

## Solubility Product

### 1. Heat of formation and solubility of microalloying carbides and nitrides

We need to quantify the solubility of different transition metal carbides and nitrides, particularly in austenite at high temperature. This is because transition metal carbides play two crucial roles in microalloy and low alloy steels. (i) The more *insoluble* precipitates, for example TiC, TiN, NbN, exist at high temperature and act as austenite grain refiners, say, during hot rolling. NbC also has a very marked effect in retarding dynamic recrystallisation of the austenite. (ii) The more *soluble* compounds, for example  $V_4C_3$  or VC,  $Mo_2C$  and chromium carbides, will enter solution in the austenite during annealing and can be precipitated as nano-precipitates to improve strength during cooling and transformation to ferrite, say, by interphase precipitation, or during tempering after a quench to strengthen martensite. Iron carbide is the most soluble of all. Actually the more soluble compounds are those having the smaller enthalpies of formation (see Figure 1). The alloy designer needs mathematical models and data that can be used to predict the distribution of carbon, nitrogen and transition metal alloying elements as functions of temperature—how much is in solution and how much exists as precipitates? We'd also like to know the size, shape, habit and orientation relation, but that's another matter.

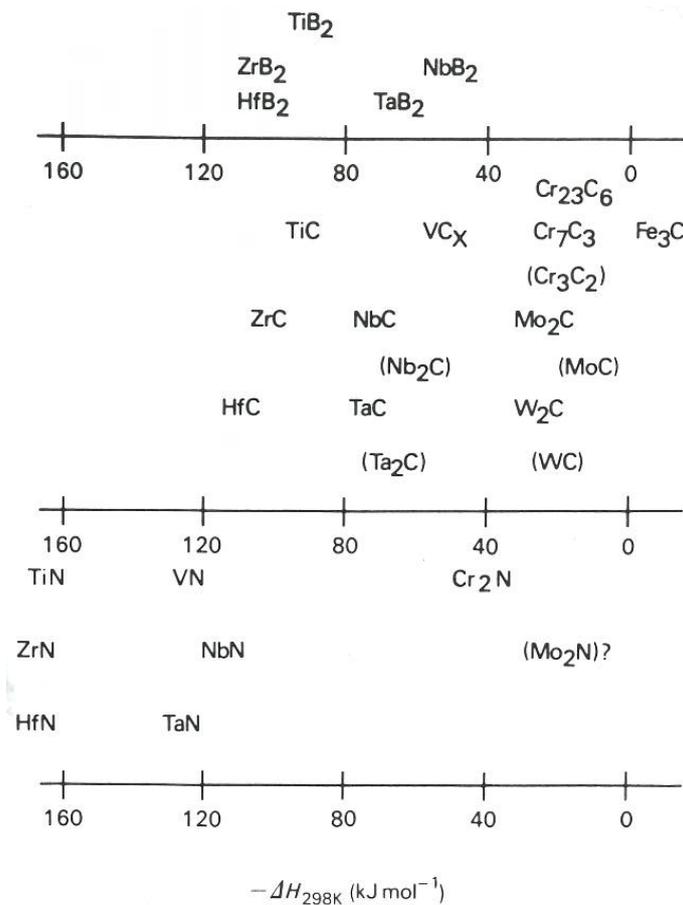
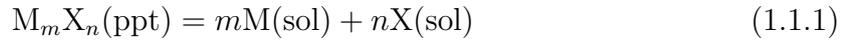


Figure 1: Heats of formation of some carbides and nitrides

### 1.1 Case of one microalloying element and single precipitate composition

Consider a chemical reaction



which describes the dissolution of a carbide or nitride  $M_m X_n$  precipitate (ppt), for example NbN or  $V_4 C_3$  into solution (sol) in austenite at some temperature  $T$ . In equilibrium the chemical potentials of components M and X are the same in the precipitate and in the solution, so we have

$$\mu_{M,\text{ppte}} = \mu_{M,\text{sol}} \quad \text{and} \quad \mu_{X,\text{ppte}} = \mu_{X,\text{sol}} \quad (1.1.2)$$

Expressing the chemical potentials in terms of standard chemical potential and activity, this becomes

$$\begin{aligned} \mu_{M,\text{ppte}}^\circ + RT \ln a_{M,\text{ppte}} &= \mu_{M,\text{sol}}^\circ + RT \ln a_{M,\text{sol}} \\ \mu_{X,\text{ppte}}^\circ + RT \ln a_{X,\text{ppte}} &= \mu_{X,\text{sol}}^\circ + RT \ln a_{X,\text{sol}} \end{aligned}$$

Now, the chemical potential of the precipitate is, in view of (1.1.1) and (1.1.2)

$$\begin{aligned} \mu_{\text{ppte}} &= m\mu_{M,\text{ppte}} + n\mu_{X,\text{ppte}} \\ &= m\mu_{M,\text{sol}} + n\mu_{X,\text{sol}} \end{aligned}$$

and therefore, again in terms of activity and standard state,

$$\mu_{\text{ppte}}^\circ + RT \ln a_{\text{ppte}} = m\mu_{M,\text{sol}}^\circ + mRT \ln a_{M,\text{sol}} + n\mu_{X,\text{sol}}^\circ + nRT \ln a_{X,\text{sol}}$$

and rearranging this last equation, I get,

$$RT (m \ln a_{M,\text{sol}} + n \ln a_{X,\text{sol}} - \ln a_{\text{ppte}}) = \mu_{\text{ppte}}^\circ - m\mu_{M,\text{sol}}^\circ - n\mu_{X,\text{sol}}^\circ$$

which is

$$\begin{aligned} RT \ln \frac{a_{M,\text{sol}}^m a_{X,\text{sol}}^n}{a_{\text{ppte}}} &= -\Delta G_{\text{sol}}^\circ \\ &= RT \ln K \end{aligned}$$

having defined

$$\Delta G_{\text{sol}}^\circ = m\mu_{M,\text{sol}}^\circ + n\mu_{X,\text{sol}}^\circ - \mu_{\text{ppte}}^\circ$$

as the standard Gibbs free energy of solution of the precipitate. This equation also serves to define the *equilibrium constant*  $K$  for the chemical reaction. I now have

$$a_{M,\text{sol}}^m a_{X,\text{sol}}^n = a_{\text{ppte}} \exp(-\Delta G_{\text{sol}}^\circ/RT)$$

The activity of a pure defect-free solid phase is constant (usually taken to be one) and for a dilute solution Henry's law tells us that the activity of a solute is proportional to the concentration  $x$  expressed as an atomic fraction. The proportionality constants,  $\gamma$ , are called *activity coefficients* and are constant, independent of temperature and composition. So if  $x_M$  and  $x_X$  are the concentrations of M and X in the solid solution and  $\gamma_M$  and  $\gamma_X$  are activity coefficients, we now have

$$(\gamma_M x_M)^m (\gamma_X x_X)^n = a_{\text{ppte}} \exp(-\Delta G_{\text{sol}}^\circ/RT)$$

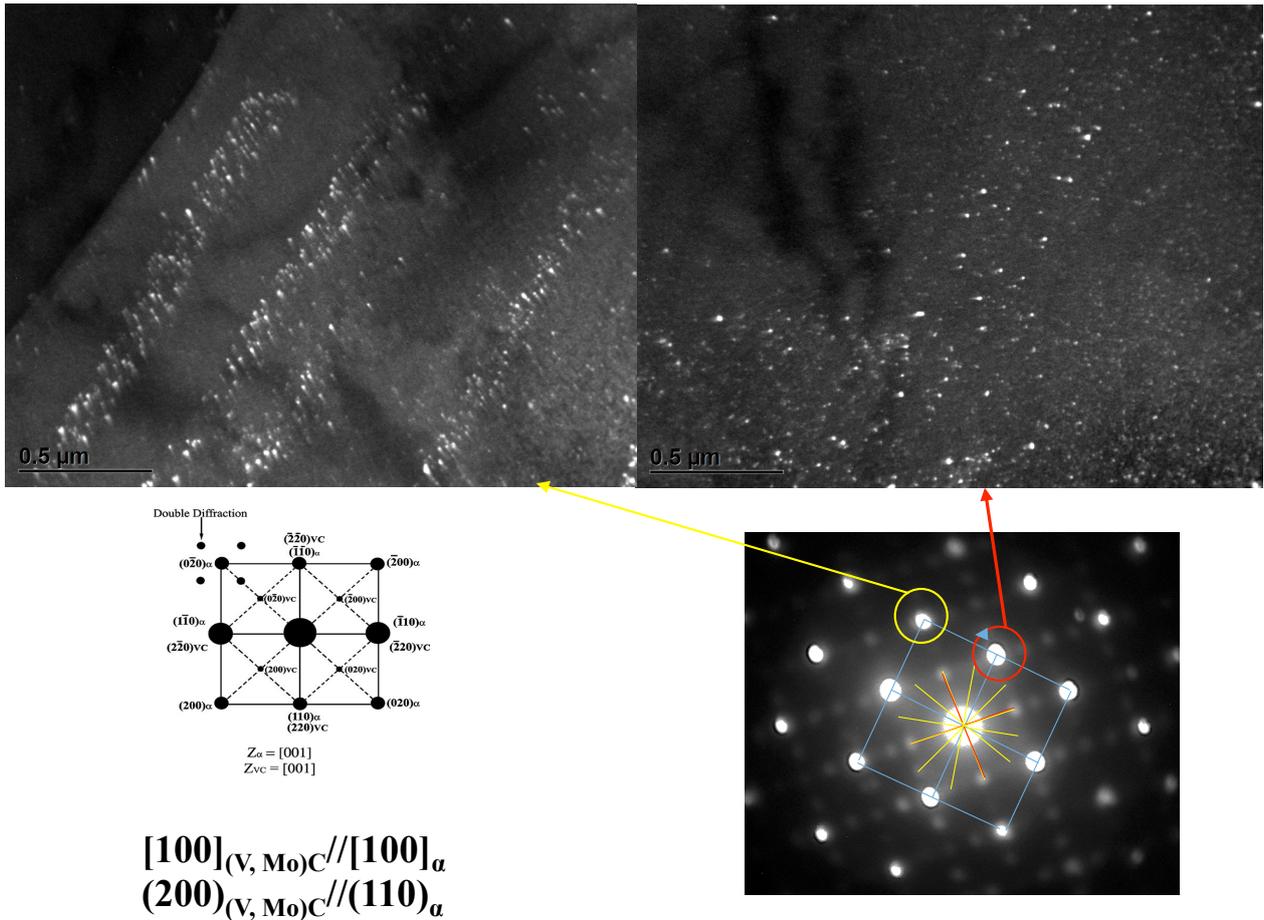


Figure 2: Dark field images of (V,Mo)C interphase precipitates in an ultra high strength 0.1C-0.2V-0.5Mo steel (courtesy of Peng Gong and W. Mark Rainforth)

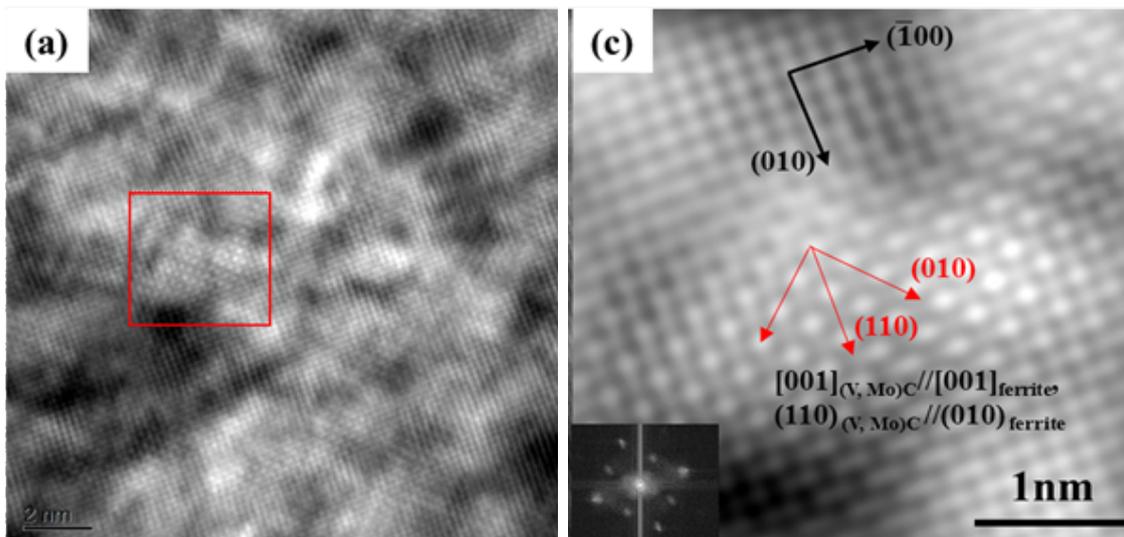


Figure 3: As figure 2 in high resolution: determination of orientation relation (courtesy of Peng Gong and W. Mark Rainforth)

