NIOBIUM IN CEMENTED CARBIDE

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Introduction

Like the other transition metals of the fourth to sixth groups of the periodic table, niobium forms hard refractory compounds with boron, carbon and nitrogen. The only significant technical application of these in materials harder than steel is that of niobium carbide in cemented carbide (partly including what is often referred to as cermets). The aim of this paper is to summarize the information available on this subject.

After some general comments on cemented carbides, the Nb-C and appropriate Nb-Me-C systems will be presented and this will be followed by an account of the effects of niobium on the composition, microstructure and properties of cemented carbides. References to original articles will be mainly confined to work that is not reported in standard text ,books and review articles (1-9). It is recalled that questions concerning the conversion of raw materials into carbide powder and sintered cemented carbide blanks will be dealt with in other papers at this conference.

A Brief Presentation of Cemented Carbides

From a modest beginning in the 1920's the annual world production of cemented carbide has now grown to about 25,000 tons. As sintered blanks, this represents a value of a good billion dollars of which close to 50% in the cost of raw materials in the form of ore concentrates, mixed carbide powder and cobalt. The leading cemented carbide product companies have spent much effort on forward integration and today offer a range of ready-made tools and often also advanced technical services. Their turnover is there-fore some four times that of the value of as-sintered blanks and their combined annual R & D budgets are of the order 200 millions dollars of which a large fraction is spent on developing new tools (10).

The first cemented carbide grades comprised about 90 percent of hard grains of WC, which crystallizes in a simple hexagonal structure, and 10 percent of a tougher cobalt binder phase in which a few percent of tungsten and carbon are dissolved. After mixing, the constituents are milled, dried into agglomerates that facilitate subsequent handling, pressed and sintered at a sufficiently high temperature for the cobalt phase to be liquid which ensures rapid shrinkage to full density.

A large part of the cemented carbide produced at present still consists of the primary WC-Co grades, which generally also have small additions of other carbides in order to inhibit grain growth during sintering. Niobium carbide can be used for this purpose but offers no advantages over the less costly carbides of vanadium and chromium and, therefore, the WC-Co grades will not be further discussed in this paper. The WC-Co cemented carbide grades react rather strongly with hot steel and therefore show poor perfor-mance in steel cutting. For this purpose another type of cemented carbide was introduced as early as 1930. In this a second (cubic) carbide - often referred to as the gamma phase - is present, which is a solid solution of varying amounts of TiC, TaC, NbC and WC. (In the following this will be denoted MC). Two groups of such grades were originally developed, one with TaC and the other with TiC as the major constituent of the cubic carbide. The former was mainly used in the United States and the latter in Europe. Residual evidence of this can still be observed, but, by and large, the same combinations of the different carbides are now used all over the world. The microstructure of a typical steel cutting grade with about 50 volume percent of the cubic (Ti, Ta, Nb, W)C carbide, 38 percent of the hexagonal WC phase and 12 percent cobalt is displayed in Figure 1. (It is important to differ-entiate between the amount of TiC, TaC and NbC added during mixing of powder and the amount of (Ti, Ta, Nb, W)C in the sintered product. In the follow-ing we shall only talk about the latter. It should be pointed out that depending on the process parameters used there may be marked concentration gradients in the cubic carbide). The established steel cutting grades contain up to about 70 volume percent of the cubic carbide phase. For speci-fic applications (such as finishing operations in hard working materials) very hard cutting materials have been developed containing only cubic carbide and no hexagonal WC. The first materials of this type were the TiC-Ni grades, generally with additions of molybdenum that have sometimes been included under the heading of "cermets". During the last few years new tougher products of this type have been introduced, containing other cubic carbides and nitrides and also WC. In some cases considerable amounts of cobalt have been added to the binder phase. In this way the region between the harder established MC-WC-Co steel cutting grades and the original TiC-Ni grades is being filled.

Figure 1. The microstructure of a typical steel
cutting carbide tool.

Of great importance in all cemented carbide grades are the carbon con-
tents, which are difficult to control due to the presence of a volatile
carbon compound during sintering. For a summary of this situation, see for
instance the recent paper by Spriggs (11). Too much carbon leads to the
formation of graphite and too little to the formation of complex carbides.
In the WC-Co as well as the MC-WC-Co systems there exists a narrow region of
carbon contents within which both these two situations can be avoided. The
exact carbon contents within the WC-Co two phase or MC-WC-Co three phase
region is also of importance since the solubility of tungsten in the binder
phase is higher at low carbon contents than at high carbon contents, and this
has a considerable influence on properties and performance. In all discus-
sions of the effects of varying compositions on the properties of cemented
carbide, the influence on the carbon balance has always to be thoroughly
considered.

