REVEALING THE WELDABILITY ADVANTAGES OF MODERN NIOBIUM MICROALLOYED LINEPIPE STEELS

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Weldability, Niobium, Heat Affected Zone, Carbon Equivalent, Toughness

Abstract

This paper addresses and comprehensively answers topical questions about the role of niobium during austenite transformation in the coarse-grained heat affected zone (CGHAZ) of modern HSLA linepipe steels during welding. It has been categorically demonstrated that there is no justification for the application of any carbon equivalent formula, containing an *additive* factor for niobium, to be used in the assessment of CGHAZ transformation for the rapid cooling regime in which resistance to cold cracking susceptibility may require consideration. *Indeed*, there is every reason to expect niobium treated steels, which are resistant to austenite grain growth during welding, to exhibit significantly superior performance in this respect.

At higher welding heat inputs, as encountered in submerged arc welding pipe manufacture with multi arc procedures or in 'double jointing' girth welding, the finer grain sized HAZ's are still encouraged to transform in an appropriate lower temperature range to achieve optimum microstructure and toughness through the role of niobium in solution in the transforming austenite. The way in which niobium achieves these unique benefits is thoroughly explained.

Introduction

It is nearly fifty years since I first became aware of comment in the technical literature claiming adverse effects of niobium on weldability [1]. It all seemed to start when welding consumable manufacturers realised they were having difficulty meeting the increasing toughness demands of submerged arc weld metals for tubular components for North Sea oil platforms. For entirely unsubstantiated reasons the finger was pointed at niobium, but that suspicion was effectively quashed by the mid 1970's [2]. However, later that same decade, the focus of attention turned to the coarse-grained heat affected zone (CGHAZ) and similar accusations against niobium became quite prevalent. The role of microalloying elements, in general, was critically reviewed in 1980 [3] and niobium specifically in 1981[4] and it was immediately obvious that interactions with carbon, both in weld metal and in the CGHAZ, were pivotal in determining the outcome.

Over the following decades many conflicting papers were published concerning the role of niobium in the heat affected zone and it became necessary for a comprehensive review to be undertaken to rationalise these. The myth that niobium levels should be restricted in steels for structural and linepipe applications was effectively dispelled in 2011 and it was demonstrated that

judicious control of carbon level was, by far, the most important factor in controlling CGHAZ microstructure and toughness [5]

Subsequently, a further comprehensive review of all possible effects of niobium on weldability was published [6] and it was demonstrated that the irresistible trend towards the use of lower carbon levels had opened the door to the more effective application of niobium microalloying.

Weldability has been defined as:

"The ability of a material to be joined using a wide range of appropriate welding processes to produce joints effectively free from significant defects and strong enough and tough enough, in all areas of these joints, to be fit for the purpose intended" [6].

In this latter context there is no doubt that, in the linepipe sector, the two areas of topical interest are heat affected zone cracking susceptibility and heat affected zone toughness.

This paper sets out to further examine the role of niobium and its specific effects in these two important areas and by critically assessing technical information, most of which is already in the public domain, makes new revelations about why niobium is so uniquely beneficial over such a wide spectrum of welding conditions.

First I will address the cold cracking susceptibility issue which is, of course, of particular concern during girth welding with lower heat inputs, and then turn my attention to heat affected zone toughness which is important both during pipe manufacture and later during 'double jointing' or field girth welding, that is, across a much wider spectrum of heat inputs.

Niobium, Hardness, Hardenability, Carbon Equivalent and Cold Cracking Susceptibility

Arguably the most serious defect that can occur during pipeline field girth welding is hydrogen assisted cold cracking. Even if promptly detected during inspection it can result in inconvenient, expensive and time-consuming repairs and, if undetected, then far more serious consequences may well result at a later date. With modern linepipe materials and construction during the spring to autumn 'window', in ambient temperatures above ten degrees centigrade, with appropriate preheat, cracking is rarely encountered. However, as linepipe materials have become stronger, wall thicknesses greater and pipe diameters larger, attention has once again, focused on the avoidance of this very unwelcome defect. With many long-distance projects now crossing hostile and elevated terrain and fabrication often taking place in adverse winter weather conditions, with temperatures down to minus thirty degrees centigrade, anything that can be done to minimise risk must be considered at the outset.

This immediately leads designers and owner-operator companies to make sure that they are procuring the best possible material for their projects and, whilst the benefits of low carbon steels are now widely accepted, questions still arise from time to time about the role of microalloying elements such as niobium. In the last few years two specific questions have repeatedly come to the

fore. These concern the role of niobium in cold cracking susceptibility and, yet again, HAZ toughness.

Question 1: Does niobium influence, hardenability and heat affected zone (HAZ) hardness and is its presence detrimental or beneficial to hydrogen-induced cold cracking susceptibility?

The role played by overall chemical composition and individual elements in determining hardenability, the generation of hard heat affected zones following welding and their susceptibility to hydrogen induced cold cracking has been the subject of extensive international research for several decades. Many technical writers, myself included, have regrettably misused the term hardenability in the welding context and, before proceeding to develop my theme, I want to correct and clarify our terminology.

In the classical or historical meaning the term ***hardenability*** refers to the ability of steel to be hardened to a particular depth from the surface during heat treatment. Normally the interest is in determining the depth to which martensite can be produced below a component surface following rapid quenching. This property was, and still is in certain industries, usually assessed using a Jominy test [7]. The steels concerned are typically of the higher carbon type.

However, in the welding of modern structural, pressure vessel or pipeline steels, which are generally lower in carbon, we are really more interested in predicting the actual ***hardness*** and nature of the microstructure which may be produced with the rapid cooling rates associated with low heat input welding processes and whether or not such microstructures will be susceptible to hydrogen induced cold cracking. In reality, therefore, what welding metallurgists should concern themselves with is the effect individual alloying elements, or combinations of elements, have on the temperature at which austenite transforms to ferrite through direct or other more subtle effects as discussed later.

So, what does the term ***hardness*** actually refer to? Hardness has been reported in some publications to be a material property in effect, resistance to penetration, but the following ASM clarification is, I personally believe, noteworthy [8].

"Hardness is not a fundamental property of a material. Hardness values are arbitrary, and there are no absolute standards of hardness. Hardness has no quantitative value, except in terms of a given load applied in a specified manner for a specified duration and a specified penetrator shape."

It follows therefore that, when comparing the behavior of different materials against an existing hardness data-base or the requirements of specific standards, cognisance must be given to the precise hardness measurement technique applied and the indenter load in question. An increasingly common mistake is to equate Vickers hardness results measured with 5 kg or 10 kg loads with microhardness data derived using 1kg or even lower loads. Such an approach might be, theoretically, acceptable for perfectly homogeneous materials but steels do not fall within that category.

It is a matter of fact that the direct roles of individual elements in influencing hardenability during component quenching and the generation of hard microstructures following welding are usually similar and it is no surprise, therefore, that various Carbon Equivalent (CE) formulae have evolved and have been used, **interchangeably**, to predict both hardenability and hardness (and later, by implication, resistance to hydrogen induced cold cracking).

There is no universally accepted carbon equivalent formula applicable to all classes of steels and the derivation of each has largely been empirical in nature resulting in formulae *the use of which is best restricted to the class of steels and circumstances for which they were devised.*

So, what about niobium?

There are, of course, a number of Carbon Equivalent formulae which have been derived by reputable researchers over the decades that do indeed include factors for niobium (9-13). However, when the background to such formulae is researched, they have usually been generated for very specific purposes. Equation 1, for example, relates to spot weldability of particular types of sheet steels [9] whilst equation 4 is an integral part of an approach, with lower carbon steels, to predict the formation and hardness of bainite [10]. Equation 2, which as originally published in 1976 by Graville [11], contained an extra term to recognise the logarithmic dependence of cracking susceptibility on hydrogen content, was developed by multiple regression of eighty data sets but the origins of his material are no longer readily accessible. Finally, in 1990, Cottrell [12] also utilised data from a wide range of disparate sources to produce equation 3 but his data covered such varied compositions and welding conditions that it never actually gained general credence in the fabrication industry.

$$CE_s = \%C + \frac{\%Mn}{6} + \frac{(\%Cr + \%Mo + \%Zr)}{10} + \frac{\%Ti}{2} + \frac{\%Nb}{3} + \frac{\%V}{7} + \frac{UTS}{900} + \frac{t}{20} \qquad 1$$

$$CE_{Graville} = \%C + \frac{\%Mn}{16} + \frac{\%Ni}{50} + \frac{\%Cr}{23} + \frac{\%Mo}{7} + \frac{\%Nb}{8} + \frac{\%V}{9} \qquad 2$$

$$CE_w = \%C + \frac{\%Mn}{14} + \frac{(\%Ni + \%Cu)}{30} + \frac{(\%Cr + \%Mo)}{10} + \frac{\%Nb}{2.5} + \frac{\%V}{6} + 3\%N + 20\%B \qquad 3$$

$$CE_B = \%C + \frac{\%Mn}{5} + \frac{\%Si}{24} + \frac{\%Cu}{10} + \frac{\%Ni}{18} + \frac{(\%Cr + \%V)}{5} + \frac{\%Mo}{2.5} + \frac{\%Nb}{3} \qquad 4$$

(To be used in conjunction with $H_B = 197CE_B + 117$)

None of these equations are now regarded as being specifically relevant to the assessment of the cold cracking susceptibility of modern structural or linepipe steels

I have deliberately separated out the widely referenced Yurioka et al [13] CEN equation below. This actually dates from 1983 and is unwieldy to use but has, very recently, been incorporated into a new International Association of Oil and Gas Producers (IOGP) supplementary specification, S616, [14] which they recommend for use in conjunction with the API 5L Standard [15] on the grounds that **"*niobium has a powerful effect on hardenability during welding*".** At this time the specification only calls for the calculation below to be carried out for information purposes.

$$CEN = \%C + A(C)[\frac{\%Si}{24} + \frac{\%Mn}{6} + \frac{\%Cu}{15} + \frac{\%Ni}{20} + \frac{(\%Cr + \%Mo + \%Nb + \%V)}{5} + 5\%B]$$

5

Where A(C) = 0.75+0.25tanh[20x(%C − 0.12)]

A variant of the above Yurioka formula is also incorporated into the Canadian Welding Standards as CE_{CSA} where A(C) is replaced by a term F, values of which can be obtained from a useful supporting table.

I will return to the IOGP rationale later and it suffices to note here that the evidence which follows in this paper firmly refutes the need for a niobium term in Yurioka's formula.

The following four carbon equivalent formulae are, however, probably the best known and most widely utilised. They can be found integrated within important national and international standards concerned with the welding of C-Mn microalloyed structural and linepipe steels [16, 17 and 18].

$$CE_{IIW} = \%C + \frac{\%Mn}{6} + \frac{(\%Cr + \%Mo + \%V)}{5} + \frac{(\%Cu + Ni)}{15}$$

6

$$CET = \%C + \frac{(\%Mn + \%Mo)}{10} + \frac{(\%Cr + \%Cu)}{20} + \frac{\%Ni}{40}$$

7

$$CE_{AWS} = \%C + \frac{(\%Mn + \%Si)}{6} + \frac{(\%Cr + \%Mo + \%V)}{5} + \frac{(\%Cu + \%Ni)}{15}$$

8

$$P_{CM} = \%C + \frac{\%Si}{30} + \frac{(\%Mn + \%Cu + \%Cr)}{20} + \frac{\%Ni}{60} + \frac{\%Mo}{15} + \frac{\%V}{10} + 5\%B$$

9

The first two equations feature in the European EN 1011-2 specification [16], the next in the American Welding Society (AWS) DI.1 specification [17] and the last in the Japanese Welding Engineering Society's code of practice [18]. The Pcm formula was specifically developed for steels with < 0.11 % carbon.

These four formulae have seen worldwide application and have **stood the test of time**. They have been successfully adopted by international line pipe material standards such as API 5L [15] and ISO 3183 [19].

Two things are immediately obvious; carbon is consistently the dominant element and these formulae have **no factor for niobium** which, given the decades of experience with their successful application, is surely, **on its own**, powerful evidence that niobium has no significant negative effect on hydrogen induced cold cracking susceptibility.

So, can we perhaps curtail our story right at this juncture and conclude that there is certainly no need to have a niobium factor in any equation of this nature?

