Applications of Niobium
as an Alloying Element

NIOBIUM IN STAINLESS STEELS

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Introduction

It is only a century ago that alloy steels began to be introduced to replace the theretofore ubiquitous carbon steels with materials of improved properties. Such alloying elements were first introduced in 1868 (1) with the tungsten air hardening steels and in 1886 (2) with the austenitic manganese steels, but it was not until 1900 that nickel, chromium and silicon were introduced into engineering, tool and magnet steels (3, 4). It is only some seventy years ago that the stainless steels were discovered, more or less accidently by Brearley in England, and Strauss and Maurer in Germany (5), Brearley being responsible for the 13 percent Cr martensitic cutlery steels whilst Strauss and Maurer discovered the austenitic 20 percent Cr, 7 percent Ni alloys. Both discoveries were made in a search for quite different types of material, but it is significant that both alloys contained more than 12 percent Cr which is the critical level for corrosion and oxidation resistance. Thus both alloys displayed what was to become universally accepted as the property of "stainless" (6).

The corrosion resistance properties quickly lead to the application of the steels to chemical plant components, and by the 1930's it had been appreciated that molybdenum additions could produce superior corrosion resistance particularly in sulphuric acid, and improve the pitting corrosion resistance. The significance of chromium carbide precipitation in intergranular corrosion in welded or reheated structures, "weld-decay", was also understood (7, 8) and the use of niobium to stabilize against such intergranular corrosion was rapidly developed (9). These stabilized steels were later selected for high temperature applications such as superheater tubes and turbine blades largely initially because of their good oxidation resistance. It is, however, interesting to realize that the stainless steels which were developed essentially for ambient temperature corrosion resistance, also have remarkably good high temperature creep resistance, and in this context the use of niobium has been crucial to the development of many creep resisting steels.

The introduction of the Argon - Oxygen - Decarburization (AOD) steel-making process in about 1970, which enabled carbon contents below 0.03 percent to be economically achieved on a tonnage production basis has had important implications for strength, ductility, corrosion resistance and toughness. Amongst other things, it has been responsible for some decline in the demand for niobium by the stainless steel industry since 1973, because stabilization against intergranular corrosion is unnecessary when the carbon content of the steel can be kept below the solubility limit for $Cr_{23}C_6$ in austenite at temperatures in the range 350-800 **C**. However, there are dangers and problems associated with ultra low carbon contents, particularly involving a tendency for increased grain growth due to the absence of pinning particles, and the need for somewhat enhanced nickel content to offset the **loss** of stabilization of the austenite by carbon. In addition, where niobium is needed to impart creep and high temperature strength, the use of ultra low carbon contents may well be self defeating.

The metallurgy of stainless steels is complex, although recent reviews of some of the basic principles have been published without concentrating on the specific role of niobium (10, 11). Also, there has been a recent overview of the structure-property relationships in stainless steels (12). Without doubt there is potential for further alloy development; indeed, this is essential if markets are to be preserved and/or created for the products supplied by the ever increasingly sophisticated and productive steelmaking and processing plant and techniques. Nor should the need for improving steel manufacture and processing methods be overlooked, there being a clear potential for applying the thermo-mechanical processing developed **so** successfully for the low alloy steels, to the stainless steels. Progress may not, however, be **so** rapid as in the low alloy and tool steels, as the necessary economic impetus may not be *so* urgent, but it would seem that increased usage of niobium will occur as new steels and processes are forthcoming.

The purpose of this paper is to summarize some of the salient features of the role of niobium in stainless steels with a major emphasis on the physical metallurgy. The reader is referred to standard text books on stainless steel for further information on the diverse range of steel grades, mechanical properties, corrosion resistance, high temperature properties, etc.

The Types of Stainless Steel

There are several major types of stainless steel.

Martensitic steels

These contain 10-17 percent Cr with 0.03-2.0 percent **C** and upto ~ *4* percent Ni. In addition, they may contain varying amounts of additional alloying elements, molybdenum, vanadium, niobium, aluminum and copper, with occasionally the very expensive alloying element cobalt for specific purposes. The alloying elements are often used to increase the tempering resistance of the martensite, or to impart a precipitation hardening effect. At solution treatment temperatures, typically 950 C-1100 C, the steels are austenitic but transform partially or completely to martensite on cooling, the extent of the martensite transformation depending on the composition, solution treatment temperature and rate of cooling. Because of their high hardenability, martensite forms in these steels even at very slow cooling rates, resulting in air hardening steels in large section sizes. The steels require tempering

to produce useful strength-ductility-toughness combinations. A major survey
of this type of steel is available (13), and in general there have been few
significant developments in recent years. Major uses for these alloys
include chemical and petrochemical plant, power generation, construction, gas
and steam turbine components such as turbine or compressor blades and discs,
and a wide range of aircraft engine and structural components, including high
strength corrosion resistant fasteners. The higher carbon steels are pre-
eminent in the fields of corrosion and heat resistant tools and bearings,
and, of course, for cutlery.

A sub-group of the martensitic steels may be considered to be the
controlled transformation or precipitation hardening (PH) stainless steels.
In these the composition or solution treatment temperature are adjusted **so** as
to control the M temperture. In the solution treated condition, therefore,

the structure may vary from fully austenitic to fully martensitic. The fully
austenitic steels may be cold formed, during which treatment there may be
partial transformation to martensite, transformation thereafter being com-
pleted by a relatively simple sub-zero treatment or by a tempering operation.
Subsequent tempering of the martensite is usually carried out at temperatures
up to *500* C, which in appropriate compositions, can produce marked precipita-
tion hardening and very high strength levels. The control of the transforma-
tion behavior is not easy, and many steels of this type have been modified to
become fully martensitic after cooling from the solution treatment tempera-
ture. Applications have been mainly in the field of high strength: weight
ratio components for aerospace and military hardware.

Ferritic stainless steels

Containing *12-26* percent Cr, generally little or no nickel, with addi-
tions of molybdenum, niobium and titanium, and low carbon and nitrogen
contents, these steels are frequently fully ferritic from room temperature to
the melting point. They are reasonably formable, can be highly corrosion
resistant, but suffer from being not easily weldable and from inadequate
toughness. A major advantage of this type of steel is its resistance to
stress corrosion cracking in chloride environments. Recent developments have
been the production of ever lower interstitial carbon and nitrogen contents,
which can exacerbate the well known tendency for ferrite grain'coursening due
to the absence of pinning particles in the forms of carbides and nitrides.
This can offset any benefit in toughness conferred by the low interstitial
contents. The chromium content has also been increased, with the introduc-
tion of appreciable amounts of molybdenum, to improve the general, and
particularly the pitting corrosion resistance. The highly stable ferrite in
such steels allows up to- *4* percent Ni to be introduced without producing
austenite, and this is reported to improve the toughness (14), but the effect
of the nickel on stress corrosion cracking requires attention. Major appli-
cations are in sheet products for kitchen-ware, architecture, automobile
trim, and in the chemical, food and transportation industries. Uses in heavy
chemical plant have been inhibited due to the low fracture toughness and the
tendency for *485* C embrittlement.

Austenitic stainless steels

The austenitic steels contain *18-30* percent Cr, *7-25* percent Ni and low
carbon contents, often below *0.03* percent. Common alloying additions are
molybdenum, niobium and titanium although many other alloys are employed for
specific purposes, e.g. precipitation hardening. These steels are predomin-
antly austenite at all temperatures, but depending on the composition can
either:

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a. Contain varying amounts of delta ferrite at the solution treatment temperature or

b. Contain varying carbide and intermetallic phases over a range of temperatures below the full solution treatment temperature or

c. be unstable with respect to martensite formation, the martensite forming during cooling from some higher temperature, during cold working or during sub-zero treatment, and being dependent on the composition and thermal treatment.

