NIOBIUM IN TOOL STEELS AND CEMENTED CARBIDES

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Abstract

Niobium is an element of high affinity towards carbon and forms a very stable carbide. Therefore it is well suited as a carbide-forming alloying element in the production of tool steels and hard metal alloys. This paper first deals with the metallurgical fundamentals, such as the influence of niobium on the solidification behaviour of high speed steels, segregation of the MC-carbides during solidification, effect of the solidification rate on the precipitation of mono-carbides, solubility of niobium in austenite, effect on secondary hardness, M_2C decomposition and methods for the achievement of higher niobium-contents in high-speed steels. In a second part selected examples of use are referred to in the categories of high speed steels, hot working tool steels, cold working tool steels and steels for plastic moulds. A short summary of niobium in cemented carbide completes the paper.

Introduction

Niobium is an element in group 5a of the periodic table and, as do the elements vanadium and tantalum of the same group and the elements of groups 4a and 6a, it forms, together with small atomic elements such as carbon, nitrogen, boron and silicon, very stable carbides, nitrides, borides and silicides, which are classified as hard metal alloys. The hard metal alloys (and also NbC) are mainly metallically bonded, have free electrons with overlapping valence - and conduction band and are suitable electrical and thermal conductors. Their high bond energy results in a high modulus of elasticity and a high melting point. In general, they have only few slip systems so that dislocation movement is difficult; this is why they are hard and brittle. Table 1 presents a survey of the carbides, nitrides and borides of the transition metals, characterized by the melting point, the electrical resistance and the hardness (1).

Table I. Some properties of metallic hard materials (1)

4a	**5a**	**6a**	**4a**	**5a**	**6a**	**4a**	**5a**	**6a**
TiC ⬡	VC ⊡	Cr_3C_2 or	TiN ⊡	VN ⊡	CrN ⊡	TiB_2	VB_2	CrB_2
Fp 3160	2830	1895 Z	Fp 2950 N	2350 NZ	1500 Z	Fp 2900	2400	2200
R 68	60	75	R 25	86	640	R 9	38	56
H 3200	2950	2280	H 2450	1520	1090	H 3480	2080	2250
ZrC ⬡	NbC ⊡	Mo_2C	ZrN ⊡	NbN ⊡	Mo_2N ⊡	ZrB_2	bB_2	MoB_2
Fp 3530	3500	2400 Z	Fp 2955 N	2630 NZ	700 Z	Fp 2990	3000	2100
R 42	35	133	R 21	~ 200		R 7	12	30
H 2560	2400	1950	H 1520	1400	630	H 2200	2600	~ 3000
HfC ⬡	TaC ⊡	WC	HfN ⊡	TaN	W_2N ⊡	HfB_2	TaB_2	W_2B_5
Fp 3890	3780	2600 Z	Fp 3330 N	2930 NZ	700 Z	Fp 3250	3150	~ 2300
R 37	25	22	R 33	128		R 15,8	21	21
H 2700	1790	2080	H 1640	1060		H 2900	2200	2700

⊡ = face centered cubic
⬡ = hexagonal close packed
or = orthorhombic
Fp = melting point °C
R = spec. electr. resistance micro-ohm · cm
H = hardness (microhardness dN/mm²)
Z = decomposition
N = with nitrogen overpressure

It can be seen that NbC has a comparatively high melting point and high hardness. It is therefore well suited as a carbide-forming alloying element in the production of tool steels and hard metal alloys.

Niobium in Tool Steels

The first niobium-alloyed tool steel produced was available in the US (2). Its composition in wt%[+)] was 0.8% C, 4% Cr, 5% V and 1.25% Nb. During the following 25 years several investigations were published on the use of niobium as an alloying element (3 - 7), but it was the discovery of huge pyrochlore deposits in Brazil (8) that reactivated the development. The contributions presented at the *International Symposium on Niobium* in San Francisco from the 8th to the 11th of November 1981, offer an excellent summary on the knowledge and the range of applications at that time (9). At this state of development, niobium was mainly used empirically, a thorough and complete metallurgical view, however, could not be achieved until

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[+)] Unless otherwise stated, the composition elements are always specified in wt%.

the 1980's. That is why this paper first deals with the metallurgical fundamentals followed by examples of use.

Metallurgical Fundamentals

The Influence of Niobium on the Solidification Behaviour of High Speed Steels

A combination of differential thermal analysis (DTA) and directional solidification was an important aid in explaining the solidification behaviour, as well as in the development of niobium alloyed high speed steels (10 - 15). In principle, solidification proceeds in the same way in all commercial high speed steels of approx. 0.7 to 1.2 wt% carbon, but at different transformation temperatures. As the temperature decreases, three reactions take place (Figure 1):

- a) primary crystallization of δ-ferrite,
- b) peritectic transformation of melt and ferrite into austenite,
- c) eutectic formation of M_2C and/or M_6C and austenite from the residual melt.

The formation temperatures of the crystallizing primary MC-phases in vanadium or niobium alloyed grades ahead of the formation of M_2C and M_6C are marked by arrows.

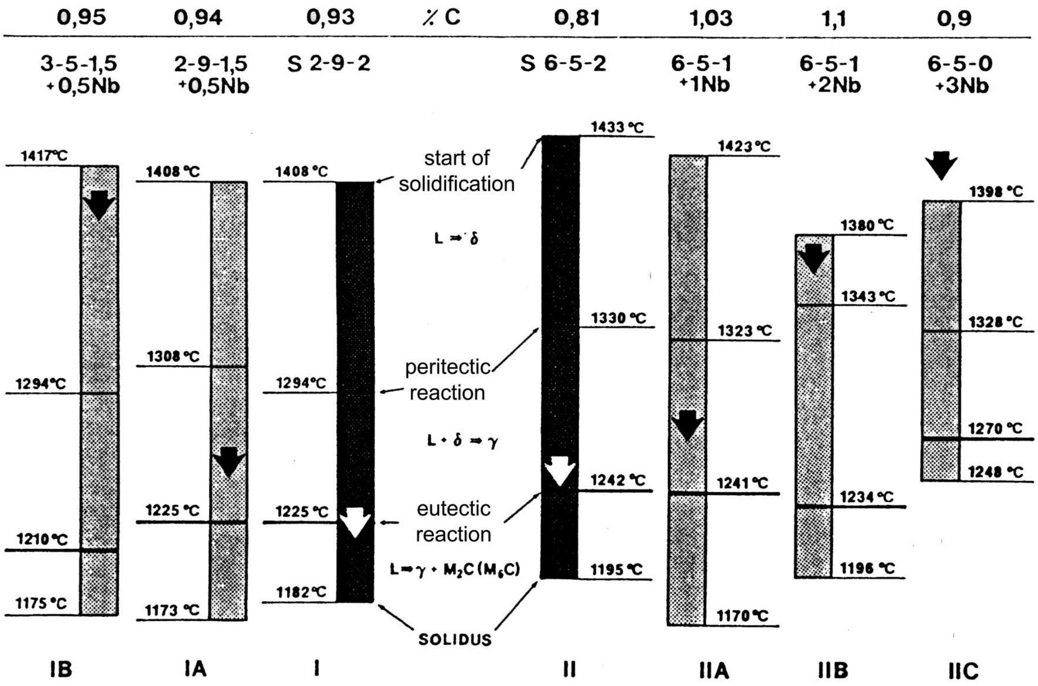

Figure 1: Solidification reactions in conventional and niobium-alloyed HSS grades based on AISI M2 and M7, as determined from DTA measurements at 0.08K/s cooling rate. Arrows mark the onset of eutectic MC formation (11).

The liquidus temperature, T_L, mainly depends on the carbon content. It decreases with increasing C-carbon content. Among all other elements, a higher niobium concentration seems to have the greatest effect on the decrease of T_L. In (16) an empirical formula for the solidus temperature of high speed steels was suggested. On the basis of own investigations, the coefficients were revised and a coefficient for the influence of niobium was introduced (17).

$$T_S = 1266 - 110\,(\text{pct C}) - 3\,(\text{pct Si}) + 4\,(\text{pct W}) + 2\,(\text{pct Mo}) + 10\,(\text{pct V}) + 15\,(\text{pct Nb})\ \text{C}$$

At the onset of MC precipitation, niobium-alloyed steels differ remarkably compared to commercial steels. In the niobium-free steels I and II, vanadium rich MC forms either eutectically or in isolation at approximately the same time as the M_2C-eutecticum. In niobium alloyed steels, niobium rich MC generally crystallizes at higher temperatures. The crystallization of primary MC in titanium and nitrogen containing melts can be initiated at higher temperatures by heterogeneous nucleation (steel IB). At very high niobium concentrations (IIB and IIC), blocky primary carbides can also be formed homogeneously (10). After the onset of primary ferrite crystallization, the precipitation of niobium rich MC proceeds mostly eutectically.

The fact that a niobium content of 2 wt% is already sufficient to lead to the crystallization precipitation of NbC from the melt, results in a special growth of the primary carbide particles, where they are pushed ahead of the tips of a dendrite front (12). The distribution curves in Figure 2 show that steels with 2 wt% niobium (14, 15) develop considerably larger carbide sizes, affecting toughness to a high degree. Experiments have shown furthermore that a rapid solidification favours finer, eutectic MC-forms (Figure 3a). In alloys containing more than 2 wt% niobium, primary niobium rich crystals with faceted crystal habit are often encountered. They are formed, still in the melt, by heterogeneous nucleation at high temperatures, before the onset of ferrite crystallization. Sizes of up to 50µm (Figure 3b) are not unusual. Their growth is barely affected by an increase in the cooling rate.

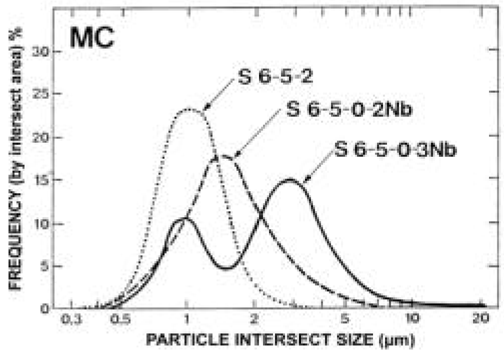

Figure 2: Size distribution of MC carbide in hardened AISI M2 and niobium analogues (14, 15, 28).

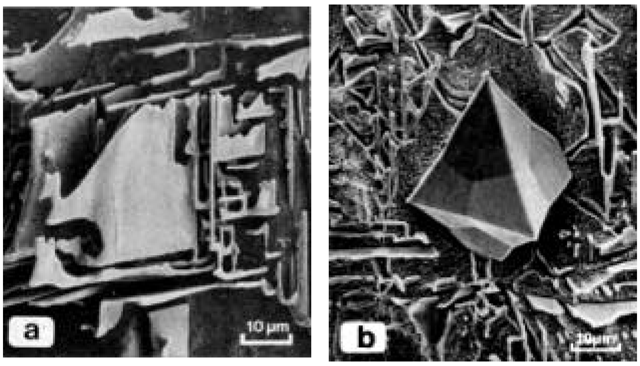

Figure 3: Niobium rich carbides in the solidification structure of niobium analogues of AISI M2; (a) eutectic (6-5-0-2 Nb) (b) primary (6-5-0-3 Nb) (14, 15, 10).

The high affinity of niobium towards carbon is the reason for the formation of coarse primary niobium carbides at niobium contents of approximately 2% and higher. Figure 4 shows a comparison of the solubility of vanadium carbide and niobium carbide in iron melts. Thermodynamic date were used from (18) and extrapolated to 1800K (19, 20). Even if Figure 4 is considered only as an approximation, the difference in the thermodynamic stability of niobium carbide is quite obvious compared to vanadium carbide. It is because of the high thermodynamic stability of niobium carbide that a melt can dissolve only comparatively small amounts of carbon and niobium (hatched area). At natural cooling rates, the precipitation of niobium rich MC-carbides straight from the melt occurs at niobium contents of approximately 2 wt%. Contrary to niobium alloyed high speed steels, a corresponding primary carbide precipitation in vanadium alloyed steels occurs at 4 to 5 wt% vanadium.

Experiments have been performed on more highly alloyed high-speed steels to evaluate the formation crystallization temperatures of primary carbides (21). They showed a very fast increase with increasing niobium content (Figure 5). These large and blocky NbC-carbides, which find enough time to grow during solidification, are the reason, together with casting voids, that the ultimate bending value strength is worse in high speed steel grades with a higher niobium content, than in commercial grades (22).

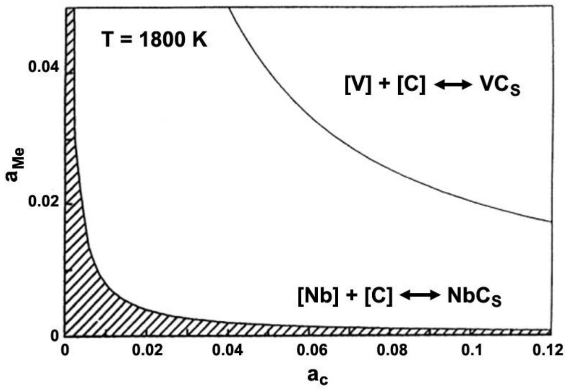

Figure 4: Calculated solution curves for niobium and vanadium carbide in iron melts at 1800 K (19, 20).