Perhaps, but in previous publications, I have presented evidence to the effect that niobium may actually be beneficial to resistance to cold cracking susceptibility [20, 21] and I believe I can now throw further light on the answer to the important question I posed at the outset.

Graville [11] was probably the first to systematically demonstrate that the effect of niobium on austenite transformation and hardness following welding varied dramatically with weld cooling rate and that it was only as cooling rate **decreased** that its *overall* effect seemed to become important. See Figure 1. This observation is entirely consistent with my own research [20, 21] and I will return to this later when explaining the effect of niobium on the development of microstructure in the CGHAZ.
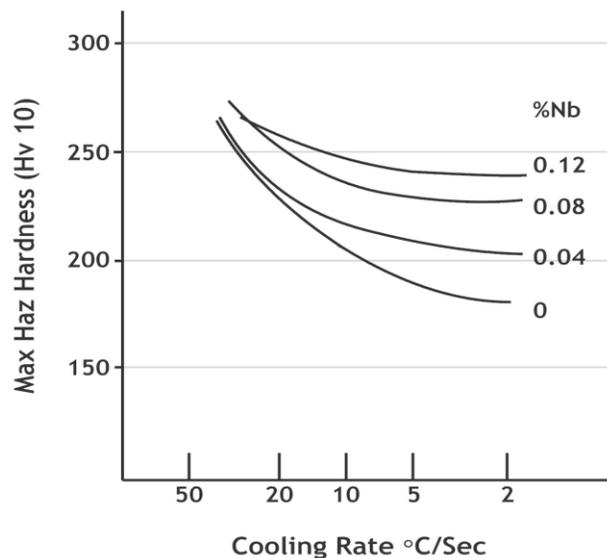

Figure 1. Effect of niobium on HAZ hardness. Adapted from Graville [11].

To further support my supposition, that niobium may actually be beneficial to resistance to cold cracking susceptibility, I now want to introduce a further carbon equivalent formula which, at first sight, appears to be entirely irrelevant to the niobium question as the element, once again, doesn't feature.

$$CE_M = \%C + \frac{\%Si}{38} + \frac{\%Mn}{6} + \frac{\%Ni}{12} + \frac{\%Cr}{1.8} + \frac{\%Mo}{2.3} + \frac{\%Cu}{9.1}$$

10

This is a formula from an intriguing Nippon Steel Technical Report published in 2007 [22]. The authors set out on a quest to demonstrate that it is not sufficient just to use a carbon equivalent formula to assess hardenability in the classical sense, **or** heat affected zone transformation behavior, without giving due consideration to the **grain size** of the transforming austenite.

Their unique research adds weight to explanations which I have forwarded in earlier publications [20, 21] to the effect that, at the rapid cooling rates associated with low heat input welding (where cold cracking might have been expected), the effect of niobium on the depression of the austenite to ferrite transformation temperature is counterbalanced, and indeed *powerfully outweighed,* by the way in which resistance to grain coarsening dominates the development of HAZ microstructure. ***Finer grain sizes, of course increase the austenite to ferrite transformation temperature.***

Amazingly, the Nippon steel report goes on to quantify the effect with the incorporation of a grain size factor expressed as a function of ASTM grain size. This led the authors to propose the relationship below and, by inference, they suggest that such a correction factor could actually be used in conjunction with other carbon equivalent formulae, not just equation 10, which is the one cited in their research.

$$CE_{effective} = CE_M - \frac{N}{35}$$

11

(Where N is the ASTM Grain Size Number)

With such an approach it is only when austenite grain sizes are very large, that is, where N = 1 or 2 that the 'effective' CE approximates to the CE_M value calculated from chemical analysis. Conversely, when the austenite grain sizes are very small and N is >9, the 'effective CE is significantly lower than the calculated CE_M value.

Table 1 and Figure 2 demonstrate the magnitude of the effect claimed by the Nippon researchers and the data in their paper is consistent with their explanation and with my own observations in the publications already alluded to.

Table 1. The potential influence of HAZ austenite grain size on effective carbon equivalent for a 'calculated' 0.40 CE_M steel.

Υ_{GS} Microns	ASTM Number N	N/35	CE (EFFECTIVE) = $CE_M - N/35$ *
254	1	0.029	.371
90	4	0.11	.290
32	7	0.20	.20
15.9	9	0.26	.14
3.97	13	0.370	.03

*From Equation 11
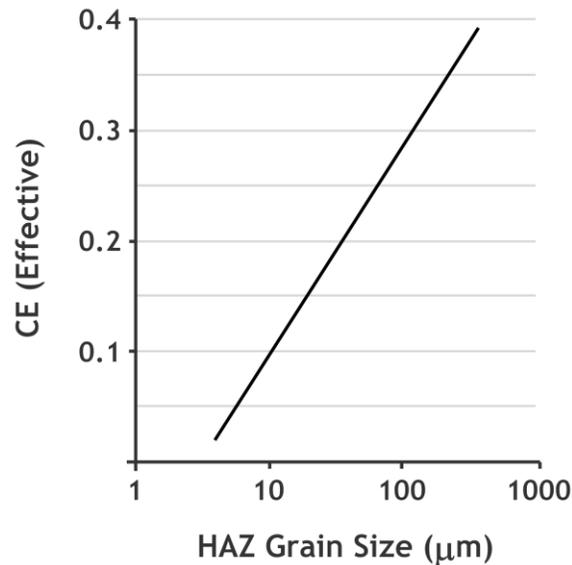
Figure 2. The relationship between CE (effective) and grain size for a calculated CE_M of 0.40 derived from [22].

Consider the significance of this contention; if we contrast the behavior of two steels with a nominal CE_M of say 0.40 then, if one had a coarse grained HAZ of average grain size 90μm which equates to an ASTM number of approximately 4 providing N/35 = 0.11, and the other a fine HAZ grain size around 16μm which equates to an ASTM grain size of approximately 9 providing N/35 = 0.26 then this suggests that the steel which resists grain coarsening will exhibit the behavior of a steel with a CE (effective) of 0.15 lower than the other; a remarkably powerful effect.

Now it has been well known for decades that niobium has a dramatic effect on grain coarsening resistance during welding, especially at the lowest heat inputs where hydrogen induced cold

cracking might be an issue and Figure 3, primarily derived from work by Hannerz [23], is an excellent illustration of the importance of this.
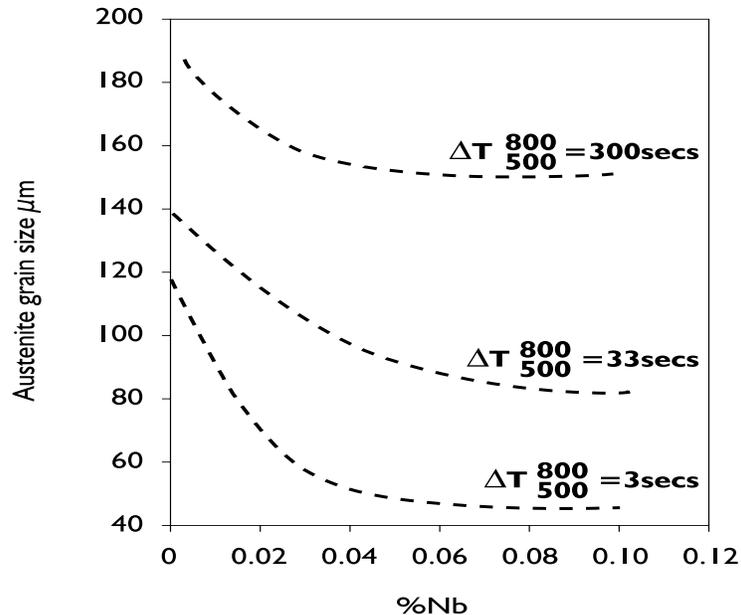

Figure 3. The effects of niobium and cooling rate on HAZ austenite grain size [23].

Much of the data in Figure 3 is from the higher carbon era and we now know that, when we study the behaviour of the low carbon higher niobium steel options which are increasingly gaining popularity for X70/80 applications, the 'Hannerz' effect is even more powerful. Steels of the latter genre which, when welded with low heat input girth welding processes, often exhibit austenite grain sizes in the 16 to 25μm diameter range, can be expected to dramatically benefit from the effect demonstrated by the Nippon researchers.

As discussed in a subsequent section of my paper this resistance to grain coarsening derives from fine distributions of Nb(CN) precipitates the efficacy of which can be augmented by the judicious use of very low titanium additions.

Even accepting that the Nippon analysis, which I have summarised [22], is probably overstating the effect there can be little doubt that any modern, low carbon, niobium treated steel must exhibit lower than expected CGHAZ hardness and better than anticipated resistance to cold cracking susceptibility.

No wonder that De Kazinczy, way back in 1963 [24], was the first to describe the potential weldability benefit of niobium in normalised steels when he astutely observed that:

"The small austenite grain size tends to decrease hardenability during welding"

Such a beneficial effect was actually experimentally noted by Ito et al [25] as indicated in Figure 4 below and by Frantov [26] who, using thermal simulation samples, compared a typical 0.07% carbon, Nb-V X70 steel with an 0.06% carbon, 0.1 % niobium X80 steel containing 0.23% chromium. Frantov observed that the higher niobium steel, **which was very resistant to HAZ grain coarsening**, could be cooled at up to 75°C/sec without exceeding the Det Norske Veritas 325 Vickers hardness limit [27] whilst the comparable conventional X70 exceeded the same hardness requirement at any cooling rate above 33°C/sec. It is noteworthy that, at slower cooling rates, there is little to distinguish the two steels in this particular study (See Figure 5).
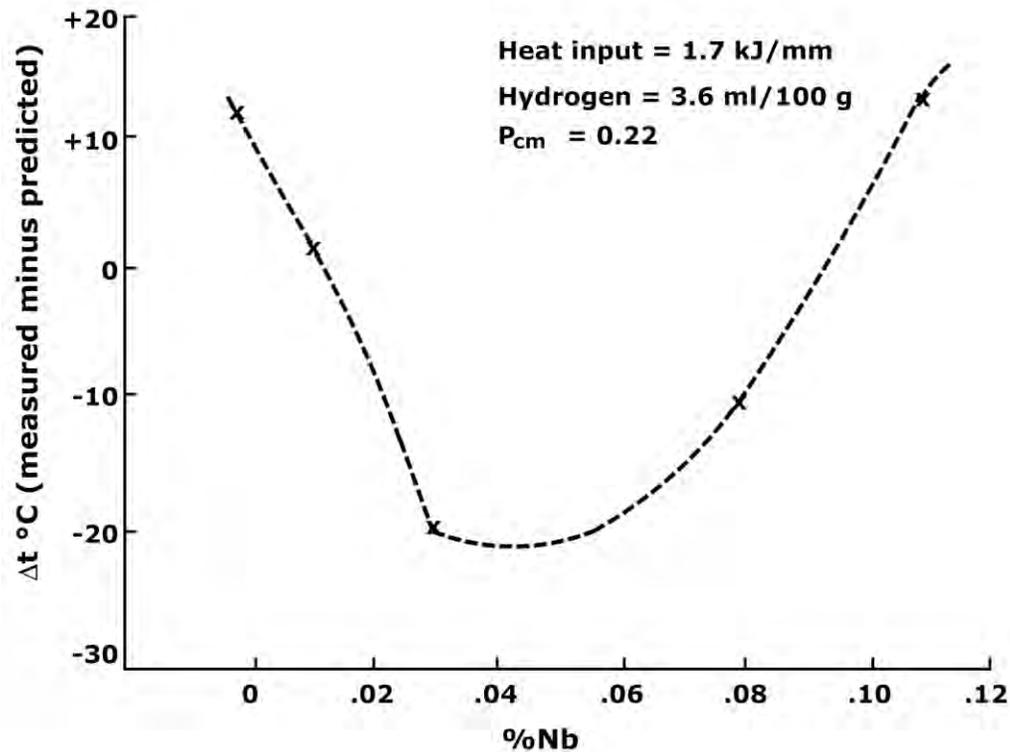