Manganese is invariably present in amounts usually up to 2 percent, and increases the solubility for nitrogen. Consequently, austenitic steels conventionally contain <u>rather hi</u>gher nitrogen contents than low alloy steels, typical values being of the order of 0.015-0.05 percent. Special high strength austenitic steels may contain up to 0.5 percent N but only if the manganese content is increased, sometimes to as much as 15 percent. However, because of the austenite stabilizing ability of manganese and nitrogen, combinations of up to 10 percent Mn with up to 0.25 percent N are used to replace the more expensive alloying element nickel, and some 4-7 percent Ni may be saved in this way. The uses of the austenitic stainless steels are too numerous to detail, but may be found in standard text books and in many steel manufacturer's brochures. Table I gives the compositions of some standard stainless steels, together with some non-standard proprietory compositions. In recent years (10, 15), there has been the development of two phase austenite - delta ferrite stainless steels, the duplex stainless steels. These comprise structures of equiproportions of delta ferrite and austenite, and frequently are produced with very fine grain sizes; the micro-duplex stainless steels. This fine grain size results naturally from the duplex structure, but is maintained by the use of niobium or titanium to form pinning carbides/nitrides which restrict grain growth, see Table I. These

Table I. Stainless Steel Types and Compositions

	AISI Type	Cr	Ni	C	Other			
Austenitic:	301	17	7	0.1				
	304	18	9	0.05				
	304 L	18	9	0.02				
	310	25	20	0.05				
	316	17	12	0.05	2.5 Mo			
	347	18	11	0.05	0.8 Nb			
	321	18	10	0.05	0.4 Ti			
Martensitic:	403	12	-	0.15				
Ferritic:	409	12	-	0.05	0.5 Ti			
	430	17	-	0.05	0.5 Ti or 0.8 Nb			
	434	17	-	0.05	1.0 Mo			
	446	25	-	0.08				
	444	18	-	0.03	2.0 Mo	0.5 Ti		
Duplex:	329	26	5	0.07	1.5 Mo			
	(FMS)	20	8	0.07	2.8 Mo	0.8 Nb		
Precipitation:	(17-4 PH)	17	4	0.04	3.5 Cu	0.25 Nb		
Hardening:	(17-7 PH)	17	7	0.07	1.2 Al			

steels have increased strength levels consequent upon their fine grain size
and the increased yield strength for ferrite compared with austenite. At
certain temperatures and strain rates they also exhibit superplastic proper-
ties. In addition, the steels are readily weldable by virtue of their delta
ferrite content, have increased stress corrosion resistance compared with the
fully austenitic steels, and are becoming widely used as corrosion resistant
castings for such applications as marine and chemical plant pumps.

The Physical Metallurgy of Niobium in Stainless Steels

Constitution

Niobium is a powerful ferrite forming element, thereby tending to
introduce delta ferrite into the solution treated microstructure in all
classes of steel. This effect is, however, complicated by the fact that
niobium combines with the austenite formers carbon and nitrogen, and removes
them from solution as undissolved NbC or NbN. Niobium, therefore, may have
an exaggerated ferrite forming capability and this will depend on the solu-
tion treatment temperature which, together with the solubility of NbC or NbN
determine the amount of carbon and nitrogen removed from solution. The
effect is further complicated by the fact that any undissolved NbC and NbN
will also remove niobium from solution in the austenite and thereby decrease
the delta ferrite forming effect. Consequently, in assessing the quantitive
effect of niobium on the constitution of a steel, only that niobium dissolved
in the metal lattice should be used, and the same applies to carbon and
nitrogen. These can be calculated from the composition of the steel, the
temperature, and the solubilities of NbC and NbN. Unfortunately, a complete
characterization of carbide and nitride solubility in the various types of
stainless steel, especially NbN solubility is not available.

A further degree of uncertainty is introduced by the fact that the
effect of niobium on the positions of the phase fields in the Fe-Cr-Ni-C
system is not known. Consequently niobium, whilst behaving qualitatively in
the same sense, i.e. as a ferrite former, will have different quantitative
effects in different base compositions. Moreover, in the fully ferritic
steels there is no data available on the solubility of NbC or NbN in high
chromium ferrite from which to calculate the amount of niobium as undissolved
NbC or NbN, although it is probable that the solubility is exceedingly
limited.

In order to overcome these imponderables, it is customary, on an empiri-
cal experimental basis, to assign a ferrite forming tendency for niobium in
terms of a "chromium equivalent". This indicates the way in which niobium
increases the ferrite content in terms of it's comparative effect with
chromium. The "chromium equivalent" for the overall composition of the steel
is then used with a similar "nickel quivalent" for the austenite forming
elements, to assess the constitution of the steel using a Schaeffler -
Schneider diagram, (16, 17, 18), Figure 1. These diagrams are useful indica-
tions, particularly for stainless steel weldments, for which much recent data
has been summarized and refined (19). It can be seen from Figure 1 that
besides indicating the delta ferrite content, the tendency for the austenite
to transform to martensite is also shown. This assumes that the assigned
chromium equivalent value is the same for both delta ferrite formation and
for the depression of the M temperature, which is not necessarily the case.

Frequently there are considerable variations for the "chromium equivalent"
value of niobium, as shown by the data presented later, which reflects the
uncertainties presented by, in particular the interaction between niobium and
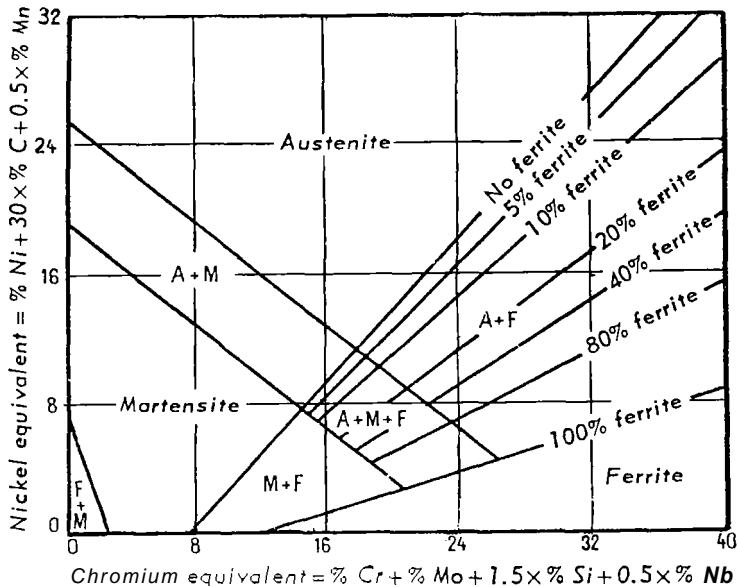carbon/nitrogen.

Figure 1.   Schaeffler ‐ Schneider Diagram.

Martensitic steels

Various chromium equivalent values have been proposed for niobium in the 12 percent Cr type steels, i.e. 1.42 (20), 1.75 (13), 2.0 (21), 3.0 (22), and 4.5 (23).   The effect can be judged from the report (24) that 1 percent Cr will increase the delta ferrite content of 12 percent Cr steels by about 14 percent.   In using these factors, it is advisable to allow for the niobium combined with both carbon and nitrogen.   There do not appear to be values available for the "chromium equivalent" value of niobium in the 17 percent Cr martensitic or PH steels.

