ranges, hot cupboards, ovens, working tops, sinks and drainers, kitchen utensils, dishwashers, trolleys, grills and tea and coffee urns. All types of cutlery and holloware.

10. High Temperature uses include furnace structural members, hangers, supports, radiation shields etc.

General applications are for such everyday objects as nuts, bolts and screws, and when cold drawn to more than 1500MN/m² proof stress, as stainless, corrosion resistant springs.

(b) Methods for improving the strength

The standard austenitic stainless steels suffer from a low proof stress, having values of ½ to ⅔ those of ferritic stainless steels or less than ¼ those of martensitic stainless steels. Consequently there is a continual need to improve the strength, without greatly impairing other properties, as this will enable thinner sections to be used and thus result in considerable economy in cost. Various methods have been used, with varying success, to increase the strength:-

(i) Cold Working

Particularly in the unstable steels which transform to martensite during cold working, very high strengths of more than 1500MN/m² proof stress can be achieved by cold working. Even in stable steels, proof stress values in excess of 1250MN/m² can be achieved. A low temperature ageing treatment at ~400°C can then, by a strain ageing effect, increase the proof stress by ~150MN/m². The achievement of high strengths by cold working, which requires some 60-80% reduction during deformation, is limited to thin flat rolled products or to wire, and one of the main disadvantages is that the strength is rapidly lost at temperatures above 600°C, and also in the heat affected zones of a weld. Relatively small amounts of high strength austenitic stainless steels are produced by cold working.

(ii) Warm working or Controlled Rolling

In this process, hot rolling is carried out at temperatures down to 750°C, i.e. below the recrystallisation temperature. At the lower rolling finishing temperatures, only dynamic recovery takes place, and the increase in strength is associated with the fine sub-grain size produced. At somewhat higher rolling finishing temperatures, recrystallisation may occur, but the grain size is fine and this also produces strengthening. The effect of composition is also of interest, in that:-

(1) Solid solution hardening by a nitrogen addition is retained at all rolling finishing temperatures.

(2) Additions of Nb (or Ti) inhibit recrystallisation and maintain fine grain or sub-grain sizes with a still further increase in strength. In addition there is probably a small amount of dispersion strengthening by strain induced NbC (or TiC) precipitation.

One of the problems associated with these controlled rolled steels is that, especially at the lower finishing temperatures obtained in thinner guage materials, some lack of uniformity in the properties can be produced. This can be overcome by a reheating treatment, which if carried out at temperatures below that required for recrystallisation, can increase the uniformity in the properties without any great loss of strength. If additions of Nb or Ti are used, which retard recrystallisation, higher reheating temperatures can be used without any major loss of strength. Some typical property levels achieved by this approach are:-

Steel	Condition	0.2 PS MN/m^2
304	Finish Rolled 800°C Finish Rolled 800°C + 850°C-5m	430 350
321	Finish Rolled 800°C Finish Rolled 800°C + 850°C-5m	480 460
304 + $0.2N_2$	Finish Rolled 800°C Finish Rolled 800°C + 850°C-5m	650 600
304 + $0.2N_2$ + 0.1Nb	Finish Rolled 800°C Finish Rolled 800°C + 900°C-5m	690 670

In these materials, the proof stress values are often more than double those obtained in solution treated standard austenitic stainless steels and due to the compositions restricting or inhibiting recrystallisation and grain growth, the properties are maintained to some extent after welding, provided the process used does not have too great a heat input. The major problem however is to obtain a weld metal with a strength matching that of the controlled rolled parent plate. Such material has potential applications in pressure vessels, storage tanks, etc.

(iii) Solid Solution Strengthening

We have already seen that the interstitial solutes are most effective, followed by the ferrite forming solutes. Carbon is not to be considered due to corrosion problems, whilst the ferrite forming substitutional solutes have such relatively small effects that large amounts are required to achieve any substantial effect. This would considerably add to the cost. Thus nitrogen becomes the most suitable solid solution strengthener, and in addition to it being made potent than carbon, it also has much less detrimental effects on intergranular corrosion. Consequently, developments have commonly tended to use up to $0.25\%N_2$ and in some cases as much as $0.5\%N_2$, which can virtually double the proof stress. The use of nitrogen particularly at the higher levels, can cause problems with regard to ingot porosity, although 0.2% can usually be accommodated without difficulty. In order to be able to dissolve such high nitrogen contents, the steels require to replace some nickel by manganese, as in the 200 series of steels. Nickel is commonly regarded as detrimental to the solubility of nitrogen whilst Mn and Cr allow more to be dissolved. Nitrogen also is a powerful austenite former, thus preventing delta ferrite formation, and also is most effective in stabilising the austenite against martensite formation. Some typical analyses and properties of nitrogen solid solution strengthened steels are:-

