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The Effects of Alloying Elements on Steels (I)

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Contents

1 Classification of Iron Alloy Phase Diagrams

It is a log-standing tradition to discuss the various alloying elements in terms of the properties they confer on steel. However, it would be impossible to include a detailed survey of the effects of alloying elements on the iron-carbon equilibrium diagram in this short literature review. In the simplest form this would need analysis of a large number of ternary alloy diagrams over a wide temperature range. However, the characteristics of the transformation in the various iron binary equilibrium systems permit a classification as in Fig. 1 as: open and closed γ-field systems, and expanded and contracted γ-field systems [1]. This approach indicates that alloying elements can influence the equilibrium diagram in two ways:

(i) By expanding the γ-field, and encouraging the formation of austenite over wider compositional limits. These elements are called γ-stabilizer.

(ii) By contracting the γ-field, and encouraging the formation of ferrite over wider compositional limits. These elements are called α-stabilizers.

The form of the diagram depends to some degree on the electronic structure of the alloying elements which is reflected in their relative positions in the periodic classification.

Type 1: Open γ-field. The important steel alloying elements Ni and Mn as well as Co and the inert metals such as Pt belong to this group. These alloying elements widens the temperature range for stable austenite by depressing the α-γ transformation and raising the γ-δ transformation. Both Ni and Mn, if added in sufficiently high concentration, completely eliminate the bcc α-iron phase and replace it, down to room temperature, with the γ –phase. So Ni and Mn lower both Ae1 and Ae3 (Fig. 1 a). It is also easier to obtain metastable austenite by

quenching from the austenite region to room temperature, consequently Ni and Mn are useful elements in the austenitic steels.

Type 2: Expanded γ-field. C and N are the most important elements in this group. The γ–phase field is expanded, but its range of existence is cut short by compound formation (Fig. 1 b). Cu, Zn and Au have similar influence. The expansion of the γ–phase by carbon, and nitrogen, underlies the whole of the heat treatment of steels, by allowing formation of a homogenous solid solution (austenite) comprising up to 2.0 wt% of carbon or 2.8 wt% of nitrogen.

Type 3: Closed γ-field. Many elements restrict the formation of γ-iron, causing the γ-area of the diagram to contract to a small area referred to as gamma loop (Fig. 1 c). This means that the relevant elements are encouraging the formation of bcc iron (ferrite), and one result is that the δ– and α– phase fields become continuous. These alloys are, therefore, not amenable to the normal heat treatments involving cooling through the γ/α phase transformation. Si, Al, Be, and P fall into this category, together with the strong carbide-forming elements, Ti, V, Mo and Cr.

Type 4: Contracted γ-field. The γ-loop is strongly contracted, but is accompanied by compound formation (Fig. 1 d). Boron is the most important element of this group, together with the carbide-forming elements Ta (tantalum), Zr and Nb.

Fig. 2 shows the influence of different alloying elements on the γ-loop of various binary systems of iron.

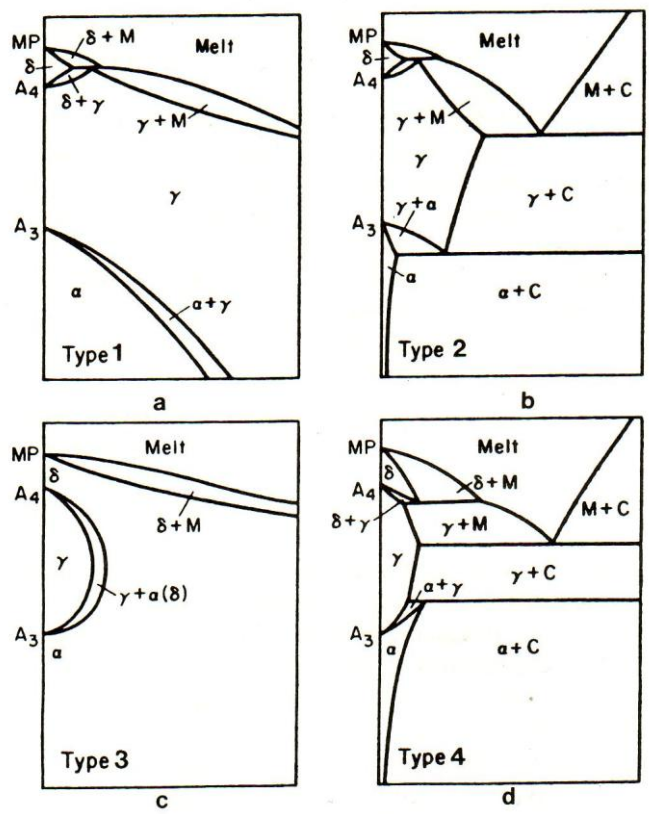

Fig. 1 Classification of iron alloy phase diagrams: (a) open γ–field; (b) expanded γ–field; (c) closed γ–field; (d) contracted γ–field [1].

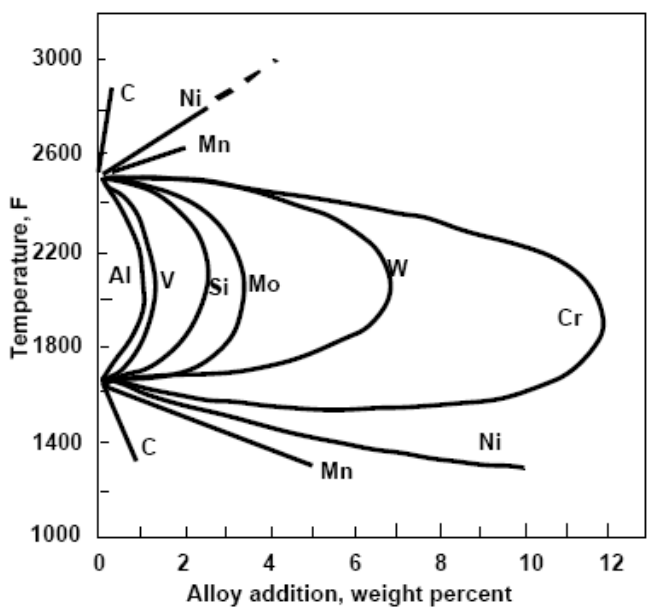

Fig. 2 γ-loops formed in various binary systems of iron.

Thus it appears from these phase diagrams that the crystal structure of solid solutions of iron at room temperature is the important basis for classifying steels. If austenite is predominant at room temperature because of the addition of sufficiently large amounts of Ni or Mn, it is called *austenitic steel*. Examples are: Hadfield steel containing 13% Mn, 1.2% Cr, and 1% C; and 18% Cr and 8% Ni austenitic stainless steel (all in wt%).

On the other hand, if the room-temperature structure consists mostly of α–iron solid solution that is made possible by the ferrite-forming elements (e.g., Cr, Si, Mo, W and Al), it is called *ferritic steel*. Examples are Fe-Cr alloys containing more than 13% Cr, and low-carbon transformer steel containing about 3% Si.

2 Effect on the Eutectoid Point

Austenite and ferrite stabilizers widen the respective phase fields. The effect of alloying elements on the Fe-Fe_3C phase diagram is strongly reflected in the eutectoid temperature, which is raised or lowered by the alloying addition. The austenite stabilizers lower the eutectoid temperature, thereby widening the temperature range over which austenite is stable. Similarly, the ferrite formers raise the eutectoid temperature, thereby restricting the γ –phase field. Fig. 3 shows the influence of alloying addition on eutectoid temperature and eutectoid carbon content.

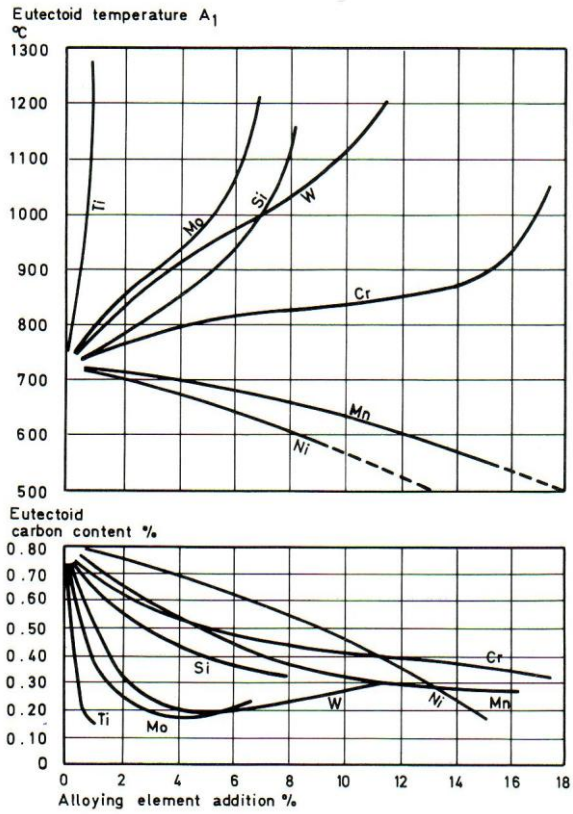

Fig. 3 Influence of alloying element additions on the eutectoid temperature and the eutectoid carbon content [4].