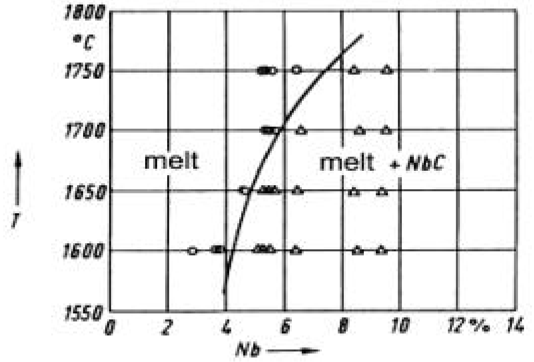

Figure 5: Liquidus temperature of niobium alloyed high-speed steels; (21, 22).
○ without blocky NbC △ with blocky NbC

Numerous experiments have also been carried out to try to improve the poor solubility of niobium in the melt of high speed steels by varying the contents of alloying elements in order to provide and so open an “alloying window” that would allow a way towards a higher niobium solubility in the melt; no experiment has yet proved successful (19). Figure 6 (23) shows that the addition of ferrite-stabilizing elements such as aluminium and silicon would increase the size of the existing δ-iron region and therefore also increase the solubility of niobium (24). Thus the idea of looking for an alloying window for the dissolution of higher niobium contents in a steel melt should not be rejected. With the addition of 1.5% Al and 1% Si to an a -typical high speed steel composition (1.4% C, 3.7% Cr, 2% Mo, 4% W, 1.1% V), niobium contents of more than 4% can be realised using ingot metallurgy without the formation of blocky-NbC (25) (see also application examples of high speed steels).

There are varying statements in the literature as to the effect of primary niobium rich MC-carbides on the further solidification process (21, 26). In (19, 20) a nucleation effect of the existing MC-carbides for ferrite is stated for only for very high cooling rates.

The morphology of primary niobium-rich carbides depends primarily on the niobium activity (14, 15). As the niobium activity in the melt decreases, a transition takes place from a smooth, octahedral shape to a dendritic form. Eventually, primary crystallization is increasingly replaced by the formation of a eutectic (Figure 7). The chemical composition of the carbide changes with decreasing formation temperature; vanadium is incorporated into the carbide as up to 25at% of the metal atoms, and thus more molybdenum is also incorporated.

Because of its high carbon affinity, niobium can better react with carbon than can vanadium. Niobium rich mono-carbides are purer and more stable than vanadium-rich MC (27 - 30). As a result, the major content of carbon is used by niobium for MC-formation, thus eutectic M_6C appears beside MC in the as-cast structure instead of eutectic M_2C. Therefore, in order to realise the formation of eutectic M_2C, the carbon-content must be increased when adding niobium. As MC-formation results in a higher carbon consumption, the quantity of these eutectic carbides formed is reduced. Figure 8 shows the considerable increase in MC-content with increasing niobium -content in the as-quenched state of these steels. The amount of M_6C decreases at the same time (14, 15).

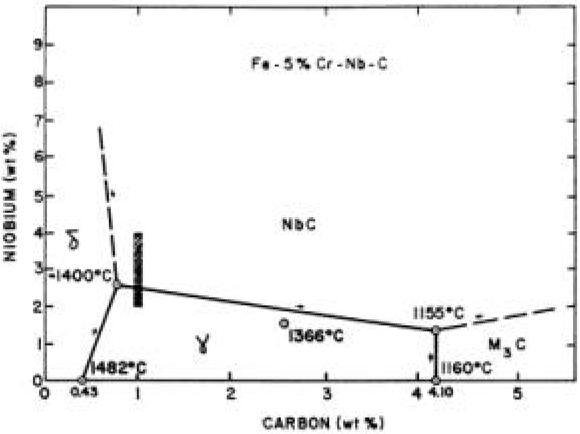

Figure 6: Liquidus surface of the pseudo ternary Fe-5Cr-Nb-C (23).

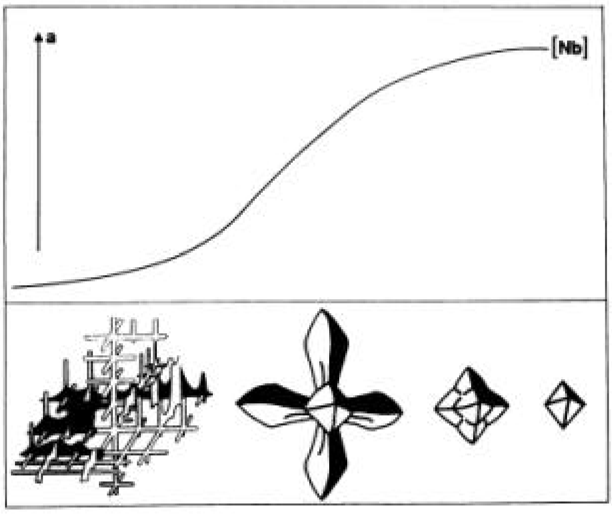

Figure 7: Morphology of NbC-type monocarbide as a function of niobium activity in the melt (schematic) (14, 15).

The ledeburitic, as-cast microstructure of the steel IIa in Figure 1 shows M_2C-, M_6C- and MC-carbides (corresponding to its composition and cooling conditions). Note the relatively high formation temperature of the niobium rich MC-eutecticum. It always appears spatially separated from the M_2C and/or M_6C eutectic regions in the as-cast structure (12).

The two primary eutectic MC-carbides show two compositions clearly diverging from each other: one vanadium rich composition high in molybdenum and low in niobium and a niobium rich composition where the increasing vanadium incorporation is accompanied by a higher molybdenum content. In this context it should be noted that a miscibility gap exists in the binary VC–NbC–system at 1470°C (31).

X-ray diffraction investigations (32, 33) on specimens of the same niobium alloyed high speed steel melts prove that the NbC-lattice parameter drops from 4.43 to 4.36Å when vanadium is incorporated, due to the smaller atomic radius of vanadium than niobium (3.03 compared to 3.3Å). Correspondingly, the VC-lattice parameter increases from 4.17 to 4.26Å with the incorporation of niobium.

Extensive carbide analyses (17) of different niobium alloyed and niobium free high speed steels revealed that M_6C does not incorporate any niobium and that in M_2C only minor (if any at all) niobium content can be detected.

Segregation of MC-Carbides During Solidification

Similar to the vanadium carbide, the niobium carbide shows a tendency towards segregation in the melt (19, 20) due to differences in density. Depending on the composition of the melt, the MC-carbides may either sink, float or form a homogeneous distribution. A density comparison of the pure carbides, the mixed carbides and the steel melt illustrates the possibility of segregation due to gravity (Table II). Alloying elements such as tungsten, molybdenum and niobium increase the density of the melt, while vanadium and carbon reduce it. Vanadium, in particular, has the strongest effect on the segregation of MC-carbides. At 1500°C a full miscibility exists in the binary system NbC-VC (34) and the alloying element vanadium is incorporated into the niobium carbide, depending on the vanadium content of the melt. This has also been confirmed experimentally (19, 20). Neglecting the low iron content of the MC-carbides and assuming a linear correlation of the density of the mixed carbides with the vanadium and/or niobium content, their density develops as illustrated in Figure 9.

Table II Density of carbides and pure iron at different temperatures (35, 41, 42)

	NbC	VC	MC Nb-rich	MC V-rich	Fe *T* = 25 °C	Fe *T* = 1500 °C
Density [g/cm^3]	7.79	5.7	7.59	6.78	7.87	7.02

In addition, Figure 9 shows the density of alloyed melts at 1500°C in correlation with the alloy content (35). Furthermore, the composition of the monocarbides in various experimental melts, and their density, are also recorded. For an alloy with Fe-4% Nb-1.2% C (specimen II/2), where monocarbides rich in niobium are formed, a decrease in niobium carbides can be expected. This has also been confirmed experimentally (19). MC-carbides were found to float, especially in systems with a higher vanadium content since vanadium rich MC with a low density is formed in this case. Within the alloying system Fe-4%Nb-1.2%C-12%W, however, a homogeneous distribution of primary niobium carbides occurs. Due to the high tungsten content, the density of the melt increases sufficiently so as to stop a further sinking of the carbides. Attention has to be paid to a segregation by gravity when the alloy content of high speed steels is increased to such a degree that, during cooling, carbides precipitate straight from the melt. To date, little importance has been attached to gravity segregation because of the minor density differences between the melt and the niobium rich MC-carbide.

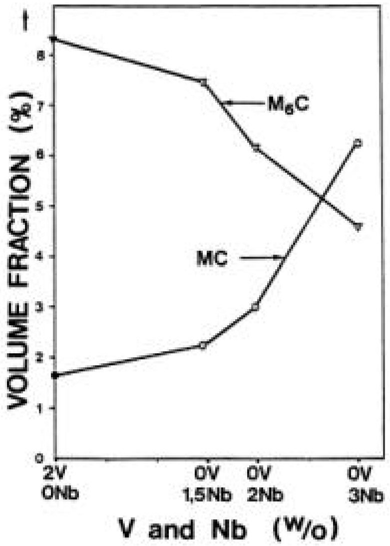

Figure 8: Influence of increasing niobium content on the volume fraction of carbides in a series of AISI M2 analogues with niobium instead of vanadium, at constant carbon level (14, 15, 28).

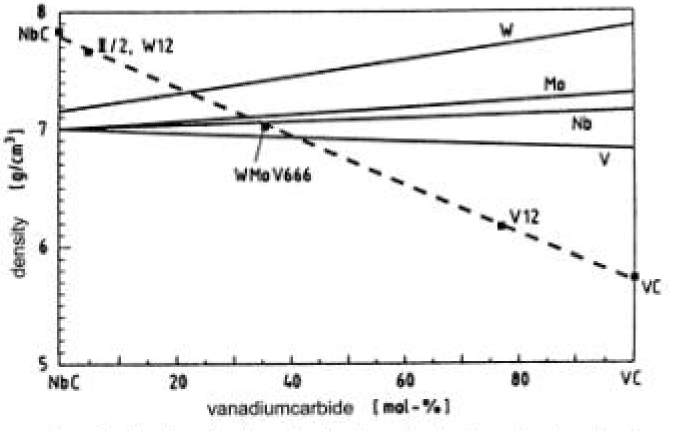

Figure 9: Dependence of the density of iron melts at 1500°C from the alloying content and density of pure and mixed carbides from some alloys.
Fe + 4Nb + 1.2C (II/2); II/2 + 12%W (W12); II/2+12%V(V12); II/2+WmoV666; (10, 19, 20)

Technically advantage can be taken of gravity segregation to establish mono-carbide structures for increased wear resistance in castings (36).

Effect of Solidification Rate on the Precipitation of Monocarbides

Thorough investigations have been made on the effect of cooling rate on primary niobium carbide sizes during solidification (21). Low cooling rates were achieved by ingot casting, high and even higher rates by gas and/or water atomization, as well as by solidification of the melt on a rotating copper disc. Figure 10 illustrates the results, i.e. the connection between cooling rate and the size of the primary niobium carbides, established in experiments (20). It also shows results achieved with a NbC laser-alloyed high speed steel containing approx. 6.5wt% niobium, fitting well with the scatter band. As expected, the size of the mono-carbides decreases with increasing cooling rate. It is remarkable that even with very high cooling rates of $\dot{T} > 10^6$ K/s, primary mono-carbides develop during cooling. The scatter in the measured values of carbide size (see Figure 10) results from nucleation effects. The literature deals with a two-stage nucleation process for MC-carbides (12, 14, 17, 37 – 40). During cooling, aluminium oxide deoxidation products develop in the high speed steel melt. These deoxidation products exist in a solid aggregate state and act as nuclei for titanium nitride TiN (and/or (TiV)(CN). The titanium nitride forms a fine border around the aluminium oxides and functions, in its turn, as a nucleus for the vanadium rich MC-carbides

$$Al_2O_3 \rightarrow TiN \rightarrow MC$$

Experiments have also revealed that the nucleation of niobium-carbide also occurs on Al_2O_3-particles (21, 40); additionally a one-stage nucleation process seems to be possible (21).