In recent years cemented carbides with coatings of TiC, TiN and Al_2O_3
(often in combinations) have been increasingly used in metal cutting opera-
tions. Some results from studies of coatings of NbC have been published (12-
16), but it appears that only in special cases do they offer advantages over
the corresponding titanium compounds (5). With the advent of coated cemented
carbide grades, modifications of the substrates have been made and these are
partly confined to the surface region in order to achieve a good adhesion of
the coating.

As evident from this brief presentation, cemented carbides are rather
complex materials; their performance in metal cutting and rock drilling
operations or as wear resistant parts also depends on a complex interplay
between more fundamental mechanical properties. Thus, it is difficult to
single out the critical effects of one element, in particular of an element
such as niobium of which common cemented carbides only contain a few percent.
Hence, it is in most cases not possible to draw anything but rather tentative
conclusions from the scattered studies that have been published on niobium in
cemented carbides.

The Nb–C System. Properties of NbC

The equilibrium diagram of the Nb–C system, mainly according to Storms (3, 4) is given in Figure 2. There are still some uncertainties in the area of compositions around Nb_2C, but this is of minor importance in this context, since only NbC occurs in cemented carbides. This phase which crystallizes in the rock–salt structure has an extended homogeneity range from $NbC_{0.65}$ to $NbC_{1.00}$. According to the study of Suzuki, et al (20) on the NbC- WC-Co system in the range WC/NbC from 90/10 to 10/90 the composition of the cubic (Nb,W)C carbide varies from $(Nb,W)C_{0.80}$ to $(Nb,W)C_{0.88}$ and a similar deviation from stoichiometry is observed for niobium carbide in steels. From the observed variation in lattice parameter one infers that the changes in composition depend on a variable fraction of the carbon sites being vacant. It seems likely that discrete phases with ordered vacant and filled carbon sites exist at lower temperatures as is the case in similar systems and there are indications, that this may be the case (18, 19), see also Figure 2. Nitrogen, and also oxygen, can substitute for carbon in NbC. Impurities of nitrogen in cemented carbides are almost certainly in the cubic carbide phase. The same applies to oxygen, but much of this element disappears as carbon monoxide during sintering. On this point we would expect a difference between cemented carbides having a high or a low TiC/TaC+NbC ratio, the former grades having a higher impurity level of oxygen due to the stronger titanium–oxygen affinity.

Some physical and mechanical properties are summarized in Table I. They are quite similar to those of related borides, carbides and nitrides. The variation of hardness with temperature is given in Figure 3. Since cemented carbide tools may attain temperatures in excess of 1000 C in metal cutting operations hot hardness is an important property. As a measure of toughness, transverse rupture strength at room temperature is generally given. Some values of this property for cemented carbides with 10 wt. percent cobalt and varying ratios of MC/WC for different MC carbides are given in Figure 4. Chemically, niobium carbide is quite inert having, for instance, a high resistance towards attack from the common acids. Of particular interest for the applications in metal cutting is the reactivity towards hot iron and steel. One would expect the latter to be closely correlated to the solubility in austenite which is much less than that of WC and VC but about the same as that of TiC (16, 24). For a more theoretical discussion of the properties of NbC and their correlation to chemical bonding we refer to the review article by Williams (9).

The NbC-WC-TiC and Related Systems

The results of a fairly recent study (25) of the NbC-WC-TiC systems are summarized in Figure 5. They agree quite well with previous publications (1, 26). The most important observation is the reduction of WC contents in the cubic carbide phase with increasing contents of NbC, this effect being quite analoguous to the TaC-WC-TiC system. From the limited results available (25, 26) it appears that the temperature dependence of the solubility of WC in the cubic carbide is greater in the system with NbC than in that with TaC, and it would be of interest to have more information on this point.