One convenient way of illustrating quantitatively the effect of an alloying element on the γ-phase field of the Fe-C system is to project on to the Fe-C plane of the ternary system the γ-phase field boundaries for increasing concentration of a particular alloying element. This is illustrated in Fig. 4 for Ti, Cr, Mo and Mn, from which, for example, it is evident that just over 1 wt% Ti will eliminate the γ-loop, whereas 20 wt% Cr is required to reach this point. Associated changes in eutectoid temperature and composition are also illustrated.

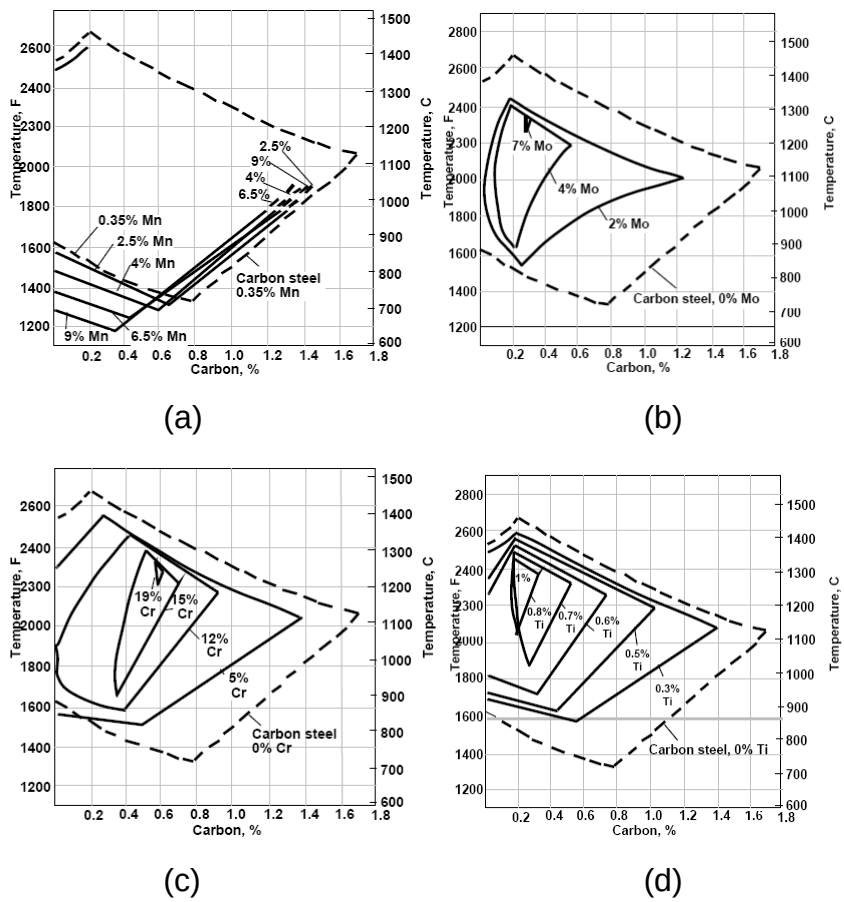

Fig. 4 Effect of alloying additions on the γ-phase field: (a) Mn; (b) Mo; (c) Cr; (d) Ti [1].

3 Distribution of Alloying Elements

In commercial alloy steels, which are multicomponent systems, alloying elements can be found (i) in the free state; (ii) as intermetallic compound with iron or with each other; (iii) as oxides, sulfides, and other nonmetal inclusions; (iv) in the form of carbides; or (v) as a solution in iron [5]. As to the character of their distribution in steel, alloying elements may be divided into two groups:

1) Elements that do not form carbides in steel (e.g. Ni, Si, Co, Al, Cu and N)
2) Elements that form stable carbides in steel (e.g. Cr, Mn, Mo, W, V, Ti, Zr, and Nb).

The first group elements do not form chemical compounds with iron and carbon, and consequently the only possible form in which they can be present in steel is in solid solutions with iron. The only exceptions are Cu and N. Copper dissolves in α-iron at normal temperatures in amounts of up to 1.0%. If the Cu content exceeds 7%, iron will contain copper in the free state as metal inclusions. Nitrogen also has a limited solubility in ferrite. When the N content is higher than 0.015%, nitrogen is found in steel in the form of chemical compounds with iron or some alloying elements (V, Al, Ti, and Cr). These chemical compounds are called nitrides.

Alloying elements whose affinity for oxygen is greater than that of iron are capable of forming oxides and other nonmetal compounds. When added at the very end of the steel melting process, such elements (e.g., Al, Si, V, Ti) deoxidize steel by taking oxygen from iron. The deoxidizing reaction yields Al_2O_3, TiO_2, V_2O_5 and other oxides. Owing to the fact that deoxidizers are introduced at the final stages of the steel melting process, the majority of oxides have no time to coagulate or to pass to slag, and as a result they are retained in the solid steel as fine nonmetal inclusions. In addition to a great affinity for oxygen, some alloying elements have a greater affinity for sulfur than iron does, and upon being introduced into steel, they form sulfides.

Alloying elements that form stable carbides in steel can be found in the form of chemical compounds with carbon and iron or be present in the solid solution. The distribution of theses elements depends on the carbon contents of steel and the concurrent presence of other carbide-forming elements. If a steel contains a relatively small amount of carbon and a great quantity of an alloying element, then, carbon will be bound to carbides before the carbide-forming elements are completely used. For this reason excess carbide-forming elements will be found in the solid solution. If a steel has a large amount of carbon and little of the alloying elements, the latter will be present in the steel mainly as carbides.

Most alloying elements, except C, N, O, B and metalloids standing far from iron in the periodic table, dissolve in great amount in iron. The elements standing to the right of iron (Co, Ni, Cu, etc.) form solutions in iron only and do not enter

into carbides. Thus one can state that alloying elements dissolve predominantly into basic phases (ferrite, austenite, cementite) of iron-carbon alloys or form special carbides [5].

4 Alloy Carbides

The addition to iron-carbon alloys of elements such as Ni, Si, Mn, which do not form carbides in competition with cementite, does not basically alter the microstructures formed after transformation. However, in the case of strong carbide-forming elements such as Mo, Cr and W, cementite will be replaced by the appropriate alloy carbides, often at relatively low alloying element concentrations. Still stronger carbide- forming elements such as Nb, Ti and V are capable of forming alloy carbides preferentially at alloying concentrations less than 0.1wt%. It would, therefore, be expected that the microstructures of steels containing these elements would be radically altered.

Carbides are formed in steels only by iron and metals that stand to the left of iron in the periodic table. The strong carbide-forming elements are shown in Fig. 5.

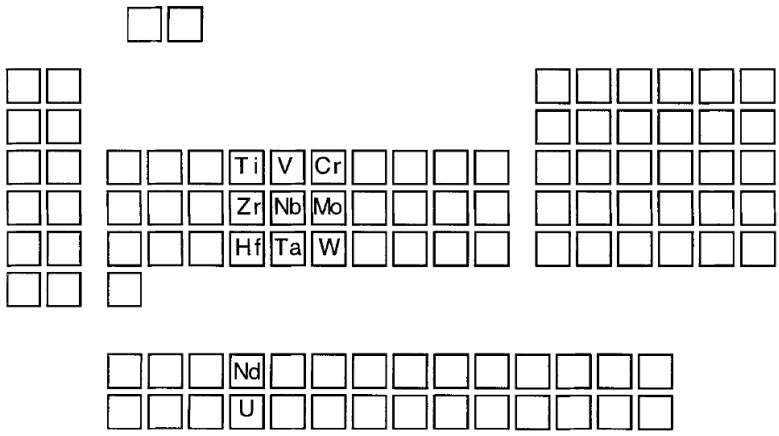

Fig. 5 The periodic table showing the positions of strong carbide-forming elements [6].

In steel six kinds of carbides can be formed as shown in Table 1, where M denotes a sum of carbide-forming (metal) elements. The carbides placed in group I posses a complicated crystal structure; an examples is cementite (Fe_3C), or $Cr_{23}C_6$. A specific structural feature of the carbides of group II as interstitial phases is a simple crystal lattice (e.g., TiC, WC, NbC and Mo_2C).

Table 1 Possible variants of carbide formation in steels.

Carbides of group I	Carbides of group II
M_3C	MC
$M_{23}C_6$	M_2C
M_7C_3	
M_6C	

The stability of the alloy carbides and nitrides in steels relative to that of cementite is shown in Fig. 6, where the enthalpies of formation (ΔH_f) are plotted (cementite is the reference, i.e. $\Delta H_{f\text{-cementite}}=0$). It should be noted that the effectiveness of the carbides as strengtheners depends on the fineness of the dispersion and the volume fraction precipitated. The fineness of the dispersion depends on the activation energy barrier (ΔG^*) for nucleation which in turn is influenced by the free energy of formation of the carbide, the interfacial energy and the misfit. Fig. 6 can be used as a guide in this regard. The finest precipitate dispersions are generally obtained from VC, NbC, TiC, TaC and HfC. Theseare all close-packed intermetallic compounds. On the other hand the carbides with complex crystal structures and low heats of formation, e.g. M_7C_3, M_6C and $M_{23}C_6$, generally form relatively coarse dispersions [7].