Material and Composition	304	316	HP 304	HP 316	201	202	347	HP 347	18-2MN	Tenelon
C%	0.08	0.08	0.06	0.07	0.15	0.15	0.06	0.08	0.10	0.10
Mn%	1.5	1.8	2.0	2.0	6.5	9.0	1.5	1.5	12.5	15.5
Cr%	19.0	18.0	18.0	17.5	17.0	18.0	18.0	18.0	18.0	18.0
Ni%	10.0	12.0	10.0	11.5	4.5	5.0	12.0	11.0	1.7	0.8
Mo%	-	2.5	-	2.7	-	-	-	-	-	-
Nb%	-	-	-	-	-	-	10xC	10xC	-	-
N_2%	0.04	0.03	0.20	0.20	0.25	0.25	0.04	0.20	0.35 min	0.35 min
Tensile Strength MN/m^2	541	571	695	695	805	740	556	710	825	860
0.2% Proof Stress	247	247	340	350	385	310	247	415	450	480
% Elongation	50	50	46	45	48	50	50	39	63	45

Strengths up to 350/400MN/m^2 0.2% Proof Stress are readily achieved, but the impact properties are slightly impaired, compared with Type 304. However the commercial exploitation seems to be limited by the availability of suitable welding electrodes, and dilution effects can lead to delta-free weld structures with consequent hot cracking problems.

(iv) Duplex Austenite-delta ferrite steels

It has already been shown than an increase of 1% in the delta ferrite content increases the tensile strength by 2.5MN/m^2 and the 0.2% Proof Stress by 2.2MN/m^2. A further advantage of the presence of delta ferrite is that it causes grain refinement of the austenite, which produces additional strengthening. These two effects can be combined, and accentuated by further refining the grain size by a controlled rolling treatment, using hot working in the range 900/950°C, or at even lower temperatures. This causes a very fine dispersion of ferrite and austenite, about in equal proportions, which can give proof stress values well in excess of 450MN/m^2. These micro-duplex steels, however, require a careful balance of the ferrite and austenite forming elements, which can lead to compositional control problems. Further advantages of this approach to increased strength are:-

(1) the material may exhibit superplastic properties, which may improve certain aspects of formability.

(2) the micro-duplex steels have greater resistance to stress corrosion cracking than the standard steels. They can therefore replace standard steels in mild stress-corrosion conditions, but cannot replace the high nickel alloys for more critical stress corrosion applications.

One major disadvantage of the micro-duplex steels is that during welding the micro-duplex structure is destroyed in the heat affected zone, giving rise to a coarse widmanstatten structure with not only a loss of strength, but also a marked impairment of the stress corrosion resistance. However this approach has considerable potential, especially if cheaper combinations of ferrite and austenite forming elements can be found which produce micro-duplex structures. The compositions and properties of two typical micro-duplex steels are as follows:-

Steel Type and Compositions	I.N.744	F.V.702
C%	0.05	0.03
Mn%	0.40	0.60
Cr%	26.0	15.7
Ni%	6.5	2.5
Mo%	-	1.0
Ti%	0.30	-
Nb%	-	0.50
Tensile Strength MN/m^2	740	690
0.2% Proof Stress MN/m^2	570	600
% Elongation	24	22

(v) Transformation Induced Plasticity (TRIP Steels)

This process of producing high strength coupled with good ductility in austenitic steels relies on the fact that, when martensite is formed during straining, the work hardening rate increases and this considerably increases the uniform ductility prior to plastic instability. At the same time the martensite which is formed increases the strength very appreciably, even more so if the martensite forms from an austenite which has been thermo-mechanically treated by processes similar to ausforming.

In particular the strength can be appreciably increased if the carbon content is increased from the conventional 0.10%C maximum, to about 0.3%. There are two main methods which can be used, although many variants on them have been investigated:-

(1) The first method requires that the composition of the steel be so adjusted that it is austenite at room temperature but the M_d temperature is above room temperature. The steel is then thermo-mechanically treated at a temperature above the M_d temperature, large deformations of ~80% at temperatures in the range 250°C to 550°C being used. This deformation of the austenite raises the M_s temperature, and consequently the M_d temperature, but the deformed austenite is still stable on cooling to room temperature. On straining at room temperature however, much of the austenite transforms to martensite, the transformation induced plasticity resulting in good ductility and the martensite giving high strength. This type of treatment can be applied to wide varieties of steel, but within any one variety the composition and thermo-mechanical treatment can be critical. A range of carbon contents up to 0.3% can be used to provide a range of strength levels. Typical properties of a steel containing 0.3%C, 2%Mn, 2%Si, 9%Cr, 8.5%Ni and 4.0%Mo after 80% reduction to sheet at 425°C are:-