I can gather the three constants into a single constant, say,  $C = a_{\text{ppte}}/\gamma_M^m\gamma_X^n$ , and write

$$x_M^m x_X^n = C \exp(-\Delta G_{\text{sol}}^\circ/RT)$$

The *weight percentages* of M and X, which we conventionally write as [M] and [X] are proportional to the concentrations so the previous equation is equivalent to

$$[\text{M}]^m [\text{X}]^n = D \exp(-\Delta G_{\text{sol}}^\circ/RT)$$

in which  $D$  is another constant involving the atomic weights of the components and factors of a hundred to convert to percent. I find

$$D = C \times 100^2 \frac{(m+n)^2}{m^2 A_M/A_X + 2mn + n^2 A_X/A_M}$$

where  $A_M$  and  $A_X$  are the relative atomic masses (or atomic weights) of the elements M and X. All this *defines* the *solubility product*,  $k_s$ ,

$$\begin{aligned} k_s &= [\text{wt}\% \text{M}]^m [\text{wt}\% \text{X}]^n \\ &= [\text{M}]^m [\text{X}]^n \\ &= D \exp(-\Delta G_{\text{sol}}^\circ/RT) \end{aligned} \quad (1.1.3)$$

Now I take logarithms to the base ten on both sides and I get

$$\log k_s = A - B/T \quad (1.1.4a)$$

where the constants are

$$A = \log D \quad \text{and} \quad B = \Delta G_{\text{sol}}^\circ/2.303R \quad (1.1.4b)$$

Then all the constants including changes from natural to base 10 logs, standard states and conversions to weight percent are accounted for by fitting experimental data to equation (1.1.4a). You will always find solubility product data in the metals handbooks and literature given by quoting the constants  $A$  and  $B$  for a particular carbide or nitride in austenite or ferrite. Of course the whole thing can be extended to multicomponent precipitates, for example (V,Mo)(C,N) a carbonitride of vanadium and molybdenum (see Figures 2 and 3) but it's a mess to write down and problems such as on page 7 require a computer to solve.

Because of equation (1.1.4a) if we plot  $\ln k_s$  (or  $2.303 \log k_s$ ) against  $1/T$  we get a straight line with a negative slope of magnitude  $\Delta G_{\text{sol}}^\circ/R$ . This is called an *Arrhenius plot*; examples are shown in Figures 4 and 5.

On the other hand, because of equation (1.1.3) it is clear that plotting  $[\text{wt}\% \text{M}]^m$  against  $[\text{wt}\% \text{X}]^n$  at any given temperature will result in a curve resembling a hyperbola as shown, for example, in the schematic in Figure 6. The way to interpret this graph is as follows. At the required temperature, say  $T_2$ , and given concentrations of M and X (these could be, say, vanadium and nitrogen) we wish to know how much of the vanadium

and nitrogen are in solution and how much are tied up in vanadium nitride precipitates. If we place a point on the graph corresponding to the known nominal compositions then *in equilibrium* if that point falls to the left and below the curve the microstructure will be a single phase austenite with V and N in solution. If the point falls above and to the right of the hyperbola then the microstructure will be a two phase mixture of VN and austenite solid solution. The curve is therefore a graph of the *solubility limit* at that temperature—if the concentrations of V and N lie on a point to the right and above the solubility limit the that limit is exceeded and some of these elements must come out of solution and form precipitates.

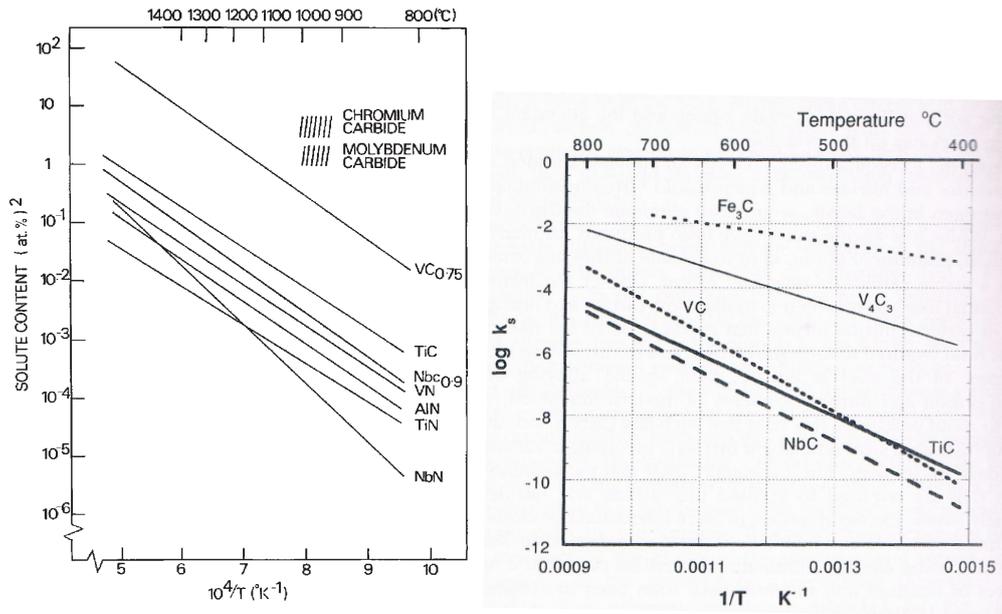


Figure 4: Arrhenius plots of solubility products in austenite (left) and ferrite (right)

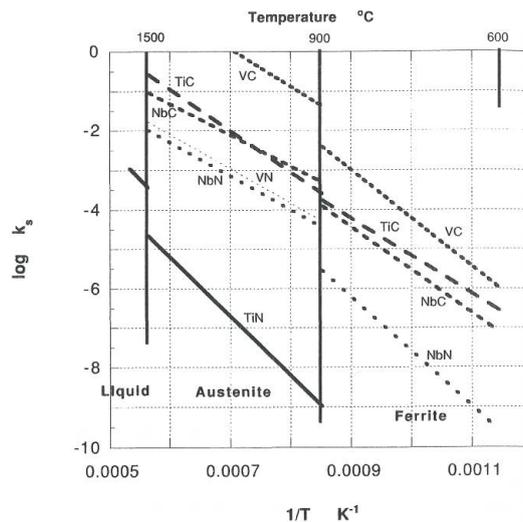


Figure 5: More Arrhenius plots of solubility product in iron. Note that the most soluble carbides and nitrides are those lines towards the top of the figure—having the largest solubility products.

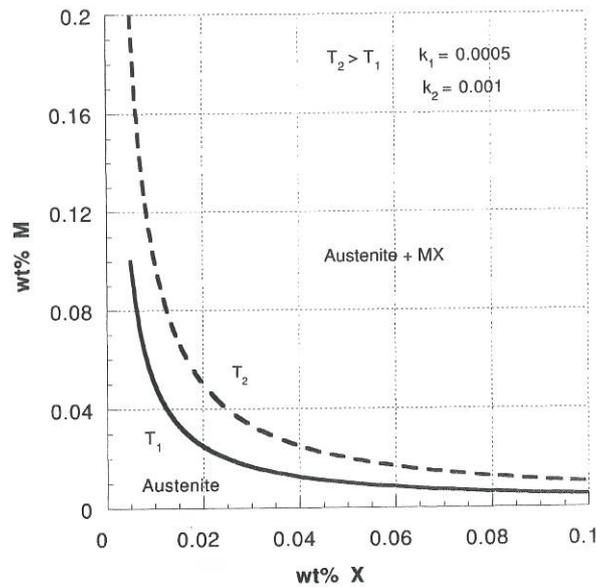


Figure 6: Schematic solubility product isotherms. Note that these two lines define the solubility limits at two temperatures. This is a kind of phase diagram—the solubility limit lines separate the single phase solid solution from the two phase solution plus precipitate fields.

Of course the next question is, *how much precipitate do I expect?* It's actually quite simple. Take the example of vanadium nitride. We first define these quantities.

$V_T$  : wt% V in alloy

$N_T$  : wt% N in alloy

$[V]$  : wt% V dissolved in austenite

$[N]$  : wt% N dissolved in austenite

$V_{VN}$  : wt% V present as VN

$N_{VN}$  : wt% N present as VN

$A_V$  : relative atomic mass of V

$A_N$  : relative atomic mass of N

Then it's easy to see by the mass balance that the total weight percentage of vanadium can be divided into that which is dissolved and that which belongs to the precipitate. The same goes for nitrogen, so we have,

$$V_T = [V] + V_{VN} \quad (1.1.5)$$

$$N_T = [N] + N_{VN} \quad (1.1.6)$$

The *atomic* percentages of V and N tied up in VN are equal because of stoichiometry. So the *weight* percentages are in the ratio of the atomic weights, leading to

$$N_{VN} = V_{VN} \frac{A_N}{A_V} \quad (1.1.7)$$

And, by definition of the solubility product we have

$$k_s = [V][N] \quad (1.1.8)$$

The rest is algebra. Let's first find a formula for the amount of dissolved vanadium,  $[V]$ . From (1.1.8) we have

$$[V] = \frac{k_s}{[N]} \quad (1.1.9)$$

and

$$\begin{aligned} [N] &= N_T - N_{VN} \\ &= N_T - \frac{14}{51}V_{VN} \\ &= N_T - \frac{14}{51}(V_T - [V]) \end{aligned}$$

using (1.1.5) and (1.1.6) and then substituting (1.1.7). Then (1.1.9) leads to a quadratic equation for the amount of dissolved vanadium, namely,

$$\frac{1}{51}[V]^2 + \left(\frac{1}{14}N_T - \frac{1}{51}V_T\right)[V] - \frac{1}{14}k_s = 0 \quad (1.1.10)$$

This can be solved using the usual formula for quadratic equations and once we have  $[V]$  we can find  $V_{VN}$  and  $N_{VN}$ , the amounts of vanadium and nitrogen that are tied up in the precipitate as functions of the nominal compositions,  $V_T$  and  $N_T$ , of V and N and their atomic weights; and the solubility product which is a measurable function of the temperature. If we had more than one possible compound, or if we are interested in carbonitrides then the thermodynamic principles remain the same. The algebra becomes a lot more complicated and requires the solution of a number of simultaneous equations. The alloy designer uses commercial computer packages.

Now examine Figure 7. This illustrates in part the perennial problem arising from the unfortunate fact that metallurgists always work in weight percent, whereas the physics and chemistry of course refers to atom percent—because atoms combine one to one in chemical reactions and so on. If the stoichiometry were one to one (which we assume in all the examples here) and if we were plotting *atomic percent* not *weight percent* then all points lying on a  $45^\circ$  diagonal would represent stoichiometric compositions. Because we actually plot weight percent then the stoichiometric line has a slope given by the ratio of the atomic weights of the two components. Now suppose we are interested in austenite with nominal concentrations of vanadium and nitrogen indicated by the point P. We construct a line with the same slope as the stoichiometric line that passes through P and it does not intersect the origin because in general an alloy does not contain equal atomic percentages of V and N. Using this construction we take the intersection of the stoichiometric line passing through P with the solubility limit curve and at the intersection we read off the concentrations of V and N that remain in solution in the austenite.