Austenitic steels

In austenitic steels, the constitution can conveniently be referred to the Fe-Cr-Ni ternary system (25).   A typical isothermal section at a solution treatment temperature of 1000 C is shown, Figure 2(a).   By studying similar ternary sections for lower temperatures, the change in constitution on ageing or during service may be predicted, Figure 2(b).   But stainless steels contain other elements than chromium and nickel, which may be converted to chromium or nickel equivalents and the corrected composition used with the isothermal section of the Fe-Cr-Ni diagram to predict the constitution.   The "chromium equivalent" value of niobium is often stated to be 0.5 (16, 17, 26, 27), but several authors (26, 27) state that the carbon and nitrogen must be taken into consideration by using the effective niobium content:
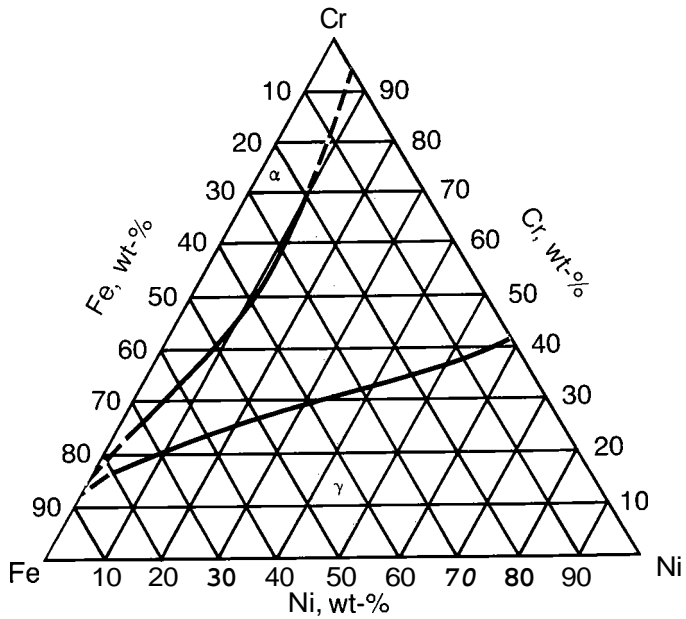
(a).   1000 C isotherm.
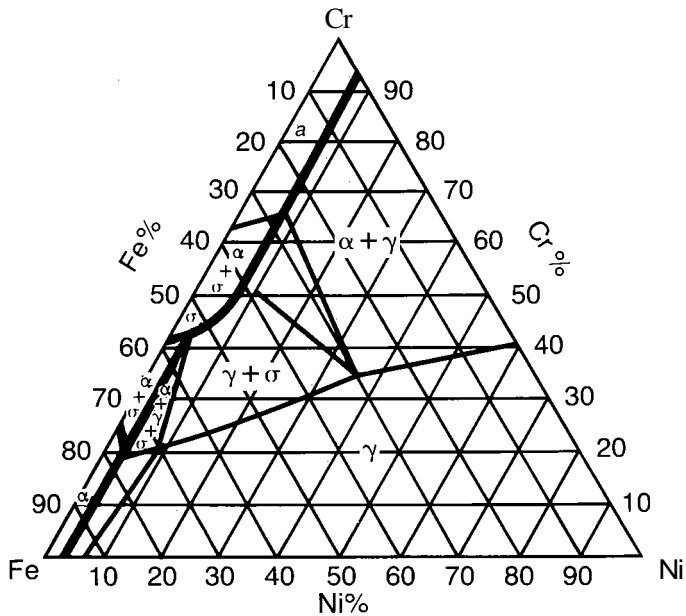
(b).   650 C isotherm.

Figure 2.   Fe-Cr-Ni Ternary System.

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$$\text{Effective Nb\%} = \text{Nb\%} - 8 (\text{C\%} - 0.03) + \text{N}_2\%]$$

$$(1)$$

A "chromium equivalent" value of 0.5 for niobium is rather low, bearing in mind the values for the martensitic steels, and also the relative amounts of chromium and niobium required to close the gamma loop (28). Using the data of Irvine et al (29), Keown has calculated that when the removal of carbon and nitrogen is taken into account the "chromium equivalent" of niobium in 18 percent Cr-Ni steels is— 1.7 (30), which is more of the order of magnitude expected. The magnitude of the effect can be judged by the fact that 1 percent Cr increases the delta ferrite content by— 15 percent. It is clear, however, that considerably more work is required before the effect of niobium on the constitution of stainless steels is adequately quantified.

The Ac_1 and Ac temperatures in transformable martensitic steels

In the transformable martensitic steels, the Ac_1 temperature controls the maximum tempering temperature which can be used without reaustenitization taking place. The only reported data (20) indicates that 1 percent Nb raises the Ac_1 temperature by 50 C. A similar figure has also been reported for vanadium (24) in 12 percent Cr steels. In view of the fact that niobium increases the A_1 temperature more than vanadium per weight percent in binary iron alloys, the above value may be low due to the presence of stable VC precipitates which decrease the effective vanadium dissolved in the ferrite, or alternatively provide nucleation for austenite and thereby produce a low Ac_1 temperature.

The Ac_3 temperature controls the temperature at which austenitization is complete, although higher temperatures than the Ac_3 will usually be required to dissolve all the NbC or NbN. There seems to be no data available on the effect of Nb on the Ac_3, but by comparing the effects of the three elements molybdenum, vanadium and niobium on the A_3 temperature in binary iron alloys (28), and the experimentally determined effects of molybdenum and vanadium on the Ac_3 temperature (31), it can be inferred that 1 percent Nb will increase Ac_3 by 190 C; this may be compared with the effect of vanadium, of 104 C per weight percent. On this basis, i.e. niobium has about twice the effect of vanadium, it might be inferred that the effect of niobium on the Ac_1 temperature may be nearer to the increase of 100 C per weight percent which as been reported for vanadium rather than the 50 C reported for niobium.

The M_s temperature and hardenability

The M temperature is predominantly dependent upon the composition of the austenite, and so will be controlled by the composition of the steel and by the austenitizing temperature, which will determine the extent of the solubility of the NbC and NbN. Little data is available for the effect of niobium on M_s, mainly due to the relatively limited use of niobium in transformable steels, and even then in very small concentrations of 0.10 percent.

It has been reported that in 0.1 percent C, **12** percent Cr steels, the M
temperature is depressed by **11** C per percent niobium **(20),** and the same value
is quoted by that work for vanadium. This depression of the M_s by niobium
seems to be small. If the effect is indeed comparable to that of vanadium,
it has been shown that in low alloy steels **1** percent V depresses M by **20**
C **(32),** whilst in **17 1/2** Cr transformable martensitic steels the effect is
increased to **32** C per **1** V. Consequently, it seems most probable that an
overall effect of niobium is to depress the M temperature by ⁻ **25** C per 1
Nb.

In the austenitic stainless steels, the formation of martensite is an
important factor in controlling the formability of the steel. When marten-
site forms during straining, the work hardening rate increases, which in-
creases the maximum uniform strain. This imparts improved stretch form-
ability, and it is found that some **3-6** percent martensite **is** formed at a true
strain of **0.2** is optimal **(34)** Figure **3,** consequently, the M_d temperature,
i.e., the temperature at which martensite starts to form during deformation,
must be controlled to be at some critical level above room temperature.
Whilst the effects of a number of common alloying elements are known on the
M_d, there is no data for niobium. It cannot be assumed that the effect of an
alloying element is the same for its effects on both M and M_d, because the
M_d will be affected by the stacking fault energy of the austenite, which will
be discussed later. The stacking fault energy controls the ease with which
the close packed hexagonal ε-martensite is formed, and ε martensite is the
pre-cursor of normal α martensite in stainless steels, the α often forming at
the intersection of ε martensite laths.

No systematic data is available on the effect of niobium on harden-
ability in **12-17** Cr steels. The effect of niobium dissolved in the austen-
ite will undoubtedly be to increase the hardenability, but as in the case of
vanadium, niobium would be expected to have variable and complex effects.
Whilst niobium dissolved in the austenite increases hardenability **(33)** any
undissolved NbC or NbN will detract from this by lowering the effective
dissolved niobium and carbon. The effect of the lower nitrogen would prob-
ably be minimal, but the lower carbon could decrease the martensitic hard-
ness. In addition, undissolved NbC or NbN will refine the austenite grain
size, which in turn will further lower the hardenability. The effect of
niobium will, therefore, depend on the composition, austenitizing temperature
and solubility relationships. However, due to the high basic hardenability
provided by the **12-17** percent Cr in these transformable stainless steels, the
overall influences of niobium, be it positive or negative, is likely to be
minimal on the hardenabilty.

Stacking Fault Energy

In austenitic stainless steels particularly, the stacking fault energy
is important because it influences the work hardening rate, which in turn has
a profound influence on the forming characteristics. Increasing the stacking
fault energy decreases the work hardening rate, and vice-versa.