Figure 4. The effect of niobium on preheat required to prevent Tekken test cold cracking in vanadium free steels. Adapted from Ito et al [25].
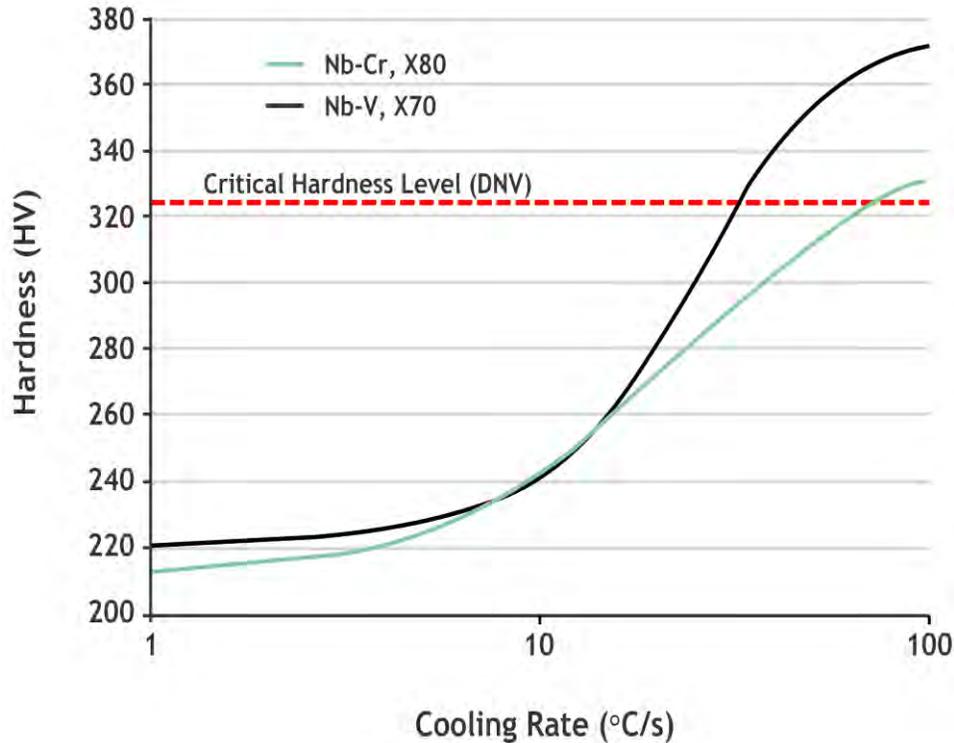
Figure 5. The effect of weld cooling rate on HAZ hardness of two different line pipe steels. The low carbon Nb-Cr steel is much more resistant to grain coarsening. After Frantov [26].

In 2013, I postulated that niobium treated steels with enhanced resistance to HAZ grain coarsening would be much less susceptible to cold cracking susceptibility [21] and it is, therefore, gratifying to find so much supportive evidence in the published literature.

My question is, therefore, answered and there is no technical justification **whatsoever** for the inclusion of a **'plus'** factor for Nb in any carbon equivalent formula concerned with the assessment of HAZ transformation at the cooling rates of interest to the consideration of cold cracking susceptibility of modern linepipe steels.

In conclusion it seems reasonable to assert that using CE$_{IIW}$ or Pcm to assess the weldability of modern niobium bearing linepipe steels provides an unduly conservative estimate of their inherent resistance to hydrogen induced cold cracking.

Niobium, HAZ Transformation Behaviour, Heat Input and Toughness

Question 2: How does niobium influence the development of GCHAZ microstructure in modern linepipe steels and is its effect beneficial or detrimental?

I want to begin by addressing the contention expressed by the IOGP and their recommended use of the Yurioka carbon equivalent formula, including a factor for niobium, to be used as an additional tool to assess the weldability of API 5L steels [8]. Of course, their understanding that niobium can depress transformation temperature is correct but, we have already seen how with rapid thermal cycles as in low heat input welding, the end result is, in practice, dominated by grain size.

Niobium depresses $\gamma \rightarrow \alpha$ transformation temperature.

It is widely understood and well reported that niobium has a powerful effect on the depression of austenite transformation temperature during steel processing [28, 29, 30, 31] and I am including a few diagrams below to demonstrate this and the way in which the effect may be influenced by cooling rate.
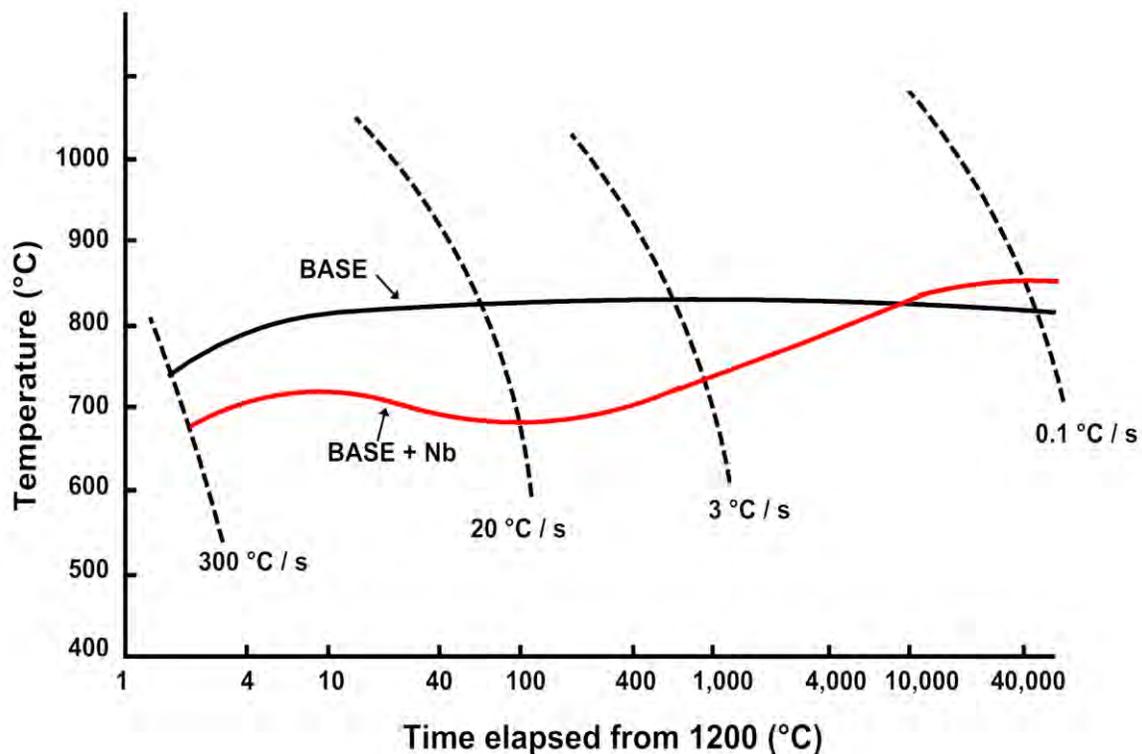

Figure 6. The effect of niobium on the depression of the austenite to ferrite transformation temperature [28]
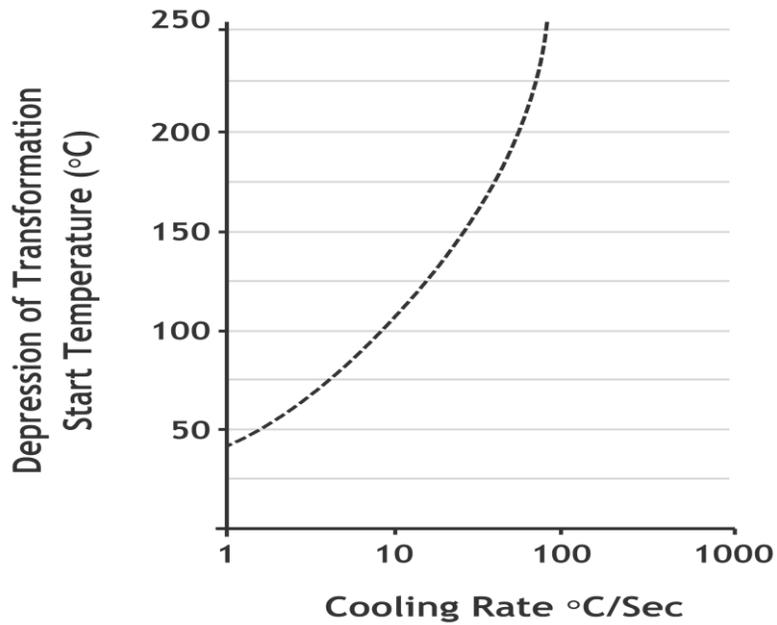
Figure 7. The effect of cooling rate on transformation temperature in niobium treated steels. Composite graph derived using data from various sources [28, 29, 30, 31]
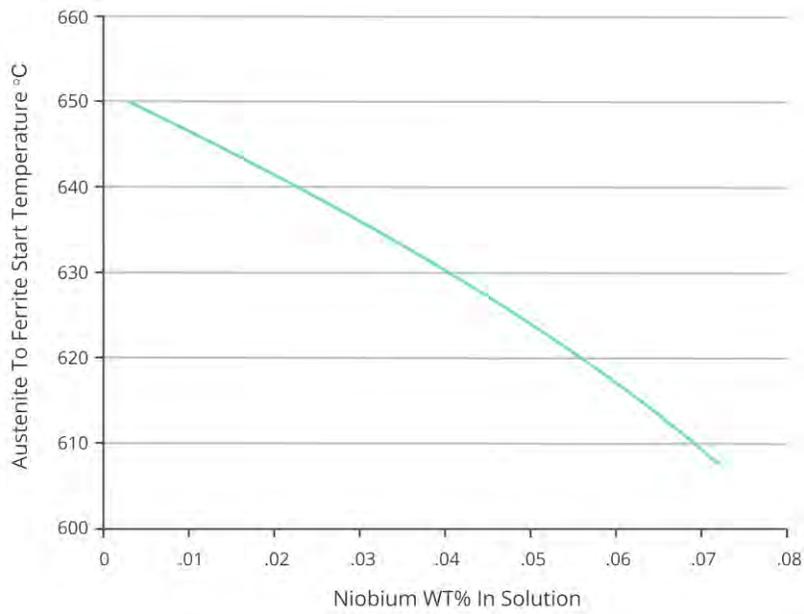

Figure 8. The effect of niobium on steel transformation temperature [30].

Many contributions to the literature have attempted to explain these dramatic effects but, arguably, the most convincing and comprehensive assessment was published by Yan & Bhadeshia [30] reporting on work sponsored at Cambridge University (UK) by Companhia Brasileira de Metalurgia e Mineracao (CBMM). This work reviewed all plausible theories and concluded that the retardation of austenite transformation is most likely due to the segregation of soluble niobium to prior austenite grain boundaries which, the authors calculate, reduces the austenite grain boundary energy by 0.076 J m^{-2} per wt% of soluble niobium.

Separating the effects of austenite grain size and niobium solute concentration, the authors further noted that 0.079% soluble niobium reduced the transformation start temperature (Ar$_3$) by forty degrees centigrade at a cooling rate of 20 degrees C s^{-1} and a prior austenite grain size of 30μm.