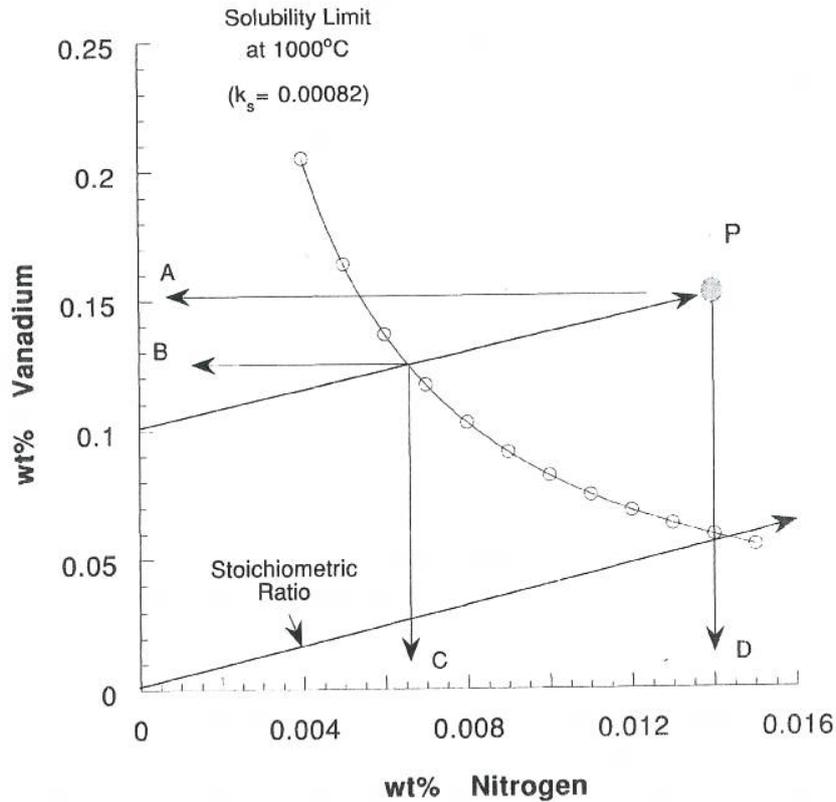


Figure 7: Construction for the determination of the amounts of V and N in solution and in precipitate. Note  $(A-B)/(D-C) = 51/14$ .

Figures 8–11 are examples of solubility limit, or solubility product, curves for a number of microalloying elements in austenite. As I have mentioned, the importance of this cannot be overemphasised as it allows the materials engineer to design alloy compositions and heat treatment schedules to obtain a desired microstructure and hence desired mechanical properties. In particular this gives control of austenite grain refiners and solution and reprecipitation to achieve particle hardening by interphase precipitation or through tempering.

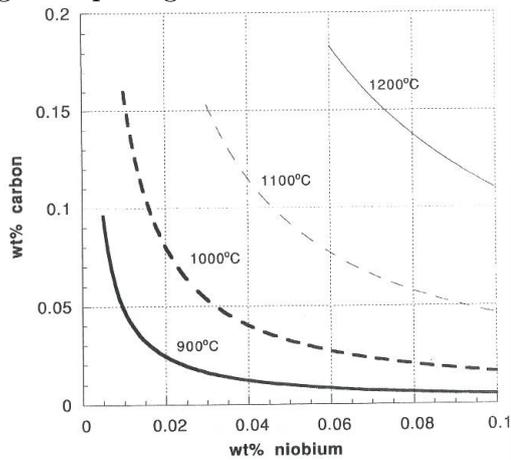


Figure 8: Isotherms for NbC in austenite

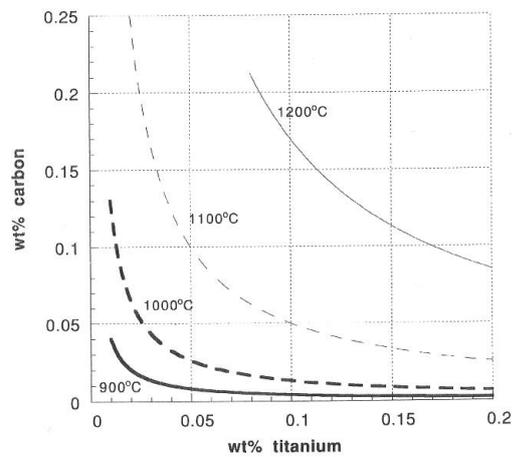


Figure 9: Isotherms for TiC in austenite

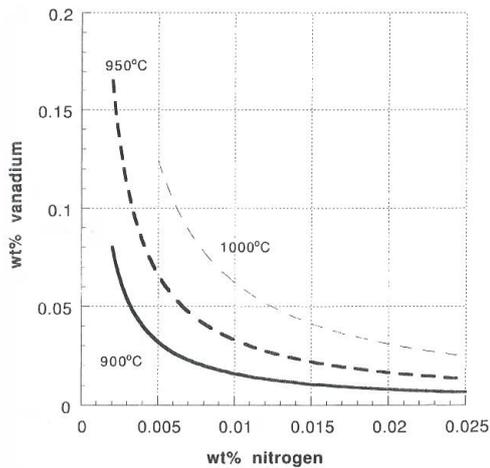
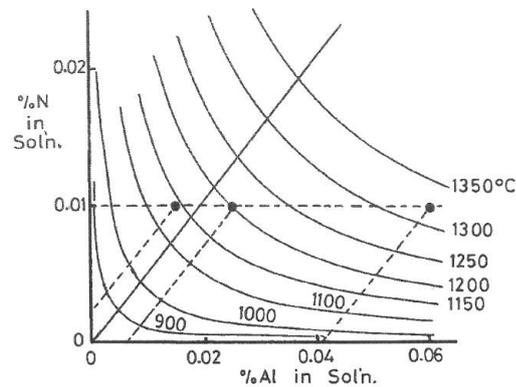
Figure 10: Isotherms for VN in  $\gamma$ -phase 1.3% Mn steel

Figure 11: Isotherms for AlN in austenite

Figure 12 illustrates what you have learned up to now. Suppose you are interested, for the sake of simplicity, in a steel with a single microalloying element, titanium, at 0.1 wt%. How can you optimise hardening precipitates that form after cooling from austenite by varying the carbon concentration? The upper diagram shows solubility limits (products) at three temperatures. Imagine that the steel requires an isothermal anneal at 1200° during which all the Ti and C are to be dissolved so that they can subsequently form, say, interphase precipitates as the austenite transforms to ferrite on cooling. You will need at least a stoichiometric amount of carbon or there won't be enough to tie up all the Ti as TiC and some Ti must inevitably remain in solution in the austenite and in the resulting ferrite—this may be fine if you are seeking some solution hardening. This is the situation if the carbon concentration falls in region A in the lower diagram. As the carbon increases from zero the amount of Ti and C that will be available to combine will increase until the stoichiometric line intersects the Ti concentration. Note that as we increase the carbon concentration the equivalent of our point P in Figure 7 is moving to the right along the horizontal broken line in the upper diagram. In region A there is more Ti than C atomic percent; beyond the stoichiometric point there is more C than Ti atomic percent. Therefore in region B, the amount of carbide that can form is fixed and at its maximum amount, given the 0.1 wt% of Ti; the remaining carbon will probably form iron or other carbides on cooling—no bad thing, perhaps. At the boundary of regions B and C the point P moves from the left and below the solubility limit to above and to its right so that at the soaking temperature of 1200° the equilibrium microstructure is austenite plus TiC. This means that not all the Ti and carbon become dissolved and that TiC that forms at 1200° is likely to grow coarse and be useless at particle hardening. At the same time these coarse precipitates tie up some of the Ti and C that would otherwise be available to form fine interphase precipitates and in consequence the cooled alloy will have the TiC fraction “limited by solubility”. The conclusion is that in this case using any carbon concentration in the range of region B will give optimum fine carbide fraction, since if the carbon concentration is less the carbide fraction is limited by stoichiometry and if it's greater some Ti and C will be tied up as useless (possibly even deleterious) large second phase particles.

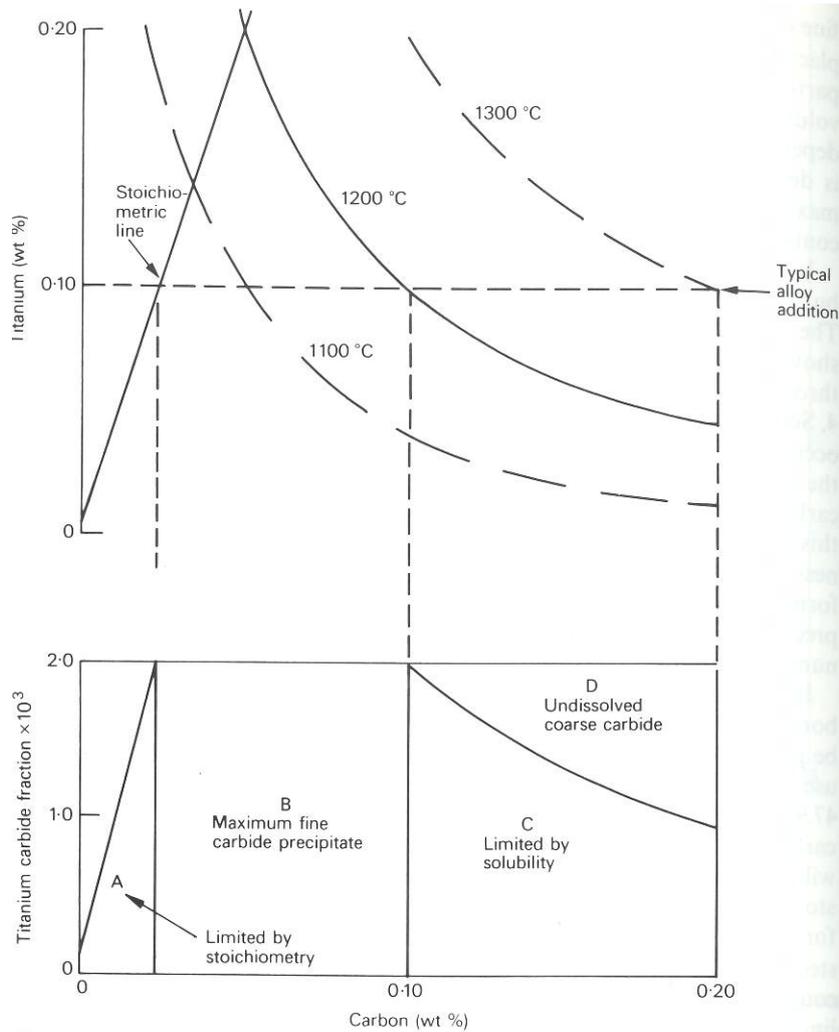


Figure 12: Effect of stoichiometry on the precipitation of TiC in a microalloyed steel

Figure 13 shows how these ideas are exploited in the design of fine grain microalloyed niobium steels. Notice that there are two effects of increasing the annealing temperature before air cooling. (i) The yield stress increases overall. (ii) The Hall-Petch slope increases. This is because at the higher annealing temperatures, more NbC is dissolved and therefore available for interphase precipitation in the ferrite in order to contribute to the particle hardening.

