Strengthening Mechanisms in Steels*

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I. Introduction

Steels have been the most important engineering materials for many years and will remain so for a very long while. This position arises from the versatility of alloys based on iron, which cover a very broad strength spectrum from the comparatively low yield strength of mild steel (12–15 t/in²) to the special alloy steels with strengths in excess of 200 t/in². This range is shown schematically in Fig. 1, where the strength range is still further extended upwards by the inclusion of iron whiskers free from dislocations which can achieve strengths well over 10⁶ lb/in². On the other hand in the downward direction we have weak iron single crystals. It is perhaps instructive to note at this stage that very pure iron crystals with substantially less than one part per million carbon impurity possess remarkably low strengths. Fig. 2 shows a stress

Fig. 1. The strength spectrum of steels (Zackay)

Fig. 2. Stress strain curves of iron crystals with approximately 5×10^{-3} p.p.m. carbon content

strain curve for such material where the initial flow stress at room temperature is only 2 000 p.s.i. and a sharp yield point is absent.¹⁾ The theme of this lecture is that the various strengthening mechanisms in steels can all now be rationalized in terms of the interaction of dislocations with solute atoms and precipitates. However, there are wide variations in individual behaviour which need further detailed study. The starting point in our strength survey is logically the role of elements in solid solution and in particular the interstitial solute carbon (and nitrogen).

II. Solid Solution Strengthening

The classical work of Cottrell and Bilby²⁾ showed that elastic interactions occur between carbon atoms and dislocations in iron with the result that carbon atoms segregate to dislocations and lock them in position. From this idea originated the theory of the sharp yield point in which the high yield stress was necessary to force the dislocations away from their carbon atmospheres. More recently³⁾ it has been appreciated that the locked dislocations rarely break away, but that the yield point develops as fresh dislocations are generated. The drop in stress τ occurs because assuming a constant strain rate the velocity v of the dislocations decreases as the number N generated increases: $\dot{\epsilon} = Nvb$

$$v = k\tau^m$$

where τ : stress
 $\dot{\epsilon}$: strain rate
 N : number of dislocations
 v : velocity
 b : Burgers vector
 k and m are constants for a given material.

There is now plenty of structural evidence that dislocations in relatively pure iron are locked effectively by the presence of iron carbide particles. For example, iron can be quenched from 650°C to form a supersaturated solid solution of carbon in α -iron. However, on quench-ageing in the range 100°–300°C, iron carbides are nucleated both on dislocations and in the matrix^{4),5)} (Photo 1). The very low equilibrium solubility of carbon in α -iron at these temperatures ensures that carbide precipitation will occur even in relatively pure iron. Even when mobile dislocations are created at the yield point, the stress to propagate them is still quite high. We conclude that the friction stress, a stress exerted by solute atoms in random solid solution on the moving dislocations is a potent

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Photo 1. Precipitation of iron carbide (ϵ) in Fe-C alloy quenched from 690°C and rested 18 months at room temperature (Hale and McLean) ($\times 24\,000$) ($1/2$)

source of strengthening.

The substitutional elements also contribute to solid solution strengthening. Data is not precise because of the interference of interstitial solute impurities, but elements like phosphorus, nickel and molybdenum are much more effective than, for example, chromium, cobalt and vanadium⁶⁾ which exerts little strengthening in iron in small concentrations (1–3 at%) (Fig. 3). If the effect of interaction with carbon is excluded, the substitutional strengthening can be qualitatively understood in terms of differences in size factor and valency.

Fig. 3. Effect of solutes on U.T.S. of α -iron (Nunes)

III. Martensite

The martensite reaction is undoubtedly one of the most impressive strengthening mechanisms in steels, although it unfortunately leads also to brittleness. The causes of the high strength of martensite have

been hotly argued, but there is little doubt that at least three mechanisms contribute:

- (i) interstitial solid solution strengthening
- (ii) high dislocation density
- (iii) presence of carbide precipitates.

Winchell and Cohen⁷⁾ have shown by experiments on iron-nickel-carbon martensites that the flow stress is a strong function of carbon concentration (Fig. 4), and concluded that the strengthening arises primarily from the interstitial solid solution strengthening. The effect is substantial because of the asymmetrical distortion introduced into the ferrite lattice by the carbon atoms, which enables them to interact more strongly with the stress fields of dislocations⁸⁾. A similar increase in carbon content in stable austenite has a very much smaller effect, because the distortions produced are symmetrical (Fig. 4).