Tensile strength = 1500MN/m²
0.2% Proof Stress = 1430MN/m²
Elongation % = 50

It is also possible to cold roll the thermo-mechanically worked material by some 15% reduction, when the strength can be increased to 1750MN/m² Tensile strength, 1620MN/m² 0.2% Proof Stress, but with a reduced ductility.

(2) The second method requires that the steel contains carbide forming elements and a carbon content of ~0.3%, and that the composition is adjusted so that M_s and M_d temperatures are below room temperature. After solution treatment, the steel is austenitic, and is then thermo-mechanically worked at 250-550°C; deformation of ~80% again being used. This not only deforms the austenite, but also causes carbide precipitation, both of which raise the M_s and M_d temperatures. The M_s may still be below room temperature, but the M_d is then above room temperature. Straining at room temperature then causes the austenite to transform to martensite with a consequent high strength and high ductility due to the transformation induced plasticity. Again the steel may be cold rolled 15% at room temperature after the thermo-mechanical deformation. By these processes, 0.2% Proof Stress values up to 2000MN/m² with ductilities of 20/25% Elongation may be achieved.

It can be seen that the process employs the thermo-mechanical working of a carefully controlled austenitic steel composition to produce controlled transformation behaviour. This controlled transformation approach is further employed by the use of a -196°C refrigeration treatment to transform the austenite to martensite after the thermo-mechanical deformation, followed by tempering or ageing at ~400°C. In fact the process can be summarised in terms of a combination ausforming and controlled transformation behaviour.

These steels have been but little used due to:-

(1) Their cost; invariably they contain appreciable amounts of nickel, some being reported as high as 20%.

(2) Difficulty in controlling the composition to give the correct transformation behaviour.

(3) Costly processing, involving wear on plant due to the low temperature deformation and high reductions which are used.

(4) The restriction of the material to flat rolled thin products, or wire.

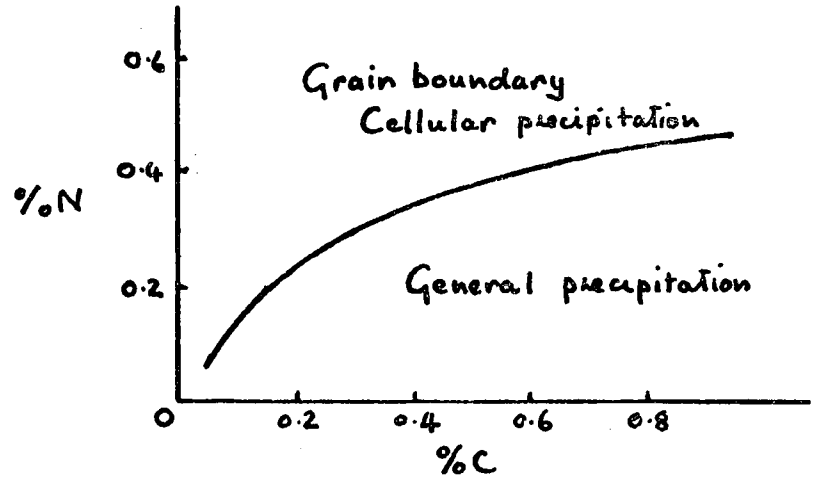
Potential applications include rocket vehicle skins, high strength stainless fasteners, surgical needles, stainless armour and high strength wire and cable; but so far this potential does not appear to have been realised.

(vi) Precipitation Hardening Stainless Steels

Age hardening stainless steels can be produced by employing a very wide range of age hardening reactions. There are three however which have possible commercial applications:-

(1) Carbon-Nitrogen

The base compositions are Cr-Ni, Cr-Mn, or Cr-Ni-Mn steels, the higher the nitrogen used, the greater the amount of Mn which is required at the expense of Ni. The carbon and nitrogen contents can be each increased up to as high as 0.8%, but usually are limited to less than 0.4%. Precipitation occurs either as a general precipitation of $M_{23}C_6$ carbide, with possibly some Cr_2N, or as a grain boundary discontinuous or cellular precipitate of lamellar nodules of $M_{23}C_6$ or Cr_2N. This latter type of precipitation is very deleterious to the ductility and should be avoided. It usually occurs at high (C+N) contents, and the limiting compositions for its occurrence are:-