Various equations have been published to describe the effect of composi-
tion on the stacking fault energy of austenitic stainless steels **(35, 36),**
but these do not include a factor for niobium. There is considerable diver-
gence of the data on the quantitative effects of the various alloying ele-
ments. Dulieu and Nutting **(37)** have concluded that niobium increases the
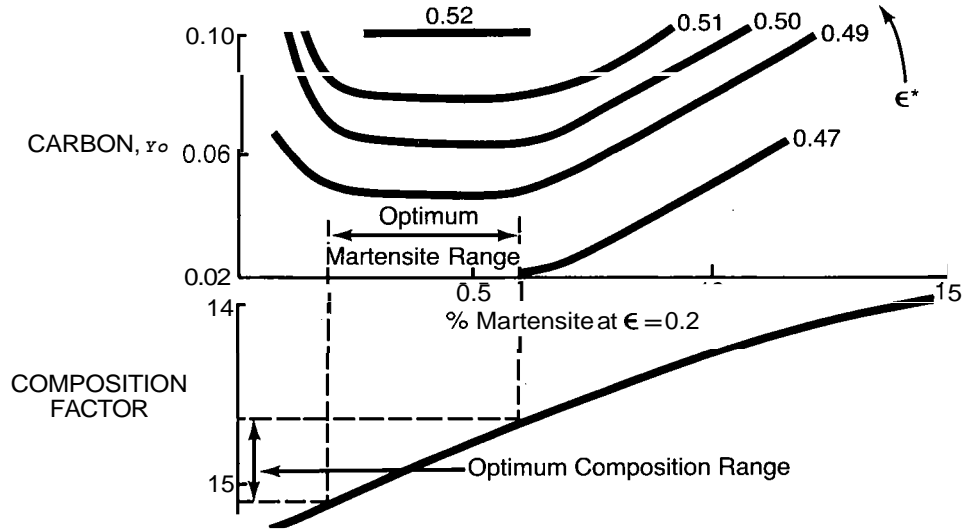
Figure 3. Nomogram showing effect of Carbon and Martensite on Strain.

stacking fault energy of austenite by approximately 2 mJ m^{-2} per weight
percent. On the other hand, the opposite effect has also been suggested
(38), although no precise value has been given. Using the results of careful
analyses of the effect of niobium on the work hardening rate of 18 percent
Cr-10 percent Ni, 18 percent Cr, 12 percent Ni, and 16 percent Cr, 25 percent
Ni austenitic steels, corrected for variations in the grain size and inter-
stitial content due to undissolved Nb(CN) (39), it was shown that dissolved
niobium slightly increased the work hardening rate at low strains but had no
effect at higher strains. It was concluded that niobium had a very small
effect on stacking fault energy, if anything slightly decreasing it. It
would appear that the increase in stacking fault energy reported for niobium
(37) may well have been due to the removal of nitrogen as NbN; it is generally
agreed that nitrogen has a marked effect in decreasing the stacking fault
energy.

Carbides and Nitrides of Niobium

The most commonly occurring carbides and nitrides of niobium in the
stainless steels are NbC and NbN. Both have f.c.c. structures with a values
of 4.46A$^{\circ}$ and 4.38A$^{\circ}$ respectively (40), and it is often suggested that NbC
has an interstitial defect lattice.   There is also evidence that NbC and NbN
are mutually soluble, forming an Nb(CN) phase, and solubility studies (41,
42) have indicated that nitrogen can fill the interstitial vacancies in what
seems to be $Nb_4 C_3$, moving the stoichiometry towards Nb(CN). NbC forms
during solidification as a eutectic with austenite after the solidification
of the primary austenite dendrites, Figure 4, whilst NbN largely forms
directly from the melt as small cuboids, and it has also been shown that in
boron steels, boron can dissolve in NbC (43).   The different solidification
pattern of NbC and NbN reflects the greater stability of NbN, the enthalpies
of formation at 298K being— $-75kJ mol^{-1}$ for NbC and— $-115kJ mol^{-1}$ for NbN
(44).

Optical Micrograph x 1,500

Figure 4.   Eutectic of Niobium Carbide and Austenite.

The different stabilities of NbC and NbN are also reflected in different solubilities in austenite, NbC being more soluble than NbN (45). Many determinations have been made of the solubility of NbC in austenite in stainless steels (42, 46-49), the results being expressed in a typical solubility equation, such as the following:

$$\log [Nb] [C] = \frac{-9350}{T} + 4.55 \quad \text{(for 18\% Cr, 13\% Ni steels)} \ (42)$$

(2)

$$\log [Nb] [C] = \frac{-8358}{T} + 4.07 \quad \text{(for 20\% Cr, 25\% Ni steels)} \ (47)$$

(3)

From these relations, all of which are very similar in quantitative terms, Harries (49) has shown that the solubility of NbC increases with increasing nickel content; a similar effect has also been observed for the chromium carbide $Cr_{23}C_6$. The solubility relationships take the form of curves such as shown in Figure 5, and such relationships have been shown to have a particularly important consequence. This is that with a steel composition in which the niobium: carbon ratio is in the stoichiometric ratio for NbC, the temperature dependence of the solubility of NbC is at a maximum (50, 51). This means that the amount of NbC available for precipitation is a maximum at the stoichiometric ratio, and decreases sharply with deviations on either side of stoichiometry, Figure 6. This phenomenon explains the maximum secondary hardening (52), precipitation hardening (33) and creep strength (42) which are observed at the stoichiometric ratio, and has also been applied to stabilization against intergranular corrosion (20) and to recrystallization after cold working (49).

With increased nitrogen in austenitic steels, it is possible to combine the nitrogen with the carbon content in terms of an effective interstitial content, and using this the solubility of Nb(CN) has been **shown** to be (41):

$$\log [Nb] [C + 6/7N] = \frac{-6750}{T} + 3.21$$

(4)

Relatively, little data has appeared on the solubility of NbN, but on the basis of reported data (54), the following approximate relationship can be deduced:

$$\log [Nb] [N] = \frac{-11600}{T} + 4.84$$

(5)

Using the solubility equations, it is generally agreed (48) that the heat of solution of NbC in austenite is— 175 kJ mol^{-1},

Introducing nitrogen into the NbC lattice to form Nb (CN) reduces the heat of solution to— 130kJ mol^{-1} as the ratio of C : N in the Nb (CN) increases, but the heat of solution of NbN in austenite is much higher at ~ 220 kJ mol^{-1} as befits its greater stability, higher enthalpy of formation and lower solubility. But the introduction of carbon into NbN, or of nitrogren into NbC appears to decrease the stability and increase the solubility.
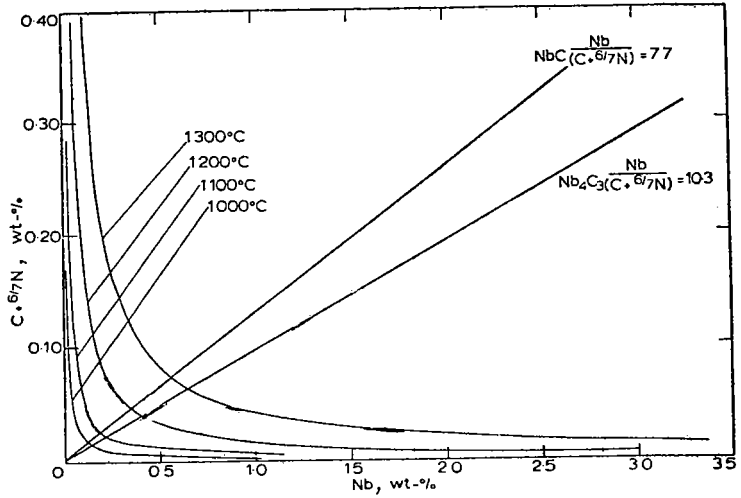
Figure 5. Solubility and Stoichiometric Compo-
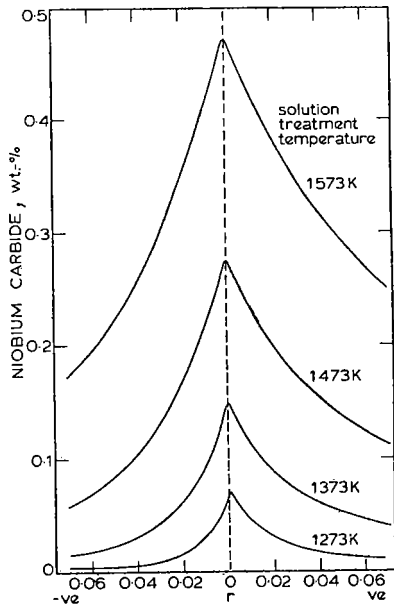sition of Niobium Carbide *(42)*.