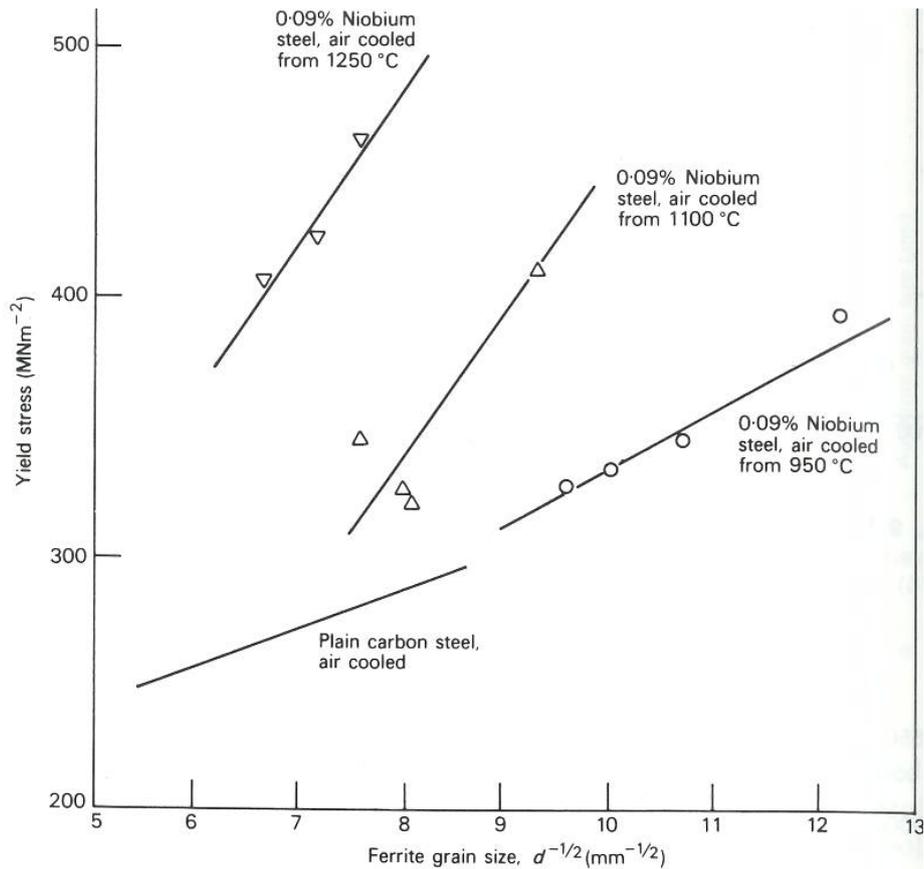


Figure 13: Effect of austenitising temperature on the yield strength of a 0.1C–0.6Mn–0.09Nb steel

## 2. More than one microalloying element

The designer of microalloy steels has a wide range of microalloying elements at her disposal. These are many transition metal elements as well as Al. Here is a list.

**Vanadium.** Vanadium carbide is very soluble in  $\gamma$ , even close to the  $A_3$  temperature. Vanadium nitride is less soluble and is used for grain refinement by including up to 0.01% N in vanadium steels (which normally have no more than 0.15wt% V). The benefit offered by high solubility of vanadium carbide is the extensive formation of interphase precipitates during controlled rolling below  $A_1$ , coiling or cooling. Vanadium microalloy steels are complicated by the existence of a number of stoichiometries and crystal structures of vanadium carbides. Their heats of formation are plotted in figure 14 and it is seen that at 0K the thermodynamically most stable is monoclinic  $V_6C_5$ . VC is the expected cubic phase having rocksalt crystal structure and  $V_4C_3$  is this same phase having a quarter of the carbon sites as vacancies.

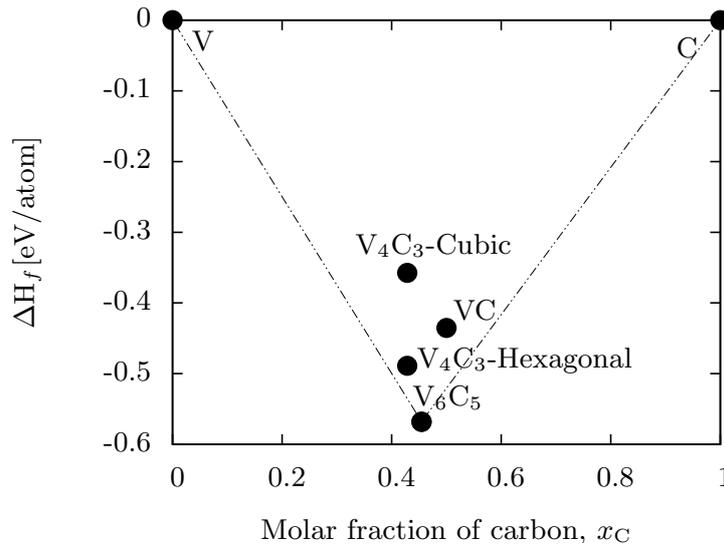


Figure 14: Heats of formation of competing vanadium carbide phases, calculated using first principles quantum mechanics (density functional theory).

Figure 15 shows the wide differences in solubility product, especially at high temperature, in comparing VC and  $V_4C_3$ .

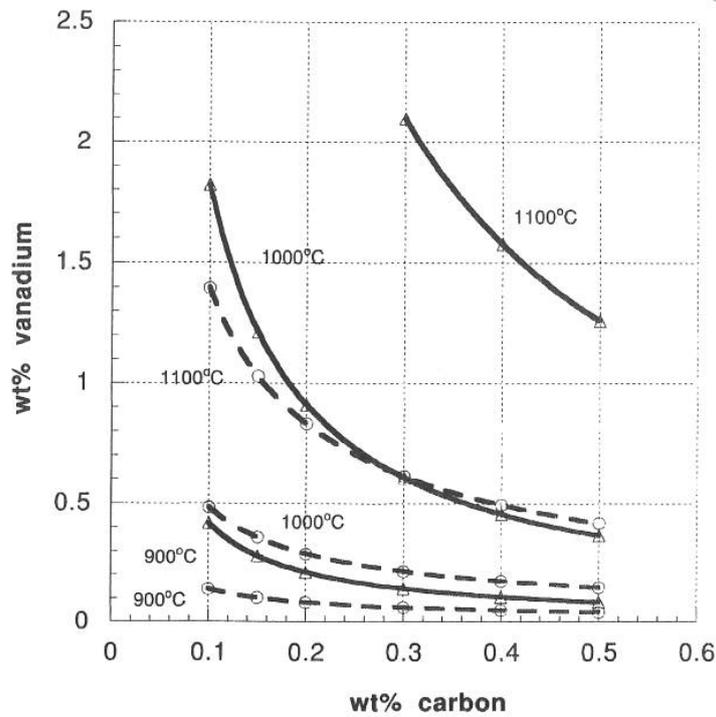


Figure 15: Solubility limits of vanadium and carbon based on cubic VC (solid lines) and  $V_4C_3$  (broken lines). This is only consistent with figure 14 if the  $V_4C_3$  is taken to be hexagonal, not cubic.

**Niobium.** Carbonitrides dissolve only at higher soaking temperatures, and so particle strengthening is restricted. Principally the carbonitrides act as  $\gamma$  grain refiners and very markedly suppress recrystallisation of the austenite under controlled rolling (Ti and V have similar but less effective roles). The change in solubility in the range 900–1300°C leads to significant deformation induced precipitation.

**Titanium.** TiN is very insoluble and will precipitate in the liquid steel to promote grain refinement. Whatever Ti remains after TiN precipitation will result in TiC which has similar solubility to NbC. Ti also is a sulphide former and so will dissolve in MnS particles and reduce their ductility during hot rolling, thus preventing their elongation.

**Aluminium** addition as a deoxidant has to some extent been superseded by vacuum melting. Any Al not combined into alumina and taken off from the liquid remains to provide AlN precipitates, having a relatively low solubility product. AlN has a different crystal structure compared to the common transition metal carbonitrides and so it provides a “mutually exclusive” precipitate system (see section 2.1, below).

**Molybdenum** is primarily added to improve hardenability, but it will combine with vanadium carbonitride to form  $V_xMo_{1-x}C_zN_{1-z}$  (see figure 3)

This all means that the treatment in section 1.1 is too elementary for the general microalloyed steel. We need to consider the equilibrium between more than one microalloy element, carbon and nitrogen and one or more, possibly complex, carbonitrides. However, if you keep your head, you will see that as in section 1.1, the mathematics while messy-looking is really very easy and only involves solving quadratic, cubic or quartic equations. The last two, of course, require a computer or graphical solution. So take a deep breath and study sections 2.1 and 2.2 below.

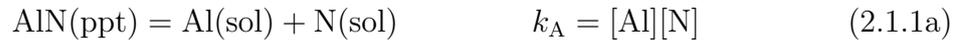
We study two cases in these notes. The simpler is the case in which two (or more) *mutually exclusive* compounds are precipitated. This is the situation in which the compounds have different crystal structures and are regarded as simultaneously in equilibrium with the austenite matrix. The second, rather more difficult problem, is the one in which one or more precipitates exist in equilibrium and are *miscible*, by virtue of their having the same crystal structure, containing more than one microalloy element or more than one interstitial element (C or N). This latter case divides into two: the case of a single transition metal carbonitride and the case of complex carbonitrides.

## 2.1 Mutually exclusive precipitates

If two or more compounds may precipitate having different crystal structures then we can consider a number of chemical reactions such as (1.1.1) as occurring independently and retaining the same solubility products as if the others were not occurring. It is expected that this is the case in vanadium microalloy steels although it is not yet known whether more than one of the vanadium carbides in figure 14 are to be found simultaneously in the same steel. There is currently some evidence of cubic VC and cubic  $V_4C_3$  being

found in the same steel but this is not necessarily a case of mutual exclusivity if we regard these as the same phase having variable carbon vacancy concentrations. This would then amount to a *third* scenario in addition to the two discussed in the previous paragraph and we will not discuss this much further in these notes.

Instead I will use the example of hexagonal AlN existing in equilibrium with cubic VN at some temperature in austenite. We write two reactions as in equation (1.1.1),



The solubility products are those of the individual reactions as taken from measurements in ternary Fe-V-N and Fe-Al-N alloys. Actually  $k_A \ll k_V$  and so if sufficient Al were present in the steel then it will tie up a stoichiometric amount of N in AlN up to the solubility limit given by  $k_A$ . Any remaining N could then result also in VN precipitation if the solubility limit  $k_V$  is exceeded. Therefore the alloy designer can manipulate the amounts of VN and AlN precipitates by adjusting the weight percentages of V, Al and N, and by choosing appropriate soaking and rolling temperatures.

Essentially as in section 1.1 we are tasked with finding out, at a given temperature, how much of each microalloy element is present in solution and how much is tied up as precipitate in equilibrium. In the case of just one microalloy element, V, and one interstitial element, N, we arrived rather easily at equation (1.1.10). In the case of *mutually exclusive* precipitates only, we may use the simplification that the activities of the precipitates are **one** as before since they exist as immiscible pure phases which have separate crystal structures. Let us now proceed to a solution.

The total nitrogen content in weight percent is

$$N_T = [\text{N}] + N_{\text{AlN}} + N_{\text{VN}}$$

namely the sum of the contributions to the total weight percentages from that in solution (so called free nitrogen), and those tied up in the separate chemical compounds. Because of the 1:1 stoichiometry we also know that

$$N_{\text{AlN}} = \frac{14}{27} \text{Al}_{\text{AlN}}$$

$$N_{\text{VN}} = \frac{14}{51} \text{V}_{\text{VN}}$$

because the atomic weights of N, Al and V are 14, 27 and 51. Combining these last three we have,

$$N_T = [\text{N}] + \frac{14}{27} \text{Al}_{\text{AlN}} + \frac{14}{51} \text{V}_{\text{VN}}$$

The weight percent of Al present as AlN is the same as the difference between the total Al,  $\text{Al}_T$ , and the dissolved Al; and similarly for the V and so we write,

$$\text{Al}_{\text{AlN}} = \text{Al}_T - [\text{Al}]$$

$$\text{V}_{\text{VN}} = \text{V}_T - [\text{V}]$$

and putting these into the previous equation results in

$$N_T = [N] + \frac{14}{27} (Al_T - [Al]) + \frac{14}{51} (V_T - [V]) \quad (2.1.2)$$

The two nitrides must each be present in amounts consistent with the independent solubility products, and so we can substitute for  $[V]$  and  $[N]$  from (2.1.1) and hence eliminate these in favour of the known solubility products to obtain a closed equation for the dissolved nitrogen. Firstly the last equation becomes, on substitution from (2.1.1)

$$N_T = [N] + \frac{14}{27} \left( Al_T - \frac{k_A}{[N]} \right) + \frac{14}{51} \left( V_T - \frac{k_V}{[N]} \right)$$

I can multiply both sides by  $[N]$  and collect terms and I arrive at

$$\frac{1}{14}[N]^2 + \left( \frac{1}{27}Al_T + \frac{1}{51}V_T - \frac{1}{14}N_T \right) [N] - \left( \frac{1}{27}k_A + \frac{1}{51}k_V \right) = 0 \quad (2.1.3)$$

It is worthwhile to compare this to (1.1.10). It is also a simple quadratic equation that can be solved analytically in terms of known quantities: the composition of the steel and the solubility products at the soaking temperature. There will not be a solution if there is only one precipitate and there may be nonsensical solutions turning up—for example if dissolved amounts predicted by equations (2.1.1) turn out to be greater than the total amounts then there will be *negative* quantities of precipitate predicted!