The reason for the proper nucleation of niobium-carbide on the Al_2O_3-particles is the appropriate lattice fitting of both phases along certain lattice planes. Figure 11 (21, 38, 40) illustrates the good correspondence of niobium atoms in (111) planes of the niobium carbide and the oxygen ions in (0001) planes of aluminium oxide. If, therefore, the aluminium content of the melt is reduced, e.g. deoxidation is achieved in another way, tertiary aluminium deoxidation products, which are homogeneously distributed in large numbers and act as nuclei for niobium carbides, develop at a very late casting stage. If there are just a few alumina particles in the melt, for example primary and secondary deoxidation products, only few, but coarse, niobium carbide particles develop (upper boundary curve). Many small tertiary Al_2O_3 -particles result in many and fine niobium carbide particles (lower boundary curve) (21).

To prevent the formation of coarse niobium carbides such as are formed at slow cooling rates, powder metallurgy is a suitable alternative process to produce high speed steels with a higher niobium content. With this process, high speed steels with up to approximately 3wt% Nb can be produced with a satisfying property profile (42, 43).

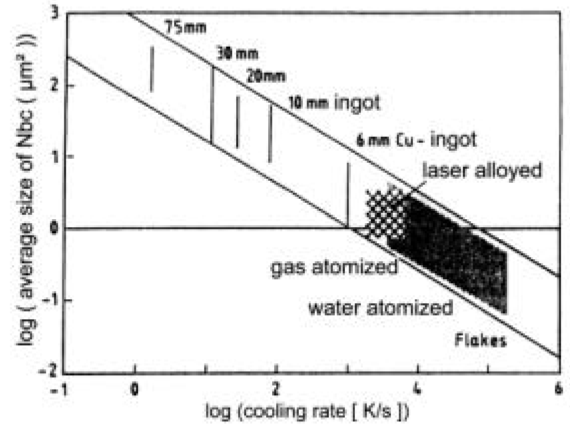

Figure 10: Average NbC-size as a function of the cooling rate (19, 20).

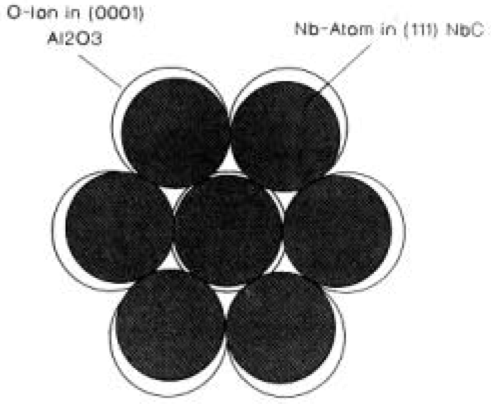

Figure 11: Fit of lattice planes (0001) of Al_2O_3 to (111) of MC (21, 38,40).

Solubility of Niobium in Austenite

The solubility product of niobium carbide in austenite is illustrated in Figure 12. Even at high temperatures it is insignificant (44). This means, on the other hand, that niobium can scarcely contribute to the secondary hardness, since there is almost no solubility in the austenite. (Therefore vanadium as the most important element for secondary hardening cannot be substituted by niobium completely.) This, however, proves that even small amounts of niobium precipitated as niobium-carbide can be used to slow or prevent the grain-growth of austenite (micro-alloying with niobium). Niobium carbides are very efficient, as there is no coarsening even at high temperatures (Figure 13) (45). These stable NbC particles thus effectively control the austenitic grain size; the higher the volume fraction of the fine particles, the finer the austenitic grain size (Figure 14) (46); see also chapter: Examples of use, especially Table V.

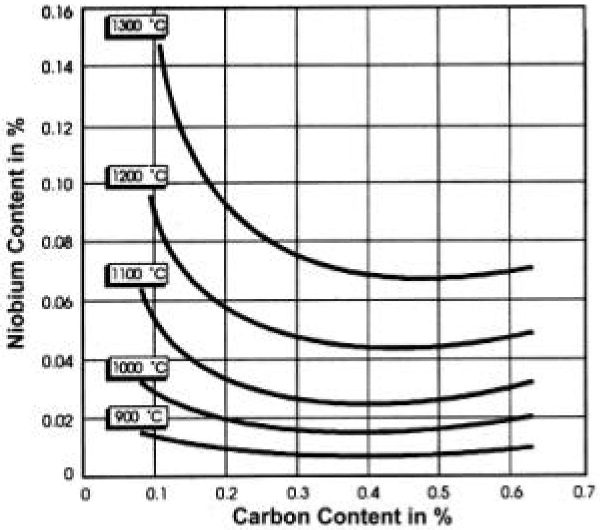

Figure 12: Solubility of NbC in austenite (44).

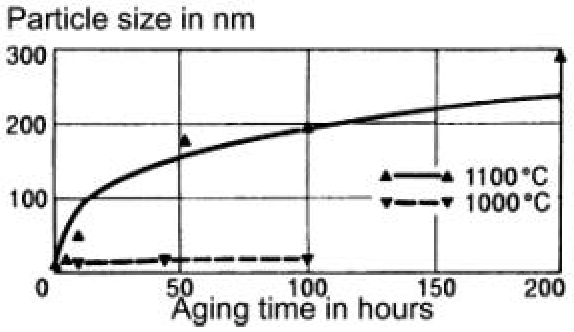

Figure 13: Variation of average particle size of niobium carbide with ageing time (45).

Effect of Niobium on Secondary Hardness

The fact that scarcely any vanadium can be dissolved in niobium carbide is an advantage, as only a small amount of vanadium is incorporated in the (coarse) MC-particles and is therefore available for secondary hardness.

With niobium alloyed steels, where primary MC is mainly formed as niobium carbide, the vanadium content can thus be reduced (14, 15). In general, the vanadium content in high speed steels is 2wt% max. An approximate schematic balance (Figure 15) on the basis of chemical carbide analyses and on a quantitative estimate of the amount of carbides, shows that in this case half of the vanadium is required for primary carbide formation and half of it for secondary hardening. Even for niobium-alloyed steels, approx. 1.1wt% of vanadium must be available for secondary hardness. As a certain amount of vanadium is also soluble in niobium rich MCs, the vanadium content should be 1.7wt%.

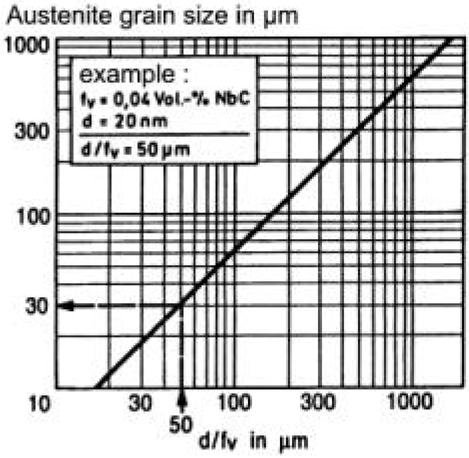

Figure 14: Dependence of austenite grain size on volume fraction (f_v) and size (d) of NbC particles (46).

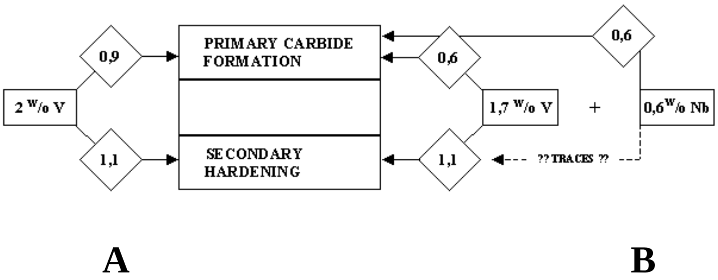

Figure 15: Balance of vanadium and niobium between primary carbide formation and secondary hardening: A = conventional alloys, B = alloys containing niobium (14, 15).

Some investigations on niobium alloyed high speed steels, show a slower decrease in secondary hardness above the secondary hardness maximum. This phenomenon seems to indicate an active role for niobium in secondary hardening (47 - 49). (Recent investigations showed similar results (50 – 52). Fine M_4C_3 carbide precipitates were found in a tempered high speed steel containing 11%W, 2%Mo, 2%V and 0.5%Nb and it is assumed that they may also have dissolved niobium and titanium.)

In one very complete investigation (53), most modern analytical methods were applied (atom probe field ion microscopy and transmission electron microscopy) to study secondary hardening carbides in the AISI grades M2, M7 and in T1, in the powder metallurgical steels ASP23, ASP30 and ASP60, as well as in a powder-metallurgical steel with the chemical composition 2%W, 3%Mo, 1.6%V, 1.6%C and 3.2%Nb. After tempering to peak hardness, all steels showed two types of precipitates: disk-shaped MC of 3 to 5nm in diameter and rod-like M_2C, 5 to 10nm long. The precipitates were of complex composition and all carbide-forming elements (tungsten, molybdenum, vanadium and chromium) were found in both types of precipitate. The MC-precipitates were rich in molybdenum, chromium and vanadium, while M_2C-precipitates were rich in molybdenum and chromium. MC-secondary hardening carbides showed a clear deficit in carbon. At the beginning of MC-formation, the carbon -content was about 0.75at%, but it decreased to 0.98at% C with increasing tempering time (54). A PM model alloy containing 3.2% Nb (corresponding to 1.9at% Nb) showed a matrix with 0.1at% Nb after hardening and 2at% Nb in MC and 1.2at% Nb in the M_2C after tempering. These thorough investigations demonstrate that the active effect of niobium on secondary hardness in high speed steels can be neglected, but in some cases a slower decrease in secondary hardness after exceeding the hardness maximum is reported.

M_2C Decomposition

The properties of commercially produced high speed steels depend on the type, amount and shape of the non-dissolved alloy carbides MC, M_6C and M_2C, as well as on their spatial- and size distribution (14). Solidification via the metastable M_2C eutectic offers the advantage of the decomposition of M_2C carbides into M_6C carbides and vanadium rich MC-carbides during subsequent deformation and heat treatment. These MC-carbides dissolve to a large extent during the hardening process and supply the matrix with vanadium for subsequent secondary hardening. The carbide distribution in the as-quenched state is thus not only determined by the microstructure in the as-cast state and the accompanying banded structure, but also by the morphology and the rate of M_2C decomposition (29, 55).

Investigations on the morphology and kinetics of M_2C -decomposition in high speed steels of grade S 3-5-1.5 + 0.5 niobium are reviewed in (56). On applying different cooling rates to a 10kg test ingot, niobium alloyed economy grades showed an area of M_2C eutectic structure with approx. 60 – 70% of a fine -lamellar structure, 20 – 30% acicular -fine flaky structure and 5 – 10% coarse flaky structure. Studies proved that the decomposition rate decreases from the fine-lamellar, to the coarse-flaky and acicular/fine-flaky structure.

When half of the vanadium content in an M2 steel (HS 6-5-2) was replaced with niobium, investigations showed that decomposition proceeded much faster in the niobium containing steel than in the commercial M2 steel. The decomposition products MC and M_6C appeared in a refined structure (29).

Stoichiometrically, the vanadium monocarbide consumes carbon to a higher extent than that of niobium. A considerable amount of vanadium is also dissolved in M_2C and in the matrix, while niobium solely occurs in MC-carbides. Due to its high affinity towards carbon, this element consumes the major amount of carbon, thus insufficient eutectic carbides can be formed subsequently and a transformation from M_2C to M_6C is the result. Therefore, in grade S 6-5-1+1%Nb (29), the proportion of carbon was increased by 0.25% (to 1.12) This means that all three types of carbides are present in the as-cast microstructure of slowly solidified specimens i.e. MC, M_2C and M_6C, while only MC and M_2C appear when rapid cooling is applied (Figure 16). When the cooling rate was changed within the cooling rate range investigated, the volume fraction of MC remained constant, while the volume ratio of M_2C to M_6C changed in favour of M_2C.

The M_2C composition in a commercial M2 steel grade scarcely changes with the cooling rate, however a more obvious modification takes place in niobium alloyed steels. As an example, comparatively low percentages of tungsten and molybdenum can be found in the M_2C of niobium alloyed steel undergoing slow cooling, while a more rapid solidification results in higher chromium and iron contents.

The varying decomposition behaviour can be explained by the thermodynamic stability and the different morphologies of the M_2C carbides. It is obvious that the decomposition tendency of M_2C is highest when it is finely distributed and only short diffusion paths need to be covered.

The peculiar diversity of M_2C composition in niobium alloyed steel grades and commercial HS 6-5-2 steel is reflected in the thermodynamic stability of the carbides. The enthalpies of formation of mixed carbides were interpolated from literature data on the enthalpies of formation of pure carbides, according to their analyses (29). The metastable M_2C-phase contains more tungsten and vanadium and less iron and chromium in niobium free HS 6-5-2 grades than in niobium alloyed steel grades. Figure 17 illustrates the ΔG-values versus the temperature for the single carbides. Hence, the stability of M_2C in niobium steels would be less than that in niobium free grades. This is also in accordance with the results of experiments that show a faster decomposition of M_2C-carbides in niobium alloyed steels. The niobium addition has therefore a positive effect, as a fine-lamellar M_2C is formed, which undergoes decomposition much more easily, and thus provides a supply of vanadium for the formation of secondary hardening carbides.