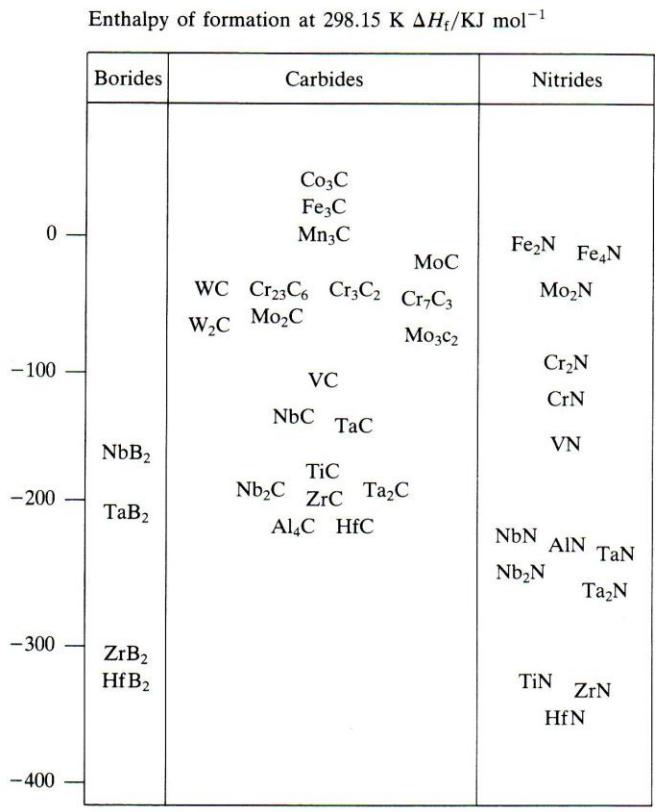

Fig. 6 Enthalpies of formation of carbides, nitrides and borides [7].

The volume fraction of carbide precipitated depends on the solubility of the alloy carbide in the austenite prior to quenching, relative to the solubility in ferrite. Fig… shows the solubility products of various carbides and nitrides in austenite as a function of temperature. The solubilities of these compounds in ferrite are very much lower and to a first approximation can be considered to be approximately equal. It is clear therefore that chromium, molybdenum and vanadium with highest solubilities in austenite, should precipitate in the highest volume fractions in the ferrite.

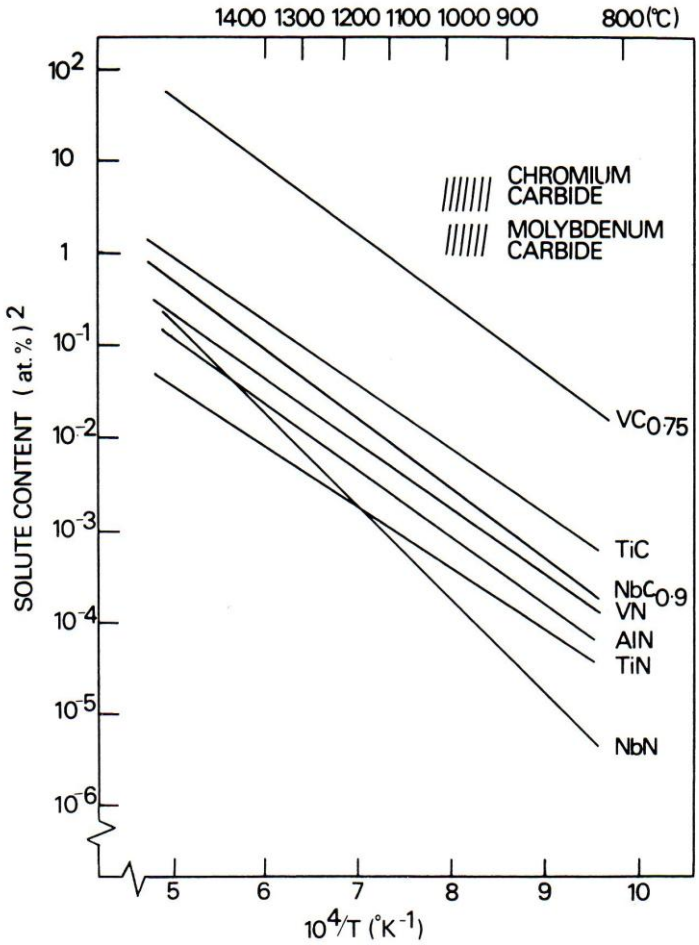

Fig. 7 Solubility product of carbides and nitrides in austenite as a function of temperature [7].

5 Effects on Transformation Diagrams

Alloying elements have considerable influence on the kinetics and mechanism of all three types of transformation of austenite to pearlite, bainite and martensite.

Alloying elements that dissolve only in ferrite and cementite without the formation of special carbides exert just a quantitative effect on the transformation processes (Fig. 8). Cobalt speeds up a transformation but the majority of elements, including NI, Si, Cu, Al, etc., slow it down.

Carbide- forming elements produce both quantitative and qualitative changes in the kinetics of isothermal transformations (Fig. 8). They (e.g., Cr, Mo, W, V, etc.) influence the austenite decomposition differently at different temperatures:

i. At 700-500 °C (pearlite formation), they slow the transformation
ii. At 500-400 °C, they dramatically slow the transformation
iii. At 400-300 °C (bainite formation), they speed up the transformation

Therefore, steels alloyed with carbide-forming elements have two maxima of the austenite isothermal decomposition rate separated by a region of relative stability undercooled austenite (Fig. 8).

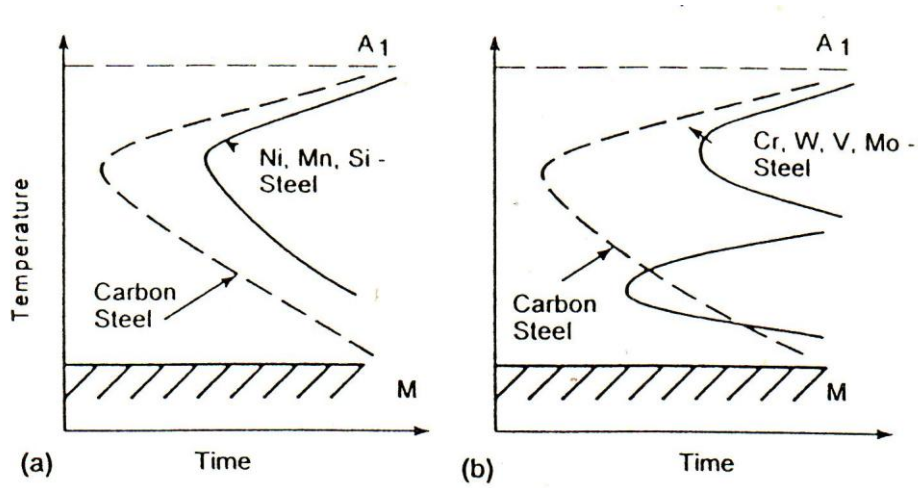

Fig. 8 Diagrams of isothermal transformation. (a) Carbon steel and steel alloyed with non-carbide-forming elements; (b) carbon steel and steel alloyed with carbide-forming elements [5].

6 Effect on Ferrite Hardness

All alloying elements that form solid solutions in ferrite affect its hardness. The hardness increase caused by substitutional solution is shown in Fig. 9. Si and Mn, the most frequently occurring alloying elements, have a relatively potent effect on the hardness of ferrite, while Cr gives the smallest hardness increase.

For this reason Cr is a most convenient alloying element in steel that is to be processed by cold working in which good hardenability is required.

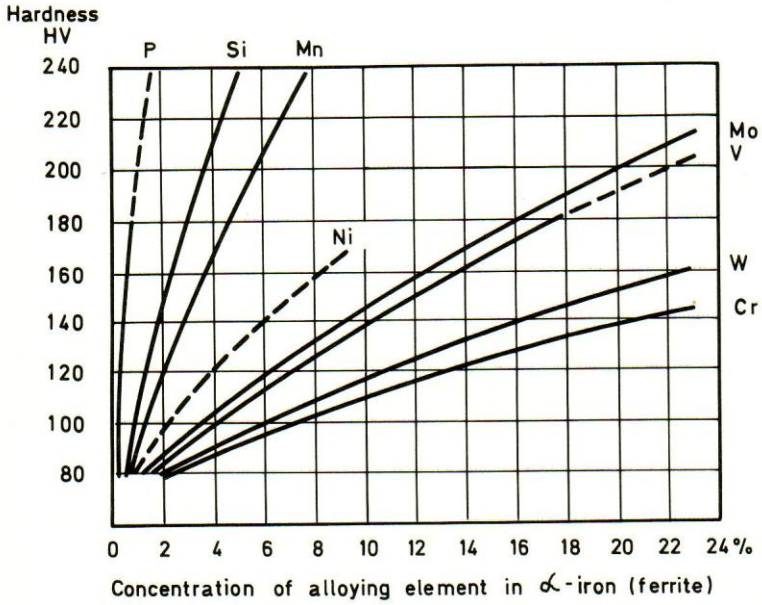

Fig. 9 Effect of substitutional alloying element additions on ferrite hardness [8].