While there is a number of approximations attendant on the derivation of (2.1.3) its predictions have been found to be in accord with experiment as shown in the example in figure 16.

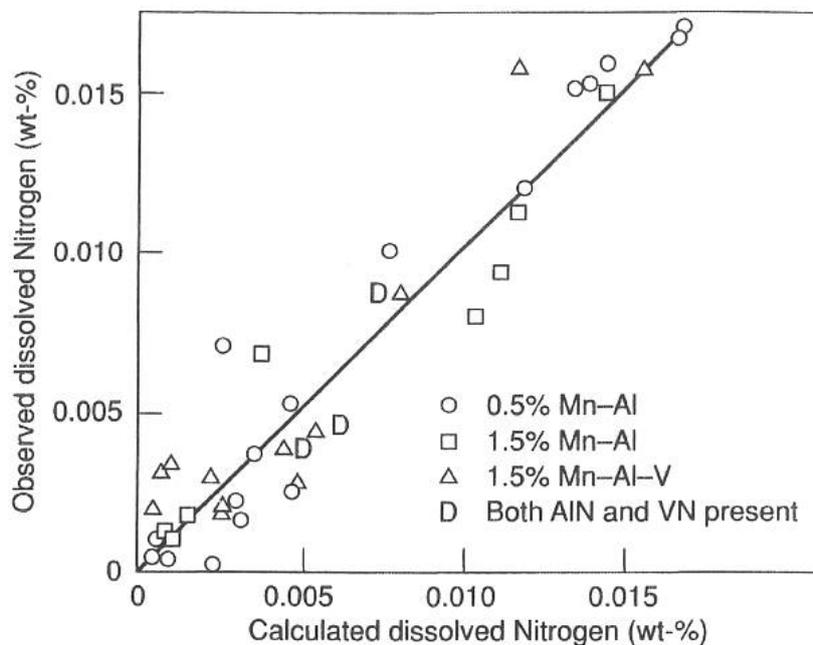


Figure 16: Comparison between prediction and experiment of free nitrogen in Al-V-N steels

As in the simpler case of section (1.1), remember that once you have  $[N]$  by solution of equation (2.1.3) then you can use mass balance and (2.1.1) to find the amounts of Al and V in both solution and in the two separate compounds and find the amount of nitrogen remaining in solution.

You can go further and use the equations that you have to construct a phase diagram showing the one, two and three phase regions as functions of the microalloy contents. Proceed as follows. From (2.1.1), since  $[N]$  is the same in both equations because the nitrogen is simultaneously in equilibrium with both precipitates we know that

$$\frac{[Al]}{[V]} = \frac{k_A}{k_V} \quad (2.1.4)$$

I now take  $[V]$  from this equation and I take  $[N]$  from (2.1.1a) and put them into (2.1.2) which leads to

$$N_T = \frac{k_A}{[Al]} + \frac{14}{27} (Al_T - [Al]) + \frac{14}{51} \left( V_T - \frac{k_V}{k_A} [Al] \right)$$

I now multiply through by  $[Al]$  and collect powers in  $[Al]$  and I get this quadratic equation,

$$\left( \frac{14}{27} + \frac{14}{51} \frac{k_V}{k_A} \right) [Al]^2 - \left( \frac{14}{27} Al_T + \frac{14}{51} V_T - N_T \right) [Al] - k_A = 0$$

So far this is just another equation like (2.1.3) but this time for the dissolved Al rather than N. But if I take the special case that the dissolved Al content is equal to the total Al content, that is,

$$[Al] = Al_T = Al_{pb} \quad (2.1.5)$$

then this defines  $Al_{pb}$  as the weight percent of Al at the phase boundary between the two phase  $\gamma+VN$  and the three phase  $\gamma+AlN+VN$  fields. In other words  $Al_{pb}$  is the largest concentration of Al that can be added to a vanadium containing steel while still preventing the precipitation of AlN. Now if I apply the condition (2.1.5) to equation (2.1.2) then the second term vanishes and as before using (2.1.1a) and (2.1.4) I find

$$\frac{14}{51} \frac{k_V}{k_A} Al_{pb}^2 - \left( \frac{14}{51} V_T - N_T \right) Al_{pb} - k_A = 0$$

which I can solve for  $Al_{pb}$ . I can follow an identical procedure to find  $V_{pb}$  and so get the locus of the  $\gamma+AlN / \gamma+AlN+VN$  phase boundary. This construction is shown in figure 17.

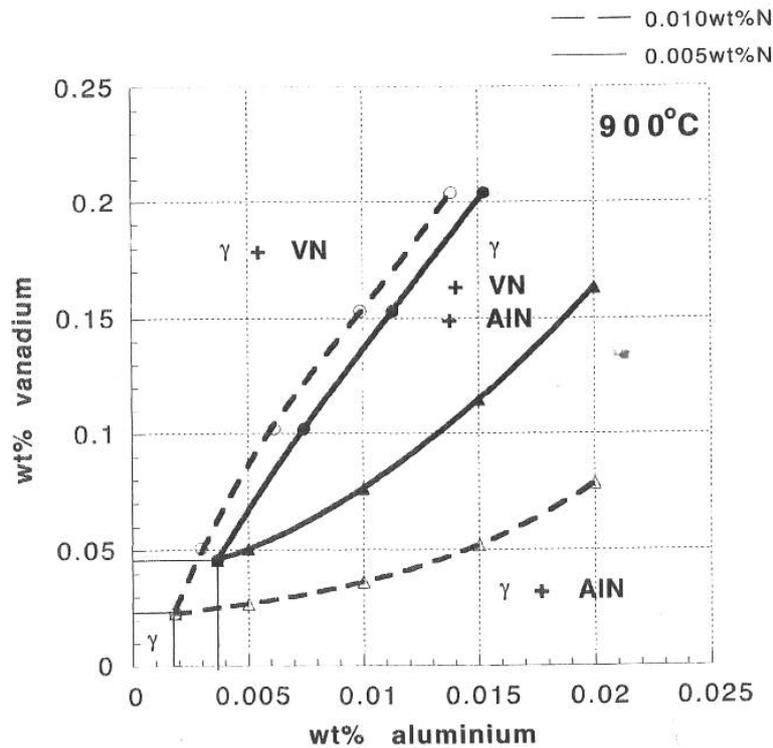


Figure 17: Calculated phase diagram

## 2.2 Carbonitrides

A simple carbonitride has a chemical formula  $M_mC_nN_p$ . In complex carbonitrides, the symbol M is taken to mean a combination of transition metal elements. In cases where these phases occur in the rocksalt structure which consists of two interpenetrating fcc lattices, then we expect the chemical formula to be  $MC_xN_{1-x}$  and  $0 < x < 1$ . The transition metal atoms occupy one sublattice and the interstitial elements the other. (Equivalently you can think of this as an fcc transition metal with C and N atoms occupying octahedral interstices—see Barrett and Massalski.) All of the sites in the first sublattice are occupied (possibly by one of several transition metal elements randomly placed). The second sublattice is occupied by C and N in the ratio  $x/1-x$ . But not all sites might be occupied. Most transition metal carbonitrides are sub-stoichiometric—a fraction of the sites are vacant. Figure 18 shows this effect in niobium carbonitrides and the resulting measured lattice parameters. This means that we should write our chemical formula as  $MC_xN_y\square_{1-x-y}$ , where  $\square$  stands for vacancy. As I mentioned in the first paragraph of section 2.1, this amounts to a third scenario which we don't look at here. Instead we will focus for simplicity on simple or complex carbonitrides having a 1:1 ratio of transition metal to interstitial atoms.

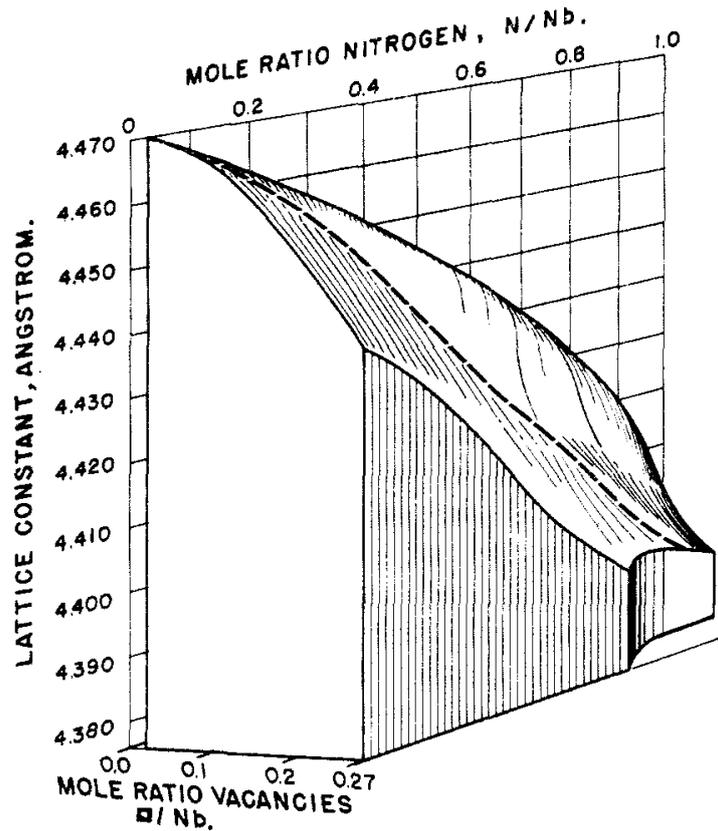
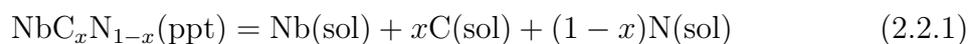


Figure 18: Measured lattice constants of cubic phases of niobium carbonitride (*J. Chem. Phys.*, **64**, 1471 (1960))

### 2.2.1 Simple carbonitrides

Let us go through an analysis for  $\text{NbC}_x\text{N}_{1-x}$  using the same procedure that we have employed in sections 1.1 and 2.1. I will make two further simplifying assumptions regarding the activities of the components. Firstly assume that the activity coefficients of all our microalloy elements and C and N are equal to **one**. This means that we are working in the Henrian standard state in the dilute limit. This point is really academic because in the end we *fit* the experimental data to an equation like (1.1.4a) and so all the constants are rolled up into the fit. It works as long as the data *does* fit (1.1.4a). It is not really possible to extend the method easily if the assumptions of constant activity coefficient are not consistent with the observations.