Figure 6. Niobium Carbide available for Precipitation as
a function of deviation from Stoichiometry (50).

The precipitation of niobium carbo-nitride has been reported in 12 percent Cr steels during tempering and creep testing (45), and has been held responsible for increased creep resistance. This may be due to the relatively slow rate for formation of Nb (CN) in ferrite due to the very high

activation energy for diffusion of niobium, which at $340 kJ mol^{-1}$, is the highest of the common alloy elements in steels. The Nb (CN) is said to precipitate in the grains, most probably on dislocations. In austenitic steels, NbC precipitates predominantly on dislocations, Figure 7(a) and this is because of its large misfit with austenite, even though it does show a cube-on-cube orientation relationship. With high degrees of supersaturation induced by high solution treatment temperatures, planar arrays of precipitates of NbC are observed, the so-called "stacking fault precipitation" occurs (54-5), Figure **7(b).** Both forms of precipitation cause marked age hardening.

There is little or no data available on the solubility of NbC or NbN in high chromium ferrite, typical of the ferritic stainless steels. However, some preliminary results (57) indicate that at 990 C in 17-25 percent Cr ferritic steels containing 0.3 percent Nb, the solubility product has a value of log [Nb] [C] = -9.1. This is an exceedingly small solubility.

Any precipitation of NbC or NbN in a ferrite matrix will occur with an orientation relationship:

$$\{100\} \; NbC \; // \; \{100\} \; a$$
$$<100> \; NbC \; // \; <110> \; a$$
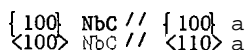
Other Carbide and Nitride Phases

In 12 percent Cr martensitic steels, the precipitate mainly responsible for secondary hardening and resistance to tempering is M_2X, where M is one of

the transition metals chromium, vanadium, molybdenum, tungsten niobium etc., and X is carbon or nitrogen. The close packed hexagonal M_2X phase is widely

occurring in many highly alloyed steels (58), and as niobium can form hexagonal carbides and nitrides, it is not surprising that it dissolves in M_2X,

increasing both the "a" and "c" dimensions of the unit cell. This probably is the reason why it accentuates secondary hardening. NbC, being isomorphous with VC, also can dissolve to large extents in VC, and give increased tempering resistance and secondary hardening in steel containing appreciable quantities of vanadium, although the vanadium also can dissolve in M_2X.

These features have been employed in the development of higher strength 12 percent Cr steels (59). Again, the M_2X largely precipitates on dislocations

in the tempered martensite with an orientation relationship:

$$\{10.0\} \; M_2X \; // \; \{100\} \; \alpha$$

$$\{00.1\} \; M_2X \; // \; \{011\} \; a$$
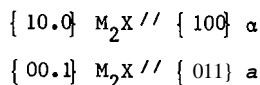
Other complex niobium bearing carbo-nitrides can also be formed during tempering the 12 percent Cr steels (60), which are based on the M_6C and M_6N

phases. Such phases are Cr_3Nb_3N which can also have iron replacing chromium, molybdenum replacing niobium and carbon replacing nitrogen. These precipitating phases, however, are predominantly confined to the grain boundaries.
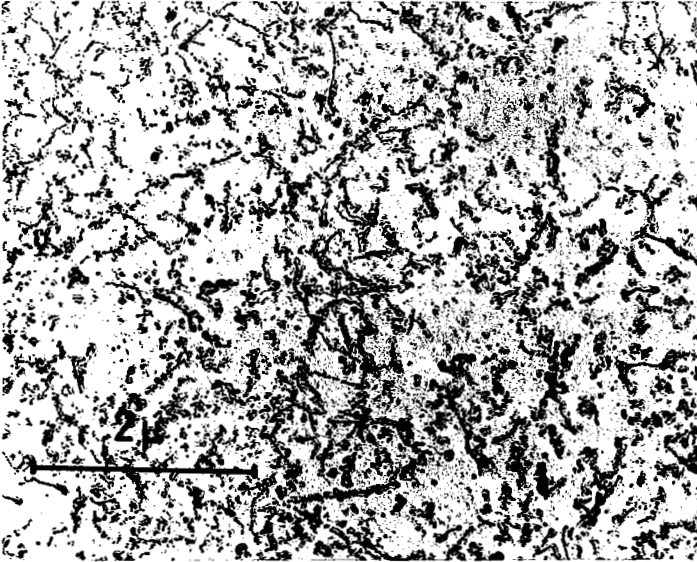
(a). Precipitation on dislocations Thinfoil x 50,000.

(b). "Stacking Fault" Precipitation. Extraction Replica x 20,000.

Figure 7.   Precipitation of Niobium Carbide in Austenite.

In the high nitrogen austenitic stainless steels containing niobium, NbN can precipitate similarly to NbC (61), but a complex chromium-niobium nitride, 2-phase, is frequently observed (62-65). This is a distorted or tetragonal body centered cubic structure in which ordering of the chromium, niobium and nitrogen atoms occurs (66) and essentially has the formula $CrNbN$. Other complex chromium-niobium nitrides are also found in nitrided iron-niobium alloys, but do not seem to precipitate in steels. A characterization of the morphology and modes of precipitation has recently been carried out in Nitronic 50 (67).

Intermetallic Compounds

Niobium can form a number of intermetallic compounds in austenitic stainless steels and superalloys, many of them leading to embrittlement. Of particular detriment in this respect is sigma phase, which is generally based on the complex cubic structure $FeCr$. Niobium can form a sigma phase with iron, and also forms in complex alloys containing molybdenum and titanium, the equally embrittling chi phase. Using the $PHACOMP$ analysis for estimating the electron vacancy number (N_v) and thus the tendency for sigma formation (68), the following equation has been developed:

$$N_v = 0.66Ni + 1.71Co + 2.66 \ Fe + 4.66 \ (Cr + Mo + W) + 5.66V + 6.66Zr + 10.66Nb$$
(6)

It can be seen that niobium markedly promotes sigma phase, which occurs when $N_v > 2.52$. However, the niobium combining with carbon and nitrogen is not active in sigma formation.

The embrittling effects of sigma and chi phases have been related to composition (69) through an equivalent chromium content:

$$Equ. \ Cr = Cr + 0.31Mn + 1.76Mo + 0.97W + 2.02V + 1.58Si + 2.44Ti + 1.70Nb + 1.22Ta - 0.266Ni - 0.177Co$$
(7)

Again, the detrimental effect of niobium in forming these embrittling phases is shown.

Sigma phase usually only forms slowly in austenite, but the presence of delta ferrite accelerates sigma formation markedly, when it occurs as a transformation product of the chromium (and niobium) enriched delta ferrite. It should be noted that niobium can readily introduce delta ferrite into the structure. In Fe-Cr alloys, sigma phase should not form above- 820 C, but sigma forming alloying elements can increase this temperature, and chi phase forms also at considerably higher temperatures than sigma phase. In general, however, sigma and chi phases form massive grain boundary constituents.