It has been equally well reported that niobium also depresses the austenite to ferrite transformation temperature of the coarse grained heat affected zone following welding eg the widely referenced work of Poole et al [32] see Figure 9 **but,** as further demonstrated by Kirkwood [20] in Figure 10, this effect only has a **dominating** influence in real welds at the very slowest cooling rates. Remember Graville's old work [11] illustrated in Figure 1.
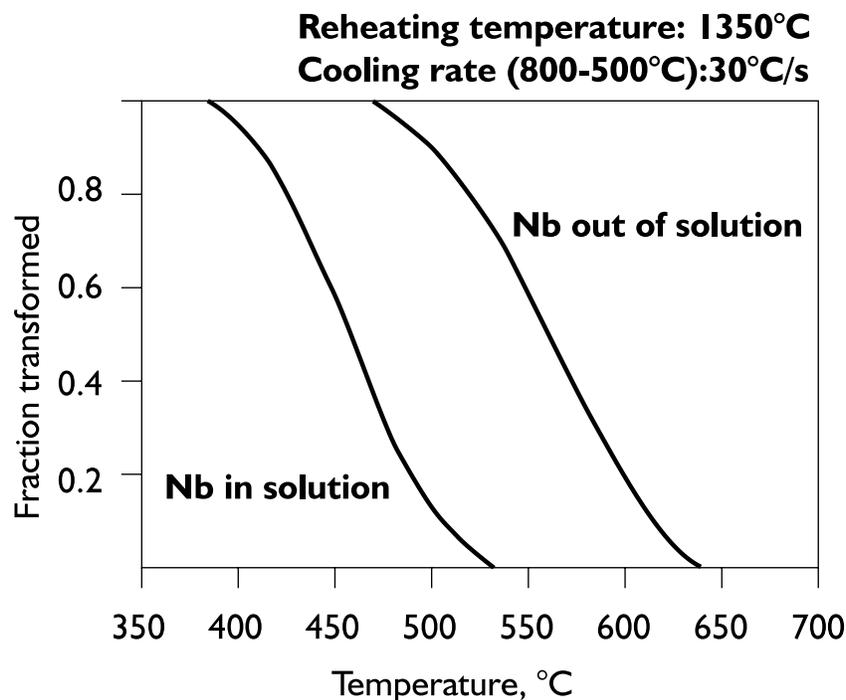

Figure 9. The effect of niobium on austenite decomposition kinetics and transformation. After Poole et al [32].
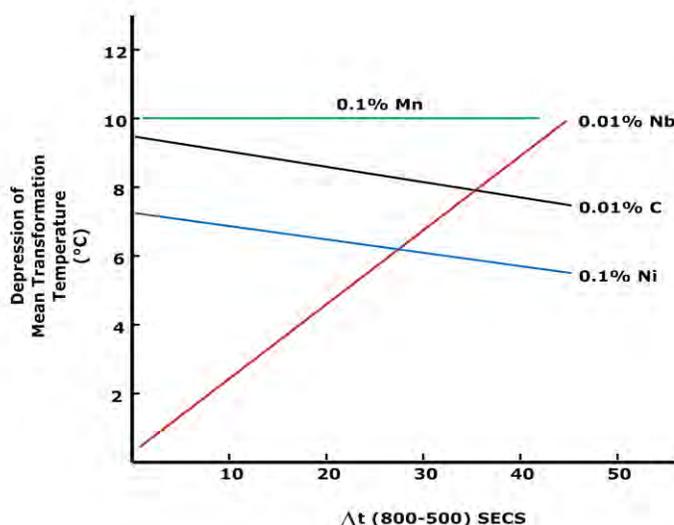
Figure 10. The effect of niobium on mean transformation temperature contrasted with the effects of other important alloying elements [20)]. The approximate effects of higher levels of each element can be computed by simple multiplication (see Table 2).

The potency of niobium, at slower cooling rates, is emphasised in Table 2 which indicates that its effect on transformation temperature, in the welding context, can be more powerful than the effects of some conventional alloying elements and, *most significantly*, as powerful as carbon.

Table 2. Approximate alloying addition required to depress CGHAZ mean transformation temperature by 40°C at a cooling rate represented by Δt (800-500) = 30secs [Derived from 5 & 20].

Element	Wt%
Carbon	0.05
Manganese	0.40
Nickel	0.67
Niobium	0.057

Weighing up all the evidence, there can be little doubt that it is the counterbalancing effect of the fine austenite grain sizes, which are experienced during the low heat input welding of niobium treated steels, which dictate the final transformation temperature and effectively negate the role of niobium in solution.

The importance of grain size is extremely well demonstrated by excellent data from Tafteh [33] across the full spectrum of CGHAZ cooling rates and I have extracted the relevant information

from Tafteh's work, for the specific case of niobium in precipitated form and re-presented it in Figure 11.
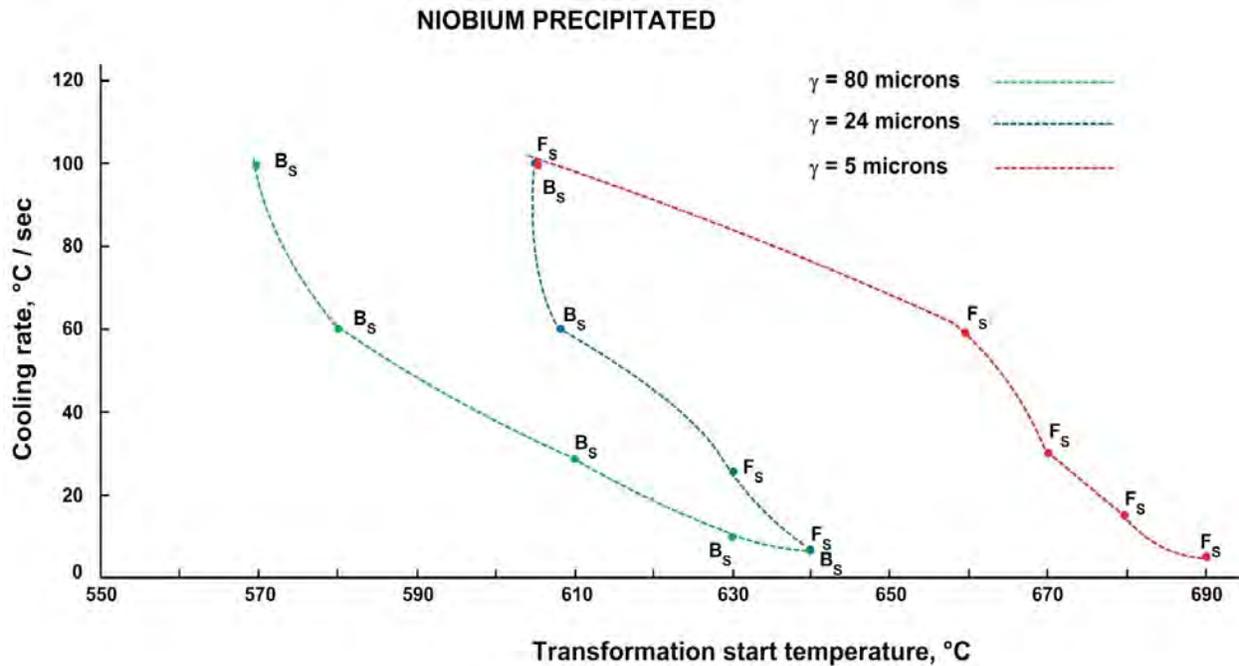

Figure 11. The overriding importance of austenite grain size on CGHAZ transformation in a 0.035% niobium steel [33].

It should be noted that at cooling rates between 40°C/sec and 60°C/sec [Equivalent to Δt (800-500) between 7.5 and 5 secs] the effect is maximised. This relates to the cooling rates experienced with low heat input girth welding processes in relatively thick walled pipe.

It follows, therefore, that whilst the IOGP rationale appears sound at first sight the practical reality is that, on balance, niobium does not depress transformation temperature at low heat inputs, because of the overwhelming effect of austenite grain size. The term for niobium in the Yurioka equation is therefore superfluous and technically unjustified.

Before continuing to address the overall effects of niobium at higher welding heat inputs it is necessary to further understand the manner in which precipitation in niobium treated steels influences grain growth across the full spectrum of welding conditions.

Figure 12, using data from various publications, schematically illustrates the observed effects of niobium on HAZ grain growth in the coarse-grained region and it is immediately apparent that this persists across a broad spectrum of weldment cooling rates.
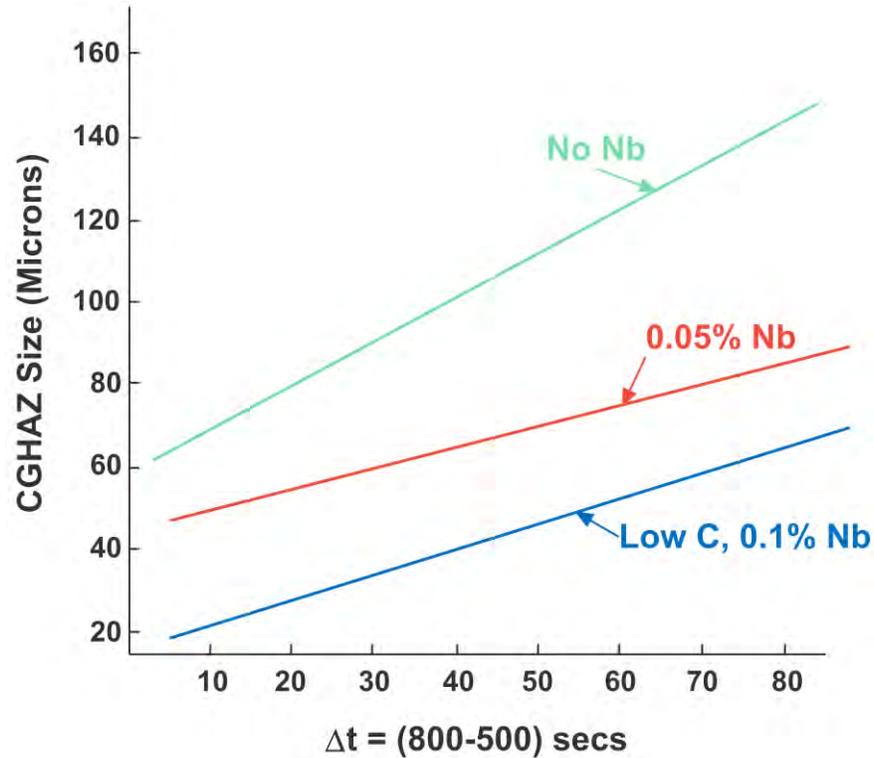
Figure 12. Schematic illustration of the effects of niobium on CGHAZ austenite grain size resulting from a range of welding thermal cycles.

The mechanism whereby niobium confers this resistance to austenite grain coarsening during welding is crucial to our understanding of the element's overall effects and whilst I, personally, believe that it is primarily a consequence of the presence of very fine Nb(CN) precipitates I have summarised the important evidence in Appendix A to enable the reader to formulate his/her own opinion and would strongly recommend the careful consideration of the key messages included therein. References [34 to 46] relate to the text of Appendix A.

Modern low carbon X70 or X80 steels containing levels of niobium in the range 0.07 to 0.11 percent generally have between forty and sixty five percent of their niobium in fine precipitate form when they are produced as strip or plate for pipe manufacture and it is these precipitates which provide such steels with their characteristic grain coarsening resistance during welding. Niobium in solution also provides a contribution but this is of much less significance in the welding context (See Appendix A).

Figure 13 provides an excellent illustration of the fine, heat affected zone, austenite grain sizes which can be encountered in low carbon, higher niobium linepipe steels processed in a manner which encourages the formation of appropriate precipitate size distributions [37]. See also Appendix A.
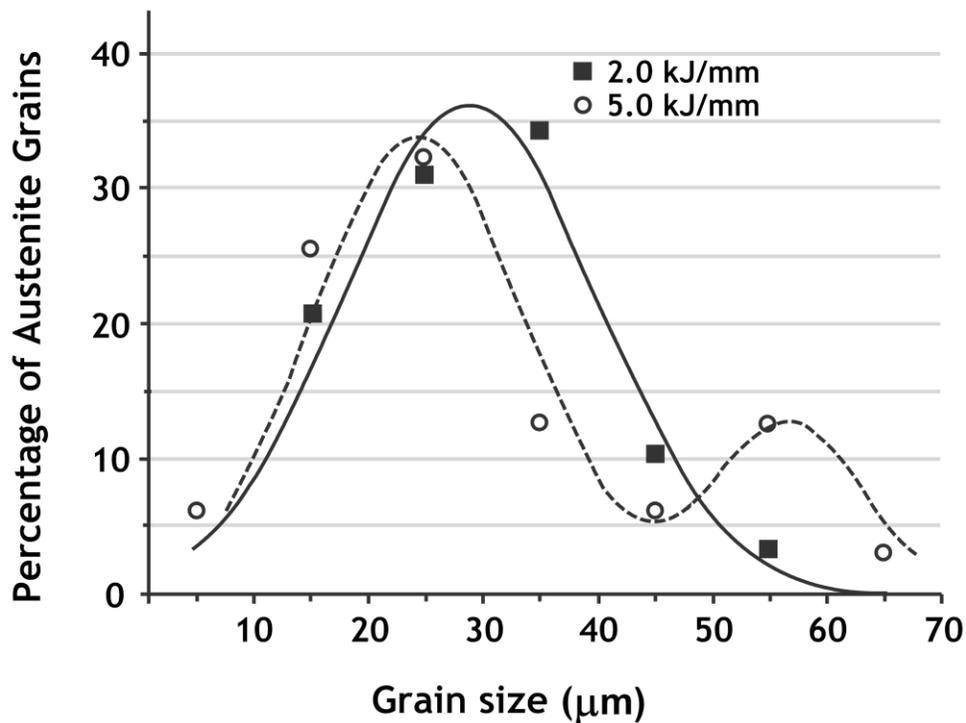
Figure 13: The effect of heat input on austenite grain diameter in a low carbon, higher niobium, high temperature processed (HTP), steel adapted from Shang et al [37]

As heat input increases and the duration of the overall thermal cycle increases the precipitates 'ripen' and begin to dissolve which inevitably decreases the efficacy of the grain refinement mechanism as illustrated in Figure 12. However, the effect remains a **major** factor in influencing CGHAZ microstructure during welding.