The hot hardness of the cubic carbide in the NbC-WC-TiC system with compositions close to the two phase regions (that is mixed carbides with nearly the maximum of WC in solid solution) has been determined by Miyoshi and Hara (22), and the results are shown in Figure 3. It is worth noting that the hardness of the mixed carbides decreases less with temperature than that of TiC.
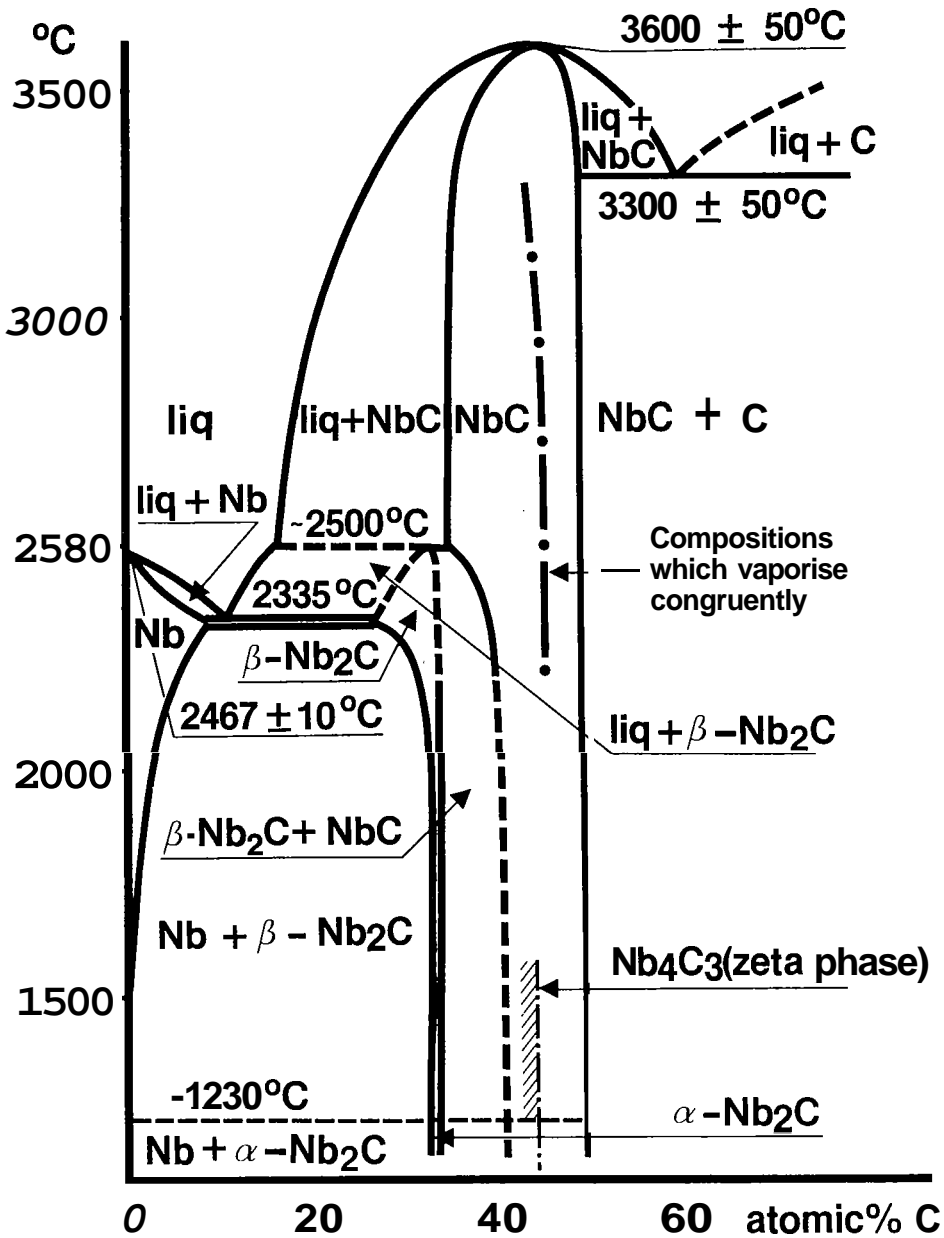
Figure 2. Equilibrium diagram of the Nb-C system (3, 4).

Table I. Some properties of niobium carbide (2, 21).

Lattice parameter (cubic structure)   (4.4702 Å
                                             (0.44702 nm
Density g cm^{-3} 7.18

Melting 'point, °C   3613 ± 26

Color   slightly brownish magenta

Coefficient of thermal expansion   6.65 10^{-6}

Microhardness HV 0.05   1800

Young's modulus, MN m^{-2} 58000 (8.41 10^{-6} psi)

Resistance (electrical), 10^{-6} ohm cm   19

Among related systems NbC-WC-HfC should be mentioned in particular since (Hf,Nb)C has been suggested as a substitute for TaC. It appears that the quasi-ternary systems with HfC are similar to those with TiC with the exception that there is a HfC-NbC (and HfC-TaC) miscibility gap at lower temperatures (25).

Niobium Carbide in Cemented Carbides

The addition of niobium to cemented carbides has effects on the composition of the various phases, the microstructure and the properties and we shall deal with these topics in turn.
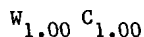
In Table II we have assembled results from a recent study of a steel cutting grade with a Field Ion Microscope (FIM) and an attached atom probe (27).   The composition found for the cubic carbide phase is marked with a cross in Figure 5 (assuming tantalum to be equivalent to niobium); it lies quite near to the boundary between the single phase and two phase region in the NbC-TiC-WC system as one would expect. Virtually all of the niobium added is dissolved in the cubic carbides. It should be recalled that if niobium carbide is added as a replacement for TiC the amount of WC in the cubic carbide will decrease, that is the volume ratio cubic carbide/tungsten carbide will decrease.