7 Effect on Martensite Transformation Temperature

Most alloying elements which enter into solid solution in austenite lower the martensite start temperature (M_s), with the exception of Co and Al (Fig. 10). However, the interstitial solutes carbon and nitrogen have a much larger effect than the metallic solutes. From Fig. 10 it can be seen that 1wt% of carbon lowers the M_f (martensite finish temperature) by over 300 °C. Note that above 0.7wt% C the M_f temperature is below room temperature and consequently higher carbon steels quenched into water will normally contain substantial amounts of retained austenite.

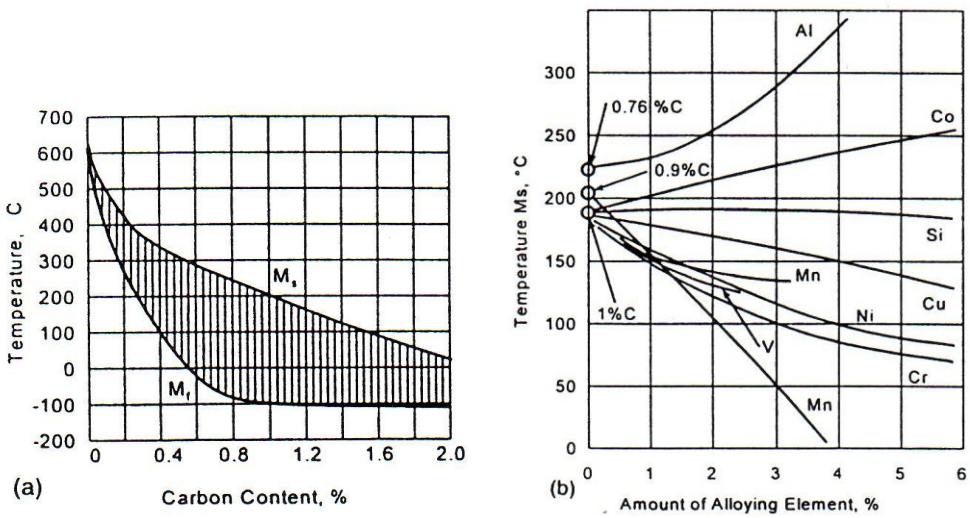

Fig. 10 Effect of (a) carbon content and (b) alloying elements at 1% C on the martensite transformation [5].

8 Nitride-forming Elements

All carbide formers are also nitride former. Nitrogen may be introduced into the surface of the steel by nitriding. By measuring the hardness of various alloy steels do treated it is possible to investigate the tendency of the different alloying elements to form hard nitrides or to increase the hardness of the steel by a mechanism known as precipitation hardening. The results obtained by such investigations are shown in Fig. 11, from which it can be seen that very high hardnesses result from alloying a steel with Al or Ti in amounts of about 1.5%. On nitriding the base material in Fig. 11 a hardness of about 400 HV is obtained and according to the diagram the hardness is unchanged if the steel is alloyed with Ni since this element is not a nitride former and hence does not contribute to any hardness increase.

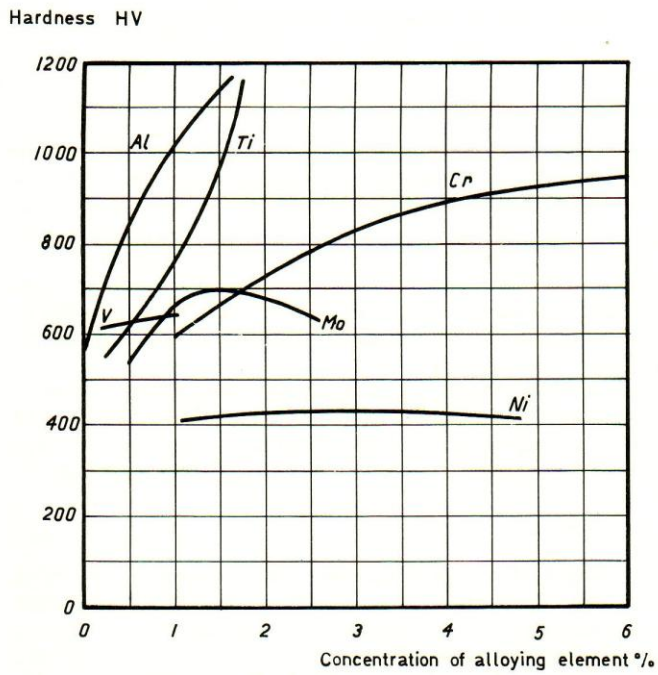

Fig. 11 Effect of alloying element additions on hardness after nitriding. Base composition is 0.25% C, 0.30% Si, 0.70% Mn [8].

9 Effect on Hardenability

The ability of a steel to form martensite on quenching is referred to as the *hardenability*. This can be simply expressed for steel rods of standard size, as the distance below the surface at which there is 50% transformation to martensite after standard quenching treatment, and this is thus a measure of the depth of hardening. Alloying elements which slow down the ferrite and pearlite reactions increase hardenability. The austenite grain size and carbon content also affect the hardneability of steels.

The severity of quench, H, was employed by Grossmann and co-workers in developing the concepts of *critical diameter* (D_0)[1] and *ideal diameter* (D_i)[2] which

[1] The diameter of a steel bar that would just transform to 50% martensite at the center when quenched into a bath having a known H value.

[2] D_0 increases as H increases, until the ideal diameter is reached when H becomes infinite.

are the bases for most producers for estimating hardenability of steels from chemical composition. The diagram correlating D_0 and D_i is shown in Fig. 12. The value of D_i obtained is hence a measure of the hardenability of the steel is independent of the cooling medium. In practice the D_i -values are used to determine the values of D_0 for bars quenched in various media, using the diagram in Fig. 12.

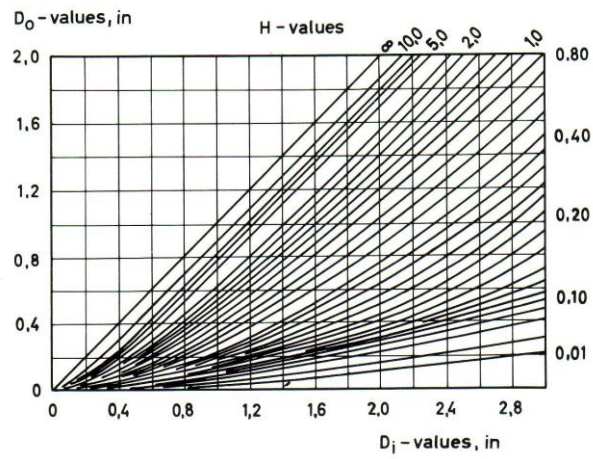

Fig. 12 Chart for determining ideal diameter (D_i) from the critical diameter (D_0) and the severity of quench (H) for carbon and medium alloy steels[8].

In order to assess the effect of alloying elements quantitatively, first step is to determine the effect of grain size and carbon content. Data are available, in so far as D_i has been determined for steels with carbon in the range 0.2-1 wt%, and for a range of grain sizes (ASTM 4-8), as shown in Fig. 13. Use of this diagram for any steel provides a base hardenability figure, D_{iC}, which must be modified by taking into account the effect of additional alloying elements. This is done by use of multiplying factors which have been experimentally determined for the familiar alloying elements (Fig. 14). The ideal diameter D_i is then found from the empirical relationship:

$$D_i = D_{ic} \times 2.21(\%Mn) \times 1.40(\%Si) \times 2.13(\%Cr) \times 3.275(\%Mo) \times 1.47(\%Ni) \quad (wt\%)$$

Further corrections have to be made for different austenitizing temperatures when dealing with high carbon steels, but, on the whole the relationship is quite effective in predicting actual hardening behavior [6].

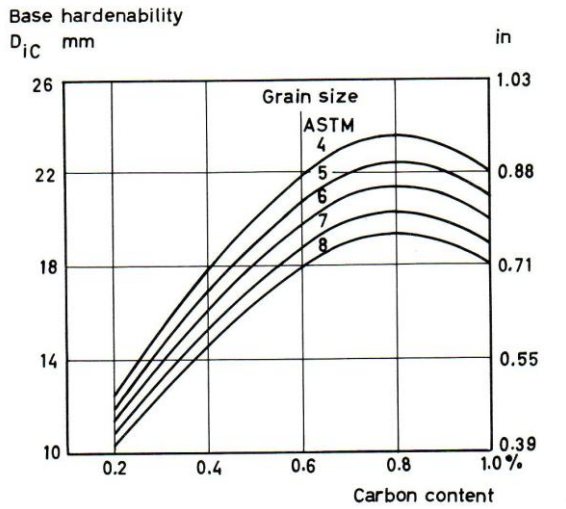

Fig. 13 Effect of carbon content and grain size on base hardenability [8].