Another common intermetallic compound which forms in both ferritic and austenitic steels containing niobium is the Laves phase, $Fe_2 Nb$ in which iron may be replaced by chromium. This phase, of close packed hexagonal structure, is isomorphous with many similar phases such as Cr_2Nb, $Fe_2 Mo$, Fe_2Ti, etc. It, thus, shows wide solubility and composition ranges. The Laves phase usually, however, only forms with the higher niobium contents, and

particularly in the hyper-stoichiometric austenitic steels (42). It occurs as massive grain boundary particles and as laths within the grains, with which it has a well defined orientation relationship, and is frequently associated with embrittlement. Less frequent phases containing niobium are the silicide analogue of the $M_{23}C_6$ carbide (70), G-phase, and μ-phase, i.e, Ni_7Nb_6, all of which tend to form grain boundary particles, and embrittle.

In the super alloys, niobium forms an integral precipitation hardening phase, γ" in some modern alloys. This is based upon Ni_3 Nb, and has a body centered tetragonal structure (72). It precipitates as disc shaped particles with an orientation relationship with the austenite showing cubic parallelism. Compared with the γ' - Ni_3 (AlTi), γ" shows slower ageing response and seems to be the more stable phase. Both chromium and iron favor γ" precipitation, but there is a tendency for γ" to transform to sigma phase on prolonged overageing. It has also been shown that niobium may substitute for titanium in γ' - Ni_3 (AlTi) in iron-base superalloys.

In the high chromium ferritic stainless steels, and in the delta ferrite of the duplex stainless steels, a precipitation process often takes place in the ferrite, leading to 485 C embrittlement. This is the result of spinodal decomposition of the alloy in the miscibility gap of the Fe-Cr equilibrium system (73), to precipitate the chromium rich α' solid solution. The embrittlement effect is also accompanied by hardening and it has been shown that niobium increases the intensity and rate of hardening, and, therefore, the embrittlement effect more than any of the other commonly occurring elements molybdenum and titanium (74), Figure 8. However, the increased embrittlement can be completely counteracted by the ferrite grain refinement produced by niobium provided there is sufficient interstitial content to provide the grain boundary pinning precipitates.


Grain size control

The use of NbC or NbN particles to control and refine the grain size in both austenitic and ferritic stainless steels is well known. In the 12 percent Cr martensitic steels, use of this effect has been made to improve the toughness by decreasing the impact transition temperature (59, 75). A similar effect has been reported for 18 percent Cr- 2 percent Mo steels (76), and for 21 percent Cr - 1 percent Cr - 1 percent Mo steels (20), both of which are fully ferritic. It is important, however, for this effect to be operative, that sufficient carbon/nitrogen are present to provide the requisite volume fraction of NbC/NbN.

The theory of grain size control by pinning particles.(77, 78) shows that the critical particle radius, r_c, required to pin a grain size of radius R_o is given by:

$$r_c = \frac{6Ro}{TT} f \left(\frac{3}{2} - \frac{2}{Z} \right)^{-1}$$

(8)

where f = volume fraction of particles
and Z = an arbitrarily defined grain size heterogeneity factor which is the ratio of the radii of a growing grain to the matrix grains.
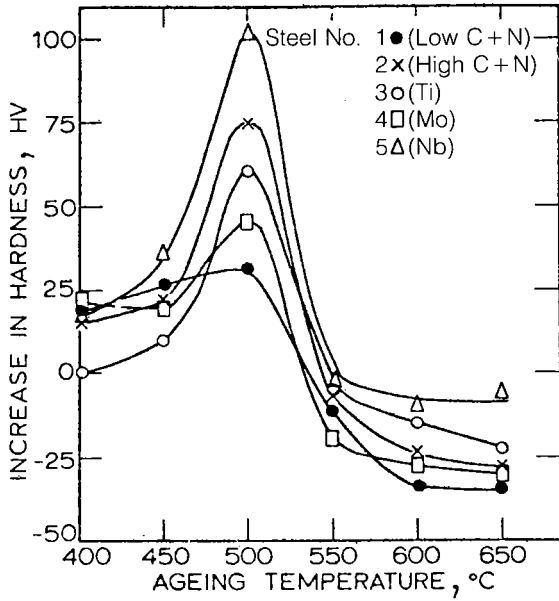
(a).　Isochronal Ageing Curves.
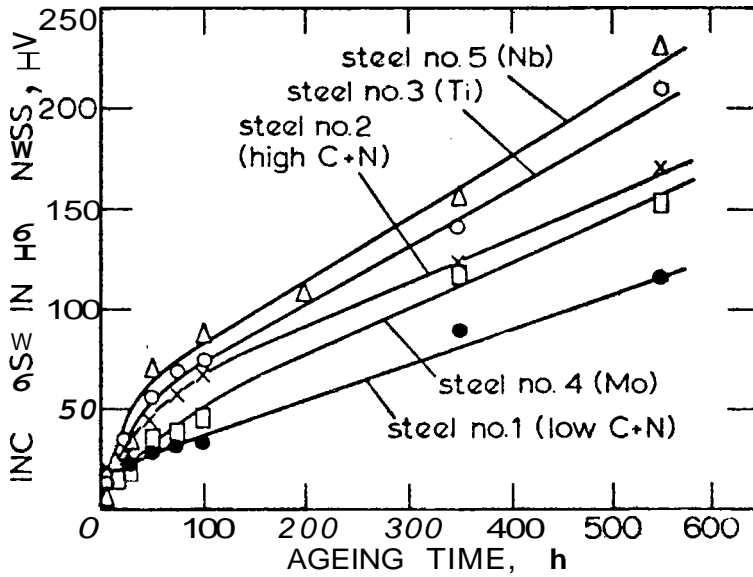
(b).　Rate of Ageing.

Figure 8.　Effect of Niobium on *485* C Embrittlement
of Ferritic Stainless Steels (76).

By using the solubility equations for Nb(CN) in austenite, it is possible from the composition of the steel to calculate f and thereby r as a function of temperature. As the temperature and time increase, the particle size, r, of the NbC will increase by Ostwald Ripening, and at the temperature at which $r > r_{cl}$ grain coarsening will commence. Data has been obtained for the Ostwald Ripening of Nb(CN) in austenite, from which r can be calculated as a function of temperature:

$$\log r = \frac{-5167}{T} + 2.593 + \frac{\log t}{3}$$

(9)

where t = heating time in hours and
      r is in μ

The grain coarsening temperature can, therefore, be calculated, providing certain assumptions are made (78). similarly, it is possible to calculate the grain size which can be effectively stabilized at any temperature, using the Zener equation (79). Whilst this approach has been successful for low alloy steels, there is no reason to suppose it cannot also be successful with the stainless steels.

Mechanical Properties

Solid solution strengthening

By virtue of its large atomic diameter, 2.94 Å for a coordination number of 12 (80), which is the largest of any of the common **substitutional** alloying elements in steel, niobium markedly strains the lattice as shown by its great effect in increasing the lattice parameter **of** austenite (81). The lattice parameter increases by 0.0051 A per weight percent niobium. This gives niobium the greatest solid solution strengthening coefficient of all the common solutes in austenitic stainless steels, namely, 40MPa per weight percent and 77MPa per weight percent respectively on the 0.2 percent proof stress and tensile strength. The greater effect of niobium on the tensile strength than on the proof stress indicates a high work hardening rate, which is greater than for other substitutional solutes and confirms both the effect on work hardening rate described earlier and the suggestion that niobium decreases the stacking fault energy. This high solid solution strengthening coefficient for niobium may be the result of substitutional - interstitial solute clustering, by Nb-C or Nb-N atom pairs, and the possibility of such clustering has been suggested to explain solid solution strengthening in the ferritic stainless steels (12) and also creep strength in austenitic steels **(83).**

Although the magnitude of solid solution hardening by niobium is apparently quite significant it should be remembered that the solubility of niobium in austenite under equilibrium conditions i.e. after slow cooling or low temperature reheating, is very low and therefore the solid solution hardening achieved is likely to be less important than strengthening due to dispersion hardening of NbCN particles or grain refinement. Very significant solid solution strengthening of austenite is only achieved when the very soluble interstitial elements nitrogen and carbon are utilized.

No quantitative data seems available on solid solution strengthening by niobium in either the martensitic or the fully ferritic stainless steels.