Table II. Preliminary results of atom probe analysis of cemented
           carbide containing 53 wt % W, 15 Ti, 11 Ta,
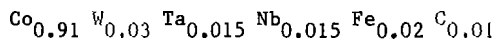   3 Nb, 9 Co, 7.8 C, 0.2 N, (27).

Cubic carbide phase (atomic composition):

$$(Ti_{0.56} \, Ta_{0.11} \, Nb_{0.05} \, W_{0.28})C_{0.85} \, N_{0.02}$$
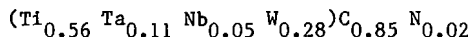
Hexagonal carbide phase:

$$W_{1.00} \, C_{1.00}$$

Cobalt binder phase:

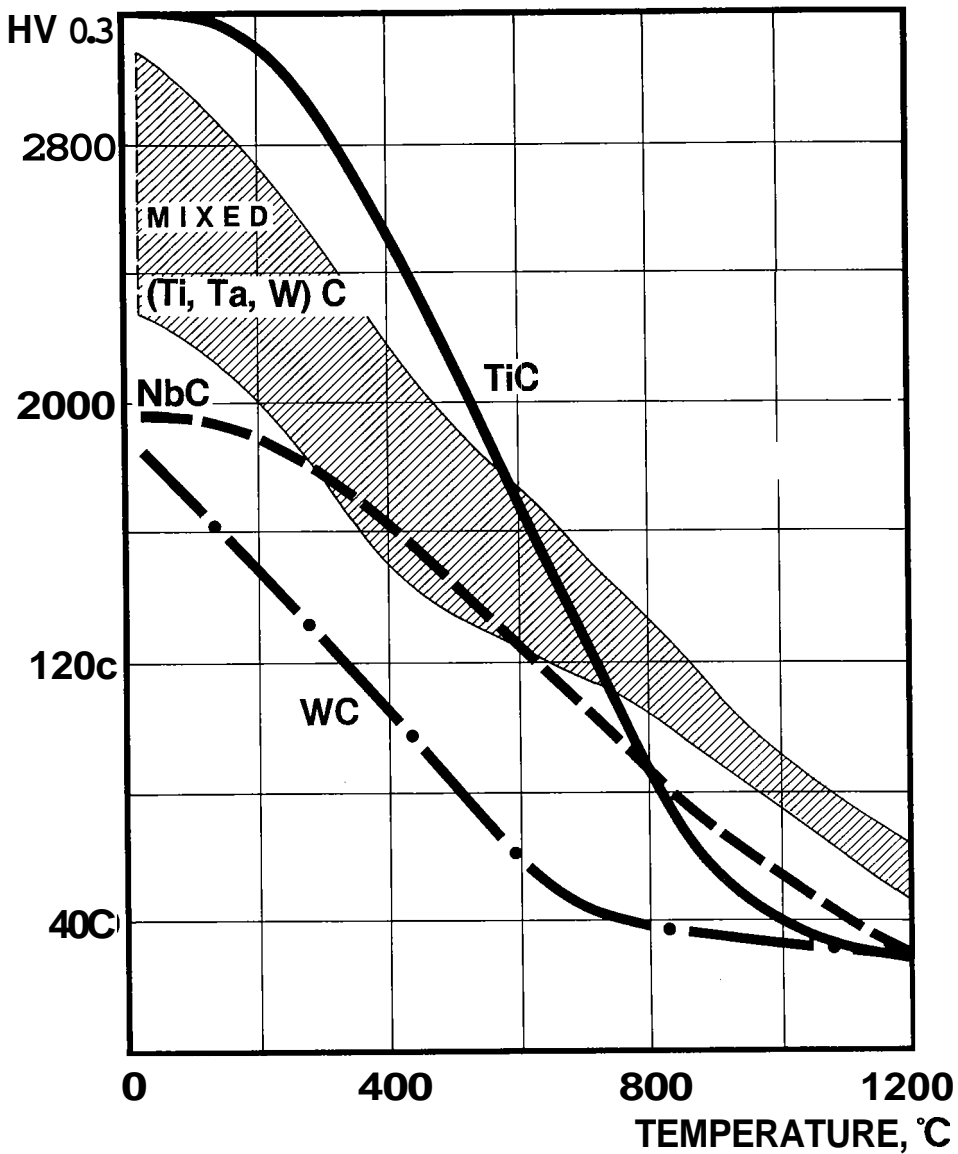$$Co_{0.91} \, W_{0.03} \, Ta_{0.015} \, Nb_{0.015} \, Fe_{0.02} \, C_{0.01}$$