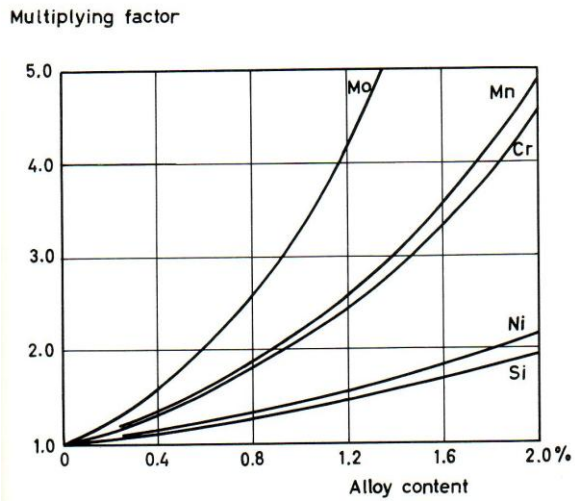

Fig. 14 Hardenability multiplying factors for common alloying elements[8].

The Boron Effect

Boron is added to steel for only one reason-to increase hardenability. Boron-treated steels have certain peculiar characteristics [9] :

1. Boron increases hardenability in hypoeutectoid steel, has no effect on eutectoid steel, and decreases hardenability in hypereutectoid stee.
2. As the austenite grain site becomes finer, the hardenability effect of B increases.
3. Austenitizing at high temperature reduces the hardneability effect of B.
4. For the maximum B effect, the concentration should be in the range 0.0005 to 0.003 wt%.
5. Increasing hardenability by adding B does not decrease the M_s temperature.

These arise because of the manner in which B produces its effect and the interactions of B with other elements in steel. To be effective, B must be in solid solution in austenite. The solubility of B in austenite is very low, for example, the solubility at 912°C is about 0.001 wt% , increasing with temperature to a maximum value of about 0.005 wt% at the eutectic. In α-iron, the solubility is essentially zero, but is influenced by the impurities present. Because of its low solubility in austenite, B can be highly concentrated in grain boundaries.

When a boron steel is cooled from the hardening temperature the solubility of boron is reduced, which results in a still greater concentration of B at the grain boundaries. Minute grains of boron carbide $Fe_{23}(BC)_6$ are formed there and to some extent they assume an orientation coherent with one of the two austenite grains between them which separate out. Atomic contact is thereby established between $Fe_{23}(BC)_6$ and austenite, resulting in a reduction in the surface tension and grain-boundary energy. The presence of boron in solid solution and coherent boron carbide in the grain boundaries delays the formation of ferrite and pearlite and also to some extent, bainite; hence increasing the hardenability of the steel [8].

The effect of B may be expressed quantitatively as the *boron factor*, which is the ratio of the ideal diameters, D_i, (according to Grossmann) for the steel with and without boron, viz.

$$B_F = \frac{D_i \; with \quad B}{D_i \; without \quad B}$$

D_i (with boron) is derived from the Jominy end-quench hardenability curve; D_i (without boron) is calculated from the chemical composition of the steel.

The optimum B content, near 0.002 wt%, for increasing hardenability in 0.2% C, 0.65% Mn, 0.55% Mo (wt%) steel is shown in Fig. 15. Boron contents above about 0.003 wt% lead to a loss in hardenability, and B in excess of about 0.004 wt% causes a loss in toughness through precipitation of Fe_2B in austenite grain boundaries.

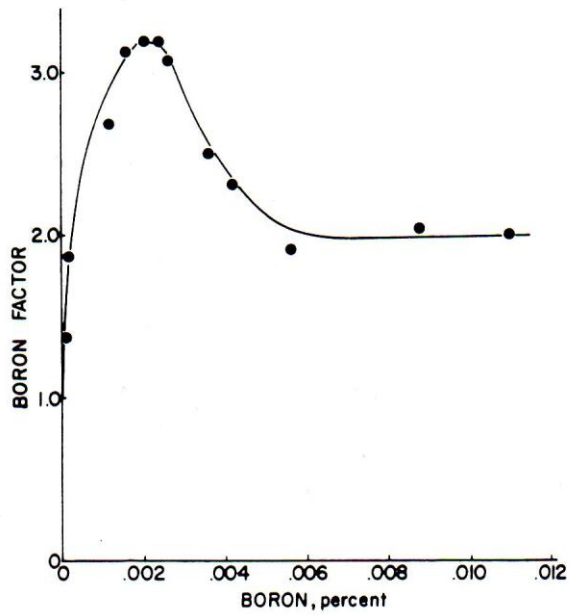

Fig. 15 Boron hardenability factor as a function of boron content in a 0.20% C, 0.55% Mo, 0.65% Mn steel [9].

10 Effect on Tempering

Martensite in steels can be a very strong and in its virgin condition rather brittle. It is then necessary to modify its mechanical properties by heat treatment in the range 150-700 °C. This process is called *tempering*, in which the microstrucrure approaches equilibrium under the influence of thermal activation[6],[3].

The general trend during the tempering of martensite begins with the rejection of excess carbon to precipitate carbides but the substitutional solutes do not diffuse during this process. The end result of tempering is a dispersion of coarse carbides in a ferritic matrix which bears little resemblance to the original martensite.

The addition of alloying elements to a steel has a substantial effect on the kinetics of the $\gamma \rightarrow \alpha$ transformation, and also of the pearlite reaction. As pointed out previously, most common alloying elements move the time-temperature-transformation (TTT) curves to longer times, with the result that it is much easier to miss the nose of the curve during quenching. This essentially gives higher hardenability, since martensite structures can be achieved at slower cooling rates and, in practical terms, thicker specimens can be made fully martensitic.

The alloying elements also retard the rate of softening during tempering by stabilizing both the transition carbides (e.g. ε-iron carbide) and the supersaturated martensitic structure to higher tempering temperature and by delaying considerably the precipitation and growth of cementite.

10.1 Effect on the Formation of Iron Carbides

The structural changes during the early stage of tempering are difficult to follow. However, it is clear that certain elements, notably silicon, can stabilize the ε-iron carbide to such an extent that it is still present in the microstructure after tempering at 400°C in steels with 1-2 wt% Si, and even higher temperatures if the silicon is further increased. The evidence suggests that both the nucleation and growth of the carbide is slowed down and that the silicon enters into the ε-carbide structure. It is also clear that the transformation of ε-iron carbide to cementite is delayed considerably. While the tetragonality of martensite disappears by 300°C in plain carbon steels, in steels containing some alloying elements, e.g. Cr, Mo, W, V, Ti, Si, the tetragonal lattice is still observed after tempering at 450°C and even as high as 500°C. It is clear that these alloying

elements increase the stability of the supersaturated iron carbide solid solution. In contrast Mn and Ni decrease the stability (Fig. 16).

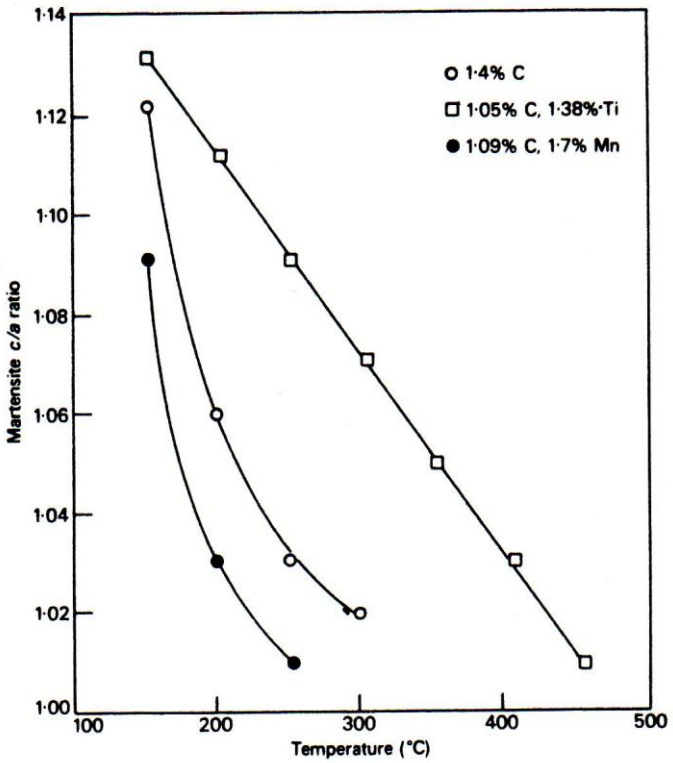

Fig. 16 Effect of Ti and Mn on the tetragonality of martensite during tempering [3].

Alloying elements also greatly influence the proportion of austenite retained on quenching. Typically, a steel with 4% Mo, 0.2% C, in the martensitic state contains less than 2% austenite, and about 5% is detected in a stel with 1% V and 0.2% C. On tempering each of the above steels at 300°C, the austenite decomposes to give thin grain boundary films of cementite which, in the case of the higher concentrations of retained austenite, can be fairly continuous along the lath boundaries. It is likely that this interlath cementite is responsible for *tempered martensite embrittlement*, frequently encountered as a toughness minimum in the range 300-350°C, by leading to easy nucleation of cracks, which then propagate across the tempered martensite laths.

Coarsening of cementite in the tempering temperature range 400-700°C, representing the forth stage of tempering, can be hindered effectively when alloying elements such as Si, Cr, Mo and W are present in steels. These alloying elements retain the fine Widmanstätten precipitation of cementite up to higher temperatures either by segregation at the carbide/ferrite interface or by entering into the cementite structure [2].