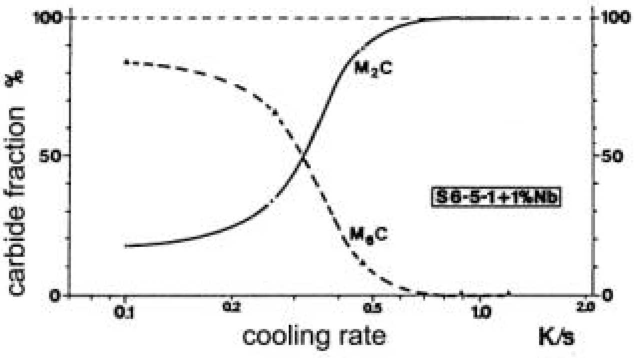

Figure 16: Part of M_6C- resp. M_2C-eutectic, related on the total amount of M_6C + M_2C eutectic (29, 10).

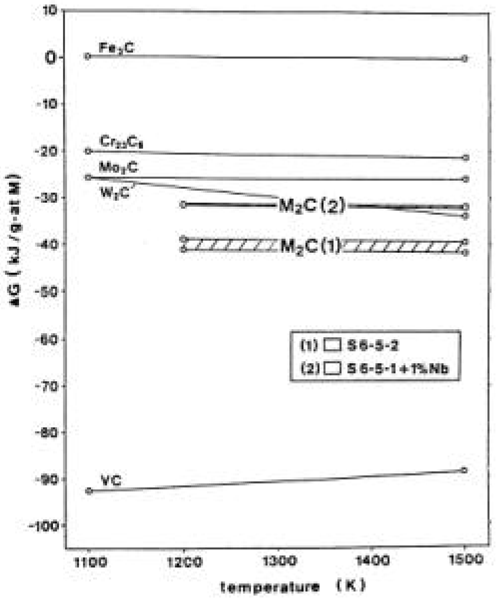

Figure 17: Free formation enthalpy of carbides (29,10).

Methods for Achieving a Higher Niobium Content in High Speed Steels

The development of highly alloyed high speed steels is restricted when using traditional melting technology. An increase in the proportion of carbide-forming elements together with a controlled increase in carbon, results in the formation of coarse eutectic structures that impair hot working capacity and toughness, or result in a precipitation of coarse carbides straight from the melt. This is particularly the case for the strong carbide formers niobium and vanadium. By atomizing the melt, fine solidification structures can be achieved; however the addition of alloying elements is restricted, as they must at least be dissolved in the melt at atomizing temperature. Powder metallurgy offers another possibility to increase the carbide content and thus close the gap between high speed steels and hard metals; that is, mixing of matrix and/or tool steel powders with carbides such as NbC, pressing and sintering.

In order to manufacture tool steels with high niobium content, different production routes were tried.

Addition of Niobium Carbide Powder to a Matrix Melt

The matrix of an optimized high speed steel, with high matrix potential, was used (57) (basic analysis 2% W, 3% Mo, 4% Cr and 1% V) to incorporate as many fine and homogeneously distributed NbC-carbides as possible. As the production of such an niobium alloyed steel by ingot metallurgy causes problems regarding the size of primary NbC, the injection of niobium carbide powder into the matrix melt using nitrogen was attempted (58). The temperature of the matrix melt was maintained between 1550°C and 1650°C. The blowing period was dependent on the desired niobium carbide content of the steel, which was adjusted to be between 3 and 6.5 % niobium, and was 5 to 20 minutes. In addition to the injection process, trials were carried out where niobium carbide powder was added to the melt by mechanical stirring, thus obtain a homogeneous distribution within the matrix melt.

A rapid dissolution of the NbC-particles in the matrix melt occurs with both methods; with injection of NbC-powder using nitrogen, as well as with stirring of the powder. During solidification of the melt, primary and/or eutectic niobium rich alloy carbides of the type MC are precipitated. In particular, the primary blocky niobium rich MC-carbides showed a large size distribution compared to an HS 6-5-2. The largest carbide cut sections were 100 to 200µm^2 (with 6.5% Nb up to 500µm^2), compared to maximum sizes of approximately 30µm^2 for the HS 6-5-2. The as-tempered hardness and the cutting performance, however, remained under the values of a usual HS 6-5-2 steel. Nevertheless, experiments on a laboratory scale have proved that, in principle, this is a viable way of producing high speed steels with high niobium carbide contents.

Atomization of Niobium Alloyed High Speed Steel Melts

To avoid a precipitation of blocky niobium carbides at higher niobium contents during the production of high speed steels by ingot metallurgy, niobium alloyed high speed steels were atomized or teemed off according to different processes. In addition to inert gas atomization and an atomization according to the PREP-process (plasma rotating electrode process), casting was also performed on rotating copper disks (59, 60). Table III shows the chemical composition of the experimental alloys. At sufficiently high melting or atomization temperatures of about 1600°C, niobium contents of more than 3% could be kept in solution (21). After atomization or melt spinning on the rotating copper disk, the niobium carbides are very fine with sizes under 1µm. The PREP-process cannot be applied for powder production, as the coarse NbC-carbides from the electrode are not dissolved and thus remain in powder particles.

Table III Chemical composition of alloys in wt% (60)

Alloy	C	Si	Mn	Cr	W	Mo	V	Nb
1	1.29	0.26	0.27	4.26	6.42	4.64	0.98	2.70
2	1.29	0.32	0.35	4.50	6.66	4.72	1.07	1.68
3	1.17	0.38	0.36	4.41	3.40	4.91	1.09	2.79
4	1.18	0.49	0.58	3.90	2.85	4.57	1.00	3.15

The matrix concept, (optimized matrix composition for the achievement of an appropriate secondary hardness potential and a sufficient content of hard carbides to resist abrasive wear), was realized by producing a steel melt corresponding to the AISI M2 grade, containing 1.3%C, 2%W, 3%Mo, 1.6%V and 3.2wt%Nb, by nitrogen atomization. Consolidation of the powder was performed by extrusion (61). After the hardening and tempering process, fine MC-carbides rich in niobium (NbC-carbides), mainly in the range of 0.5 to 1µm, could be observed. Vanadium rich MC were found to a lesser extent. Table IV is a survey of the chemical compositions and the lattice parameters of the carbides and the matrix in the as-quenched as well as in the tempered state. The simultaneous development of vanadium and niobium rich MC-carbides had already been noticed in earlier investigations (62). As in (62) a systematic connection between the chromium, molybdenum, tungsten and vanadium contents and the niobium content in the niobium carbides could also be found in this investigation (Figure 18).

Table IV. Chemical composition and lattice parameters of carbides and matrix in hardened and tempered state (61)

	Chemical composition (wt%; $\sum M = 100$)						
Phase	W	Mo	V	Nb	Cr	Fe	Lattice parameters (Å)
Matrix	1.89	2.72	1.18	0.22	4.0	bal.	2.876 ± 0.003
Niobium-rich MC	3.7	5.9	8.2	78.4	0.6	2.8	4.420 ± 0.003
Vanadium-rich MC	17.2	24.3	29.7	21.5	3.8	3.5	4.294 ± 0.003
AISI-M2 matrix	3.8	3.5	1.0	-	4.3	bal.	
AISI-M7 matrix	1.0	4.3	0.9	-	3.6	bal.	

The fine distribution of the tiny niobium rich MC carbides contributes to the stabilization of a considerably finer austenitic grain compared to the AISI M2 grade produced by ingot metallurgy. At 1250°C (Figure 19) the austenitic grain size is especially affected. The presented investigations, however, were performed at an austenitizing temperature of 1275°C. Compared to AISI T1 and AISI M2-grades, very promising results were achieved in cutting tests.

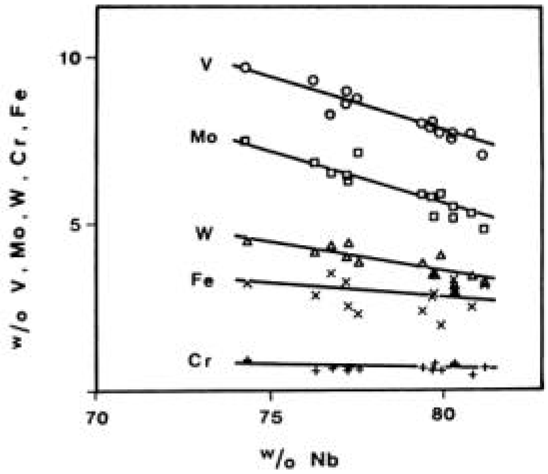

Figure 18: Composition of MC particles determined by STEM-EDX (61).

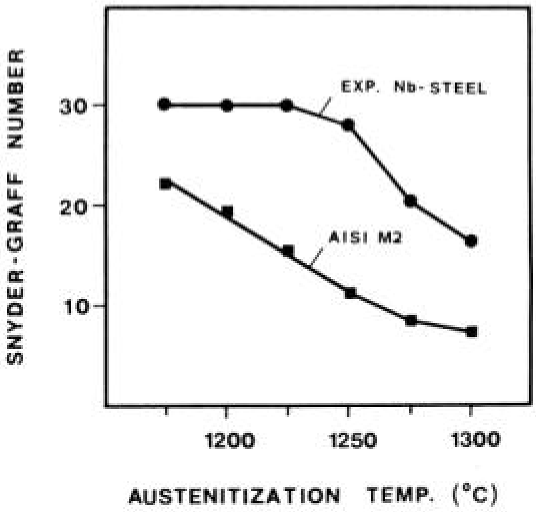

Figure 19: Effect of austenitizing temperature on intercept grain size in the experimental Nb steel and in AISI M2 (61).

Increase of the Niobium Content by a Reduction of the Carbon Content in the Melt

The niobium content cannot be considerably increased over 3%, not even with atomization of the melt, since otherwise the precipitation of large niobium carbide particles would occur ahead of the atomization at the usual melting and atomizing temperatures. From a technical point of view, very high atomizing temperatures cannot be realized: in addition to the high load that the refractory material is subjected to, the powders show higher oxygen contents and a larger number of exogenic inclusions can be found.

Higher niobium contents of more than 3wt% can be taken into solution by reducing the carbon content (19). Subsequent to or during the atomization, the powder has to be carburized, however, to guarantee a sufficiently high carbon content in the metallic matrix. When an oil-atomization was applied to a low carbon melt of 0.8%C, 2%W, 3%Mo, 2%V and 6%Nb, carburization took place during the atomization, but the intended value of approx. 1.6wt% C could not be achieved. A maximum carbon pick-up occurs with powder particles between 100 and 150µm in diameter, whereby the carbon content increases up to 1.4wt% C. Another and much more controllable method of adjusting the carbon content is a later treatment (carburization or nitriding) of the powder. These experiments have proved that it is possible to atomize high speed steel melts with reduced carbon contents and niobium contents of 6wt% at 1600°C without large, blocky primary carbides being formed.

Powder Metallurgical Production Routes

Powder metallurgy also offers the possibility of mixing an iron and/or a steel matrix powder with larger amounts of hard phases e.g. niobium carbide and sintering. An experiment has been carried out (63, 64) whereby 10-30 vol% niobium carbide was added to an iron matrix in addition to other hard phases. The tests showed that a satisfactory density can only be achieved after mechanical alloying and sintering, when boron or boron + carbon are added in such contents that a liquid phase is produced during sintering. Thus, satisfactory densities of 97 to 99% could be obtained by sintering in hydrogen at 1280°C, when 10-30vol% NbC, TiC or Al_2O_3 were added. Satisfactory fatigue strength values could also be achieved following mechanical alloying, whereby niobium carbide showed obvious advantages in mechanical properties when compared to other hard materials such as TiC, TiN, Al_2O_3 or VC.

Reference is also made in the literature to experiments investigating the strengthening of powder metallurgical, atomized high speed steels with ceramic particles such as Al_2O_3, titanium-nitride and other carbides (65). As an example, one paper can be mentioned that deals with a water atomized M3/2 high speed steel powder that was mixed with commercially available Nb-carbide of 99.5% purity. In this manner, the niobium carbide content could be varied to 2.5, 5 and 8 vol% (66). The specimens were sintered under high vacuum. When the sintering temperature was below the solidus temperature, insufficient sintering ability was guaranteed and pores were present in the microstructure. Further experiments deal with the addition of tantalum carbide and copper-phosphorus to support liquid phase sintering (see also 64, 65). The papers report satisfactory wear tests where niobium and tantalum carbides were present. It was also found that the presence of niobium carbide displaces the vanadium from the primary MC-carbides during the sintering process and mixed carbides of (V,Nb)C are formed.

Addition of Niobium Carbide by Laser-alloying

In laser-alloying, the material is locally melted on the surface by means of an efficiently focused laser beam. A small molten metal bath is formed by the interaction of the laser beam and the substrate, where various additions can be made, e.g. via injection of powders using inert gas. Due to the high efficiency of the laser, the metal bath can be overheated and bath temperatures of more than 1800°C are within reach. These high melt temperatures enable thermodynamically stable chemical compounds such as mono-carbides of niobium and vanadium to be dissolved in the melt in a large amount. After the alloying process, solidification takes place, due to the small bath volume with a high heat dissipation to the substrate and with cooling rates often over 10^3 K/s (67).