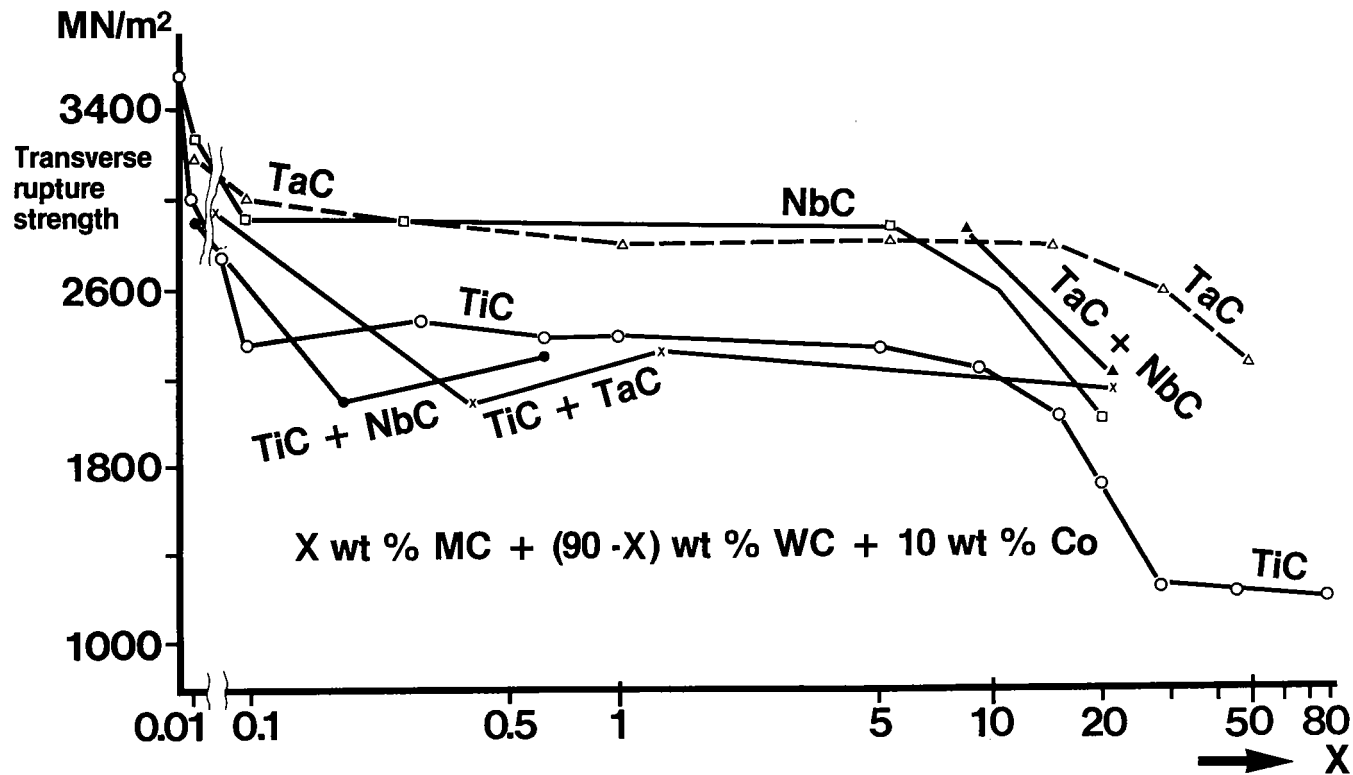Figure 3. Variation of hardness with temperature for various carbides.