10.2 The Formation of Alloy Carbides (Secondary Hardening)

A number of the familiar alloying elements in steels form carbides which are thermodynamically more stable than cementite. It is interesting to note that this is also true of a number of nitrides and borides. Nitrogen and boron are increasingly used in steels in small but significant concentrations. The alloying elements Cr, Mo, V, W and Ti all form carbides with substantially higher enthalpies compared to the iron carbide, while the elements Ni, Co and Cu do not form carbide phases. Manganese is a weak carbide former, found in solid solution in cementite and not in a separate carbide phase [3].

It would therefore, be expected that when strong carbide-forming elements are present in a steel in sufficient concentration, their carbides would be formed in preference to cementite. Nevertheless, during the tempering of all alloy steels, alloy carbides do not form until the temperature range 500-600°C, because below this the metallic alloying elements cannot diffuse sufficiently rapidly to allow alloy carbides to nucleate. The metallic elements diffuse substitutionally with low diffusivities, therefore, high temperatures are needed for the necessary diffusion of the alloying elements prior to the nucleation and growth of the alloy carbides and, in practice, for most of the carbide-forming elements this is in the range 500-600°C.

It is the ability of certain alloying elements to form fine alloy carbide dispersions in the range 500-600°C, which remain very fine even after prolonged tempering. Indeed, the formation of alloy carbides between 500°C and 600°C is accompanied by a marked increase in strength, often in excess of that of the as-quenched martensite (Fig. 17). This phenomenon, which is referred to as

secondary hardening, is best shown in steels containing Mo, V, W, Ti and also in chromium steels at higher alloy concentrations. This secondary hardening process is a type of age hardening reaction, in which a relatively coarse cementite dispersion is replaced by a new and much finer alloy carbide dispersion. In Fig. 17 the effect of increasing Mo content is demonstrated in a series of steels containing 0.1 wt% carbon.

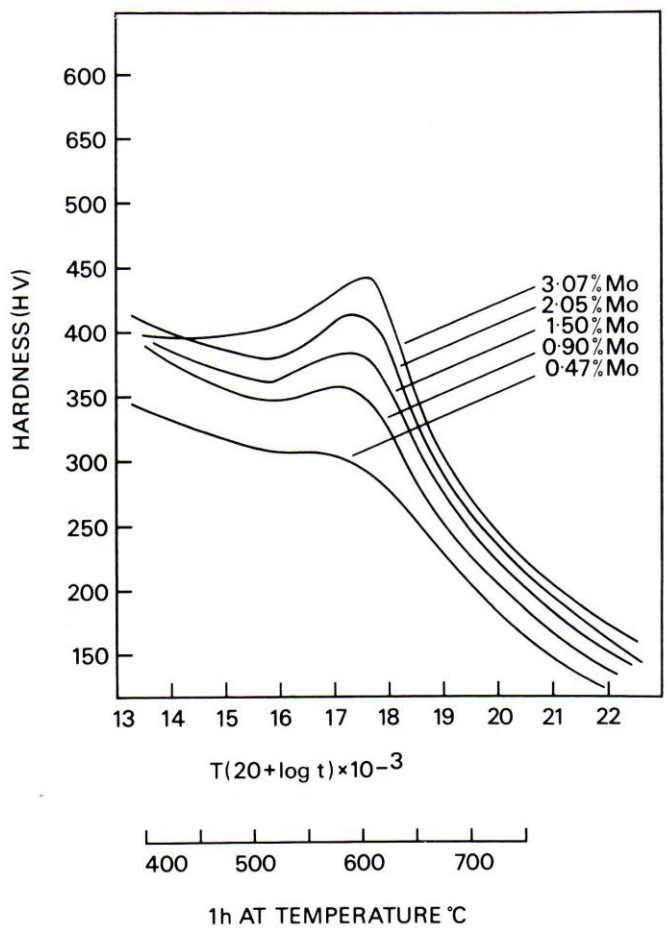

Fig. 17 The effect of molybdenum on the tempering of quenched 0.1 wt% C steels [7].

The effects of C and some alloying elements on the tempering of a 10%Ni steel are illustrated in Fig. 18. Beginning with an alloy of Fe-10%Ni, successive additions of C, Co, Cr, and Mo were made. Co, although it does not enter the

carbide, delays tempering. The addition of Cr provides an increase in strength during tempering, and Mo gives a sharp secondary hardening peak.[9]

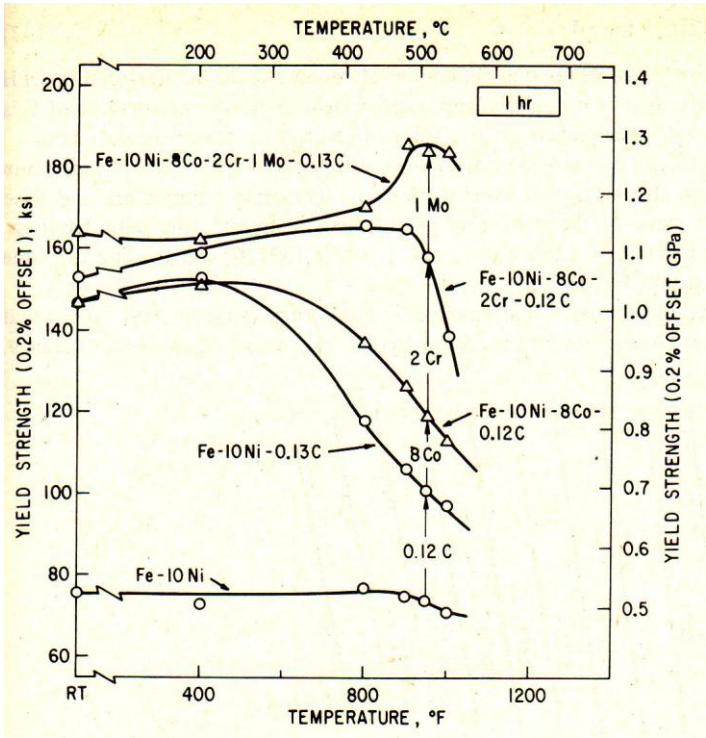

Fig. 18 Effect of carbon, cobalt, chromium, and molybdenum on tempering of 10%Ni steels [8].

Tempering of Steels Containing Vanadium

Vanadium is a strong carbide former and, in steel with as little as 0.1 wt% V, the FCC vanadium carbide (VC) is formed. It is often not of stoichiometric composition, being frequently nearer V_4C_3, but with other elements in solid solution within the carbide. Many steels containing vanadium will exhibit extensive vanadium carbide precipitation on tempering, because of the stability of this carbide (VC or V_4C_3), not only with respect to cementite but also the several chromium carbides and molybdenum carbide. The large effect of V is presumably due to the formation of VC or V_4C_3 carbides which replace cementite-type carbides at high tempering temperature and persist as fine

dispersion up to A_1 temperature. V is an important constituent of steels for elevated temperature service [2],[3],[9].

Tempering of Steels Containing Chromium

In chromium steels, two chromium carbides are very often encountered: Cr_7C_6 (trigonal) and $Cr_{23}C_6$ (complex cubic). The normal carbide sequence during tempering is:

$$\text{Matrix} \rightarrow (FeCr)_3C \rightarrow Cr_7C_3 \rightarrow Cr_{23}C_6.$$

While this sequence occurs in higher-chromium steels, below about 7wt% Cr, $Cr_{23}C_6$ is absent unless other metals such as molybdenum are present. Cr is a weaker carbide former than V, which is illustrated by the fact that Cr_7C_3 does not normally occur until the chromium content of the steel exceeds 1 wt% at a carbon level of about 0.2 wt%.

In steels up to 4 wt% Cr, the transformation from Fe_3C to Cr_7C_3 occurs mainly by nucleation at the Fe_3C/ferrite interfaces. Steels up to 9 wt% Cr do not show secondary hardening peaks in tempering curves (Fig. 19). however, theses curves do exhibit plateaus at higher Cr content, which are associated with the precipitation of Cr_7C_3. Chromium diffuses more rapidly in ferrite than most metallic alloying elements, with the result that Cr_7C_3 is detected during tempering at temperatures as low as 500°C, and in comparison with vanadium carbide, chromium carbide coarsens rapidly. Thus, in a 2 wt% Cr-0.2 wt% C steel, continuous softening will normally occur on tempering between 500°C and 700°C, although addition of other alloying elements, e.g. Mo, can reduce the rated of coarsening of Cr_7C_3.