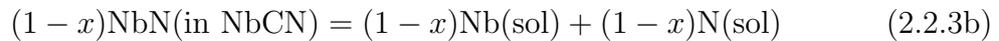
The chemical reaction I am interested in is, by comparison with (1.1.1),



The solubility product associated with this reaction is, by association with equation (1.1.3),

$$k = [\text{Nb}][\text{C}]^x[\text{N}]^{1-x} \quad (2.2.2)$$

so this depends on the stoichiometry of the carbonitride through  $x$  which is unknown as a function of composition and temperature. If I break down the reaction (2.2.1) into two half reactions I can assert that (2.2.1) *is the sum of* these two reactions



(I am using NbCN as a shorthand for  $\text{NbC}_x\text{N}_{1-x}$ .) These two reactions taking place simultaneously assert an equilibrium in which in (2.2.3a) Nb and C in solution are in equilibrium with the component NbC and in which in (2.2.3b) Nb and N in solution are in equilibrium with the component NbN. Here we imply that NbC and NbN are two *components* that make up the carbonitride. The fact that I've multiplied through by  $x$  and  $1 - x$  doesn't change the reactions and so the solubility products for the two reactions are

$$k_1 = \frac{[\text{Nb}][\text{C}]}{\text{activity of NbC in NbCN}} \quad (2.2.3c)$$

$$k_2 = \frac{[\text{Nb}][\text{N}]}{\text{activity of NbN in NbCN}} \quad (2.2.3d)$$

We now make our second simplifying assumption and assume that the carbonitride is an *ideal* solid solution of NbC and NbN so that the activities of each of those components are just  $x$  and  $1 - x$  respectively which are the concentrations of each of these components of the carbonitride. Since we assume an ideal solution of NbN and NbC in  $\text{NbC}_x\text{N}_{1-x}$  the activities in (2.2.3c) and (2.2.3d) are just the concentrations  $x$  and  $1 - x$  so solubility products for the two half reactions are

$$k_1 = [\text{Nb}][\text{C}]/x \quad (2.2.3e)$$

$$k_2 = [\text{Nb}][\text{N}]/(1 - x) \quad (2.2.3f)$$

I raise the first of these equations to the power  $x$  and the second to the power  $1 - x$  and multiply the two resulting equations together,

$$\begin{aligned} k_1^x k_2^{1-x} &= \frac{1}{x^x (1-x)^{1-x}} [\text{Nb}]^x [\text{C}]^x [\text{Nb}]^{1-x} [\text{N}]^{1-x} \\ &= \frac{1}{x^x (1-x)^{1-x}} [\text{Nb}][\text{C}]^x [\text{N}]^{1-x} \end{aligned} \quad (2.2.4)$$

Comparing the solubility product (2.2.2) for the reaction (2.2.1) with (2.2.4) it is seen to be equal to

$$k = k_1^x k_2^{1-x} x^x (1-x)^{1-x} \quad (2.2.5)$$

or, if you prefer, by taking logarithms of both sides,

$$\log k = x \log k_1 + (1-x) \log k_2 + x \log x + (1-x) \log(1-x) \quad (2.2.6)$$

This has the very pleasing structure of the weighted sum of the two solubility products for reactions (2.2.2) plus an ideal entropy of mixing term. From this sublime height it

all becomes a bit horrible, but I can develop formulas for the amount of dissolved Nb at a given temperature and composition in the same way as we have done up to now, using the conservation of mass and the stoichiometry (see page 6),

$$\text{Nb}_T = [\text{Nb}] + \text{Nb}_{\text{NbCN}} \quad (2.2.7a)$$

$$\text{Nb}_{\text{NbC}} = x \text{Nb}_{\text{NbCN}} \quad (2.2.7b)$$

$$\text{Nb}_{\text{NbN}} = (1 - x) \text{Nb}_{\text{NbCN}} \quad (2.2.7c)$$

$$\text{C}_T = [\text{C}] + \text{C}_{\text{NbCN}} \quad (2.2.7d)$$

$$\text{N}_T = [\text{N}] + \text{N}_{\text{NbCN}} \quad (2.2.7e)$$

$$\text{C}_{\text{NbC}} = \frac{12}{93} \text{Nb}_{\text{NbC}} \quad (2.2.7f)$$

$$\text{N}_{\text{NbN}} = \frac{14}{93} \text{Nb}_{\text{NbN}} \quad (2.2.7g)$$

$$\text{C}_{\text{NbCN}} = \frac{12}{93} x \text{Nb}_{\text{NbCN}} \quad (2.2.7h)$$

$$\text{N}_{\text{NbCN}} = \frac{14}{93} (1 - x) \text{Nb}_{\text{NbCN}} \quad (2.2.7i)$$

Again, I have used NbCN as a short hand for  $\text{NbC}_x\text{N}_{1-x}$  and the atomic weights (relative atomic masses) of C, N and Nb are 12, 14 and 93.

There are two possible approaches, which I describe in the next two sections, 2.2.1.1 and 2.2.1.2.

### 2.2.1.1 The *quartic* equation

I can rewrite equations (2.2.3e) and (2.2.3f) like this, using the mass balance equations above,

$$xk_1 = [\text{Nb}][\text{C}] = [\text{Nb}] \left( \text{C}_T - \frac{12}{93}x (\text{Nb}_T - [\text{Nb}]) \right) \quad (2.2.8a)$$

$$(1 - x)k_2 = [\text{Nb}][\text{N}] = [\text{Nb}] \left( \text{N}_T - \frac{14}{93}(1 - x) (\text{Nb}_T - [\text{Nb}]) \right) \quad (2.2.8b)$$

Then these are expanded out and like terms in  $x$  are collected; after which the first is divided by the second which eliminates  $x$ . The result is

$$\begin{aligned} 0 = & - (12 \times 14) [\text{Nb}]^4 \\ & + (12 \times 14 \times 2\text{Nb}_T - 12 \times 93 \times \text{N}_T - 14 \times 93 \times \text{C}_T) [\text{Nb}]^3 \\ & + (12 \times 93 (k_2 + \text{N}_T\text{Nb}_T) - 12 \times 14 \times \text{Nb}_T^2 + 14 \times 93 (k_1 + \text{C}_T\text{Nb}_T)) [\text{Nb}]^2 \\ & + (93^2 (\text{N}_T k_1 + \text{C}_T k_2) - 93 \times 14 \times \text{Nb}_T k_1 - 93 \times 12 \times \text{Nb}_T k_2) [\text{Nb}] \\ & - 93^2 \times k_1 k_2 \end{aligned} \quad (2.2.9)$$

This is a quartic equation for the dissolved niobium weight percent. Note that these equations, while still horrible, would look a lot less cluttered if we used atomic rather than weight percent so that the numbers would all go away. (I printed the numbers

deliberately small on pages 14–16 so as not to obscure the structure any more than necessary.)

Once  $[\text{Nb}]$  is known then the amount of Nb tied up as carbonitride is

$$\text{Nb}_{\text{NbCN}} = \text{Nb}_T - [\text{Nb}]$$

Then the stoichiometry of the carbonitride is found as follows. Combining (2.2.7d) and (2.2.3e) with the stoichiometric formula (2.2.7h) we find

$$x = C_T \left( \frac{k_1}{[\text{Nb}]} + \frac{12}{93} \text{Nb}_{\text{NbCN}} \right)^{-1} = C_T \left( \frac{k_1}{[\text{Nb}]} + \frac{12}{93} (\text{Nb}_T - [\text{Nb}]) \right)^{-1} \quad (2.2.10)$$

Once we have the amount of dissolved Nb from solving (2.2.9) and the stoichiometry of the carbonitride (2.2.10) then we can find the amount of Nb, C and N in solution and tied up as carbonitride from (2.2.7a), (2.2.7d–e) and (2.2.7h–i).

### 2.2.1.2 The *quadratic* equation

The solubility products,  $k_1$  and  $k_2$ , depend on  $x$  and we don't know how to get them from experiment. However we do know the solubility products for the binary NbC and NbN precipitates, from separate measurements of Fe-Nb-C and Fe-Nb-N alloys,

$$\text{NbC}(\text{ppt}) = \text{Nb}(\text{sol}) + \text{C}(\text{sol}) \quad ; \quad k_{\text{C}} = [\text{Nb}]_{\text{C}}[\text{C}]_{\text{C}} \quad (2.2.11\text{a})$$

$$\text{NbN}(\text{ppt}) = \text{Nb}(\text{sol}) + \text{N}(\text{sol}) \quad ; \quad k_{\text{N}} = [\text{Nb}]_{\text{N}}[\text{N}]_{\text{N}} \quad (2.2.11\text{b})$$

By comparison of (2.2.3e) and (2.2.3f) with (2.2.11), we are *tempted* to write

$$k_{\text{C}} = xk_1 \quad (2.2.12\text{a})$$

$$k_{\text{N}} = (1 - x)k_2 \quad (2.2.12\text{b})$$

However this is not correct, as I've indicated with subscripts “C” and “N” in (2.2.11): the amounts of carbon and nitrogen in solution,  $[\text{C}]$  and  $[\text{N}]$ , in equilibrium with  $\text{NbC}_x\text{N}_{1-x}$  in a Fe-Nb-C-N alloy *are not the same as* the amount of carbon  $[\text{C}]_{\text{C}}$  in equilibrium with NbC in a Fe-Nb-C alloy and the amount of nitrogen  $[\text{N}]_{\text{N}}$  in equilibrium with NbN in a Fe-Nb-N alloy.

But if I admit the assertion (2.2.12) then I can replace the left hand sides of (2.2.8) with  $k_{\text{C}}$  and  $k_{\text{N}}$ . I then eliminate  $x$  between these two equations and obtain

$$\frac{1}{93}[\text{Nb}]^2 + \left( \frac{1}{14}\text{N}_T + \frac{1}{12}\text{C}_T - \frac{1}{93}\text{Nb}_T \right) [\text{Nb}] - \frac{1}{12}k_{\text{C}} - \frac{1}{14}k_{\text{N}} = 0 \quad (2.2.13)$$

This is a quadratic equation that can be solved to find the amount of dissolved Nb.

Once we have that then we can find the amount of Nb tied up as precipitate, using (2.2.7a),

$$\text{Nb}_{\text{NbCN}} = \text{Nb}_T - [\text{Nb}]$$

We've assumed, or approximated, that equation (2.2.11a) is the same as

$$k_C = [\text{Nb}][\text{C}]$$

that is,

$$[\text{Nb}] = [\text{Nb}]_C = [\text{Nb}]_N \quad (2.2.14a)$$

$$[\text{C}] = [\text{C}]_C = [\text{C}]_N \quad (2.2.14b)$$

$$[\text{N}] = [\text{N}]_C = [\text{N}]_N \quad (2.2.14c)$$

(*cf.* (2.2.2) and (2.2.11).) By stoichiometry (2.2.7h),

$$C_{\text{NbCN}} = \frac{12}{93} x \text{Nb}_{\text{NbCN}}$$

Equation (2.2.7d) leads to

$$[\text{C}] = C_T - C_{\text{NbCN}} = C_T - \frac{12}{93} x \text{Nb}_{\text{NbCN}} = \frac{k_C}{[\text{Nb}]}$$

and solving for  $x$  we find

$$x = \frac{1}{\frac{12}{93} \text{Nb}_{\text{NbCN}}} \left( C_T - \frac{k_C}{[\text{Nb}]} \right) = \left( \frac{12}{93} (\text{Nb}_T - [\text{Nb}]) \right)^{-1} \left( C_T - \frac{k_C}{[\text{Nb}]} \right)$$

Finally using (2.2.7d–e) we can find the amounts of dissolved carbon and nitrogen, and we have the complete picture then.