Whilst at the very fast cooling rates the dominance of the grain size effect is welcome it might have been anticipated that, as welding heat input increases and cooling rates decrease, the niobium free steels might be expected to exhibit the lowest transformation temperatures and, in some circumstances, better microstructures but this is **not what is actually observed in practice**.

In fact, in this higher heat input regime, it is the effect of niobium in solution (the level of which is increasing as the precipitates gradually dissolve) which now outweighs the grain size effect and depresses transformation temperature thus maintaining excellent, still relatively fine grain sized bainitic microstructures [41] without polygonal ferrite or other unfavourable microstructural components.

It is this unique ability of niobium to provide microstructural control across the full spectrum of weld cooling rates which differentiates it from any other microalloying element and makes it an indispensable ingredient of any modern low carbon, high strength linepipe steel.

It is worth re-emphasising that all the niobium related metallurgical mechanisms discussed in this paper have their efficacy enhanced in lower carbon steels, ideally containing less than 0.06% carbon.

Before providing some examples of how all this works to our advantage in the pipe manufacturing industry, and during field welding, it is worth briefly considering the range of microstructural types which may be encountered and the factors influencing their formation.

Figure 14 below provides an excellent diagrammatic illustration of the way in which microstructural development varies with transformation temperature. In simple terms if we wish to optimise microstructure and toughness we need to avoid the higher temperature transformation products at the right-hand side of the diagram and those at the extreme left where, particularly with higher carbon levels, martensite or less favourable bainites might be encountered.
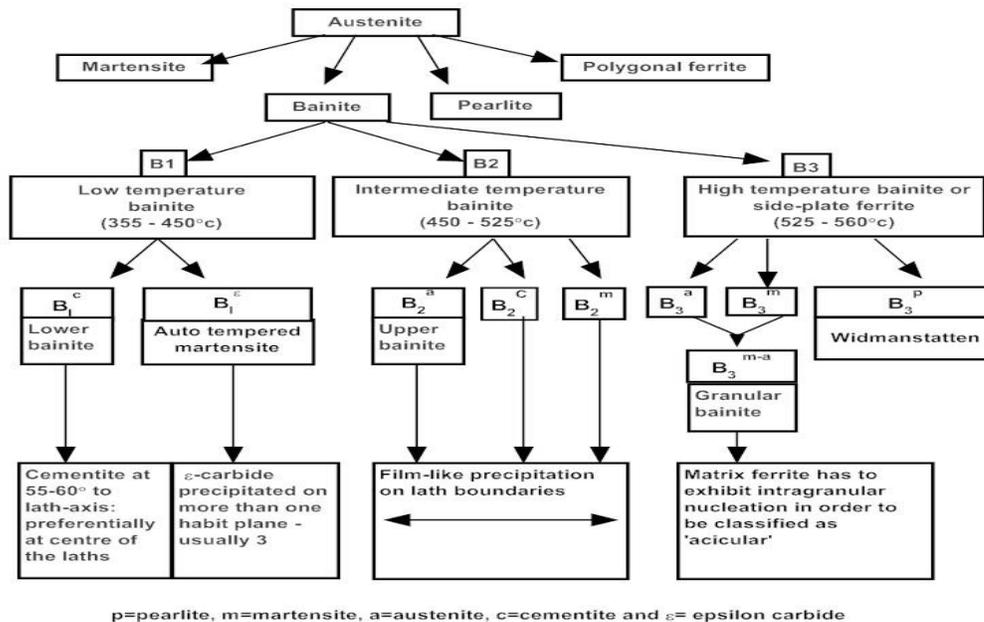
Figure 14. Possible austenite decomposition products after Bramfitt & Speer [47]

In very simple terms microstructures to the left of this diagram are encouraged by increasing conventional alloying, large grain sizes and fast cooling rates. To the right, lean alloying, fine grain sizes and slow cooling rates are important contributors.

The existence of an optimum transformation temperature, for varying carbon levels, in which toughness is maximised was demonstrated theoretically by Batte & Kirkwood [48] and Figure 15

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indicates the importance of this. Later, using experimental results from commercial steels, I will demonstrate the significance of having a proper understanding of this phenomenon and the importance of low carbon.
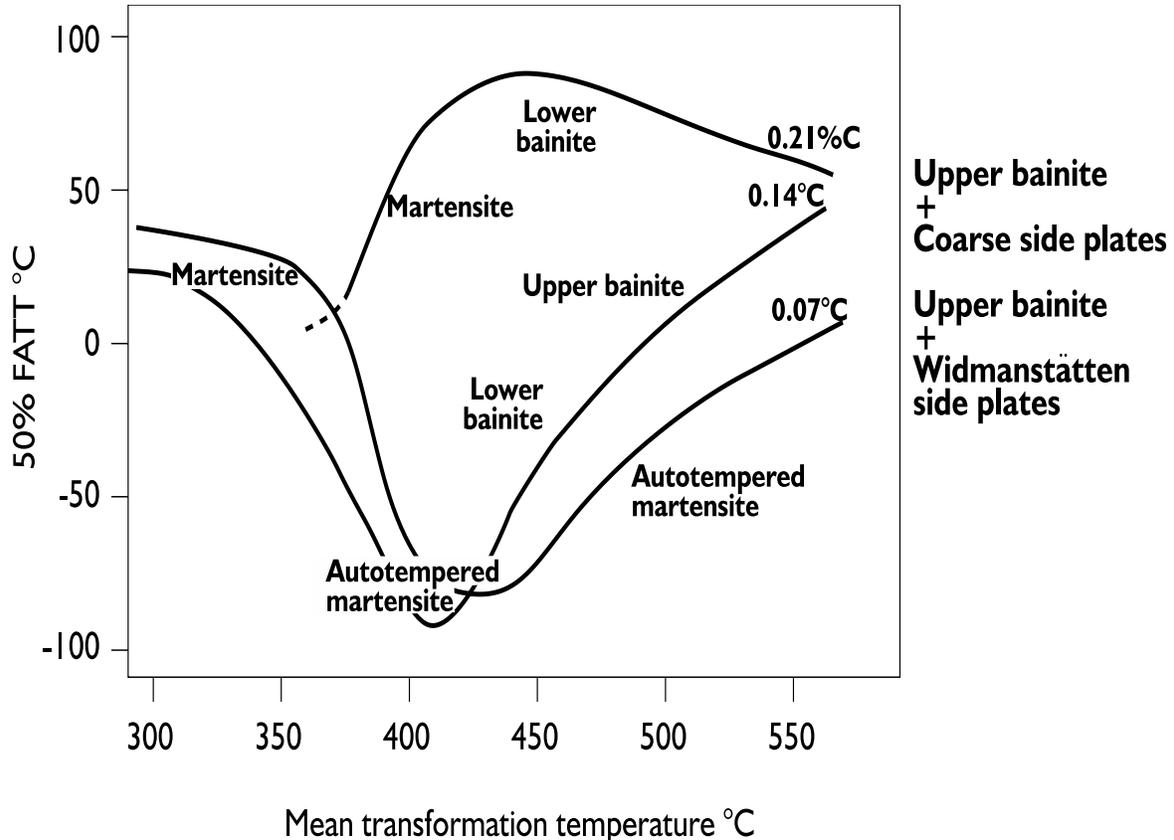
Figure 15. Theoretical relationships between toughness and transformation temperature as influenced by carbon content after Batte & Kirkwood [48].

Practical toughness results in niobium treated steels

There are many excellent references, including important contributions from Australia, China, Europe, North America and in CBMM publications, which can be cited to confirm the efficacy of niobium technology in practical line pipe steels such as the X80 used in the West-East II pipeline project and many researchers have, in recent years, made valuable contributions which could readily form the subject of a comprehensive review paper. However, for current purposes, and to emphasise the effects described in the preceeding paragraphs, I have elected to present selected results from two very valuable references which perfectly illustrate the weldability benefits which can accrue from the use of low carbon niobium treated steels in linepipe applications. The

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following graphs have all been generated from commercial steels with carbon levels ranging from 0.05% to 0.07%.

Figure 16 is a summary of published data from well documented sources. The Cheyenne Plains Project was the first significant use of X80 strength material in North America and employed low carbon steel with niobium at around the 0.095% level. A similar composition was subsequently used here in China in the extensive West-East II Project. The European spiral pipe results are representative of a similar chemical analysis that was eventually used in sections of the Southern Gas Corridor X70 project across Turkey and Greece [49].
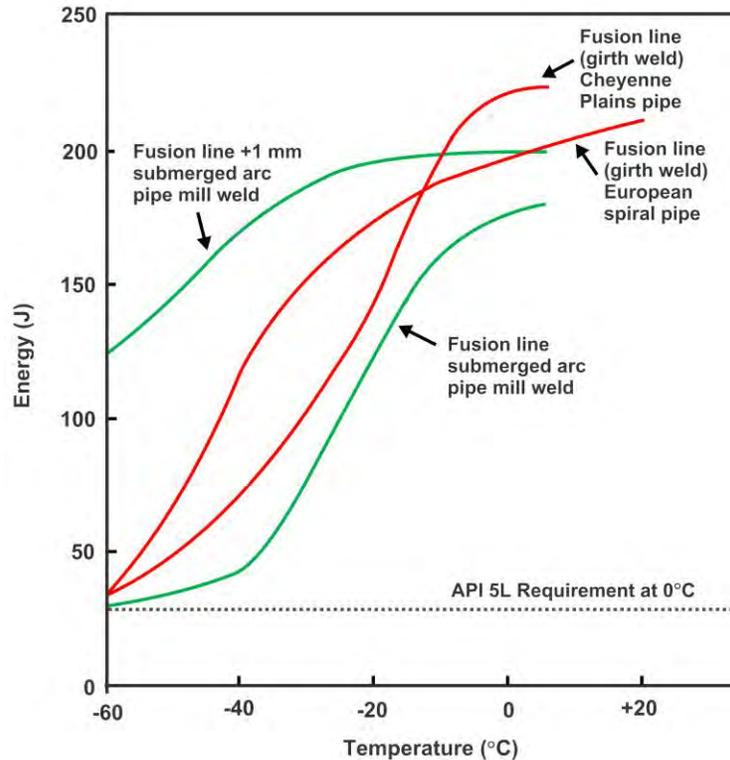
Figure 16. Published data for CGHAZ toughness from commercial production welds in low carbon, 0.095% niobium, X80, linepipe steels. [50].

The second source of my selected data comes from a very comprehensive paper published in 2013 by Frantov et al [26] the result of a joint programme between CBMM and TsNII Chermet (Moscow). This research work was specifically aimed at contrasting the behaviour of conventional Nb-V X70 linepipe steels with higher niobium X70 and X80 options with enhanced grain coarsening resistance.

A number of commercial plate/pipe materials were studied but, for present purposes, I am focusing on data from those identified in the Table 3 below.

Table 3. Compositions of selected commercial steels studied by Frantov et al [26]

	C%	Si%	Mn%	Ti%	Nb%	V%	Cr%	Al%	Mo%	Ni%
Nb-V X70	.07	.39	1.67	.013	.032	.042	-	.031	.18	.23
Nb-Cr X70	.05	.33	1.73	.013	.056	.001	.17	.033	.002	.012
Nb-Cr X80	.06	.30	1.56	.014	.094	.002	.23	.037	.01	.13

In Frantov et al's paper the vertical axis (as reproduced in the following graphs) records 'Specific Energy' in J/cm^2 to correct for the use of sub-size 5mm x10mm HAZ Charpy test pieces and, where appropriate, I have converted the horizontal axis from cooling rate °C/sec to Δt (800-500) in secs for ease of cross reference with earlier diagrams. The source paper [26] explains more precisely how the presented vertical axis data has been derived.