In contrast, a 12 wt% Cr steel will exhibit secondary hardening in the same temperature range (Fig. 19) due to precipitation of Cr_7C_3. additionally, $Cr_{23}C_6$ nucleate at about the same time but at different sites, particularly formes austenite grain boundaries and at ferrite lath boundaries. This precipitate grows at the expense of the Cr_7C_3 which eventually disappears from the microstructure,

at which stage the steel has completely over-aged. This transition from Cr_7C_3 to $Cr_{23}C_6$ in high-chromium steels is by separate nucleation and growth. Further alloying additions can promote one or other of these carbide reactions, e.g. addition of W encourages formation of $Cr_{23}C_6$ by allowing it to nucleate faster, while V tends to stabilize Cr_7C_3. in doing so, it decreases the rate of release into solution of Cr and C needed for the growth of $Cr_{23}C_6$. Clearly, V would be a preferred addition to W, if fine stable Cr-carbide dispersion is needed in the temperature range 550-650°C. [3]

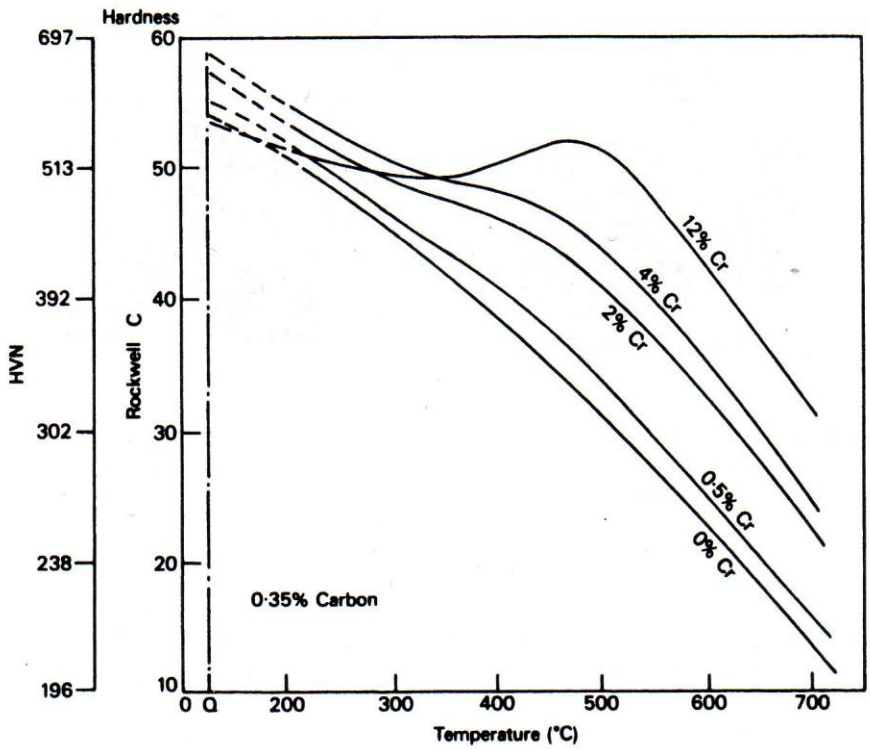

Fig. 19 The effect of Cr on the tempering of a 0.35 wt% C steel [3].

Tempering of Steels Containing Molybdenum and Tungsten

When Mo or W is predominant alloying element in a steel, a number of different carbide phases are possible, but for composition between 4 and 6wt% of the element the carbide sequence is likely to be:

$$Fe_3C \rightarrow M_2C \rightarrow M_6C.$$

The carbides responsible for the secondary hardening in both case of W and Mo are the isomorphous hexagonal carbides Mo_2C and W_2C, both of which in contrast to vanadium carbide, have a well-defined rodlet morphology.

M_2C also nucleates at former austenite and ferrite lath boundaries. As in the case of vanadium steels, M_2C precipitate nucleates both on dislocations in the ferrite, and at the Fe_3C/ferrite interfaces, but the secondary hardening arises primarily from the dislocation-nucleated dispersion of M_2C.

On prolonged tempering at 700°c, the complex cubic M_6C forms predominantly at grain boundaries as massive particles which grow quickly, while the M_2C phase goes back into solution.

For similar atomic concentrations, the secondary hardening response in the case of tungsten steels is less than that of molybdenum steels. The M_2C dispersion in the former case is coarser, probably because the slower diffusivity of tungsten allows a coarsening of the dislocation network prior to being pinned by the nucleation of particles.

11 Effect on Grain Growth

The elements Al, Nb, Ti and V in small amounts from 0.03 wt% to 0.10 wt% are important factors in inhibiting grain growth at the austenitizing temperature. This is because these elements are present as highly dispersed carbides, nitrides or carbo-nitrides (Al only as nitride) and that a high temperature is required to make them go into solution. Fig. 20 shows that in a steel containing about 0.05 wt% Nb or Ti and 0.20 wt% C the niobium and titanium carbides are not dissolved until the temperature exceeds 1200°C.[8] For V and N contents of 0.1 wt% and 0.010 wt% respectively the vanadium nitrides remain undissolved at temperatures up to and somewhat above 1000°C. Should the temperature rise so high that the phasesinhibiting grain growth pass into solution there will be a

pronounced increase in grain size. The above-mentioned elements have found great use as microconstituents in the high strength low ally steels (HSLA).

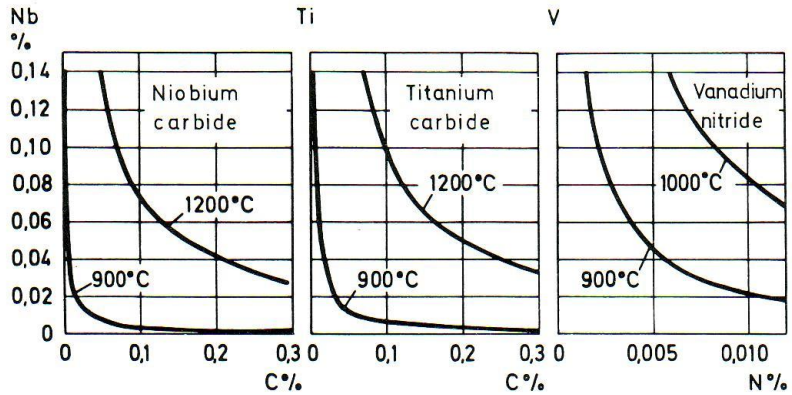

Fig. 20 Solubility isotherms of niobium carbide, titanium carbide and vanadium nitride in steel at different temperatures [8].

Ferrite grain refinement in ferrite-pearlite steels is accomplished through restricting the growth of austenite grains during hot rolling and/or by inhibiting the recrystalization of austenite during hot rolling so that the $\gamma \rightarrow \alpha$ transformation occurs in unrecrastalized austenite. For example, in the hot rolling of semikilled carbon steels, recrystalization of austenite occurs at temperature down to about 760°C. A 30% reduction at 815°C is sufficient for about 10% recrystalization. In a similar steel containing 0.03 wt% Nb, 10% recrystalization occurred after the steel was reduced 50% at 925°C. This explains why it is so difficult to refine grains in carbon steels until the rolling temperature drops below 815°C. It is usually less expensive to normalize a carbon steel than to obtain grain refinement by controlled rolling. In contrast, grain refinement in niobium steels can be obtained at finishing temperatures as high as 925°C.

In most instances, all Nb, C and N are in solution at the start of the hot rolling of austenite, but precipitation occurs during the rolling as the temperature of the steel drops. The precipitate particles hinder growth of austenite grains, and at still lowertemperatures the particles (or precipitation clusters) inhibit recrystalization of the deformed austenite grains. As indicated in Fig. 21, the effectiveness of

microalloying elements in refining ferrite grains is in the same order as the solubility of their carbides in austenite (see Fig. 20).

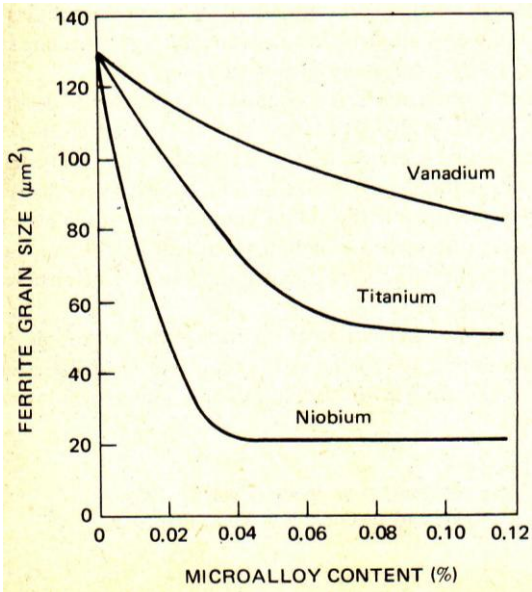

Fig. 21 Effect of microalloy content (Nb, Ti and V) on the ferrite grain size of as-hot-rolled low-carbon steel strip [9].

Grain coarsening in microalloyed and Al-killed steels in the temperature range of 900-1300°C is, however, characterized by continuous growth at low and high temperatures; between these temperature regions is a narrow temperature range where abnormal grain growth occurs. The influence of Nb on austenite grain growth characteristics in various concentrations is illustrated in Fig. 22. Increasing Nb content causes an increase in the abnormal or discontinuous grain growth temperature.

A general overview of the effects of microalloying additions on the grain coarsening of austenite is shown in Fig. 23. In Al, V, and Ti steels, these are largely controlled by the microalloying level and the nitrogen content, due to the pronounced stability of the nitrides compared with their respective carbides. The differential between the solubilities of the carbide and nitride is somewhat reduced in the case of Nb (see Fig. 7) and, NbC can be stable at quite high temperatures (1200°C) with modest Nb additions to high carbon steels. However,

the extremely low solubility of TiN in austenite (Fig. 7) has resulted in the development and extensive application of TiN technology.