Fig. 4. Effect of carbon on the hardness of austenite and martensite (Cohen)

Thin film electron microscopy studies⁹⁾ have shown not only that martensite has a very high dislocation densities, but also that very fine twins about 50–200 Å wide are frequently formed in the lamellae (Photo 2). There is little doubt that the dislocations raise the strength in the same way as in heavily cold worked metals which possess similar dislocations densities, and the presence of fine twins should have an additional strengthening effect¹⁰⁾. However this twinned structure is already present in low carbon iron-nickel martensites where the hardness is quite low (Fig. 4), so the contribution of the twins to strengthening cannot

Photo 2. Martensite in a 1%C carbon steel, showing fine twins (Kelly and Nutting) ($\times 30\,000$) ($1/2$)

be very substantial.

The work of Winchell and Cohen showed conclusively that virgin martensite, that is, martensite which formed at very low M_s temperatures (-40°C) was substantially softer than martensite allowed to rest at room temperature (Fig. 5). It is now known that ageing of martensite occurs even at sub zero temperatures, as a result of the mobility of carbon atoms, and the resultant formation of fine carbide precipitates. It is difficult to assess precisely the contribution of precipitates, but a recent estimate¹¹⁾ for 0.8C steel indicates that approximately half the strength of high carbon martensite arises from the solid solution effect, and that carbon segregation to dis-

Fig. 5. Effect of ageing on the yield stress of martensite (Winchell and Cohen)

locations, or even very fine precipitate must account for most of the additional strength. Most martensitic structures contain fine carbide precipitates but it is only in martensite formed at low (i.e. sub-zero) temperatures that a marked age-hardening reaction can be induced.

IV. Tempering of Martensite

In plain carbon steels there is a progressive softening accompanied by an increase in ductility as a quenched martensite is tempered in the range 100° – 700°C . Structurally this is a result of the growth of cementite from a fine Widmanstätten array of rodlets to coarse spheroidal particles as the temperature is raised. If however carbide forming alloying elements such as molybdenum, vanadium, tungsten, etc. are added to the steel, a further strengthening reaction sets in over the range 500° – 600°C , as a result of which hardnesses approaching that of the as-quenched alloy are frequently achieved (Fig. 6).

Tempering curves for a 2%V-0.2%C-Fe alloy

Fig. 6. Secondary hardening in a pure iron-2%vanadium-0.2%carbon alloy (Raynor and Honeycombe)

The strengthening is a result of the replacement of cementite which goes back into solution by alloy carbides such as V_4C_3 and Mo_2C which form initially as very fine coherent precipitates primarily on the dislocations inherited from the as-quenched martensite.^{11),12)} These precipitates have been detected well before the secondary hardening peak while at peak hardness Mo_2C needles are typically $100\text{ \AA}$ long and about $15\text{ \AA}$ dia. Vanadium carbide is in the form of thin plates on cube planes, about $100\text{ \AA}$ dia. and $10\text{ \AA}$ thick at peak hardness.

The secondary hardening reaction can be made even more effective by further alloying additions. In particular small concentrations ($<0.1\%$) of strong carbide formers such as niobium titanium increase the peak hardness substantially and tend to delay over-ageing¹³⁾. Structural studies have shown that the effect is due primarily to the formation of a fine dispersion of a second carbide phase (Photo 3), e.g. NbC , TiC , although an influence on the rate of growth of

Photo 3. An iron-4% molybdenum-0.1% niobium-0.2% carbon alloy quenched and tempered 6 hr and at 700°C ($\times 50\,000$) ($1/2$)

the primary alloy carbide phase cannot be excluded.