Due to the nature of the process, the metal bath volume is very small and thus laser-alloying is primarily suited for partial alloying of highly loaded locations on structural components, such as the cutting edges on tools.

When appropriate process parameters are selected, niobium contents of over 20wt% can be realized in laser-alloyed surface melting, corresponding to a mean carbon content of more than 2.8wt% in the surface melt (68).

Even minor niobium carbide additions affect the solidification structure to a high degree. Figure 20 summarizes the structure modifications dependent on the average niobium content of laser-alloyed melting beads. For up to 4wt% niobium, metallic dendrites and two different eutectics occur in the rapidly solidified structure. At niobium contents over 4wt%, solidification begins with the precipitation of niobium rich mono-carbides from the melt. Figure 21 illustrates the solidification structure of an HS 6-5-2 substrate alloyed with niobium carbide. The niobium content amounts to approximately 6.6wt%. The solidification structure shows star-shaped, niobium rich mono-carbides and eutectic cells with a second eutectic structure between them. Due to the high cooling rate, the mono-carbides remain fine in their size. At low niobium contents they appear in blooms whereas at higher niobium contents they develop an increasingly dendritic morphology. The carbide size achieved in laser alloying fits very well into the scatter band of melts with different solidification rates (Figure 10). Analyses prove that mono-carbides produced via the laser-alloying process are rich in niobium and incorporate only small amounts of other alloying elements. The niobium content of the metallic dendrites is close to the detection limit. Thus, the conclusion can be drawn that almost all of the niobium is present in the mono-carbides precipitated from the melt and in the mono-carbides of the eutectic cells (this is also true of other production processes). With laser-alloying, the amount of wear resisting mono-carbides can be increased by adding niobium. However, remarkable improvements in the secondary hardness behaviour cannot, however, not also be expected.

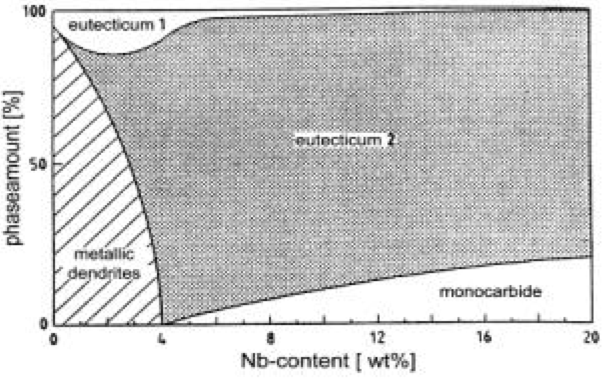

Figure 20: Structure diagram of NbC laser-alloyed HS 6-5-2 (AISI M2) (cooling rate $6 \cdot 10^3$ K/s) (20).

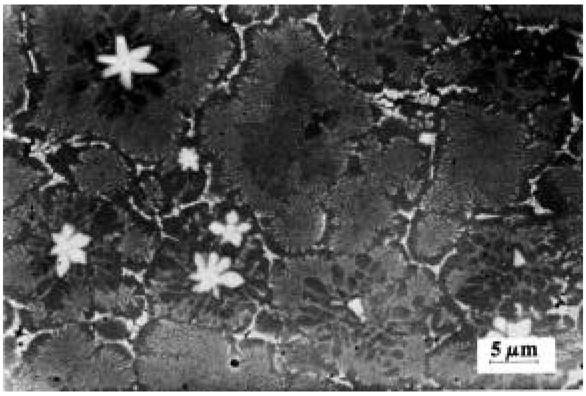

Figure 21: Microstructure of NbC laser-alloyed HS 6-5-2 (AISI M2) with about6.6 wt% Nb (cooling rate $6 \cdot 10^3$ K/s) (20).

The direct precipitation of mono-carbides from the melt at niobium contents above about 4wt% corresponds approximately to the eutecticum in the quasi-binary Fe-NbC-system (69, 70). Due to the poor interaction of the alloying elements of HS 6-5-2 with the niobium carbide, the solidification behaviour of the NbC laser-alloyed HS 6-5-2 can be approximately described using the existing quasi-binary and quasi-ternary phase diagrams, despite the high cooling rate.

Examples of Use

The use of niobium as an alloying element in tool steels has increased remarkably during the last 20 years. Thus, only a small selection of the outstanding examples can be presented in the following. The fact that niobium is a strong carbide-forming element is utilised at small niobium contents of 0.01 to max. 0.20wt.% for the prevention or the retardation of austenitic grain growth by fine and stable carbides (addition as micro-alloying element), or, at higher contents, for the formation of wear-resistant carbides (71, 72) offer an appropriate survey on the current use of niobium in high speed steels (Table V).

Table V Examples of Nb-alloyed tool steels (72)

	Chemical composition in wt%					
Application	C	Cr	Mo	V	Nb	others
Nb-microalloyed						
cutting teeth of power saws	0.60	-	-	-	0.04	
shop tool	0.12	-	0.18	-	0.10	1.8 Mn
plastic mould tool (122)	0.12	0.35	-	-	0.10	2.0 Mn – 3.5 Ni – 1.2 Cu – 1.1 Al
die casting tool for Al-alloys (103)	0.37	5.35	1.25	0.35	0.07	
hot-working of Cu-alloys (106)	0.38	2.60	2.60	0.75	0.10	1.7 Mn – 0.006 B
rolls for cold-working (112)	0.80	2.00	0.50	0.20	0.10	
Punching/coining die (115)	1.10	8.30	2.10	0.50	0.10	1,0 Al
Machining of tough tools (Ni, Ti)	1.10	4.30	5.00	1.90	0.07	6.4 W – 1.1 Al
Primary NbC						
warm forming (108)	0.58	4.50	2.70	0.80	0.45	1.8 W
hot working of valve steels (107)	0.58	4.00	2.50	1.00	1.50	3.0 Co
cutter knife	0.80	13.00	1.30	0.90	0.70	
metal drill	1.10	4.40	4.60	1.60	0.70	2.0 W
metal drill (92)	1.00	4.00	3.00	1.20	2.60	3.0 W
high-speed milling cutter (85, 86)	1.10	4.00	4.40	0.50	2.20	8.2 W – 10.0 Co
beater in mills	1.50	16.00	2.00		5.00	
extremly hard welded facings	5.30	20.00	6.50	1.00	6.50	2.5 W
Nb-stabilized						
Multilayer bonding jigs	0.03	16.50	-	-	0.40	4.4 Ni – 4.1 Cu
Nb in intermetallics						
press die	0.04	19.00	3.10	-	5.30	52.5 Ni – 0.6 Al – 0.9 Ti – 0.005 B

Depending on their application, the working properties of tool steels are manifold. Essential working properties are: hardness, red hardness, hardenability, tempering resistance, compression strength, fatigue strength, toughness, hot toughness, wear resistance, cutting tool endurance, thermal conductivity, thermal shock resistance, corrosion resistance, dimensional stability, hot-working capacity, cold workability, machinability, grindability, polishability.

The effect of niobium on these working properties should not be over-simplified by considering only that niobium is a strong carbide-forming element and therefore higher amounts of niobium carbide are formed when niobium is added, causing only the wear resistance to increase. In the section on metallurgical fundamentals, it was clearly illustrated that the addition of niobium greatly influences the allowing concept of tool steels, for instance allowing higher austenitizing temperatures and thus affecting the saturation of austenite with alloying elements, releasing vanadium for secondary hardness, influencing the carbides formed during solidification and so affecting and modifying further properties such as hardness, red hardness, tempering resistance, ductility and hot ductility as well as the life of the cutting tool directly and indirectly.

The direct influence of niobium, as a micro-alloying element, on the austenitic grain growth has already been dealt with in the section "Solubility of niobium in austenite". The wear resistance of tool steels, which is an important property for many applications, depends to a high degree on the amount of carbides present (Figure 22) (73). Consequently, there is a strong connection between the niobium content and the wear resistance in high speed steels (21) (Figure 23).

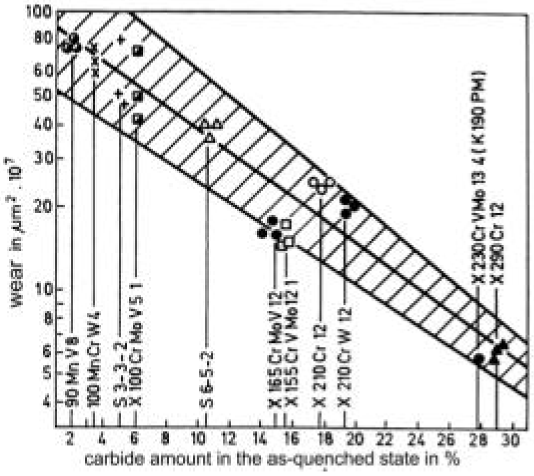

Figure 22: Wear (cross punch/matrix) dependent from the carbide amount of hardened tool steels (73).

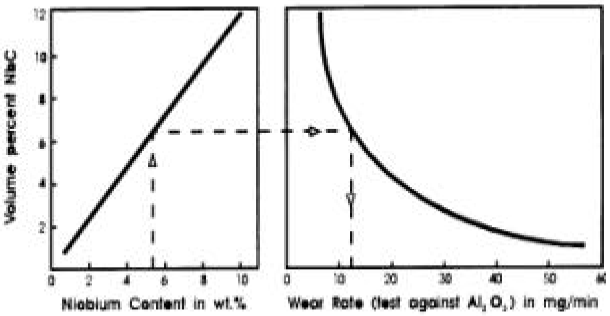

Figure 23: Results of wear tests of high speed tool steel as a function of NbC content(71) according to (21).

From the manufacturer's point of view, tool steels are divided into four categories, i.e. cold work tool steels, hot work tool steels, high speed steels and steels for plastic moulds (74).

In the following, selected examples from each of these categories are presented. However, not in all cases have these grades been produced, or will be produced, on a large technical scale. In many cases, the examples deal with laboratory and/or experimental melts with interesting results that definitely offer the prospect of large-scale production in future.

The alloying compositions conceived in these cases are often far beyond standard compositions, so that the correct classification according to the four selected categories cannot always be guaranteed.

High Speed Steels

It has been known for quite some time that niobium is a useful and effective addition to high speed steels (75-77). The application as an alloying element in high speed steels was hindered by the fact that niobium was not available at satisfactory costs for quite a long time, and that the development of high speed steels was carried out highly empirically for almost half a century by developing appropriately balanced property profiles. Intensified investigations on the use of niobium in high speed steels started in the mid seventies (4, 5, 27, 32, 33, 62, 78-83). The papers (6, 7, 27) deal with niobium as an alloying element in the high speed steel M2, whereby either part or all of the vanadium was replaced by niobium. In these studies, the as-cast structure showed, in addition to the usual M_2C-eutectic, a niobium-containing mixed carbide-eutectic or, at increasing Nb-contents in the melt, an M_6C-eutectic. At higher niobium contents, primary NbC was also found. The addition of niobium resulted in a carbon deficit within the matrix. The existing literature as yet includes no references to increasing the carbon content as compensation for this carbon deficit. The best results are achieved with a steel of 6%W, 5%Mo, 4%Cr, 1%V, 1%Nb and 0.9%C. That is, an HS 6-5-2, where half the weight percentage of vanadium is replaced by niobium. References (6, 7) refer to the essential fact that the complete replacement of vanadium by niobium does not result in a sufficient secondary hardness, and that niobium containing steels can be austenitized at higher temperatures than Nb-free grades. Vanadium containing steels showed higher hardnessvalues than niobium-steels. Thus it is highly probable that vanadium is an essential element for secondary hardness and should therefore not be completely replaced.

Other papers known at this time (84, 92) deal with an M2 high speed steel where the carbide-forming elements molybdenum and tungsten were replaced by adequate amounts of niobium. It must, however, be stated, that the complex role of niobium has not yet been investigated to its full extent.

As already stated (84), the carbon content must be redefined for higher niobium-additions to ensure sufficient matrix saturation and secondary hardness. An increase in carbon from 0.82% to 1% in a steel with 2%W, 5%Mo, 4%Cr, 1%V and 4%Nb resulted in a remarkably high secondary hardness maximum. In Brazil (Aços Villares), a high speed tool steel containing 1.3% C, 4.25% Cr, 4.5% Mo, 8% W, 2.7% V and 10% Co has been produced (85, 86), whereby the carbon was adjusted and the vanadium partly and also completely replaced by niobium. So e.g. 3% V was replaced by 2.2% Nb + 0.5% V in a T42 (S 10-4-3-10) steel grade. The result was again a better perfomance. This steel, VILLARES VK-10N, was regularly produced for more than a decade.