Increasing the nitrogen content and also increasing the ageing temperature promotes cellular precipitation, whilst increasing the carbon content promotes general precipitation. Ageing is usually carried out at 650°-800°C, but there is a tendency for rapid overageing to occur at the higher ageing temperatures. It appears that with the increased tensile strength brought about by ageing, the ductility and impact values are greatly reduced. Carbon is more effective than nitrogen in promoting ageing, but nitrogen is more detrimental than carbon in terms of the ductility and impact strength. Ageing at 700°C gives the best properties, some typical values being:-

Base Composition 21%Cr, 4%Ni, 9%Mn. S.T 1050°C, Aged 700°C-100h	Carbon and Nitrogen Contents	
	0.2%C 0.03%N	0.4%C 0.025%N
Tensile Strength MN/m^2	755	1050
0.2% Proof Stress MN/m^2	320	650
% Elongation	44	14
Impact value J at 20°C	88	42

Certain stainless valve steels of the 21/4 NS type are based on this approach to strength.

(2) Carbon-Phosphorus

Phosphorus can be used considerably to augment the age hardening due to carbon, and does not need the addition of nitrogen. This means that phosphorus can be used to give increased age hardening in simple higher carbon Cr-Ni austenitic stainless steels. The precipitating phase is $M_{23}(CP)_6$, or $(Cr.Fe.P)_{23}C_6$, the phosphorus entering into solution in the precipitating carbide. A problem again arises with respect to the formation of embrittling grain boundary cellular precipitates at the higher (C+P) contents, which must be avoided. Therefore the carbon is generally limited to $\sim$0.30%, and a similar limitation is applied to phosphorus. One disadvantage again is that fairly rapid overageing occurs at the higher ageing temperatures, and generally the optimum ageing temperature is 700°C. Some typical compositions and properties of these types of steel are given in the following table, proof stresses in excess of $750MN/m^2$ being achieved. These steels have not however been widely used.

Steel Type	Armco 17/10P	Crucible H.M.N.
Composition C%	0.15 max	0.30
Mn%	1.0 max	3.5
Si%	1.0 max	0.5
Cr%	17.0	18.5
Ni%	10.8	9.5
P%	0.30	0.25
Properties aged 700°C		
Tensile Strength MN/m^2	950	1120
0.2% P.S. MN/m^2	610	830
% Elongation	25	18

(3) Nickel-Aluminium-Titanium

These alloys usually contain at least 20%Ni in order to form the γ'-$Ni_3(AlTi)$ phases which provide age hardening. In all these steels, the initial stages of age hardening are due to zone formation, the zones being face centred cubic and of similar lattice parameter to that of the austenite matrix. The composition of the steel, however largely controls the rate of overageing and the nature of the overaged precipitate.

In steels age hardened only with Al, body centred cubic NiAl is the overaged precipitate, and this occurs as widmanstatten laths and plates. The addition of titanium results in a similar phase, Ni(AlTi) which at still higher titanium contents undergoes an ordering reaction to Ni_2AlTi. Further additions of titanium result in, γ', face centred cubic $Ni_3(AlTi)$ being the overaged precipitate, which maintains the

spherical form of the initial zones, and maintains coherence for long periods. At still higher titanium contents, close packed hexagonal Ni_3Ti forms either as widmanstatten laths or as a grain boundary cellular precipitate. The age hardening effect is due to coherency strains and general dispersion strengthening, and can be increased by increasing the volume fraction of precipitate, or by increasing the coherency strains by increasing the misfit between the zones and the matrix. The volume fraction of the precipitates or zones increases as the (Al+Ti) content increases, whilst the misfit between precipitate and matrix is increased by increasing the Ti:Al ratio. The rate of overageing should also be minimised, as this gives greater flexibility in heat treatment conditions, and also means that the steels can be used at elevated temperatures, for which in fact they were originally designed. Indeed, these alloys are often known as the iron-based superalloys and employ similar principles to the Ni-based superalloys in terms of their metallurgical characteristics. $Ni_3(AlTi)$ is by far the more slowly overaging phase of those observed, and also gives the maximum age hardening effects. Thus the use of Al and Ti contents to produce first zones and then $Ni_3(AlTi)$ precipitates, are necessary. However, the amount of (Al+Ti) which can be used is limited as too much (Al+Ti) will produce delta ferrite, whilst too high a Ti:Al ratio results in the undesirable cellular Ni_3Ti precipitation. The optimum age hardening alloys will fulfill the following conditions:

(1) Delta ferrite must be avoided, as this gives a lower age hardening response, a tendency for sigma phase formation, and the possibility of hot working difficulties. The formation of delta ferrite can be prevented in a 20%Cr, 25%Ni steel by the following condition:-

$$4Al + 3Ti < 20$$

(2) Sigma phase must not form, and although this can be achieved by eliminating delta ferrite, a sigma type phase can form in high titanium, ferrite-free steels. This means that Ti contents should be below 3%, which means that the Al is limited to $\sim 2\frac{1}{2}\%$.