V. Further Strengthening of Martensite

In recent years new methods have been adopted for the improvement of the strength of martensitic steels. Ausforming which is perhaps the best known, involves the deformation of the steel while it is still in the austenitic condition in the so called austenite bay formed at subcritical temperatures^{14),15)}. In these circumstances the austenite is supersaturated with respect to carbon, and the result of the working operation is to generate a dense network of dislocations with an associated very fine dispersion of carbide precipitate on which the subsequent martensitic reaction, which occurs on cooling after ausforming, is superimposed. During ausforming the austenite grains will be elongated in the rolling direction and the resulting martensite needles tend to be smaller. The evidence suggests that fine grained original austenite and the refinement of martensite lamellae both contribute to increased strength in ausformed steels. The ausformed martensite also shows less tetragonality than conventionally heat treated steels, and this may well be a factor in determining the improved ductility which is a characteristic of many (but not all) ausformed steels.

However a great deal remains to be understood about ausforming. The greatly dissimilar responses of steels of different compositions is hard to explain although it is clear that the work hardening characteristics and the stacking fault energy of the austenite are important factors, as well as the particular carbide which are likely to precipitate during ausworking.

VI. Maraging

Another major development in high strength steels has been the maraging steels in which carbide precipitation is eliminated by lowering the carbon to 0.02% or so, and precipitation of intermetallic compounds is achieved during tempering of the low carbon martensite. Recent work by Miller and Mitchell¹⁶⁾ has

shown that in an 18%Ni-8%Co-7%Mo the precipitate which gives rise to marked hardening during tempering is Fe_2Mo , while if the molybdenum is replaced by 1.5% titanium Ni_3Ti is formed. The commercial maraging steel has both molybdenum and titanium in it, and it has been found that both Fe_2Mo and Ni_3Ti form, the former as discs and the latter as needles. The improved toughness of the steels probably arises from the better distribution of the precipitates, for example, molybdenum prevents the tendency to precipitate formation at prior austenite grain boundaries.¹⁷⁾

VII. Austenitic Steels

Austenitic steels in general possess better high temperature properties than ferritic steels. This behaviour which is already evident in the solid solution before the structure is complicated by the superimposition of precipitation reactions, can be explained in general terms by the different behaviour of dislocations in the f.c.c. (austenitic) and b.c.c. (ferritic) crystal lattices. The facility of dislocations in the b.c.c. lattice to avoid obstacles by climb or thermally activated cross slip is much greater than in the f.c.c. lattice. This arises partly from the fact that self diffusion occurs more readily in ferrite than in austenite at equivalent temperatures, and partly because of differences in the crystallography of the deformation processes. As these mechanisms are important in recovery processes leading to the development of sub-structures, it follows that softening during creep will occur more readily in ferritic than in austenitic steels, other things being equal.

However austenitic solid solutions vary very much in their creep resistance depending on the detailed structure of the dislocations. Dislocations in all f.c.c. structures dissociate to a greater or lesser degree depending on the stacking fault energy of the matrix. (Fig. 7). The lower the stacking fault energy the greater the tendency of dislocation to dissociate into partial dislocations separated by stacking fault, and the more difficult will become the processes associated with recovery, i.e. cross slip and climb.

We now know something about how the stacking fault energy (S.F.E.) changes with composition, for example, nickel raises it while chromium lowers it.¹⁸⁾ A rough indication is given by whether or not an alloying element increases the frequency of annealing twins, and in unstable compositions, by the incidence of ϵ -martensite (Photo 4) (hexagonal c.p.). In general metals of higher valency such as chromium and manganese and silicon lower the S.F.E., while monovalent metals such as nickel and copper have little effect, or raise the S.F.E.

It is thus possible to suggest austenitic matrixes which would be useful starting points for achieving creep resistance, other factors being equal. For example the replacement of an iron-nickel chromium matrix by an iron-manganese-chromium matrix will produce a lower stacking fault energy. The stacking fault energy is also relevant in considering the streng-

Fig. 7. Dissociations of dislocations in face-centred cubic structure (Seeger)

Photo 4. ϵ -martensite in an iron-14%chromium-14% manganese steel (Sanderson and Honeycombe) ($\times 300$) ($1/2$)

thening of austenite by cold work. Elements such as manganese and chromium increase the rate of work hardening,¹⁹⁾ because by lowering the stacking fault energy they make it more difficult for dynamic recovery by cross slip, the process which is associated with stage 3 deformation in f.c.c. metals and alloys. The greatest increases in strength occur when unstable austenitic compositions are used, and martensite is formed during working, however if stable austenites are investigated, the separate role of stacking fault energy becomes clear.