The effect of niobium and carbon on the microstructure and tool life of high speed steels of the type HS 6-5-2 (M2) was investigated (80). The goal of this investigation was to compare conventional high speed steels of the type M2 with those where half the weight percentage of vanadium had been replaced by niobium. A comparison of the steel grades was made for three different carbon contents. The compositions of the steels are listed in Table VI. The table also shows the carbon contents required for complete carbide formation.

Table VI Chemical composition of experimental melts, calculated carbon contents and hardening temperature (80)

wt%						C calculated (%)		
C	W	Mo	Cr	V	Nb	With Cr	Without Cr	Hardening temperature (°C)
0.91	6.60	4.88	4.15	0.94	0.97	1.10	0.85	1 230
1.10	6.80	5.06	4.26	1.15	0.85	1.13	0.87	1 230
1.17	6.45	5.05	4.10	1.12	0.81	1.11	0.86	1 230
0.94	6.80	4.73	4.38	1.77	-	1.16	0.92	1 220
1.05	6.81	5.13	4.51	1.88	-	1.18	0.91	1 210
1.17	6.59	5.19	4.19	2.16	-	1.23	0.98	1 210

The equivalent carbon values were adopted from the literature (16) on the assumption that vanadium forms a V_4C_3 carbide, that two atoms of tungsten or two atoms of molybdenum each are combined with one atom of carbon in an M_6C-carbide and that chromium to a large extent is precipitated as $Cr_{23}C_6$. Niobium is found as NbC. These values are obviously estimations, as mixed carbides in high speed steels are much more complex. Experience has proved that chromium, in niobium-free steel grades, must only be taken into account for the carbon balance at higher carbon contents. From these considerations it can be seen that in the vanadium-steel grades, the lowest carbon content of 0.94% C is balanced, and the other two melts are slightly overcarburized with 1.05 and 1.17% C. In the niobium-containing steels, the steel with a mean carbon content of 1.10% is balanced, whilst the other two demonstrate one insufficient carbon content and one slightly higher carbon content.

In all six experimental melts, increasing the carbon content resulted in a coarsening of the MC-carbides in the as-cast state. In the supersatured states, weaker carbide forming elements are incorporated into MC as well as into M_6C-carbides except for NbC, where purer primary carbides are precipitated with an increasing carbon content in the melt. As expected, a higher carbon content in niobium free steel grades results in a higher proportion of retained austenite in the as-quenched state. With slight overcarburization, the maximum secondary hardness will be achieved.

The same tendency can be observed in niobium-containing steels. Niobium shows a stronger affinity towards carbon, therefore, even with a carbon content of 0.95wt%, the full content of niobium is precipitated as MC, appearing as niobium rich primary carbides and niobium-vanadium mixed carbides in a ledeburitic structure. With a balanced carbon content, niobium-vanadium-iron mixed carbides, with a large homogeneous range, precipitate from the melt as eutectics. With increasing carbon content (supersaturation), the niobium-vanadium-iron mixed carbides disappear and primary niobium-carbides are precipitated in addition to the niobium-vanadium-mixed carbides (80).

On comparing the secondary hardening potential (13) of the matrix and the amount of precipitated carbides with the perfomance results, it turns out that the classical high speed steel grades such as HS 6-5-2 and HS 2-9-2 show a higher amount of carbides than would be necessary to account for their performance. This knowledge lead to the development of an niobium alloyed, economical high speed steel with a composition of 3%W, 5%Mo, 1.5%V and 0.5%Nb (13, 87). In this new steel, that is patented (88) and has also been produced on an industrial scale, niobium replaces vanadium in the formation of wear-resistant primary carbides. Therefore, the content of vanadium can be reduced to the level that guarantees an optimum matrix saturation and thus a favourable secondary hardening behaviour (Table VII).

Table VII Chemical composition, calculated carbon content and hardening temperature (13)

Steel grade	Composition [wt%]						C-content calculated [%]		Hardening temperature
	C	Cr	W	Mo	V	Nb	with Cr	without Cr	°C
S 3-5-1.5-0.5 (Nb)	0.95	3.98	3.05	4.65	1.38	0.50	0.97	0.73	1180 – 1200
S 6-5-2	0.91	4.18	6.08	4.70	1.87	-	1.14	0.89	1190 – 1230

The experiments proved that the hardening temperature should be restricted to 1210°C, since these economic high speed steel grades tend towards a coarse grain formation during the hardening process, due to the lower density of carbide particles. In spite of the low hardening temperature, the HS 3-5-1.5-0.5(Nb) has the same suitable matrix potential as the conventional HS 6-5-2 and a similar decomposition behaviour of the retained austenite. Investigations established a comparable performance at average load conditions when turning, drilling, sawing- and milling processes were carried out (Figure 24). It is only at higher cutting speeds that the performance of the economic high speed steel decreases below the performance of conventional steels, as, despite a sufficient secondary hardness, the density of carbide particles is much lower. This results in a heavier temperature load on the cutting edge when cutting materials with higher strength and at higher cutting speeds.

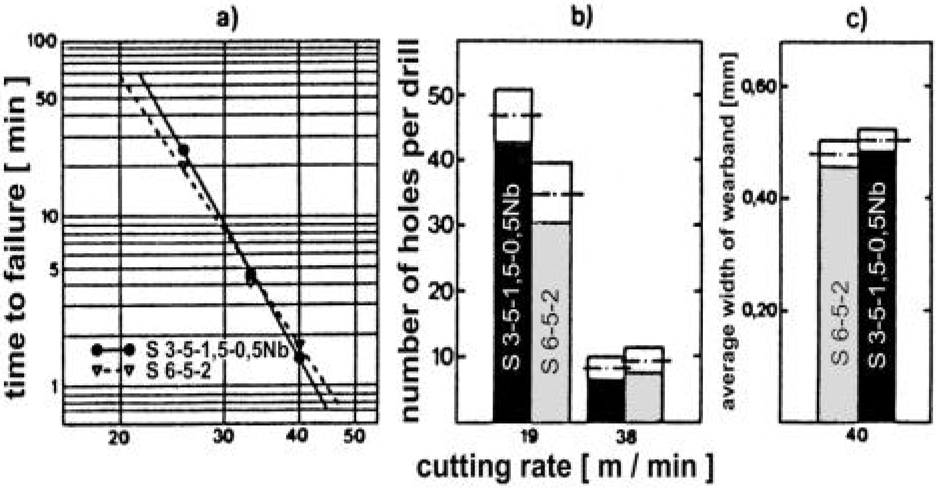

Figure 24: a) Tool performance of AISI M2 and a Nb-alloyed economic grade in continuous cutting. Work material: AISI 02 heat treated to 960N/mm^2; Feed: 0.2mm/rev. Criterion: total blunting; b) Drill performance of M2 and a Nb-alloyed economy grade. Work Material: as a) Drill size: ∅ 8mm. Hole depth: 25 mm. Criterion: total blunting; c)Average flank wear in slot milling (∅ 100mm). Work material: plain carbon steel with 0.6% C (700N/mm^2). Feed: 80mm/min. Milled Section: 2 x 10mm.

The composition of the economic high speed steel grade obviously presents an optimum alloy composition for saving on expensive carbide-forming elements. A further decrease, e.g. towards an HS 1-5-2, results in a greater reduction in performance. Also, the increase in carbon content combined with an increase in cost-saving carbide formers such as niobium and vanadium fails, because of the growth of primary carbides during solidification (12).

The question of whether the positive effects of elements such as calcium, nitrogen, boron and cobalt can also be used in the S 3-5-1.5-0.5(Nb) economic high speed steel, was tackled in (89) (Table VIII). This investigation dealt with the effect of these elements on the solidification path, carbide precipitation, M_2C decomposition, microstructure and hardness behaviour. A summary of this investigation shows that no general improvement can be achieved by the addition of these elements, but that potential improvements for certain application are a possibility.

Table VIII Analyses of the alloys investigated (in wt%) (89)

Alloy	C	Cr	Mo	V	W	Nb	Ca	Co	B	N
N1	0.86	3.98	4.48	1.54	2.95	0.60	-	-	-	-
N2	0.88	4.11	4.72	1.56	2.99	0.65	0.015	-	-	-
N3	0.93	4.06	4.73	1.54	3.10	0.65	-	4.94	-	-
N4	0.90	4.15	4.95	1.54	3.04	0.66	-	-	-	0.077
N5	0.88	3.98	4.39	1.61	2.83	0.63	-	-	0.01	-
N6	0.95	4.07	4.71	1.50	3.13	0.62	-	-	0.03	-

Many more examples can be shown for the use of niobium in high speed steels. Böhler Edelstahl in Kapfenberg has developed a high speed steel S 620 (90) to save the addition of expensive cobalt. The nominal composition of this steel is 1.1% C, 4.3% Cr, 6.4% W, 5% Mo, 1.9% V, 1.1% Al and 0.07% Nb. This steel is used in particular for intermittent cutting of nickel-based and titanium-based alloys and it performs better than the remarkably more highly alloyed M42 (HS 2-10-1-8) or T42 (HS 10-4-3-10) grades which have cobalt contents of up to 8 and 10%. The matrix concept was also used for the development of a steel where all primary carbides existing in M2 were substituted by niobium-carbide (92). This lean-alloyed steel grade has a matrix composition of 1% C, 4% Cr, 3% W, 3% Mo, 1.2% V and 2.6% Nb. Investigations proved that niobium-carbides of up to only 20 µm in size were found in the hardened matrix. Compared to a standard M2 steel, this test steel had a secondary hardness value which was lower by 1.5 HRC, however it also had excellent ductility values in bending tests. While turning softer materials such as austenitic steels, the test steel showed an improved performance compared to M2.

The largest tool steel manufaturer in Romania, i.e. Tirgoviste Works, has developed a high speed steel with the composition 1.1% C, 4.4% Cr, 4.6% Mo, 2% W, 1.6% V and 0.7% Nb using titanium as an inoculant. The inoculation of primary niobium carbide using titanium-nitride resulted in a superior carbide distribution within the matrix. Tools (drills, screwtaps) made from this steel showed an increase in performance of about 15 % compared to the higher alloyed M2 at hardness values of 65 HRC (71).

Based on an earlier high speed steel development called “Matrix niobium” (83) the following chemical composition of 1.1% C, 4% Cr, 3% Mo, 3% W, 2% V, 2% Nb and 0.1% Ti was used for a steel grade that was produced on an industrial scale (93). This steel could be used successfully in drilling processes and was equal in its performance to an AISI M2 steel. In another investigation (94), varying proportions of cobalt, aluminum and silicon were added to this steel (Table IX).

Table IX Studied high speed steels; chemical composition (94)

STEEL	C	Cr	Mo	W	V	Co	Nb	Si	Al
I (M42)	1.06	3.86	9.37	1.58	1.24	8.19	----	0.28	----
II (M2)	0.83	3.81	4.84	6.23	1.86	0.43	----	0.20	----
III	1.10	4.19	3.20	3.36	2.00	0.17	1.68	0.24	----
IV	1.08	4.21	3.38	3.28	1.90	4.38	1.81	0.36	----
V	1.13	4.29	3.27	3.40	1.97	0.28	1.77	0.95	1.49
VI	1.03	4.45	3.68	3.33	1.91	5.11	1.83	1.12	0.89

On the one hand, a comparison with the AISI M2 and AISI M42 was to be established and on the other hand the question of whether cobalt could be replaced by aluminum and silicon was to be answered. The aluminium and silicon additions resulted in a higher volume fraction of insoluble carbides, a smaller austenitic grain size and a minor amount of retained austenite with secondary hardness values after tempering of 65.5 to 66 HRC.

Experiments were also carried out on an M7 steel (HS 2-9-2) where 1%V and 0.8%W were substituted by 2%Nb (95, 96). The results showed that (without consideration of the carbon deficit) the niobium-alloyed grade could not quite achieve the tool performance of an M7 or an

M2 steel. The experiments also proved that the volume fraction of MC was higher, and that the amount of the eutectic fraction remarkably lower, than in a M7 steel.

Based on a composition of Fe + 5%Cr + 1%C, experiments were carried out to develop a steel with niobium-contents of up to 4 % by adding ferrite-stabilizing elements. A 10kg melt with a matrix composition of 2%W, 4%Mo, 1.1%V, 3.7%Cr, 4%Nb + 1.5%Al and 1%Si was designed for a laboratory test (25). Carbon content was established according to the empirical equation for stoichiometric carbides (16).

$$S_c = 0.033\ \%\ W + 0.063\ \%\ Mo + 0.06\ \%\ Cr + 0.235\ \%\ V + 0.13\ \%\ Nb$$

The two ferrite stabilizing elements, aluminum and silicon, together with the specially selected matrix composition of the steel allowed the addition of over 4% Nb without the formation of any coarse niobium-carbides during solidification.