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Figure 4. Transverse rupture strength as a function of composition for various carbide systems.
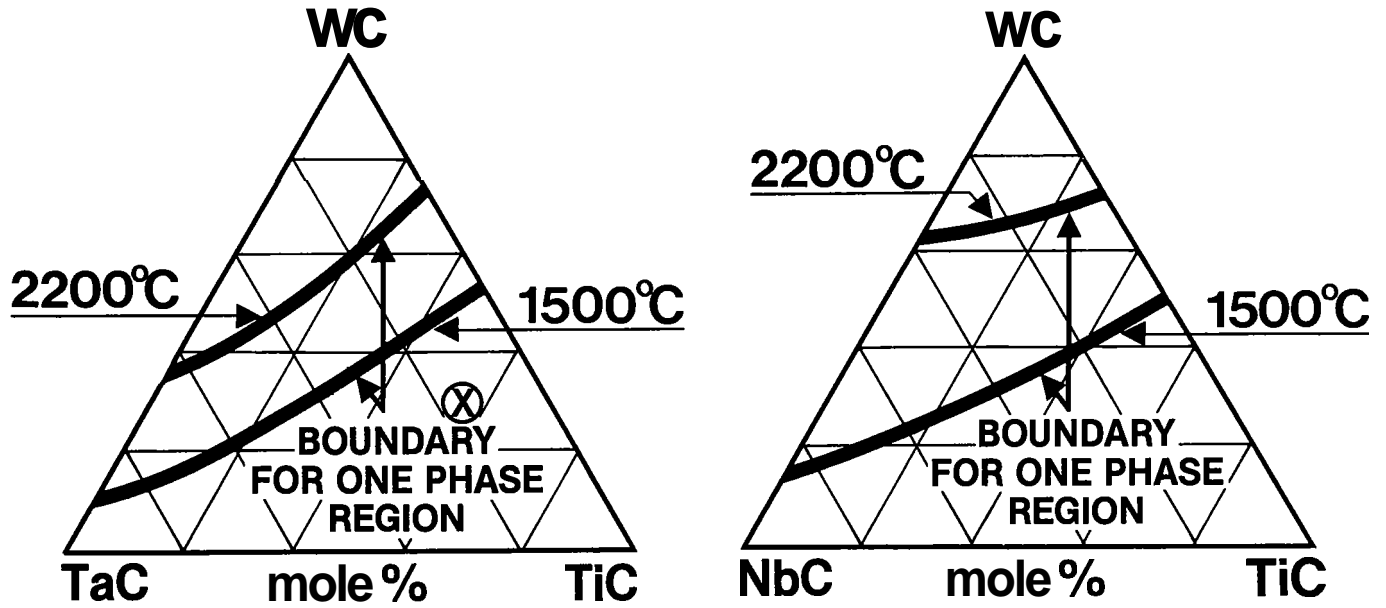
Figure 5. NbC–WC–TiC system.

Additions of niobium have no effect on the hexagonal tungsten carbide phase which appears to have a virtually constant composition, WC, in all commercial cemented carbide grades. Niobium may have a minor effect on the cobalt binder phase in which it has a small solubility. It is also very possible, as suggested by Suzuki and Yamamoto (28), that a high volume fraction of cubic carbide may retard the precipitation of WC from the super-saturated solution in the binder phase. At present it is not possible to draw any firm conclusions on this point and, in particular, the effect of niobium on WC precipitation in the binder phase is not know. Nor can much be said about the effects of niobium on the microstructure of cemented carbide (except for the changes of the cubic carbide/tungsten carbide volume ratio). Unpublished work from this laboratory indicates that the average (carbide) grain size increases somewhat with increasing NbC/TaC ratio, which would be consistent with the somewhat higher solubility of NbC in the binder phase, but it is uncertain how this is influenced by the particular processes used.

In an investigation of the NbC-WC-Co system Suzuki and Yamamoto (20) showed that, for a narrow range of total carbon contents, there is a ternary (Nb,W)C-WC-Co region (Figure 6) for NbC/WC ratios from 10/90 to 90/10. Hence, cemented carbides with sound microstructures (avoiding graphite or the Co-W ternary carbides) can be produced up to very high concentration of NbC. Regarding the influence of niobium on properties of cemented carbides not much can be said. This is already apparent if we confine ourselves to the four properties, which are often used in the characterization of cemented carbides, namely hardness, transverse rupture strength, flank and crater wear, in themselves rather complex properties depending on many parameters that have to be more or less arbitrarily fixed. In Figure 7 we have indicated how these properties vary with average carbide grain size and volume fraction of cubic carbide. We can predict with some certainty the effect of niobium on volume fraction of cubic carbide, but we know very little of its effects on average carbide grain size. While the effects of niobium on the composition of the cubic carbide is well established, there are no systematic studies on the effect of cubic carbide composition to which this can be correlated. From published information it cannot be inferred which mixture of these effects lies behind the results of Kieffer et al (25). His results concerning cemented carbides with varying NbC/TaC ratios are summarized in Figure 8.