Ductility and formability

In austenitic stainless steels there are conflicting reports of the effect of niobium on tensile ductility. In *18* percent Cr, 10 percent Ni steels niobium seems to decrease ductility at fracture, whilst in *16* percent Cr, 25 percent Ni steels increasing niobium first increases ductility and then decreases it at higher niobium contents *(84)*.

These effects are believed to be due to the varying effects of niobium on strain induced martensite formation in base compositions of very different M_d temperature. It has also been shown that in austenitic stainless steels, increasing the volume fraction of undissolved Nb (CN) particles, exponentially decreases the tensile ductility **(85)**. This is the effect expected from any large second phase particles. No quantitative data is available on the effect of niobium on the ductility of ferritic or martensitic stainless steels.

There is also no quantitative data on the effect of niobium on the formability of either the ferritic or austenitic stainless steels, although niobium, by affecting the M_d temperature, should have some influence on stretch formability, which will be also affected by the influence of niobium on the work hardening rate. In ferritic steels, it has been shown that undissolved NbC particles are capable of nucleating for the $\{111\}$ recrystallization texture which is beneficial to deep drawability *(86)*. Also in ferritic stainless steels, one of the major problems is "roping", which is due to an unfavorable texture formed during hot rolling. Niobium, by introducing undissolved Nb (CN) particles can minimize roping by promoting recrystallization and a more random texture of fine grain size (84). A new steel developed by Sumitomo Metal Industries containing **17** Cr **0.35** Cu and *0.6* Nb for example is said to be completely free from "roping".

The effect of most of the alloying elements untilized in austenitic stainless steels have been systematically investigated for their influence on hot workability **(93-95)** but in the only work reported **(95)** for niobium steels it is likely that the strong ferrite-forming tendency of niobium was not fully allowed for in designing the steels and delta ferrite was probably influencing the data. It is well known that small percentages of ferrite or large precipitates or inclusions will reduce the hot ductility of austenitic stainless steels **(93)** and that some elements in solid solution such as molybdenum, chromium, nitrogen and carbon will also reduce the ductility by **substitutional/interstitial** effects **(93)**. It is likely, therefore, that the hot workability of austenitic stainless steels containing niobium will be inferior *(96)* to simple austenitic steel such as type **304** *(18* Cr **10 Ni)**, Figure **9.**
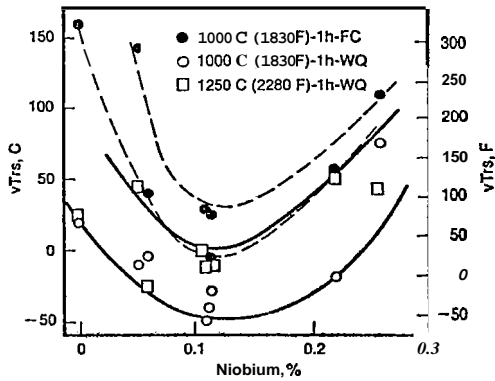
Toughness

As already described, the grain refinement of the austenitic in **12** percent Cr martensitic steels has been used to produce increased toughness and lower impact transition temperatures **(59, 75)**. An interesting effect of niobium on the transition temperature of fully ferritic stainless steels *(76, 98)*, is shown in Figure 10. It can be seen that an increase in the niobium content first decreases the transition temperature as interstitials are scavenged from the ferrite and the resulting particles refine the grain size. Further additions of niobium then either exert solid solution strengthening, or Laves phase Fe_2Nb will be formed as stoichiometry is exceeded. In either case there will be an embrittling effect, *so* that the transition temperature increases with increasing niobium content.
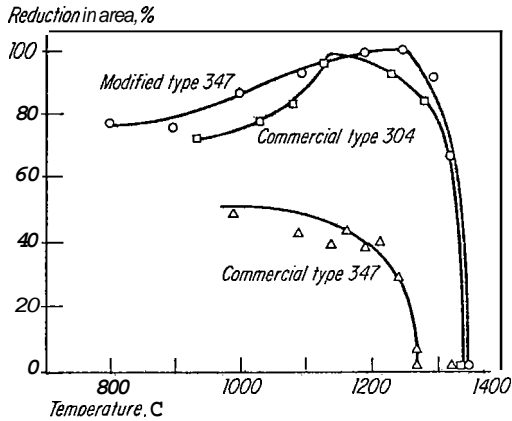
Comparison *of* Commercial Type *304* and *347* Steels and a lower carbon, lower niobium austenite steel.

Figure 9.   Hot Workability of Austenitic Stainless Steels (96).

Impact Transition Temperature of 21 Cr - 1 Mo Steels (C + N = 0.010 to 0.015%).

Figure 10.   Effect of Niobium on Toughness of Ferritic Stainless Steels (98).

High temperature properties

As previously indicated, although stainless steels were initially de-
veloped for corrosion resistance, it soon became apparent that some of the
more highly alloyed steels such as type 316 (18Cr 12Ni 2 1/2Mo) and type 347
(18 Cr 11Ni 0.8Nb) offered an excellent combination of high temperature creep
strength and high temperature oxidation resistance. These two grades have
been the main contenders for many elevated temperature applications for
almost forty years.

More recently two alloys containing both niobium and molybdenum have
emerged in the U.K. to provide possibly even better creep strengths. These
steels are FV548 (16 1/2Cr 11 1/2Ni 1 1/2Mo 1Nb) and Esshete 1250 (15Cr 10Ni
6Mn 1Mo 1Nb 0.3V 0.006B).

It is generally accepted, but not necessarily proven, that the creep
strengthening mechanisms provided by molybdenum and niobium are quite differ-
ent. Molybdenum is thought to impart creep strengthening by it's influence
in solid solution whilst niobium carbides are considered to be the main
factor in retarding dislocation movement at creep testing and operating
temperatures. In support of this latter viewpoint is the data obtained by
Keown and Pickering (42) on a systematic microstructural and statistical
investigation of a large number of austenitic stainless steels containing
variable amounts of niobium and carbon.

Because of the effect of stoichiometry on the temperature dependence of
the solubility of NbC in austenite, it was observed that the rupture life of
austenitic stainless steels is a maximum at the stoichiometric ratio. This
is due to the maximum amount of NbC being available for precipitation, and,
therefore, creep strengthening. The maximum in rupture life is also associ-
ated with a maximum rupture ductility. It has been possible to produce
equations to describe the rupture life and rupture ductility in terms of
amount of NbC available for precipitation, NbC_p, and the amount of undissolved
NbC, available for precipitation NbC_u (42):

$$\log \text{ rupture life} = 2.44 + 7.66 \text{ } NbC + 1.24 \text{ } NbC_u \tag{10}$$