One investigation (97) dealt with the effect of titanium and niobium on the properties of a tungsten-free high speed steel containing 0.99%C, 6.1%Cr, 3%Mo, 2.51%V, 0.65%Si and 0.53%Mn, to which up to 0.9%titanium and up to 2.0%niobium were added. The authors reported satisfactory results, i.e. a finer austenitic grain and good bending test values under comparable conditions resulting from the addition of niobium.

In addition to the examples in the section "Powder metallurgical production routes" that aim for the use of higher proportions of niobiumcarbide, specific niobium contents have also been adjusted in single cases in powder-metallurgical high speed steels. ASP-steels, which have been produced by Erasteel Kloster/Söderfors since the 1970´s developed better mechanical properties after the application of the ESH (electro-slag-heating) process, which results in a steel with a low non-metallic inclusion content. Reference (98) refers to ASP 2017 (0.80% C, 4.2% Cr, 3% Mo, 3% W, 1% V, 8% Co, 1% Nb) which is characterized by its good combination of hardness and toughness properties. It is used in cutting processes as a low-alloyed, PM high speed steel that meets demands for high toughness. When 1.9% Nb and/or 1% Ti were added to an atomized high speed steel powder of the type CSN 19830 and investigations of microstructure and tool performance were carried out (compaction of the steels was achieved in extrusion), compared to high speed steels produced in ingot metallurgy, the steels manufactured by powder metallurgy showed a remarkable increase in carbide content and an obvious improvement of the tool performance resulting from the niobium and titanium additions (99).

Thyssen Edelstahl developed two niobium-containing PM-steels, called TSP 1 and TSP 8, for which a patent has been applied (124). The TSP1, containing 0.80%C, 6.2%Cr, 3.0%Mo, 1.1%V, 3%Co and 1.0%Nb is an intermediate high speed steel produced by powder metallurgy and it is used for forging tools in warm forming processes. The alloy content as well as the performance lie between those of hot work tool steels and conventional high speed steels. The PM tool steel TSP 8 containing 2.4%C, 6.2%Cr, 3%Mo, 8%V, <0.8%Co and 1.8%Nb provides an improved performance compared to PM tool steels but a lower one compared to hard metals. The extremely high vanadium content in addition to the high niobium content results in an excellent wear resistance combined with adequate toughness. The TSP 8 is used for compacting dies in powder metallurgy and tools for cutting highly abrasive materials such as paper, paperboard or glass-fiber reinforced plastics.

Tests of materials incorporating varying high amounts of niobium-carbide and titanium-carbide in high speed steel powders of grade M3/2, i.e. an HS 6-5-2/3 steel, in order to achieve an improved wear resistance, were not successful. The addition of 7.7% niobium carbide and/or 5% titanium carbide and/or 5 to 15% manganese-sulphide resulted in poor bending values in the three-point bending test, due to clustering of the carbides and/or MnS (100). (Without mechanical alloying, a sufficiently fine carbide distribution in the matrix seems not to be possible.)

Finally, it should be mentioned that tests were also performed on an M2-steel to investigate the effect of an addition of boron (up to 1%) and niobium (up to 1.8%) on the stucture and properties, when the steel is transformed into a mixed amorphous-crystalline state by the melt spinning process. It could be proved that the thermal stability of the amorphous strips is increased by up to 100 to 150°C due to the addition of niobium, as compared to niobium free but boron alloyed HS 6-5-2 (101).

Hot Work Tool Steels

In many cases, a small amount of niobium is added to hot work tool steels to inhibit the austenitic grain growth. The matrix composition of an AISI H13 steel grade is 0.4% C, 5% Cr, 1.5% Mo with an addition of about 1% V to improve hot hardness. However, investigation show that at a temperature of 1020°C this austenite cannot dissolve more than 0.59% V (102). Further tests were carried out to reduce the vanadium content to 0.5% and at the same time add 0.1% niobium for grain stabilization. The authors report that the experimental steel could be produced at lower costs and with a finer austenitic grain size and that it showed the same properties as a H13 grade with a vanadium content of 0.95%.

These studies were continued, and a two-tonne melt with the composition 0.37%C, 5.35%Cr, 1.25%Mo, 0.35%V and 0.07%Nb was made (103). The results show that the austenitizing temperature should be adjusted to 1020°C to avoid austenitic grain growth, and that tempering at 540°C will result in optimum tensile strength and toughness properties. This was the background to an industrial application for this steel e.g. in tools for aluminum die casting.

In references (104, 105) further investigations on the same steel grade are presented. They confirm the finer austenitic grain size and the finer carbide distribution compared to vanadium containing steel, as well as a better toughness.

A more highly alloyed hot work tool steel W335 with 0.12% Nb was developed at Böhler Edelstahl Kapfenberg for extruding-press and die casting tools used in the processing of heavy, non-ferrous metals such as copper and copper alloys (106). This steel (composition: 0.38%C, 0.65%Si, 1.70%Mn, 2.60%Mo, 0.75%V and 0.15%Nb max.) permits austenitizing temperatures of up to 1080°C with an outstanding high-temperature strength at temperatures up to 600°C and above (Figure 25).

Carpenter Technology (107) has developed a hot work tool steel called “Thermowear” for extruding-press tools whose composition is 0.58%C, 4%Cr, 2.5%Mo, 1.0%V, 3%Co and 1.5%Nb and whose life is up to 100% longer than that of the more highly alloyed AISI H19. In addition to higher austenitizing temperatures of up to 1100°C without an inacceptable grain growth, the addition of niobium to the Thermowear resulted in the formation of wear-resistant carbides.

A new steel, “VTM”, for hot-forging processes was developed at Aços Villares (Brazil) showing an excellent combination of strength, ductility and wear-resisting properties. The steel has the composition 0.58%C, 4.5%Cr, 2.7%Mo, 1.8%W, 0.8%V and 0.45%Nb. This steel is considerably better in its creep resistance than H13 and four to five times better in its impact toughness than the AISI M2 at comparable hardness values of 57 to 62 HRC. Here too, niobium forms insoluble carbides in a fine distribution and increases wear resistance without affecting impact toughness (108).

Hitachi developed the niobium alloyed steel YXR33 with an estimated analysis of 0.5%C, 0.1%Si, 0.4%Mn, 4.2%Cr, 2.1%Mo, 1.2%V, 0.7%C, 1.6% W and 0.15% Nb (109) for application in the field of warm forming, where high toughness and strength values are required. In addition to a superior high temperature strength, this steel possesses excellent toughness properties within a hardness range of 54 to 58 HRC. In particular, it proves to be wear resistant and resistant against the appearance of clinks.

When weld deposits are made on hot work tool steels to decrease wear, then welding electrodes frequently contain a certain percentage of niobium carbide. Examples of an X32CrMoV33 (DIN 1.2365) steel and welding electrodes containing approx. 3% NbC are given in publications (110, 111).

Cold Work Tool Steels

Cold work tool steels are used under conditions where the temperature does not exceed 250°C. As cold work tool steel grades must possess a particularly high wear resistance, the highest possible carbide amounts are present here. A high toughness is also required when the tool surface is subject to great tensile stresses, e.g. during cold working or punching. Compressive strength and machinability are also important properties. Here too, niobium contents of 0.10% (micro-alloying) play an important part in the existence of stable carbides during heat treatment, as they inhibit austenitic grain growth and result in a fine-grained structure with improved toughness properties. The 0.10% niobium addition to a medium-alloyed steel that is used for rollers in a cold rolling mill (estimated composition 0.8%C, 2%Cr, 0.5%Mo and 0.2%V) results in an improved depth of hardness , and a reduction of retained austenite and thus provides an improved performance as compared to a non micro-alloyed grade (112).

The 12% ledeburitic chromium steels e.g. DIN W.Nr. 1.2379 (1.55%C, 12%Cr, 0.7%Mo and 1.0%V) characteristically have a particularly high abrasive wear resistance, due to their high carbide content, but they have only insignificant toughness properties. The 5% chromium steels e.g. DIN W.Nr. 1.2363 (1%C, 5.3%Cr, 1.1%Mo and 0.2%V) have remarkably improved toughness values, but a poorer wear resistance. At Böhler Edelstahl, a new cold work tool steel designated Böhler K 340 ECOSTAR was developed that combines the good wear resistance and compressive strength of the 12% chromium steels with the adequate toughness of low-alloyed 5% Cr-steel grades (91, 113-115). This secondary hardening, air hardenable cold work tool steel, poor in dimensional stability, (with a chemical composition of 1.1%C, 0.9%Si, 0.4%Mn, 8.3%Cr, 2.1%Mo and 0.5%V + 1.0%Al + 0.13%Nb) has a high toughness combined with good compression strength and high wear resistance. Due to the alloying agents, carbides are distributed more homogeneously and in finer grain sizes than in the 12% ledeburitic Cr-steel grades. This steel shows a good machinability and a very high tempering resistance (Figure 26); and is well suited for nitriding and coating. Böhler K 340 ECOSTAR is being used for cutting, blanking and punching tools (shear blades, dies, punches and mandrels) and cold forming tools (drawing, deep drawing, extrusion, embossing and threading tools).

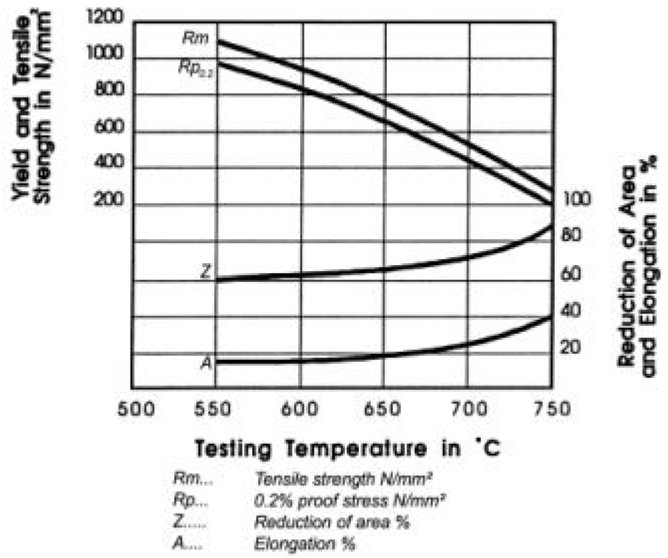

Figure 25: Hot strength chart of Böhler W335(heat treated to Rm = 1550N/mm^2) (106).

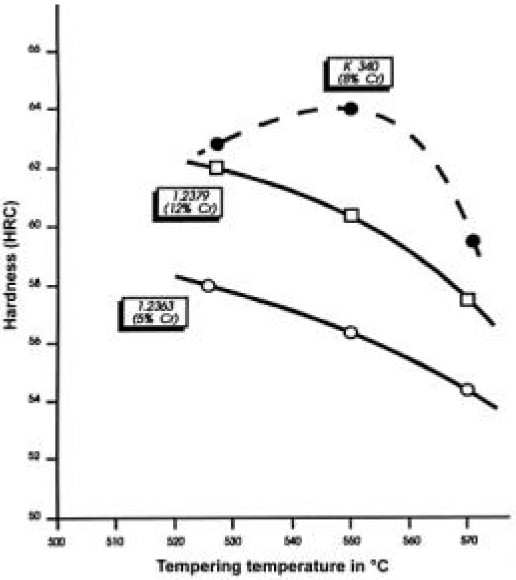

Figure 26: Long time tempering response of high chromium tool steels compared with Böhler K 340 (71) adapted from (113).

Böhler Edelstahl has recently succeeded in the development of a new ledeburitic cold work tool steel designated Böhler K 360 that realizes a further improvement in wear resistance and toughness. This steel grade combines the high toughness properties of K 340 with the excellent wear properties of DIN 1.2379 (X155CrVMo12 1). A patent has been applied for, for the Böhler K 360 steel, with a named composition of 1.25%C, 0.9%Si, 0.35%Mn, 8.7%Cr, 2.7%Mo, 1.2%V, 0.8%Al and 0.5%Nb (116). With a hardness value of 61 HRC, its bending strength lies over 5000N/mm^2, and with a hardness of 64HRC its toughness properties are remarkably better than those of the 12%-ledeburitic chromium steel at a hardness value of 61HRC. The compression strength values are also above those of the 8% Cr-steels and 12% Cr-steels; the abrasive and adhesive wear behaviour of K 360 is also better than that of the other steel grades. Thus the recently developed Böhler K 360 steel is the superior grade due to its outstanding combination of toughness, wear resistance, hardness and compressive strength (117).

Thyssen Edelstahl has developed a steel with the composition 1.1%C, 8.3%Cr, 2.2%Mo, 0.3%V and 0.8%Nb called FOR 821/Thyrodur 2393 (125). It shows a good dimensional stability, high compression strength and wear resistance, very good retention of hardness, good machinability and grindability. This grade combines also the characteristic advantages of the 5% Cr (AISI A2) and 12% Cr steel (AISI D2).