Figure 17 shows CGHAZ toughness data for these steels from multi pass, low heat input, gas shielded welding trials. The microstructural control with the niobium chromium options, as described earlier in this paper, results in fine grained, tough bainite to much low temperatures compared with the conventional Nb-V steel type. This is entirely consistent with expectations and with the data presented in Figure 16 for Nb-Cr X80 linepipe.

This is the regime where the fine CGHAZ size dominates behaviour overriding the effects of niobium in solid solution trying to depress the austenite to ferrite transformation temperature.
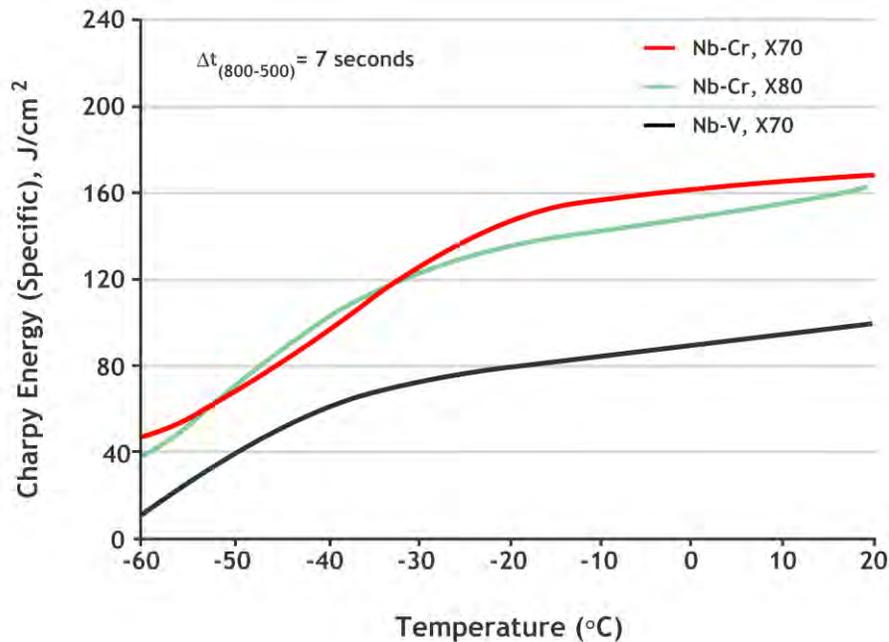

Figure 17. CGHAZ toughness data for low heat input GMAW (multi pass) welds [26].

Turning to the higher heat input welds, I have chosen simply to present the comparison between the conventional Nb-V X70 steel and the Nb-Cr X80 steel {The Nb-Cr X70 reveals very similar data to its X80 counterpart [26]}.
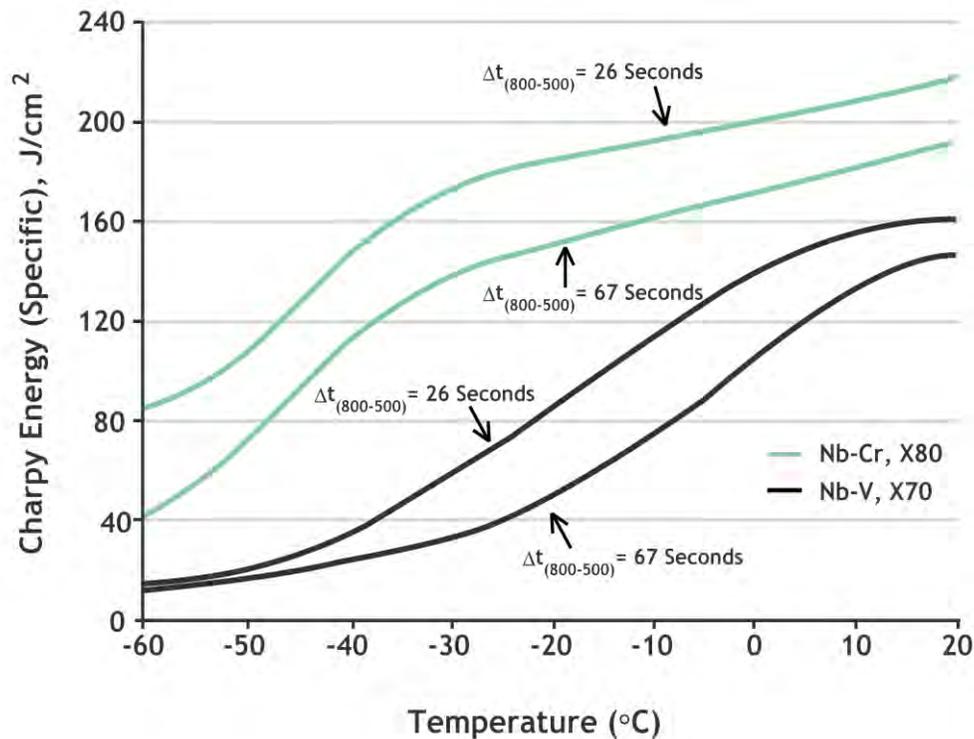
Figure 18. The CGHAZ toughness advantages of Nb-Cr X80 compared with Nb-V, X70 [26].

The results in Figure 18 confirm the predicted benefits of maintaining relatively fine grained bainite even when the heat inputs are increased up to the levels encountered in multi headed submerged arc pipe mill welding.

Recalling the predictions of Figure 15, Frantov et al's paper [26] provides excellent evidence of the anticipated effects where cooling rates become excessively fast or excessively slow and it is clear that there is, indeed, an optimum cooling rate (and by inference an optimum transformation temperature) for each alloy type. This is clearly demonstrated in Figure 19 below and it is gratifying to note that the higher niobium-chromium approach provides significantly greater flexibility at practically relevant cooling rates and lower test temperatures.
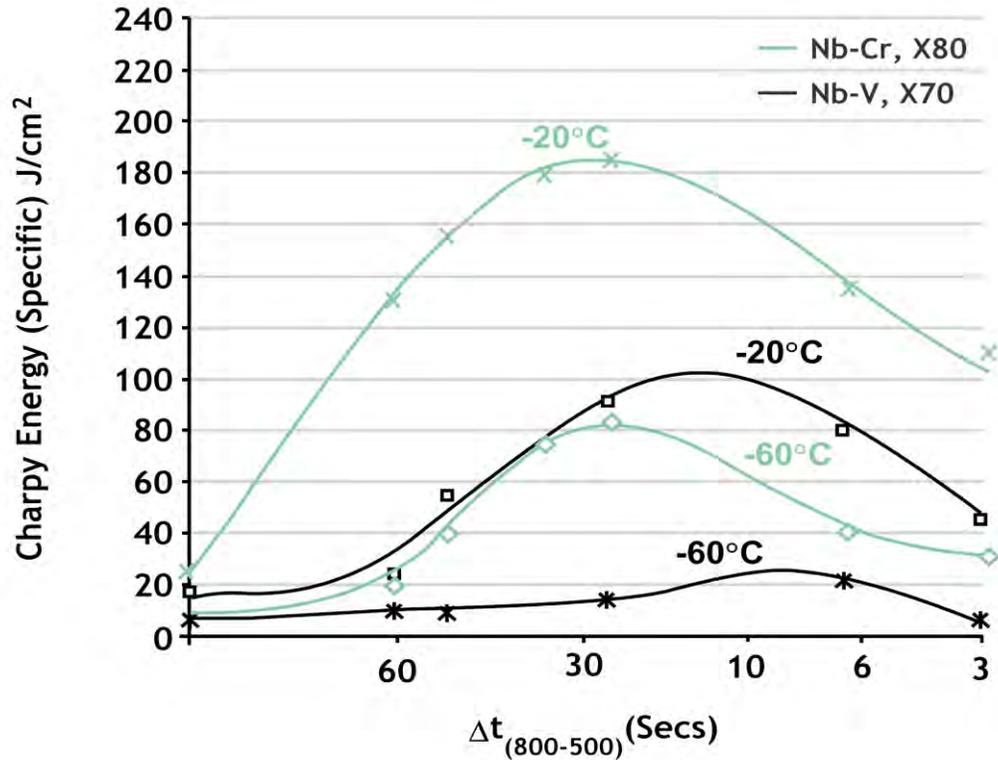
Figure 19. The effects of alloy selection and cooling rate on CGHAZ Charpy toughness at different temperatures [26].

My second question is, therefore, also answered and niobium, particularly in combination with modern steel lower carbon levels, is clearly very beneficial to CGHAZ toughness.

It is exciting to reflect on the alloy design flexibility which niobium provides and there is no other element which can simultaneously provide enhanced weldability across the full spectrum of practically relevant heat inputs and their associated thermal cycles. The way in which the grain coarsening resistance, conferred by niobium, interacts with its effect on the depression of austenite to ferrite transformation temperature is unique. I now refer to this as the:

NIOBIUM TRANSFORMATION DICHOTOMY
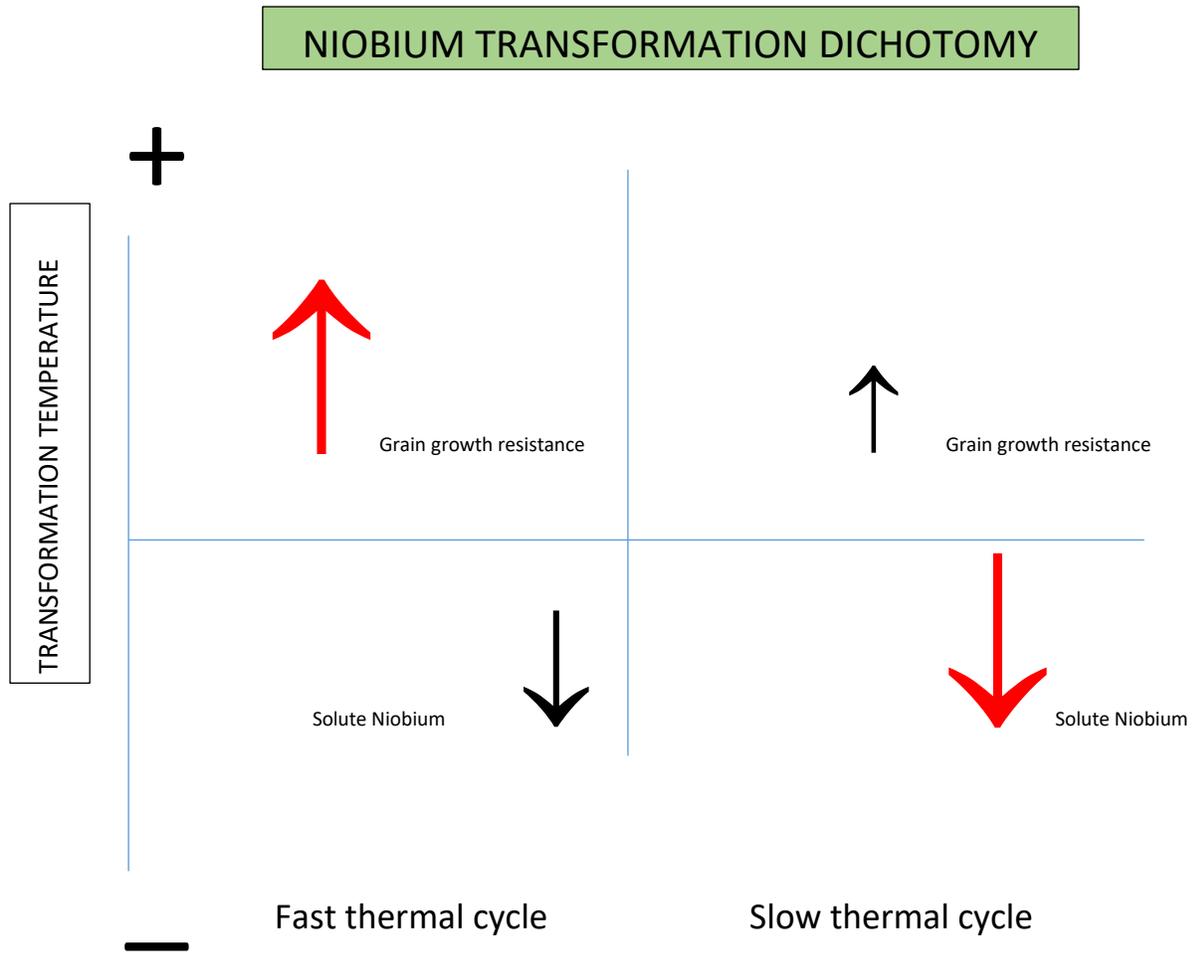
Figure 20. Niobium Transformation Dichotomy

The relative size of the 'vectors' dictates the final transformation outcome and is the key to the unique flexibility which niobium provides, conferring benefit irrespective of heat input.