$$\% \text{ elongation} = 30.06 - 48.34 \text{ } NbC_p \tag{11}$$

$$\% \text{ R of A} = 73.16 - 99.03 \text{ } NbC_p \tag{12}$$

The role of undissolved NbC in increasing the rupture life is interesting,
and is due to the creation of dislocations around undissolved NbC particles
due to differences in thermal expansion between the carbide and the matrix.
This, in effect, internally warm works the matrix, providing sites for NbC
precipitation and more pinning of dislocations with a consequent increase in
rupture life. Whilst the interpretation invokes precipitation of NbC as the
creep strengthening mechanism, other workers (83) have suggested it is due to
a solute drag effect by Nb-C atom pairs as more niobium would be in solution
and available to form solute clusters and provide solute drag on the disloca-
tions. Recent work has shown that very small additions of niobium (0.05%)
can give remarkable creep properties (97), Figure 11.
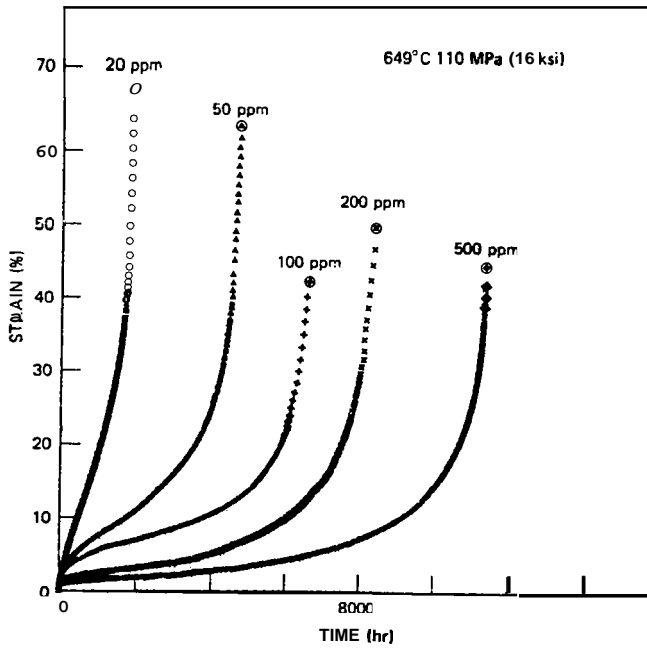
(a). Effect on Creep Curves.
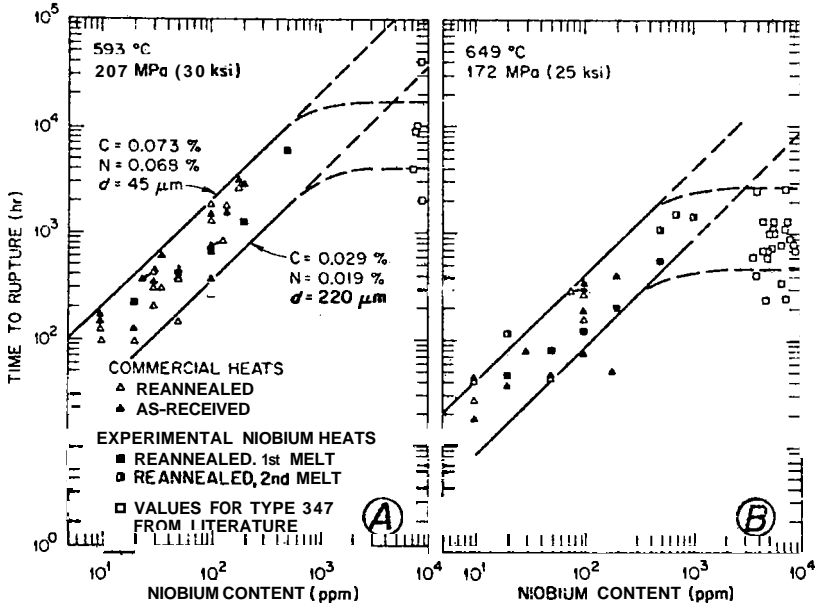
(b). Effect on Rupture Strength.

Figure 11. Effect of small Niobium additions on Creep
Properties of Austenite Stainless Steels (97).

The subject of the effect of niobium on the weldability of stainless steels can only be summarized briefly (10). In ferritic stainless steels, niobium can be beneficial by providing pinning particles which restrict grain growth in the heat affected zone. The ferrite forming effect of niobium can also prevent austenite forming, and hence transforming to martensite, in both the weld and heat affected zone; this helps to minimize weldment embrittlement. Moreover, niobium can produce finer grained and more equiaxed weld metal and hence more tough and ductile welds (87). However, in niobium steels, post weld annealing may precipitate NbC in the ferrite and cause hardening and embrittlement (88) but niobium can prevent an intergranular corrosion effect in the heat affected zone.

In austenitic stainless steels, niobium obviously has had a beneficial effect in minimizing intergranular corrosion and weld decay in the heat affected zone. It may also be useful in producing controlled ferrite content weld metal, and thus less tendency for crater cracking. However, it is also responsible for two important problems which occur in the welding of austenitic stainless steels. By forming a low melting point austenite – NbC eutectic, niobium can induce both weld metal and heat affected zone liquation cracking. Also, the high temperatures in the heat affected zone close to the weld can dissolve so much NbC that during stress relieving or subsequent service, heavy strain induced NbC precipitation occurs which can lead to low creep ductility and cracking (89–92), see equations (11) and (12). Liquation cracking of type 347 has been one of the reasons for decline of this grade for superheater tube applications, type 316 being preferred. However, in line with reducing carbon in stainless steels by use of the A.O.D. and other steelmaking processes, it is now proposed (49, 96) that the niobium and carbon should both be reduced in their stoichiometric ratio from approximately 1 percent Nb 0.2 percent C to 0.2/0.3 percent Nb, 0.02/0.03 percent Cr. This will eliminate liquation cracking problems whilst still maintaining the same amount of niobium and carbon in solid solution for creep strengthening, Figure 12.
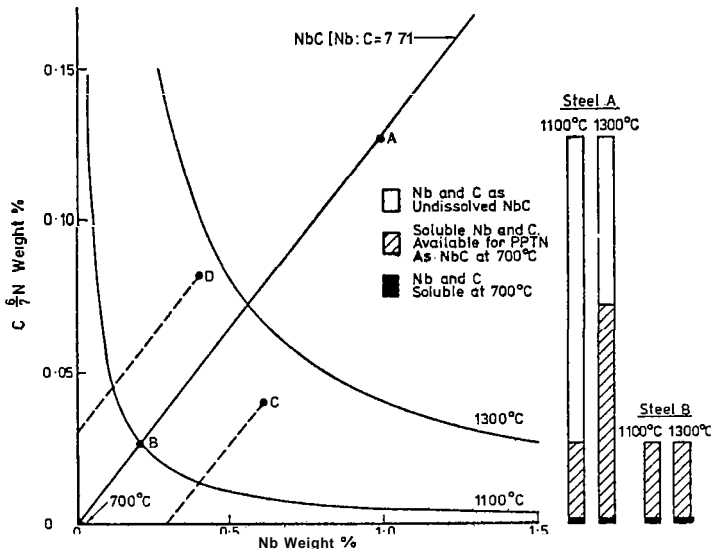

Figure 12.   Development of Lower Carbon Lower Niobium
Austenitic Stainless Steel (49).

Conclusion

The use of niobium as an alloy element is stainless steel is nearly always to produce niobium carbide to either remove carbon, which would otherwise form the detrimental chromium carbide, or to create a precipitation hardening dispersion of carbides. The former is important in corrosion resisting stainless steels and the latter in heat resisting stainless steels.

Over the last ten years the development of the A.O.D. steelmaking process facilitating low interstitial grades of stainless steel has caused a decline in the use of niobium in the stabilized austenitic grades for corrosion resistance. At the same time liquation cracking of weldments in niobium austenitic grades has caused some users to avoid this grade despite its excellent creep resisting properties. Recent developments, however, are suggesting that small additions of niobium may be essential for complete freedom from intergranular corrosion and that a reduction of niobium from 1 percent to about 0.3 percent Nb will overcome liquation cracking problems. Other austenitic grades containing Nb-N for corrosion resistance and Nb-Mo for creep resistance are being introduced quite successfully.

Many grades of martensitic stainless steel contain niobium for improved creep resistance and there has been no change in the demand for these steels which are usually forged or cast into the required component form. Recent heat treatment developments for these grades have shown how the niobium addition can be further utilized to give improved toughness by grain refinement.

The new ferritic stainless steels are increasingly using niobium for the optimum stailization of interstitials to avoid intergranular corrosion, to improve toughness and to prevent ridging or roping of the surface of cold rolled strip. These developments represent a growth area in the use of niobium, as ferritic stainless steels are making significant inroads into the traditionally austenitic stainless steel market.

It is probably true to say that the scientific understanding of the role of niobium in stainless steels has lagged behind the empirical development of these steels as it has with most steel grades. Over the last few years major developments in steelmaking and thermomechanical processing coupled with a better understanding of structure/property relationships have revolutionized many types of steel including stainless steels. Economic and strategic element situations are also being superimposed onto alloy development requirements *so* that continuing significant developments are confidently predicted for stainless steels containing niobium in the next decade.

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