Having produced a strong matrix, the next step is to achieve further strengthening by controlled precipitation. The possible reactions are extremely numerous so emphasis will be placed mainly on underlying principles which are gradually emerging from the mass of data.

Two main types of precipitate have been found to be effective.

Carbides

These include $M_{23}C_6$, NbC, TiC, etc. all of which can by suitable heat treatments be dispersed finely in an austenitic matrix.

Intermetallic Compounds

These again have numerous possibilities, but the most effective precipitate is the face-centred cubic γ' precipitate of the composition Ni_3Ti or $Ni_3(Ti Al)$.

This corresponds to the precipitate responsible for the strengthening of nickel-base high temperature alloys.

We shall now examine in greater detail the morphology of precipitation of carbides and intermetallic compounds to determine this role in achieving high temperature properties.

VIII. Precipitation of Carbides

Carbide precipitation occurs in a number of different morphologies which have varying effect on the mechanical properties.

They are

- (i) grain boundary precipitation
- (ii) precipitation on dislocations
- (iii) matrix precipitation
- (iv) precipitation on stacking faults

Little strengthening arises from grain boundary precipitation in the ordinary way. For example precipitation of $M_{23}C_6$ in the grain boundaries of an 18/10 stainless steel has little effect on room temperature strength, although the ductility is adversely affected. However at elevated temperatures, grain boundary precipitation may be beneficial, because it can reduce grain boundary sliding and the resultant intergranular cavitation leading to creep fracture.

Most of the carbides found in austenitic steels e.g. $M_{23}C_6$, NbC, TiC etc. tend to nucleate preferentially on dislocations. This is particularly pronounced with the simple cubic carbides NbC, TiC, V_4C_3 which have been found to nucleate on dislocations both during ageing heat treatments, during cooling in welded zones and in service at elevated temperatures. While this phenomenon can lead to increased strength under conditions of high temperature service, it can also drastically reduce ductility (Fig. 8) by immobilizing dislocations within the grains, and encouraging grain boundary sliding. Steels of the 18/12/1 Nb type also subjected to high solution treatments as in welding have a high concentration of NbC in solid solution which subsequently precipitates on dislocations, and in the extreme case, causes weld cracking. One solution to the problem is to leave out the niobium and to add molybdenum and boron as in the following steel.²⁰⁾

	C	Cr	Ni	Mo	Nb	B
FV.555 (type 316)	0.05	16.5	11.5	2.4	—	0.005

Fig. 8. Relationship between ductility and rupture stress for an 18/12/1 Nb steel between 550° and 700°C (Irvine et al.)

The boron addition has a significant effect on the rupture strength, which is achieved by lowering the carbon solubility, and causing the formation of larger primary carbides in the grain boundaries, where they reduce intergranular sliding. There is also a possible reduction in the grain boundary diffusion rates.

Turning to matrix carbide precipitation this is not often very dense in austenitic steels, possibly because carbon contents are usually low (<0.1), but also because the solubility of most of the carbides in austenitic is low, and consequently the precipitates occurs preferentially at grain boundaries and on dislocations. However, $M_{23}C_6$ (also V_4C_3) is more soluble and in steels of higher carbon content (0.3%) forms a dense matrix precipitate.²¹⁾ One important feature of matrix precipitation is the depleted zones which often occur in the vicinity of the grain boundaries, and arise primarily from vacancy depletion caused by the vacancies diffusing to the boundaries, with the result that they are not available to act as nuclei for matrix precipitation. These zones will be weaker than the rest of the crystal, so at elevated temperatures tend to be regions in which creep deformation concentrates. Ideally they should be avoided and the grain boundaries should be stabilized to cause embrittlement.

Recent work has shown that the simple cubic carbides NbC, TiC, TaC and V_4C_3 also some nitrides can be precipitated on association with stacking faults to form discs of very fine precipitates up to 5 microns in diameter,^{22),23)} Photo 5. We know that these sheets of precipitates occur by gradual extension of the faults, as the partial dislocations move out and act as nucleating centres for carbides precipitation. When the precipitate particles grow to a critical size, the partial dislocation is repelled and climbs away to a new position where the nucleation process is repeated. In this way sheets of precipitate are formed which eventually meet each other and divide the grains into a special form of substructure. This results in a marked