### 2.2.1.3 Comparison of the two approaches

The principal difference between these two approaches is evident when you note that (2.2.13) is the equivalent of (2.1.3) in the mutually exclusive case. This means that in the quadratic approach we are ignoring the miscibility between NbC and NbN. This amounts to our assumptions (2.2.14); that is that the amounts of dissolved elements in equilibrium with NbC in the absence of N, and with NbN in the absence of C are the same as in the equilibrium (2.2.1). A good way to get a feel for the effect of the miscibility and the precipitation of carbonitride is to look from the point of view of equations (1.1.4) and (2.2.6). In view of (1.1.4), the logarithm of the solubility product is proportional to *minus* the standard free enthalpy of solution at some fixed temperature. As (2.2.6) shows the logarithm of the solubility product,  $k_1$ , for the solution of the carbonitride is the weighted average of the logarithms of the solubility products for the separate solutions of the carbide and the nitride,  $k_1$  and  $k_2$ , *plus* an entropy of mixing term which is negative. So  $k$  is *smaller* than the weighted average from the individual reactions, meaning that the standard free enthalpy of solution is *increased* by allowing the carbide and nitride to mix. Hence the carbonitride is, loosely speaking, more stable than the carbide and nitride and hence *less soluble*. This means that the effect of nitrogen addition to a carbon microalloyed steel, enabling the formation of carbonitride, is roughly speaking to *reduce* the solubility of the resulting carbidonitride (compared to

the carbide and nitride) and hence to promote precipitation, or equivalently to *raise* the temperature at which all the Nb is dissolved.

The quartic approach was taken by Hudd *et al.*, *J. Iron and Steel Institute*, **209**, 121 (1971). However because  $k_1$  and  $k_2$  are not known as functions of  $x$ , Hudd *et al.* assumed that

$$k_1 = k_C \quad (2.2.15a)$$

$$k_2 = k_N \quad (2.2.15b)$$

That is, for  $k_1$  and  $k_2$  they used published solubility product data from Fe-Nb-C and Fe-Nb-N alloys. This is arguably an even more drastic approximation than (2.2.11) and (2.2.12) used in the quadratic approach, namely,

$$k_1 = k_C/x \quad (2.2.16a)$$

$$k_2 = k_N/(1-x) \quad (2.2.16b)$$

because at least here the solubility products implicitly depend on  $x$  as they should. We could argue that *in principle* the quartic approach is the more rigorous, but the approximation that needs to be made to solve it is more drastic than the approximation of exclusive carbide and nitride, albeit combined into a single stoichiometry carbonitride precipitate. But we see now that this is incorrect.

Figure 19 illustrates the comparison using as examples Fe-0.03Nb-0.1C-0.01N and Fe-0.08Nb-0.1C-0.01N steels. The red and blue circles correspond to solutions of equation (1.1.10) for the cases that either nitrogen or carbon are absent, and show the weight percent of Nb expected to be tied up in precipitate as functions of the austenitising temperature. For the quaternary alloys we show solutions obtained from the quartic (as solid lines) and quadratic (as dotted lines) connecting the green circles.

The quadratic approach, which amounts to the mutually exclusive case, practically predicts the same amount of precipitate as for the case of the Fe-Nb-C alloy. This is because (2.2.13) essentially reduces to (1.1.10) because  $k_N$  is an order of magnitude smaller than  $k_C$  (figure 5) and  $N_T$  is an order of magnitude smaller than  $C_T$ .

On the other hand, the quartic approach properly takes account of the enthalpy of mixing. As argued above this has the effect of increasing the thermodynamic stability of the  $\text{NbC}_x\text{N}_{1-x}$  and so its solubility is less and a greater amount of precipitate is predicted compared to the mutually exclusive (quadratic) approximation. There still remains the fact the ansatz (2.2.15) cannot be right. The qualitative features of the theory are evident in figure 19, but this does not mean that the quantitative predictions are correct. It may be possible to calculate  $k_1$  and  $k_2$  from electronic structure theory. It may also be possible to do experiments as suggested by equations (2.2.3e) and (2.2.3f) in which as a function temperature, using different compositions of Fe-Nb-C-N alloys, both the equilibrium concentrations of dissolved N and C *and* the stoichiometry,  $x$ , of the  $\text{NbC}_x\text{N}_{1-x}$  can be measured.

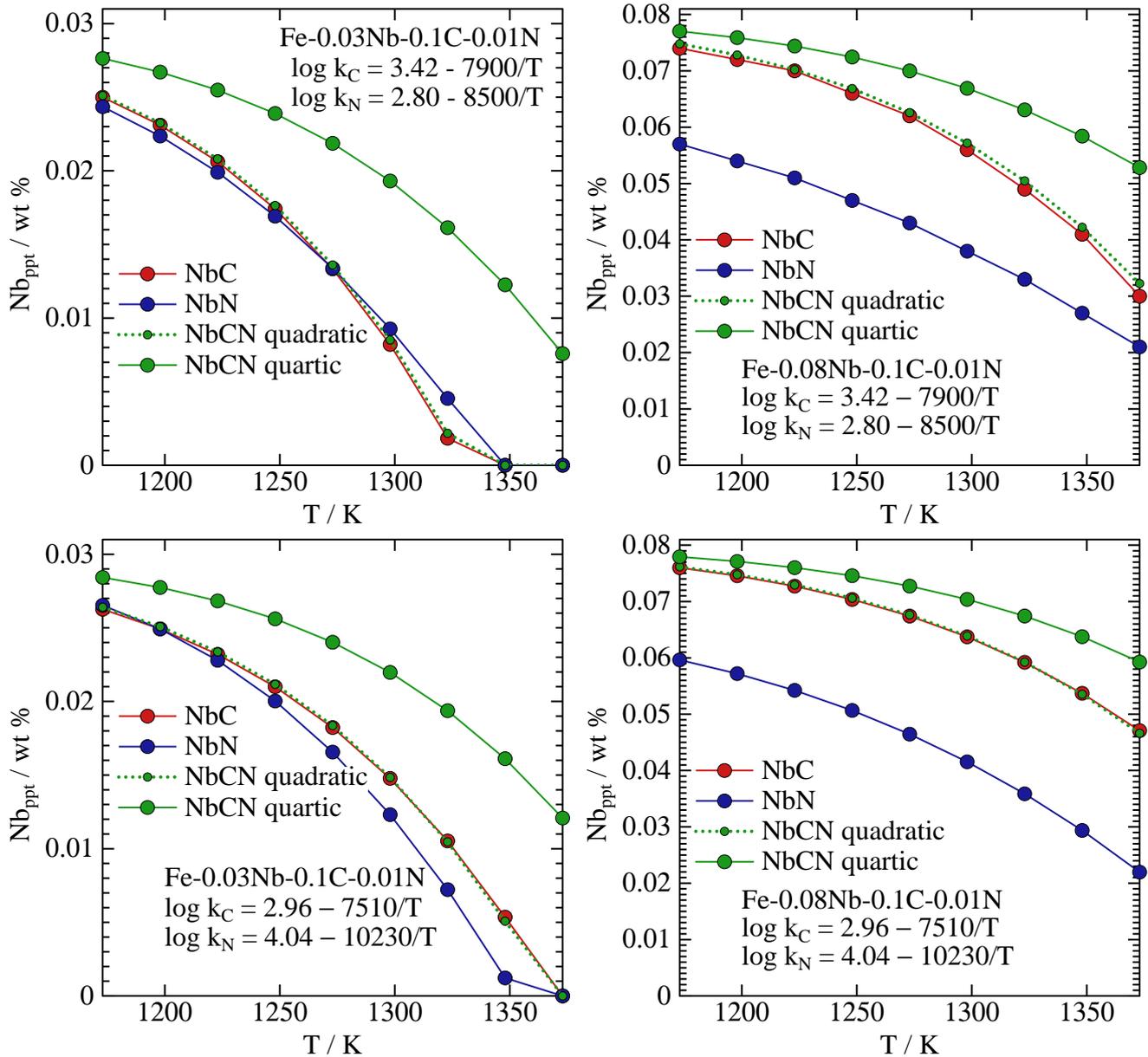


Figure 19: Weight percent of Nb in precipitate as a function of soaking temperature. These are solutions of equations (1.1.10) (red and blue circles corresponding to the ternary Fe-Nb-C and Fe-Nb-N alloys), (2.2.9) and (2.2.13) which are respectively the quartic and quadratic approaches described in the text. The solubility parameters used are shown in the figure.

It is significant that the results shown in figure 19 are quite insensitive to the choice of parameterisation (1.1.4) for the solubility products. The top two graphs are calculated using a parameterisation

$$\log k_C = 3.42 - 7900/T ; \quad \log k_N = 2.80 - 8500/T$$

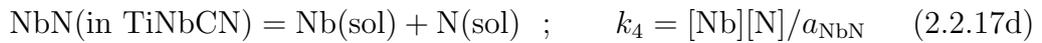
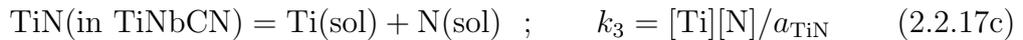
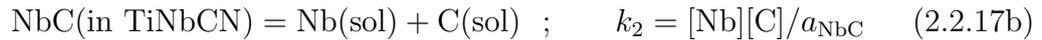
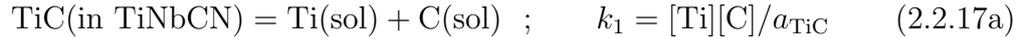
which is cited by Gladman as due to measurements of Narita; and the lower two used

$$\log k_C = 2.96 - 7510/T ; \quad \log k_N = 4.04 - 10230/T$$

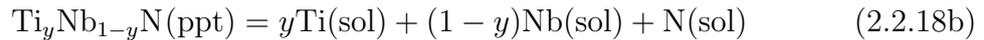
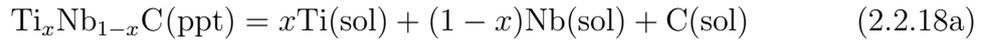
which are the parameters quoted by Hudd *et al.* Since the assumption (2.2.15) is that  $k_1 = k_C$  and  $k_2 = k_N$  and since we expect that  $k_1 < k_C$  and  $k_2 < k_N$  as argued above, then the solubility of  $\text{NbC}_x\text{N}_{1-x}$  is *overestimated* and we expect that actual amounts of precipitate to be even larger than predicted.

## 2.2.2 Complex carbonitrides

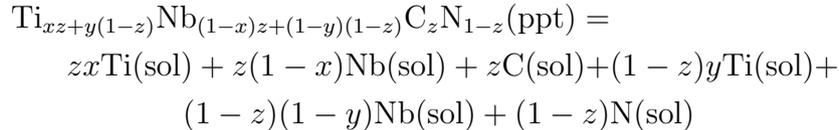
Imagine a steel with composition  $A$  wt%Ti,  $B$  wt%Nb,  $C$  wt%C and  $D$  wt%N. In comparison to equations (2.2.3a,b) we have these equilibria,



in which  $a$  is the activity of the precipitate. Again, we may not take these as being one. Consider the dissolution of a complex carbide of Ti and Nb, and a complex nitride of Ti and Nb,



As in the case of the simple carbonitride we envisage the formation of the complex carbonitride in two stages: first the formation of the carbide and the nitride (2.2.18), followed by their mixing to form the carbonitride. The formation of the complex carbonitride is described by the equilibrium,



in which we essentially mix  $z$  moles of (2.2.18a) with  $(1-z)$  moles of (2.2.18b).