Thus, this survey of niobium in cemented carbide ends up with more questions than answers. It is even difficult to give a completely satisfactory explanation to the extensive practical observations that up to 50 percen of the tantalum in TaC can be replaced by niobium without any significant adverse effect on process costs or properties. The results of Suzuki and Yamamoto (20) as well as of Kieffer et al (25) indicate that higher concentrations of niobium may well be used without any marked deterioration of hardness or transverse rupture strength, but there are no indications that there would be any significant improvements of properties. It appears that very much the same can be said about the substitution of (Hf,Nb)C for TaC, In more commercially oriented debates, fairly strong views on the merits of niobium in cemented carbide are sometimes aired. What is proposed may be correct for the particular process parameters chosen by a certain manufacturer and for the set of tests that has been chosen. However, it is obvious that the effects of variations in niobium contents are rather limited and therefore, quite extensive studies of various factors indicated above have to be carried out before we can draw more general conclusions.
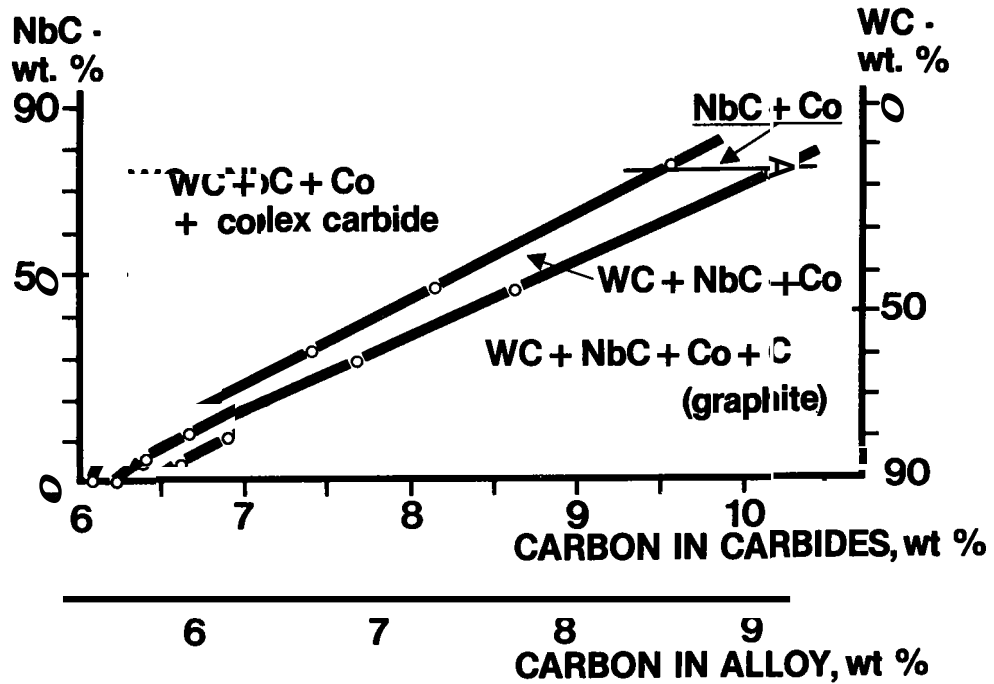
Figure 6. Location of ternary (Nb, W) C-WC-Co region.