The following table provides a perfect illustration of how the relative contributions of each 'vector' influence the outcome.

Table 4. Data extracted from Tafteh thesis (33) for a 0.035% niobium steel

| Δt 800-500 (secs)	Cooling rate °C/sec	Niobium precipitation state	Grain Diameter (microns)	Transformation Start Temperature (°C)
5	60	Precipitated	24	610
30	10	In solution	80	570

In considering this data, account should be taken of the fact that, in this instance, it is not the grain size change which is significant. The lower transformation temperature is actually more to do with the fact that the niobium is now in solution.

Tafteh's data (33), for the situation with niobium in solution, contrasts markedly with that shown in Figure 11 when the niobium had all been precipitated. In this case, as shown in Figure 21, grain size and cooling rate are of secondary importance. The much lower transformation temperatures indicated are clearly associated with niobium in solution.
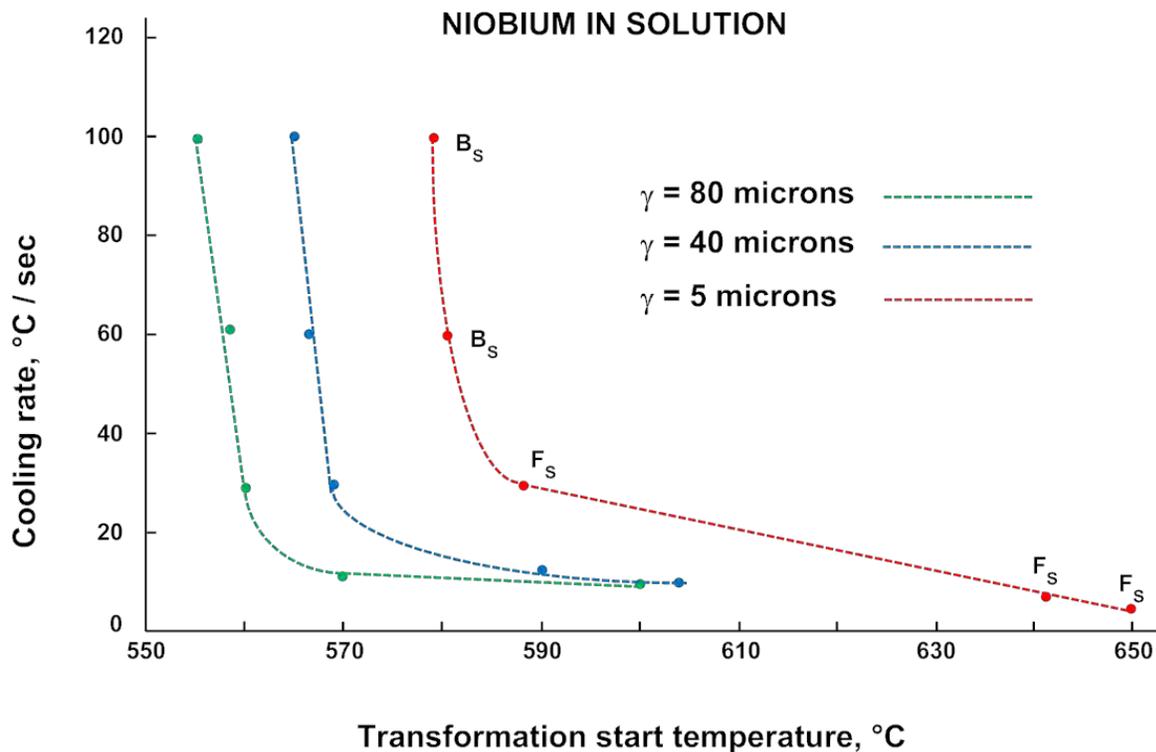

Figure 21. The reduced effect of austenite grain size on CGHAZ transformation in a 0.035% niobium steel [33].

It has taken time but the advantages of low carbon, higher niobium steels, which typically finish rolling at higher temperatures (HTP) are now much more widely appreciated and the timeline diagram included in Appendix B demonstrates this [51].

Conclusions.

1. Modern, low carbon, niobium bearing linepipe steels are particularly resistant to austenite grain coarsening across the full spectrum of practically relevant welding heat inputs. This property primarily derives from the presence of fine dispersions of Nb(CN) usually augmented by the presence of very low levels of titanium.

2. At low heat inputs and in situations where there is concern about the possible generation of high hardness levels leading to cold cracking susceptibility, the grain coarsening resistance of niobium treated steels dominates austenite transformation behavior and overbalances the effect of solute niobium which would otherwise have depressed the transformation temperature.

3. Low carbon niobium bearing steels are, therefore, less likely to generate high hardness levels in their heat affected zones and, in consequence, are significantly more resistant to hydrogen induced cold cracking.

4. There is no evidence to support the inclusion of any 'plus' factor for niobium in any carbon equivalent formula which seeks to predict the CGHAZ hardness or cold cracking susceptibility of modern, low carbon, niobium treated linepipe or structural steels when welded with low heat inputs.

5. At low heat inputs the fine grain size of the transformed austenite in modern low carbon niobium bearing steels ensures optimum HAZ toughness and significant benefits over more traditional Nb-V linepipe steel options.

6. At higher heat inputs, up to and including those associated with large diameter pipe manufacture in modern pipe-mills, low carbon niobium bearing steels are still resistant to austenite grain coarsening but their HAZ transformation behavior is now dominated by the role of niobium in solution and this combination ensures that the best possible microstructure and toughness continues to be generated.

7. Niobium has unique attributes in terms of the aspects of weldability discussed in this paper and no other element can offer the exclusive benefits across the full range of relevant welding conditions. Niobium is, therefore, and must always be an indispensable ingredient of modern low carbon linepipe steels.

Acknowledgements

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APPENDIX A

THE MECHANISM OF GRAIN GROWTH RESISTANCE DURING WELDING

There has been some debate about the precise mechanism through which niobium confers resistance to austenite grain coarsening during welding and, whilst most researchers have concluded that precipitation holds the key, others have speculated about a significant contribution from solute drag effects. This short summary assesses appropriate, relevant, evidence and concludes that precipitation effects are of overriding importance.

The ability of fine dispersions of precipitates to resist grain growth was first treated theoretically by Zener and published by Smith in 1948 [34] and, in the equation below, R_c is the critical maximum grain radius, r is the radius of the pinning particles and f is the volume fraction of the particles.

$$R_C = 4r/3f \hspace{4cm} 12$$

This equation has been modified many times over the decades, as comprehensively reviewed by Manohar et al [35], but in simplistic terms, a decrease in grain size results from a decrease in particle size (*within limits*) and or an increase in the volume fraction of particles.

Many years ago, Gladman [36] calculated the precipitate sizes which would maximise this effect and his classic diagram in Figure A1 is very much in line with recent experience with modern low carbon, higher niobium steels. See Figures A2 and A3.
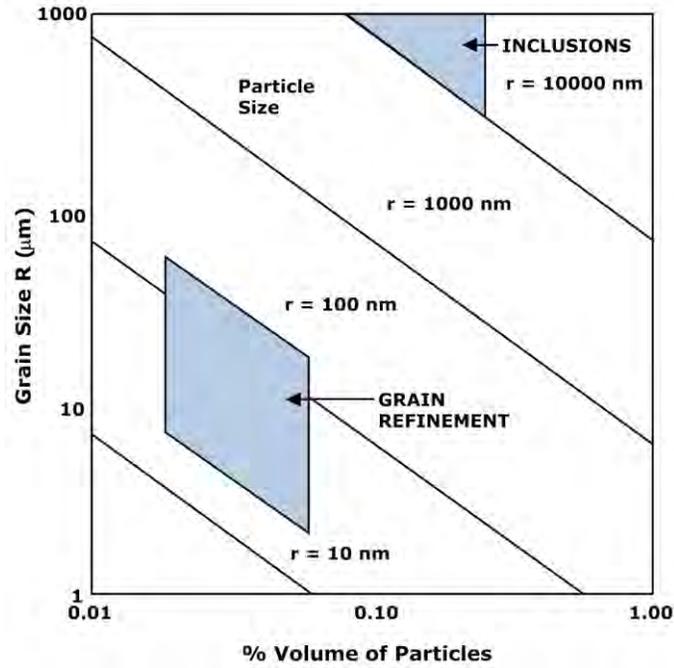
Figure A1. The relationship between grain size, precipitate size and volume fraction [36].
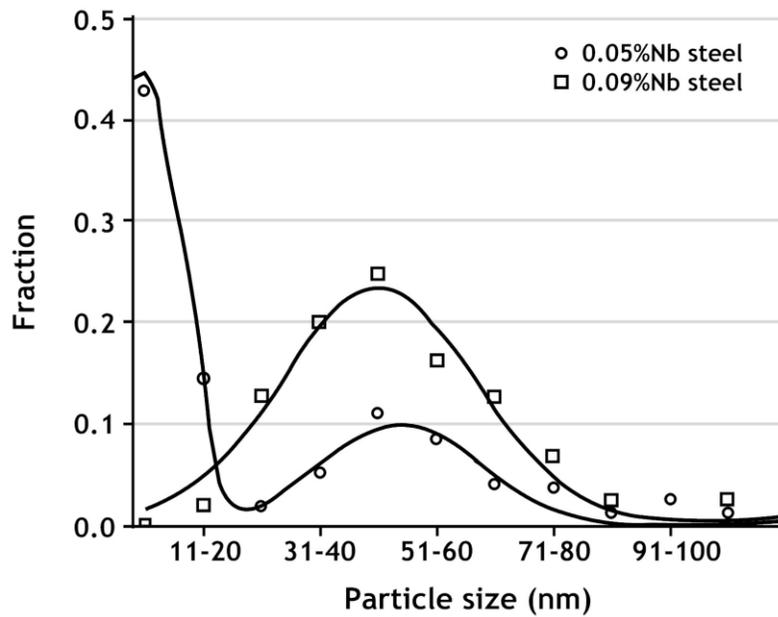
Figure A2: Size distributions of precipitates in the CGHAZ of line pipe steels with different niobium contents. Heat input 3kJ/mm. After Shang et al [37].
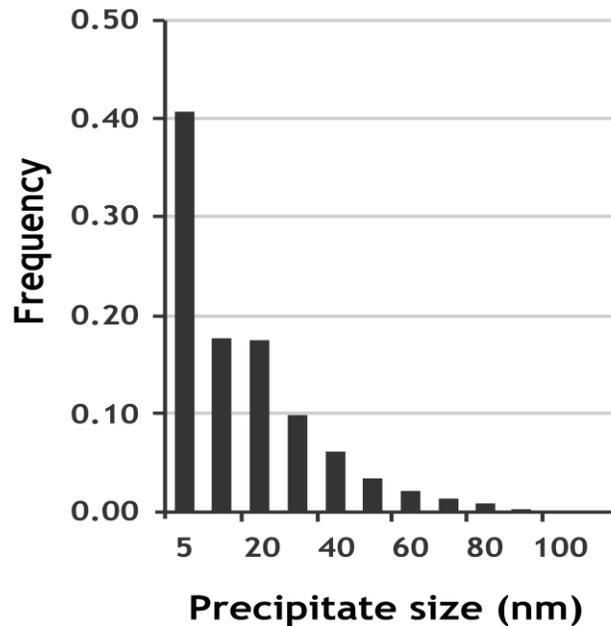
Figure A3. Size distribution of precipitates in a low carbon, 0.09% niobium, X80 steel prior to welding. After Di Shino [38, 39].