As in section 2.2.1 we assume that the complex carbonitride is an ideal solid solution of the component complex carbides and nitrides then we can assert that

$$a_{\text{TiC}} = xz \quad (2.2.19a)$$

$$a_{\text{NbC}} = z(1-x) \quad (2.2.19b)$$

$$a_{\text{TiN}} = y(1-z) \quad (2.2.19c)$$

$$a_{\text{NbN}} = (1-y)(1-z) \quad (2.2.19d)$$

We proceed in the same vein as before exploiting the mass balance identities, stoichiometries and the irritating atomic weight ratios. The weight percentage of N in the austenite matrix is  $[\text{N}]$  and so the weight percent nitrogen in the carbonitride is  $D - [\text{N}]$ , and the weight percent carbon in the carbonitride is  $(12/14)(D - [\text{N}])z/(1-z)$ . The weight percent of Ti in the carbonitride is the sum of that weight percent that came from the

formation of TiC in the first step of the thought experiment plus that coming from the TiN,

$$\text{wt\%Ti in carbonitride} = \text{Ti}_{\text{carbonitride}} = \frac{48}{14} (D - [\text{N}]) \frac{xz + y(1 - z)}{1 - z}$$

in the same way

$$\text{wt\%Nb in carbonitride} = \text{Nb}_{\text{carbonitride}} = \frac{93}{14} (D - [\text{N}]) \frac{(1 - x)z + (1 - y)(1 - z)}{1 - z}$$

Now we can find the matrix compositions of C, Ti and Nb in terms of [N] and the alloy composition and stoichiometry of the carbonitride (remember that the steel composition is  $A$  wt%Ti,  $B$  wt%Nb,  $C$  wt%C and  $D$  wt%N, so in our notation,  $A = \text{Ti}_T$ ,  $B = \text{Nb}_T$ ,  $C = \text{C}_T$  and  $D = \text{N}_T$ ),

$$\begin{aligned} [\text{C}] &= C - \frac{12}{14} (D - [\text{N}]) \frac{z}{1 - z} \\ [\text{Ti}] &= A - \frac{48}{14} (D - [\text{N}]) \frac{xz + y(1 - z)}{1 - z} \\ [\text{Nb}] &= B - \frac{93}{14} (D - [\text{N}]) \frac{(1 - x)z + (1 - y)(1 - z)}{1 - z} \end{aligned}$$

Putting these into the second column of equations (2.2.17) for the solubility products we get, bearing in mind (2.2.19),

$$\begin{aligned} k_1 &= [\text{Ti}][\text{C}]/a_{\text{TiC}} \\ &= \frac{1}{xz} \left( A - \frac{48}{14} (D - [\text{N}]) \frac{xz + y(1 - z)}{1 - z} \right) \left( C - \frac{12}{14} (D - [\text{N}]) \frac{z}{1 - z} \right) \end{aligned} \quad (2.2.20a)$$

$$\begin{aligned} k_2 &= [\text{Nb}][\text{C}]/a_{\text{NbC}} \\ &= \frac{1}{z(1 - x)} \left( B - \frac{93}{14} (D - [\text{N}]) \frac{z(1 - x) + (1 - y)(1 - z)}{1 - z} \right) \times \\ &\quad \left( C - \frac{12}{14} (D - [\text{N}]) \frac{z}{1 - z} \right) \end{aligned} \quad (2.2.20b)$$

$$\begin{aligned} k_3 &= [\text{Ti}][\text{N}]/a_{\text{TiN}} \\ &= \frac{1}{y(1 - z)} \left( A - \frac{48}{14} (D - [\text{N}]) \frac{xz + y(1 - z)}{1 - z} \right) [\text{N}] \end{aligned} \quad (2.2.20c)$$

$$\begin{aligned} k_4 &= [\text{Nb}][\text{N}]/a_{\text{NbN}} \\ &= \frac{1}{(1 - y)(1 - z)} \left( B - \frac{93}{14} (D - [\text{N}]) \frac{z(1 - x) + (1 - y)(1 - z)}{1 - z} \right) [\text{N}] \end{aligned} \quad (2.2.20d)$$

If  $y$  is made the subject of (2.2.20c) and this then substituted into (2.2.20a, b and d) then, after making  $x$  the subject of these, three further equations result,

$$x = \frac{f_1([\text{N}], z)}{f_2([\text{N}], z)} \quad (2.2.21a)$$

$$x = \frac{f_3([\text{N}], z)}{f_4([\text{N}], z)} \quad (2.2.21b)$$

$$x = \frac{f_5([\text{N}], z)}{f_6([\text{N}], z)} \quad (2.2.21c)$$

in which the six functions as defined in (2.2.21) are

$$\begin{aligned}
f_1 &= A(1-z)k_3 \left( C(1-z) - \frac{12}{14}z(D-[N]) \right) \\
f_2 &= z \left( (1-z)k_1 \left( (1-z)k_3 + \frac{48}{14}[N](D-[N]) \right) \right. \\
&\quad \left. + \frac{48}{14}(D-[N])k_3 \left( C(1-z) - z\frac{12}{14}(D-[N]) \right) \right) \\
f_3 &= \left\{ \left( (1-z)k_3 + \frac{48}{14}[N](D-[N]) \right) \left( \frac{93}{14}(D-[N]) - B(1-z) \right) \right. \\
&\quad \left. - A[N](1-z)\frac{93}{14}(D-[N]) \right\} \left( c(1-z) - \frac{12}{14}z(D-[N]) \right) \\
&\quad + z(1-z)^2 k_2 \left( (1-z)k_3 + \frac{93}{14}[N](D-[N]) \right) \\
f_4 &= z(1-z) \left\{ (1-z)k_2 \left( (1-z)k_3 + \frac{48}{14}[N](D-[N]) \right) \right. \\
&\quad \left. + \frac{93}{14}(D-[N]) \left( C(1-z) - z\frac{12}{14}(D-[N]) \right) \right\} \\
f_5 &= B(1-z)[N] \left\{ (1-z)k_3 + \frac{48}{14}[N](D-[N]) \right\} \\
&\quad - \left\{ (1-z)k_4 + \frac{93}{14}[N](D-[N]) \right\} \left\{ (1-z)^2 k_3 + \frac{48}{14}[N](D-[N]) - A(1-z)[N] \right\} \\
&\quad + z(1-z)[N](D-[N]) \left( \frac{48}{14}k_4 - \frac{93}{14}k_3 \right) \\
f_6 &= z(1-z)[N](D-[N]) \left( \frac{48}{14}k_4 - \frac{93}{14}k_3 \right)
\end{aligned}$$

We seek values of  $[N]$ , the dissolved nitrogen concentration, and  $z$ , the fraction of the interstitial sites that are occupied by carbon (as opposed to nitrogen—there are no vacancies in this problem) such that equations (2.2.21) are consistent; that is, such that each of those three ratios,  $f_1/f_2$ ,  $f_3/f_4$  and  $f_5/f_6$ , is equal to a number,  $x$ , which must of course be between zero and one (since it is the fraction of transition metal sites occupied by Ti, as opposed to Nb). Equating the three equations (2.2.21) results in just two independent equations,

$$\begin{aligned}
\frac{f_1}{f_2} &= \frac{f_3}{f_4} \\
\frac{f_1}{f_2} &= \frac{f_5}{f_6}
\end{aligned}$$

equivalently

$$\begin{aligned}
f_1 f_4 &= f_2 f_3 \\
f_1 f_6 &= f_2 f_5
\end{aligned}$$

Two further functions of  $[N]$  and  $z$  are defined, namely,

$$\begin{aligned}
F_1 &= f_1 f_4 - f_2 f_3 \\
F_2 &= f_1 f_6 - f_2 f_5
\end{aligned}$$

and it follows that when both of these are zero a solution is found as long as it results in sensible values of  $[N]$  and  $z$ , namely that  $0 < [N] < D$  and  $0 < z < 1$ .

This provides the basis of a computed solution of the problem of determining the amount and the stoichiometry of the complex carbonitride in the steel of a given composition and temperature.

The procedure is illustrated in figure 20. The computer selects systematically trial values of  $z$  (between zero and one) from which  $[N]$  is found by iteration. For each pair  $(z, [N])$  the functions  $f_1$  to  $f_6$  are evaluated and hence functions  $F_1$  and  $F_2$ . In figure 20, the solid line shows the concentration of free nitrogen,  $[N]$ , as a function of  $z$  for which  $F_1 = 0$ , and the broken line shows the same for which  $F_2 = 0$ . For those values of  $[N]$  and  $z$  for which both  $F_1$  and  $F_2$  are zero, namely at the intersection of the two lines, we have a solution of the problem at the chosen composition and temperature. Of course it assumed that data are available for the solubility products,  $k_1$  to  $k_4$ , for the ternary equilibria (2.2.17).

Figure 21 shows a full solution of the problem for a 0.1C-0.009N-0.01Ti-0.03Nb steel (that is  $A = 0.01$ ,  $B = 0.03$ ,  $C = 0.1$ ,  $D = 0.009$ ). The calculated weight percentages of the components in solution and in carbonitride are shown as a function of the temperature. CN is shorthand for carbonitride.

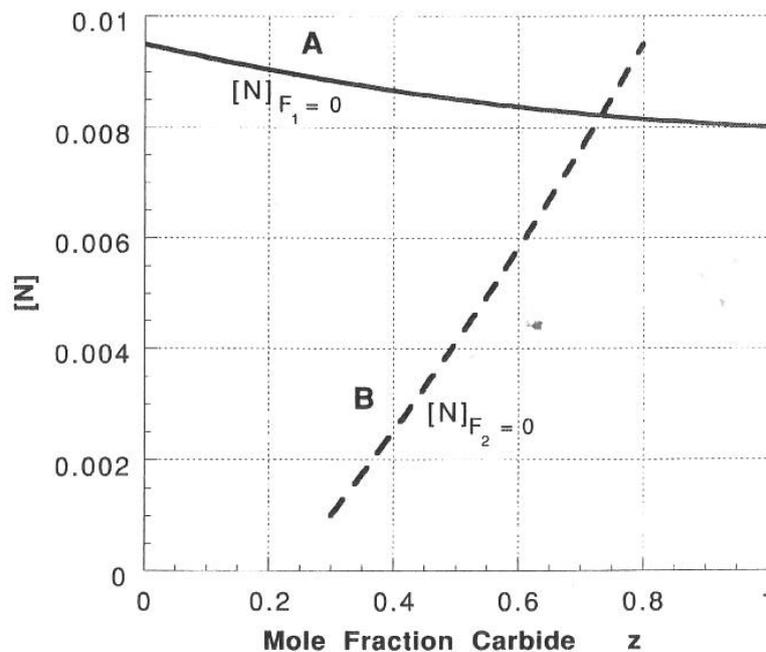


Figure 20: Schematic illustration of the solution to equations (2.2.21)

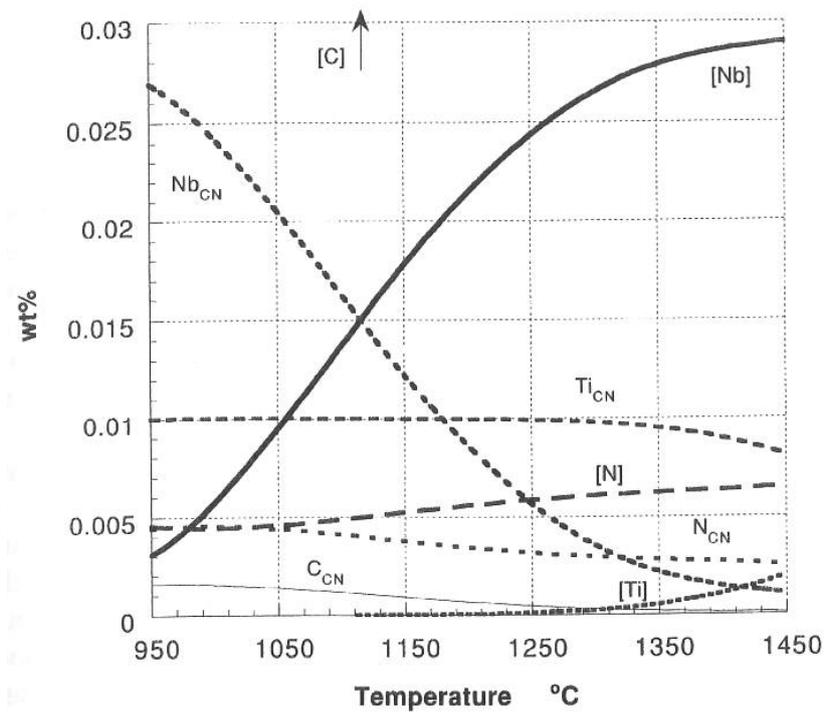


Figure 21: Calculated concentrations Ti, Nb, C, N in solution in austenite and as carbonitride precipitates in a 0.1C-0.009N-0.01Ti-0.03Nb steel

### Further reading

T. Gladman, "The Physical Metallurgy of Microalloyed Steels," Published by Maney, for the Institute of Materials, 1997