Photo 5. An 18/12/2 Ta/0.1C steel aged 100 hr at 700°C. Extraction replica. ($\times 14\,000$) ($1/2$)

Fig. 9. Mechanical properties of an aged 35%Ni, 15%Cr, 1%Ti, 0.1%C alloy (Harding and Honeycombe)

enhancement of mechanical properties both at room and elevated temperatures. Fig. 9 shows the enhancement of yield stress at room temperature when a 35Ni/15Cu/1Ti/0.1C austenite is aged at 700°C after solution treatment at 1 300°C. Stacking fault precipitation commences after about 10 hr at 700°C and raises the yield stress from 22 000 lb/in² to 60 000 lb/in²²⁴⁾ while a pre-strain of 3% on the solution treated condition raises the yield stress to nearly 70 000 lb/in².

The rise in strength is in part due to the increased density of stacking faults, but also to the large increase of precipitation of NbC (or TiC) on undissociated dislocations. Tensile and creep tests at elevated temperatures reveal that the strengthening due to stacking fault precipitation is still appreciable at 800°C. This strengthening primarily arises from the inhibition of the movement of dislocations by the walls of fine precipitate, which in this sense act as grain boundaries, but do not exhibit the grain boundary tendency towards cavitation and intergranular cracking at elevated temperatures.

IX. Precipitation of Intermetallic Compounds

The highest strengths in austenitic steels are achieved

ved by precipitation of intermetallic phases, because the solubility of the relevant alloying elements e.g. Al and Ti varies so greatly with temperature, that much larger volume fractions of precipitates are possible with intermetallic compounds than with carbides. For example, it has been found that 6at%Al plus 2.75at%Ti can be dissolved at 1200°C in a 15%Cr, 25%Ni iron alloy.²⁵⁾ Aluminium and titanium allow the precipitation of the phase which corresponds to the formula $Ni_3(Al, Ti)$ and is face centred cubic. This phase contributes markedly to the strengthening of austenitic steel in which it first precipitates as a coherent Widmanstätten array. In high Nb (and Ta) alloys the phase is replaced by the orthorhombic Ni_3Nb phase which is also a very effective strengthener. The strengthening effect of Ni_3Ti is illustrated in Fig. 10 where a pure alloy containing 15%, 35%Ni, 3.5%Ti, 0.25%C shows a marked increase in strength during ageing at 700°C initially due to stacking fault precipitates but latterly also due to the precipitation of Ni_3Ti , the combined effect raising the strength to about 120 000 lb/in² (Fig. 10).

Fig. 10. Mechanical properties of an aged 35%Ni, 15%Cr, 3.5%Ti, 0.25%C alloy (Harding and Honeycombe)

One difficulty in these austenitic steels is to prevent the γ' phase being replaced by other phases when overageing takes place. For example the hexagonal ϵ phase, also Ni_3Ti , can form either as coarse needles or flakes or as a grain boundary cellular structure. Both morphologies are harmful to the mechanical properties. There are also the hexagonal Laves phases Fe_2Mo and $Fe_2(TiNb)$ which can have some strengthening effect when uniformly distributed, but they often form coarse plates or occur massively at grain boundaries with detrimental effects on strength.²¹⁾ Other harmful phases which form as equilibrium is approached include the tetragonal sigma phase and the cubic chi phase, which again have a predilection for the grain boundaries. Clearly one way of improving the high temperature mechanical properties of this class of steel is to stabilize the γ' phase by further alloying additions which have the effect of reducing the mismatch between precipitate and matrix.²⁶⁾ The closer the matching of matrix/precipitate

parameters, the slower is the overageing process. This is achieved by decreasing the parameter of the matrix, for example by adding cobalt or increasing the nickel content. Alternatively the lattice spacing of the Ni_3X precipitate can be increased, for example, additions of titanium and molybdenum increase the lattice-spacing of Ni_3Al .²⁷⁾

X. Conclusions

In this lecture I have only had time to discuss very briefly a few important strengthening mechanisms in steels. Much work remains to be done, but thanks to the application of modern techniques, we now are able to study in detail the structures which give rise to high strength. However, there are still great difficulties in predicting precise compositions and heat treatments likely to give improved results. Nevertheless some guiding principles are emerging to the extent that development of new steels should gradually become rather less empirical than is the case at present.

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