Fig. 23 illustrates that the grain coarsening during reheating in C-Mn steels with microalloyed additions that form with a volume fraction of ~0.0005 of alloy carbides and/or nitrides. It also illustrates that γ-grains grow very little with increasing temperature during continuous grain growth, while grain growth becomes very rapid during abnormal or discontinuous grain growth. It is thus apparent that steels containing microalloyed second phases are susceptible to grain coarsening in particular temperature range.

Increased amounts of V above 0.14 wt% refine the γ-grain size at temperatures up to ~1000°C and do not contribute any marked effect above 1100°C due to appreciable solubility of VCN in austenite [2]. The grain coarsening temperature in Al-killed steel is above 1050°C. Nb-bearing steels have sufficiently higher grain coarsening temperature than the V-bearing steels and Al-killed steels. The grain refinement of austenite by Nb addition is more effectively accomplished (relative to Ti, V, and Zr addition) on both the reheated grain size and recrystalized grain size when Nb content is up to 0.1 wt% and the temperature is up to 1200°C. Ti addition up to 0.040 wt% causes the formation of stable nitride, which raises the grain coarsening temperature to about 1300°C during both isothermal soaking and hot deformation.

It should be noted that the solubility of carbide particles in the austenite increases in the order NbC, TiC, VC, while the nitrides with normally lower solubility increase in solubility in the order TiN, NbN, AlN, VN (see Fig. 7). It is thus apparent that NbC and TiN are the most stable particles and the most effective grain size refiners. However, Al, V, and Ti are more effective in high-nitrogen steels, by forming comparatively stable AlN, V(CN), and Ti(CN) in austenite, which may be potent in preventing grain coarsening on reheating but not effective in preventing recrystalization [2].

Fig. 24 also illustrates the difference in coarsening rates between vanadium nitride and titanium nitride at 1100°C. As expected, VN shows a much more rapid rate of coarsening than is shown by TiN.

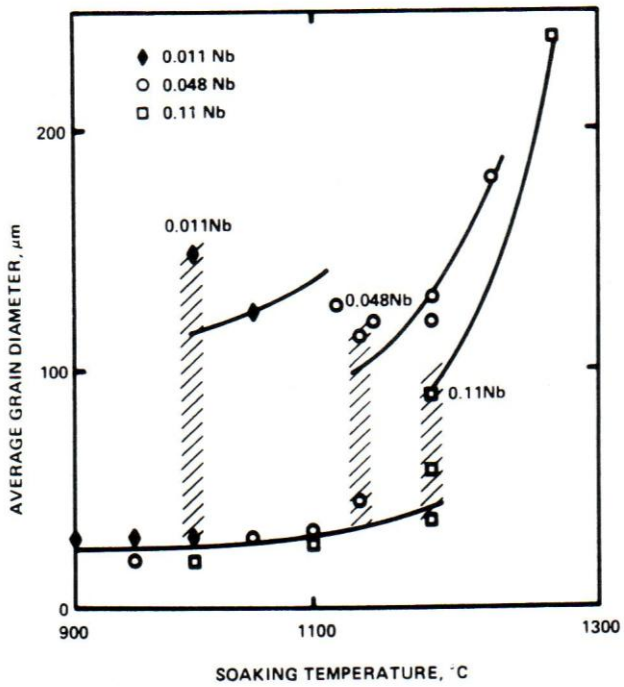

Fig. 22 Austenite grain growth characteristics in various Nb steel. Hatched bars represent the range of duplex grains produced at the coarsening temperatures [2].

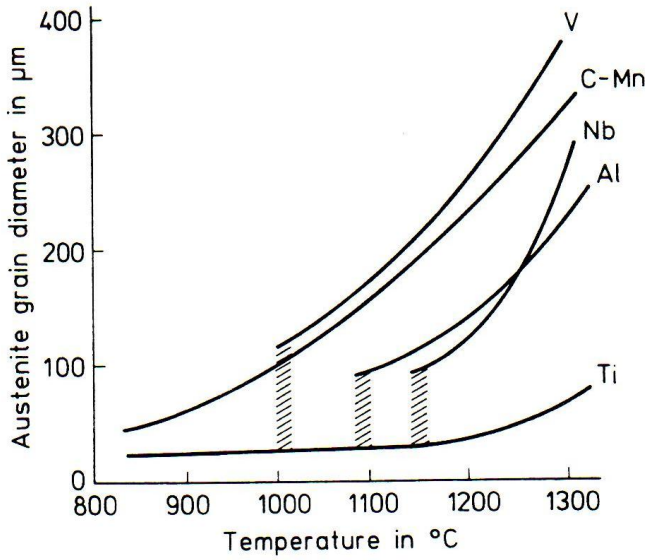

Fig. 23 The general effect of microalloy additions on the grain coarsening temperature of austenite in C-Mn steels contating a volume fraction of 0.0005 of alloy carbide or nitride. Specific grain coarsening temperatures are dependent upon microalloy content, nitrogen content, and the effects of prior thermal or thermomechanical cycles on the precipitated particle size [2],[10].

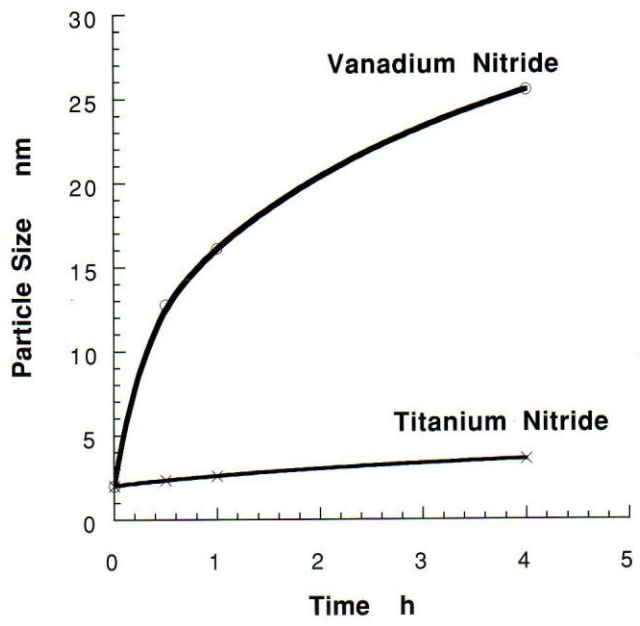

Fig. 24 Comparison of the calculated particle coarsening rates of vanadium and titanium nitrides at 1100°C [10].

The effects of various microalloy additions and concentrations on the recrystalization temperature are shown in Fig. 25. Niobium additions cause a more marked increase in the recrystalizytion temperature than are observed with other microalloys. To some extent, niobium is an ideal microalloying element to consider for the hot rolling and controlled rolling processes in that it can exhibit most of the effects that microalloying elements may have [10]. In particular

(i) The niobium carbo-nitride can be substantially dissolved at commonly used soaking temperatures prior to hot rolling.

(ii) Of the microalloying elements dissolved, niobium has by far the largest effect in retarding recrystalization.

(iii) Strain inducement of niobium carbo-nitride occurs at temperatures between about 1000°C and 800°C which represent a commonly used temperature range for the completion of the hot rolling process.

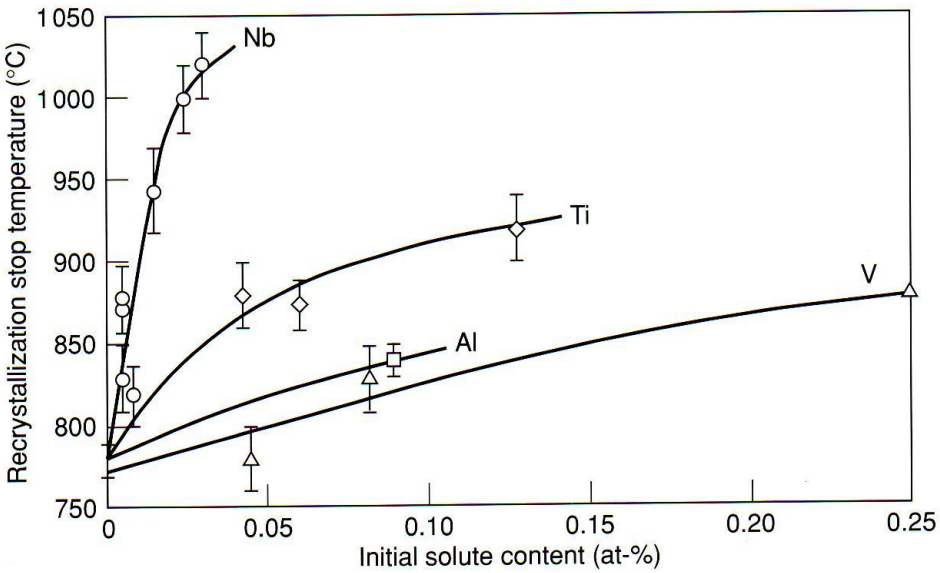

Fig. 25 The effects of microalloying addtitions on the recrystalizytion temperature of austenite in a low carbon 1.4wt% Mn steel [10].

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