MC · RICH

MC · POOR

LARGE   SMALL
GRAIN SIZE

MC · POOR

MC · RICH

LARGE   SMALL
GRAIN SIZE

HV 3

MC · RICH

≈1500

MC · POOR

LARGE   SMALL
GRAIN SIZE

T.R.S.
MN/m²

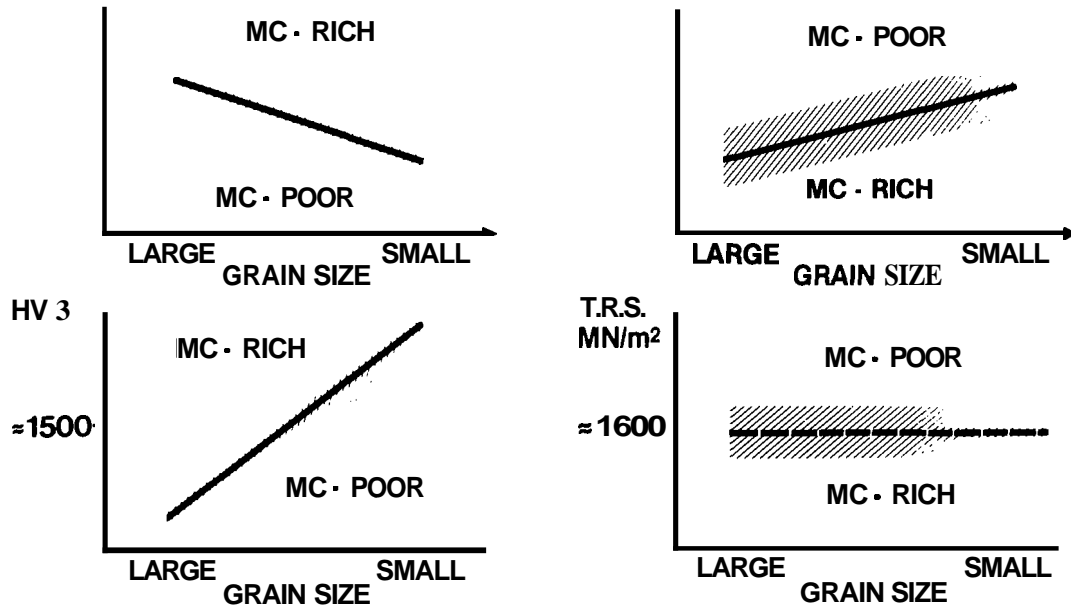MC · POOR

≈1600

MC · RICH

LARGE   SMALL
GRAIN SIZE

Figure 7.   Effect of carbide grain size and volume fraction
of cubic carbide on various properties.
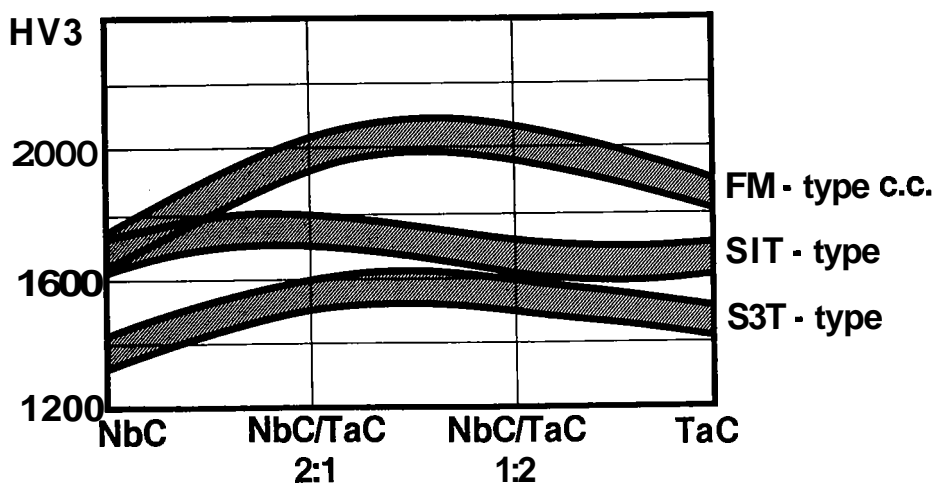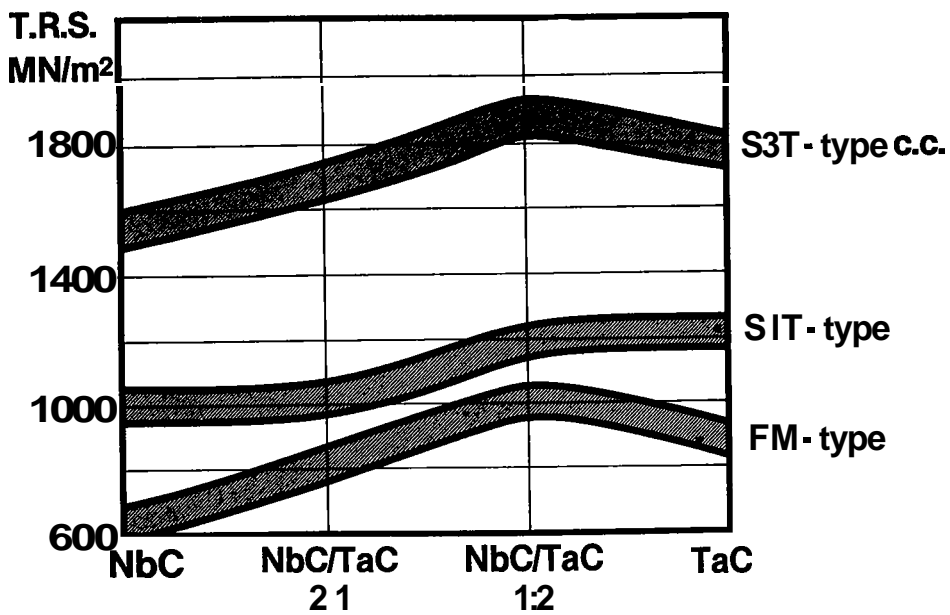
Figure 8.   Effect of NbC/TaC ratio on properties
after Kieffer et al (25).

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R. Kieffer	US Pat *3 463 621* Fr Pat *1 594 539*	making HfC-NbC mixed crystals using NbC + HfC additions instead of TaC
Komatsu (Toyota)	US Pat *3 887 443* US Pat *3 922 405*	precipitating Group V carbides (incl NbC) on cemented carbide or steel substrates n salt bath containing molten borate salts.
Dzodziev et al	DGR Pat *131 182*	Nb as addition to TiC Ni–Mo alloys.
Jun Nemeth	UK Appl *2 038 879*	composite aterial: TiB_2 + NbN + binder metal.