Modern low carbon X70 or X80 steels containing levels of niobium in the range 0.07 to 0.11 percent generally have between forty and sixty five percent of their niobium in fine precipitate form when they are produced as strip or plate for pipe manufacture and it is these precipitates which provide such steels with their characteristic grain coarsening resistance during welding. Niobium in solution also provides a contribution but this is considered to be of much less significance in the welding context as alluded to in the following paragraphs.

Bhattacharya (40) has reported the outcome of an interesting experiment carried out on a low carbon 0.05%, 0.095% niobium X80 line pipe steel which throws light on this debate. One section of pipe had a 3.2 kJ/mm sub arc weld prepared on it and then, the average CGHAZ diameter was metallographically assessed. A second, adjacent, section of pipe was then austenitised at 1230 degrees centigrade for one hour and then water quenched. The welding experiment was then repeated.

The CGHAZ results are included in Table A1 below which also includes details of the solute and precipitated niobium.

Table A1. The effect of original precipitate state on the CGHAZ diameter of X80 pipe following sub-arc welding at 3.2 kJ/mm.

	TOTAL Nb	Soluble Nb	Precipitated Nb	CGHAZ Diameter (μm)	Calculated Volume Percent of Nb(CN)
Original Pipe	0.095	0.0336	0.0614	48	6.97×10^{-2}
1230 °C + Quench	0.095	0.0688	0.0262	75	2.97×10^{-2}

Additionally, Figure A4 indicates that the 1230 degrees centigrade austenitising treatment has dramatically altered the ***volume size range*** distribution of the precipitates prior to welding and, as would be expected, the calculated volume percentage of precipitates was also dramatically reduced.
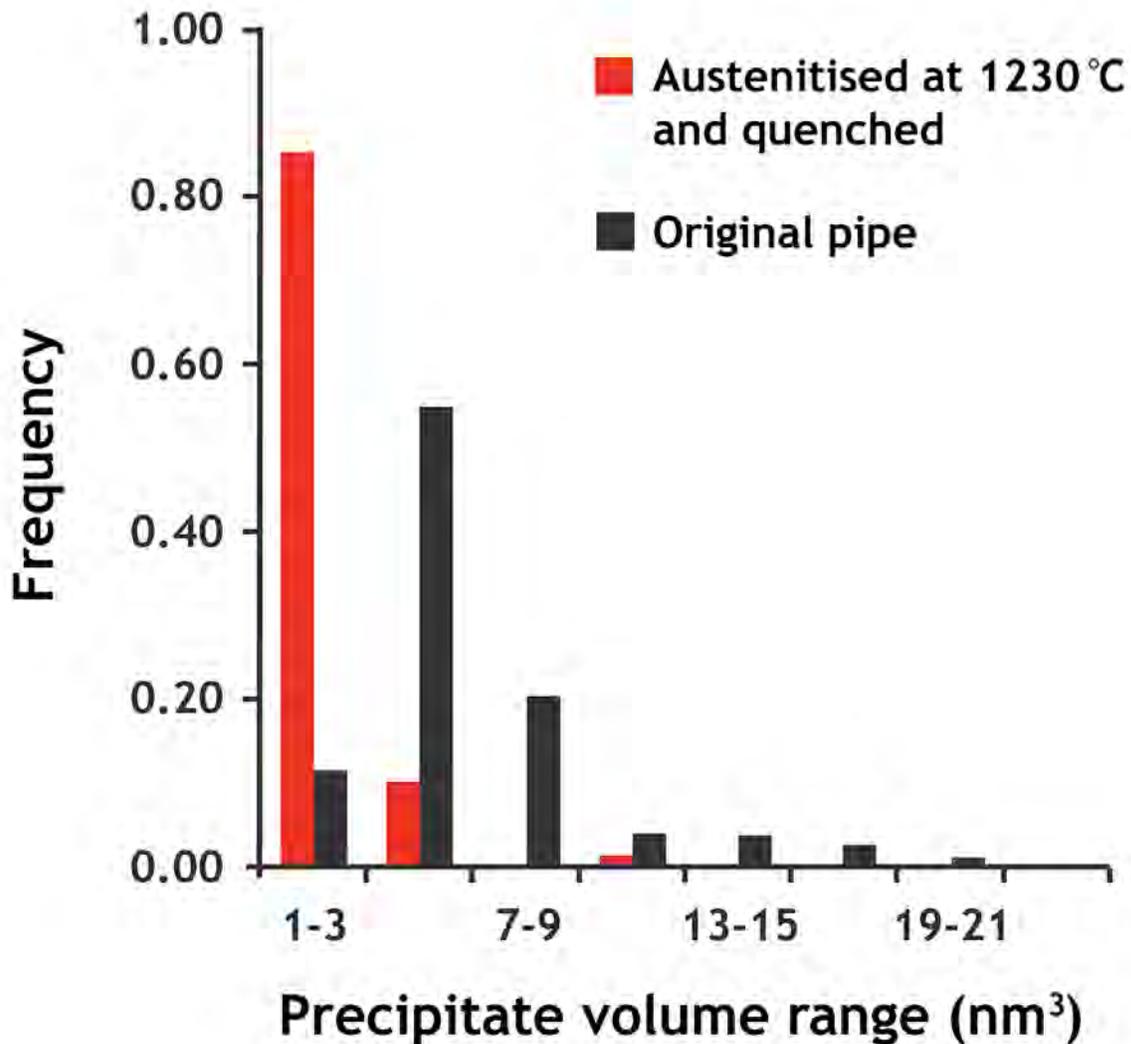
Figure A4. Change in precipitate distribution following austenitising at 1230°C [40].

These precipitate measurements were made using a small angle x-ray scattering (SAXS) technique at the High Energy Materials Science beamline facility at Deutsches Elektronen Synchrotron [DESY].

It can immediately be appreciated that the state of precipitation is of critical importance to CGHAZ growth and that the dissolution of more of the niobium and the destruction of the original 'effective' precipitates has dramatically reduced the grain coarsening resistance of the steel. In fact, Bhattacharay [40] also observed that in the pipe material which had been austenitised and quenched, before welding, many of the residual fine precipitates were TiN or TiCN which, not unexpectedly, survived the 1230 degrees centigrade treatment. These are undoubtedly the

nucleation material on which Nb(CN) precipitates have been observed to form in modern linepipe steels [42]).

This important observation not only confirms that the reduced volume fraction of precipitates partially negates the steel's grain coarsening resistance but, crucially, strongly suggests that TiN or TiCN, on its own, doesn't have the ability to provide the very fine CGHAZ sizes we get in modern low carbon, niobium microalloyed steels. This is consistent with the observations of Subramanian et al who have demonstrated that the Zener force resisting austenite grain growth is much more powerful with the composite Nb(Ti)(CN) than with Ti(CN) or Nb(CN) alone [43].

Ikawa et al [44] have indicated that 60-80 percent of austenite HAZ grain growth, during welding, occurs during the heating cycle reaching a maximum growth rate just before peak temperature whilst, during cooling, the growth rate slows very rapidly even in the early stages of the cooling cycle.

Fujiyama et al [45] have also studied the relative roles of the solute drag effect and precipitates in titanium microalloyed steels during CGHAZ growth and a diagrammatic illustration of their findings, reproduced here in Figure A5, confirms the overriding role of precipitates versus the solute drag contribution.
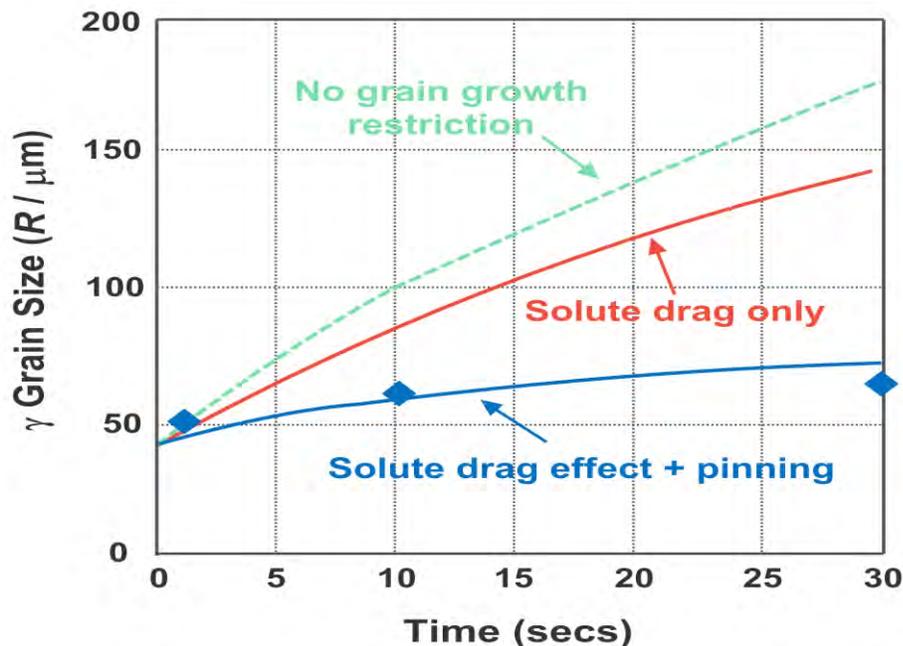
Figure A5. The relative contributions of solute drag and pinning in a titanium microalloyed steel held at 1200°C [45].

Of course, the relative contributions will change slightly dependent on the precise composition of the precipitates under consideration but the principles Fujiyamam et al set out in their paper are consistent with other evidence in the literature and the author's own experience.

Whilst it is dangerous to generalise and make tenuous assumptions when comparing the roles of niobium during thermo mechanical controlled processing (TMCP), recrystallisation and during the

thermal cycles associated with welding, Hutchinson et al [46] have theoretically demonstrated that, in austenite containing 0.1wt% niobium, fine precipitates make the dominant contribution to grain coarsening resistance in preference to any solute drag mechanism. This seems to be particularly the case the higher the austenite temperature and when the precipitates exceed 2-3nm radius in size.

As heat input increases and the length of the overall thermal cycle increases the precipitates ripen and begin to dissolve which inevitably decreases the efficacy of the grain refinement mechanism as illustrated in Figure 12 in the main text of this paper. However, the effect remains a major factor in influencing CGHAZ microstructure during welding.

In the current author's opinion, it seems reasonable to conclude that it is the role of precipitation which is dominant in conferring austenite grain coarsening resistance on niobium treated steels during welding. Solute drag may also be involved, but the evidence suggests that its contribution is much less significant.

APPENDIX B

1960s
Research provides stimulus for development of low carbon steels with niobium levels up to at least 0.12 percent.

1971
'Pearlite free' low carbon X70 steel with niobium and molybdenum commercially applied in Canada.

1972
First 'Arctic' grade X80 molybdenum free linepipe steel produced based on a low carbon, 0.10 percent niobium concept.

1980
Low carbon, nickel X70/80 developed in Italy with 0.14 to 0.16 percent niobium with outstanding properties.

1983
Full scale demonstration heat of the chromium-niobium HTP steel produced in Japan, sponsored by CBMM, and evaluated internationally.

1990s
Further refinements of low carbon pearlite free steels now commonly referred to as acicular ferrite or bainitic ferrite steels.

1998
The Pemex Cantarell project uses the pure HTP concept for a Gulf of Mexico, thick wall X70, sour service (pH=5) pipeline.

2003
HTP concept pipe also used for the Cameron Highway crude oil project in the Gulf of Mexico, the largest offshore pipeline system in the USA.

2004
Cheyenne Plains - First onshore X80 pipeline in the USA and a significant portion of the gas line utilizes HTP low carbon, niobium-chromium steel.

2008
Half of the steel for the Kinder Morgan 1,323 mile gas pipeline uses HTP steel similar to that used for Cheyenne Plains.

2010
China adopts HTP technology and applies it successfully in their 5,500 mile X80, West-East II high pressure gas pipeline.

2015/16
310,000 tonnes of X70 low carbon, niobium HTP steel supplied for a key section of the TANAP gas pipeline project, and a further 75,000 tonnes to the TAP project.

2017+
Low manganese, 'sour service' variants of HTP steels and optimized 'OHTP' steels with carefully tailored chemistry will become available.

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Niobium Nb

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