Developments in 13% chromium steels (DIN 1.4153 with 13%Cr, 0.5%Mo, 2%V, 0.8%C) also showed that a niobium addition can result in a further improvement in the property profile (118). Figure 27 shows that an improvement in toughness of 25% can be achieved at the same hardness level when the fine and homogeneous distribution of primary niobium carbides is combined with secondary hardening through vanadium. The increased molybdenum-content results in a better corrosion resistance. The wear of highly alloyed, ledeburitic cold work tool steels is essentially determined by the amount and hardness of the carbides. It is therefore an obvious development to take advantage of the harder niobium- and also tantalum carbides as compared to the softer M_7C_3-ledeburitic carbides (119). 12%-Cr-steels (X210Cr12) were therefore produced with a composition of 1-7%NbC, 1-5%TiC and 2.5%(Nb,Ti)C (120).

Investigations showed that the flank wear decreases with an increasing fraction of MC-carbides. The wear rate is highly dependent on carbide size and distribution. Due to the random distribution of MC-carbides, no increase of possible edge breakage was observed when alloying with niobium- or titanium carbide.

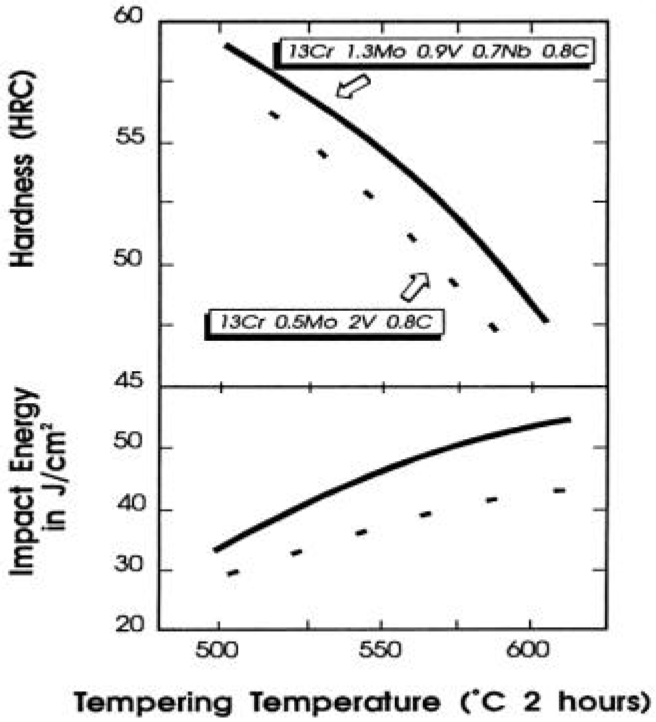

Figure 27: Properties of steel for cutting knives (118).

For hard-facing highly loaded tools, electrodes are used that are basically ledeburitic steels and that have a high content of carbide-forming elements. In this context reference is made to an electrode material of 4%C, 25%Cr, 7%Mo, 7%Nb + V and W where a surface hardness of up to 67HRC can be achieved by deposit welding. In addition to the use of Fe-Nb-powder, ferro-niobium-carbides can also be used successfully in electrodes (121).

Steels for Plastic Moulds

Steels for plastic moulds have a typical composition of approx. 0.40%C, 1.50%Mn, 2%Cr and 0.20%Mo. When manufacturing the moulds, it is important that the steels show a good machinability at high hardness values, and that they have an appropriate dimensional stability and appropriate nitriding ability. In service, acceptable compressive strength and wear resistance are necessary. The microstructure must be homogeneous with the lowest possible macro and micro-segregation. In the plastics industry, more and more aggressive materials containing various additives are being produced; the chromium content of the steel is thus increased to improve resistance to wear and corrosion. Niobium is also used as a micro-alloying element in these steels. As an example, Böhler M 261-steel, which has a typical composition of 0.13%C, 0.30%Si, 2%Mn, 0.35%Cr, 3.50%Ni, 1.20%Cu, 1.20%Al, 0.10%S and 0.06%Nb, might be mentioned (122, 123).

When tools are manufactured from this material, a tensile strength of 1250MPa can be achieved at a hardness value of 44 HRC by a simple ageing treatment and without any additional steps or surface modifications; the result is an obvious increase of compressive strength and wear resistance. Typical applications are in the injection molding of camera or electronic parts, or in compression molding dies such as the dies for plastic containers.

In reference (126) the positive effect of niobium on substituting copper in age-hardenable tool steels used for plastic processing is reported. EWK (Edelstahl Witten-Krefeld) has applied for a patent for a soft-magnetic steel for plastic moulds containing 0.05%C, 11%Cr and 0.3%Nb. The publication (127) refers to the properties of this steel, called PH X Supra.

Niobium in Cemented Carbides

Since the comprehensive study on the role of niobium in cemented carbide alloys about 20 years ago (128), scarcely any other reference can be found in the literature which would provide a more thorough metallurgical knowledge. So this paper (128) must be the main source in any summary. In the following, a short summary is presented on the role of niobium in cemented alloys, based on the results from reference (128), but also from later studies.

The most important group of hard metals are the WC-Co cemented carbide alloys. The proper wettability of WC by the binder, cobalt, which also results in appropriate toughness values, depends on a considerable solubility of WC in the metallic alloys, in particular at higher temperatures. Occasionally, small additions of other carbides are used to stabilize grain growth during the sintering process. Furthermore, WC does not form firmly adhering, high-melting-point oxide layers. WC-Co cemented carbide alloys are therefore relatively easily corroded or dissolved by the hot chips produced during machining, and that is why pure cemented carbide alloys are not suited to the machining of steels. On the contrary, TiC forms high melting-point and firmly adhering oxide layers that prevent oxidation during heating in air.

The tendency towards diffusion into the hot steel chip is much lower in the case of titanium titanium carbide and titaniumniobium carbide and their mixed carbides with WC, than it is with pure WC. On the one hand, this is related to the much lower solubility of those carbides in ferro-metals, and on the other hand to their tendency towards the development of firmly adhesive oxide layers that hinder diffusion. Furthermore, titanium-carbide and titanium-niobium-carbide additions improve high-temperature strength which is important for the machining of steel. Low temperature toughness, however, is decreased by these additions. That is why cubic carbides of varying compositions are added to WC-Co cemented carbide alloys, resulting in a cubic mixed carbide in the sintered product (1).

Tungsten carbide has a hexagonal close-packed crystal structure, while the other carbides mentioned have a fcc crystal structure. Some miscibility exists, however, since the hexagonal WC-lattice can be transformed into a cubic structure by a relatively minor shifting of the lattice components. This also explains the good solubility of tungsten carbide in cubic carbides, in particular in titanium carbides.

Investigations proved that when niobium carbide is added to a hard metal, niobium prefers the cubic carbide, exists in the cobalt binding phase only in minor amounts, and is not incorporated into the hexagonal WC (129) (Table X).

Table X Preliminary results of atom probe analysis of cemented carbide containing 53 W, 15 Ti, 11 Ta, 3 Nb, 9 Co, 7.8 C and 0.2 N (all in wt%) (129)

Cubic carbide phase (atomic composition):

$(Ti_{0.56}\ Ta_{0.11}\ Nb_{0.05}\ W_{0.28})\ C_{0.85}\ N_{0.02}$

Hexagonal carbide phase:

$W_{1.00}\ C_{1.00}$

Cobalt binder phase:

$Co_{0.91}\ W_{0.03}\ Ta_{0.015}\ Nb_{0.015}\ Fe_{0.02}\ C_{0.01}$

The hardness of the carbides decreases with increasing temperature. It should be mentioned that red hardness in mixed cubic carbides decreases more slowly at higher temperatures than the hardness of pure carbides TiC, NbC or WC (Figure 28).

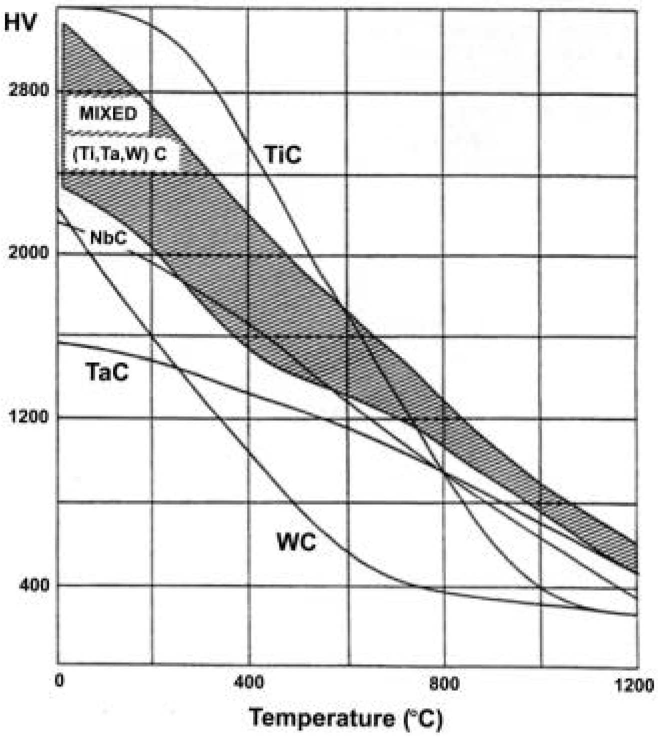

Figure 28: Variation of hardness with temperature of various carbides (130, 133).

Tantalum and niobium are similar in their chemical properties and nearly always occur together in the ore.

For the production of hard metals, not only the very expensive TaC with max. 1% NbC, but also the cheaper TaC with a higher niobium content (tantalum : niobium = 6 : 1 to 1 : 1) is used (1).

Niobium carbide has similar properties to TaC and is soluble with TaC in all ratios. It is therefore the natural and most commonly used carbide in combination with TaC. As far as its valuable properties in cemented carbide are concerned, NbC can be ranked between TaC and TiC. There are different opinions about the degree to which NbC can replace TaC in the different grades without reducing their performance. US producers still prefer the pure or Ta-rich grades; 90:10, 80:20 TaC:NbC, however 60:40 TaC:NbC has been used in Europe for some time; Japanese production falls between the two extremes (134).

Hard metal grades used for the milling of steel generally contain a relatively high amount of TaC. These TaC additions increase the toughness and decrease thermal shock resistance (1). However, TaC is expensive. Any substitute is of interest, as long as the properties of the hard metals manufactured with the substitute at least match the properties of conventional hard metal alloys containing mixed crystals of TiC-TaC-NbC. While these substitutions do not significantly change the usual mechanical and physical properties of the cemented carbide and have also been successfully used in hard metal for turning, high levels of substitution lead to premature fracture and chipping in milling applications (135). Thus, the maximum NbC substitution in phosphorus-hardened grades has been found to be 30% (136).

The carbon content of hard metals, in combination with the carbide-forming elements, must be balanced in such a way that the carbon content is neither too high to result in a graphite precipitation during liquid phase sintering, nor too low to result in the formation of complex carbides. Investigations illustrate that there exists a narrow range for the carbon content in the ternary system (Nb,W)C-WC-Co where an NbC/WC- ratio of 10/90 to 90/10 can be adjusted without the appearance of too high or too low a carbon content (131).

Apart from cobalt, the elements nickel and iron can also be used as a binding phase. The solubility of the various carbides in these binding phases is completely different (Table XI). It can be seen that niobium carbide and also titanium and tantalum carbides, are significantly less soluble in the binding phases than tungsten-carbide.

Table XI Solubility of different carbides in cobalt, nickel and iron at 1250°C (1)

Carbide	wt% Co	Wt% Ni	Wt% Fe
Tungsten-carbide	22	12	7
Titanium-carbide	1	5	< 0.5
TiC-WC 1 : 1	2	5	0.5
Tantalum-carbide	3	5	0.5
Niobium-carbide	5	3	1
Molybdenum-carbide	13	8	5
Vanadium-carbide	6	7	3
Chromium-carbide	12	12	8

Table XII contains a summary of cemented carbides of WC/Co type used nowadays and current variations of cubic carbides.

Table XII Some examples for application of WC/Co based cemented carbides, adapted from (1)

Hard material	Binder	Wt% Binder	Grain size µm	Remark
WC	Co	2 – 6	0.5 - 1	0.5 – 2 wt% TiC, VC, NbC fine-grained microstructure
WC	Co	6 - 12	0.5 - 2	0.5 – 2 wt% TiC, VC, NbC
WC	Co	6 - 12	> 2	
WC, TiC, NbC (TaC)	Co	8 – 15	1 - 2	6 – 20 wt% cubic carbides
WC, TiC, NbC (TaC)	Co	8 - 15	1 - 2	20 – 50 wt% cubic carbides

Niobium carbide is added not only to cemented carbides, but also to hard ceramic materials to improve the tool performance. Reference (132) deals with the addition of 5 – 40 wt% NbC to Al_2O_3 where, after liquid phase sintering, a composite material developed and where increasing niobium carbide concentration resulted in an improved wear resistance.

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