(3) Neither widmanstatten nor cellular Ni_3Ti should form as these cause poor ductility. This can be achieved in the higher Ti steels by the addition of 1%Al, which inhibits Ni_3Ti formation. The 1%Al is thus necessary even though it gives a slight reduction in the intensity of age hardening by decreasing the lattice parameter of the γ' and thus decreasing the misfit between the matrix and the precipitate.

(4) Within the confines imposed by the above conditions, the steel should have maximum response to age hardening, and therefore should contain a maximum (Ti+Al) content and a maximum Ti:Al ratio.

An optimum composition is 15/20%Cr, 25%Ni, 1/1½%Al, 3/3½%Ti with low carbon. Often such an alloy will contain some Mo for solid solution strengthening, high temperature strength and creep resistance. Ageing in this steel follows the sequence:-

$$\text{Matrix} \rightarrow \text{zones} \rightarrow \gamma' \rightarrow \text{equilibrium } Ni_3(AlTi)$$

and occurs at temperatures of 600°-850°C. For maximum strength, consistent with a reasonable ageing time, 750°C is used as the ageing temperature, but at 800°C ageing is more rapid, and the ductility is slightly improved due to the lower strength achieved.

Some typical steels and properties achieved are as follows:-

Steel Type	A286	Unitemp 212	15Cr 25Ni 3¼Ti
Composition C%	0.05	0.08	0.02
Cr%	15.0	13.5	15.05
Ni%	26.0	26.0	20.04
Mo%	1.2	1.75	-
Al%	0.15	0.15	0.15
Ti%	2.0	3.0	3.27
V%	0.30	-	-
Tensile Strength MN/m^2	1000	1300	1200
0.2% Proof Stress MN/m^2	700	920	860
% Elongation	25.0	23.0	21.0
	Aged 750°C	Aged 700°C	Aged 750°C

A summary of the optimum properties obtained in Ni-Al, Ni-Ti and Ni-Al-Ti age hardened steels is as follows:-

Tensile Strength MN/m^2	Ni-Al Steels			Ni-Ti Steels			Ni-Al-Ti Steels		
	0.2%PS	%El	Impact J	0.2%PS	%El	Impact J	0.2%PS	%El	Impact J
770	385	35	65	430	39	115	370	37	102
925	555	26	37	555	30	85	525	30	77
1080	760	18	31	710	20	47	680	23	52

It can be seen that compared with the Ni-Al and Ni-Ti steels, the Ni-Al-Ti steels have the best ductilities and impact values at the highest strength levels.

There have also been attempts to produce quantitative relationships between the age hardening achieved and the microstructural parameters. A recent analysis indicated that the maximum increase in age hardening, ΔH, was described by:-

$$\text{Log}\,\Delta H = 1.59 + 1.10\,R + 0.16 \log \delta$$

where R is the average radius of the γ' particles
δ is the difference in lattice parameters between the matrix and the precipitate, i.e. misfit.

It should be noted that the volume fraction of γ' does not enter into the equation because all the alloys used had a virtually constant Ti content and no Al, i.e. a constant volume fraction of γ'. The equation for ΔH can be re-stated as:-

$$\Delta H \doteq 0.15\, R^{\frac{1}{2}} \delta^{\frac{1}{2}}$$

This has a similar form to the coherency hardening relationships developed by Gleiter and Hornbogen, viz:-

$$\Delta T = k\, R^{\frac{1}{2}} . \delta^{m} . f^{n}$$

where f is the volume fraction of precipitate.

Whilst these steels can produce attractive combinations of properties, they are both expensive and may be difficult to hot process. In addition they frequently require to be vacuum melted. Consequently they are restricted for use to high strength:weight ratio applications, particularly at high

temperatures. In fact these γ' age hardened austenitic stainless steels could be a future generation of high temperature power plant steels. A consideration of their high temperature and creep properties is, however, another subject and overlaps very much into the metallurgical developments of the superalloys based on both nickel and cobalt.

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