

The gamma/WC solubility boundary in the quaternary TiC-NbC-TaC-WC system at 1723 K

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The composition of the gamma phase in equilibrium with tungsten carbide has been experimentally determined at 1723 K by use of the electron microprobe. The systems studied are the ternary TiC-TaC-WC, TiC-NbC-WC, NbC-TaC-WC systems and the quaternary TiC-NbC-TaC-WC system at two TaC/NbC ratios.

1. Introduction

Cemented carbide grades for metal cutting are comprised of a cobalt binder, tungsten carbide (also known as alpha phase) and gamma phase. The latter phase has the B1 crystal structure and is a solid solution of TiC, NbC, TaC and WC. The particular properties of metal cutting grades are partially obtained by varying the total amount of carbides in the cemented carbide. Thus when designing new grades or when trying to replace one carbide by another it is helpful if the solubility of WC in the gamma phase in the quaternary TiC-NbC-TaC-WC phase diagrams is known.

No information on this solubility in the quaternary system has been found in the literature. In the work reported here an attempt has been made to define the region of compositions of interest to cemented carbide manufactures by measurement of the composition of the gamma phase in equilibrium with WC in a number of standard and specially manufactured grades. An article has already been published in which this approach has been used to determine solubility in the ternary TiC-TaC-WC system [1].

2. Materials and experimental details

The composition of the grades studied are given in Table I. All grades were manufactured after commer-

TABLE I Composition of grades studied (wt %)

Grade	TiC	NbC	TaC	WC	Co	at % TaC at % NbC
1	19.0	3.8	12.2	55.5	9.5	1.75
2	12.0	2.0	3.0	74.8	8.2	0.82
3	9.8	3.7	5.7	70.0	10.8	0.84
4	4.3	3.7	12.1	69.9	10.0	1.78
5	11.9	4.0	6.0	68.6	9.5	0.82
6	2.6	2.4	3.6	85.9	5.5	0.81
7	4.0	1.9	6.1	77.0	11	1.75
8	2.34	0	11.29	76.37	10	∞
9	1.13	0	14.63	74.24	10	∞
10	5	0	4	81	10	∞
11	6.0	0	1.0	83.0	10	∞
12	0	20	0	70	10	0
13	5	5	0	80	10	0
14	0.3	2.0	6.2	86.9	5.1	1.69
15	2.7	1.8	2.63	86.7	6.0	0.85

cial practice. Appropriate mixtures of the various pure carbides and cobalt were ball milled in alcohol and the resulting slurry spray-dried. Specimens suitable for this study were pressed from the powder and sintered at 1723 K in argon at reduced pressure. After this standard sintering procedure the mean particle size in the specimens was about 1.5 μm .

After being sintered in the standard manner, all specimens were resintered at 1723 K for 24 h in argon to both coarsen the gamma phase particles to make their composition easier to measure using the electron microprobe, and to ensure a closer approach to equilibrium. Resintering took place in graphite-lined furnaces which ensures that the carbon activity, a_c , in the specimen is close to unity. After resintering, the specimens were cooled as rapidly as possible to ensure the retention of the gamma phase composition occurring at the equilibrium temperature of 1723 K. The initial cooling rate was 15 K min^{-1} from 1723 to 1520 K.

Specimens were sectioned, ground and polished and the gamma phase composition measured using a Camebax electron microprobe. As the mean gamma particle size is about 3 μm , beam spreading was minimized by using an accelerating voltage of 15 kV and a specimen current of 20 nA. Pure element standards were used together with the Camebax on-line program for correction of the intensity ratios. Carbon was, as before [1], determined "by difference" because of known inaccuracies in its determination by measurement.

The lattice parameter of the gamma phase in all samples was determined by X-ray diffractometry using a Rigaku diffractometer equipped with a rotating anode operated at 9.5 kW. To correct for peak shifts due to specimen positioning errors the tungsten carbide in the specimens was used as an internal standard.

The volume fraction of the various phases in the samples was determined from photomicrographs using the linear intercept method [2].

3. Experimental results

The results of all these measurements are given in Tables II and III. In Table II (microprobe results) are

TABLE II Composition of gamma phase (at %) microprobe results

	Ti		Nb		Ta		W		Co		C(by diff)	
	\bar{x}	$\pm S$	\bar{x}	$\pm S$	\bar{x}	$\pm S$	\bar{x}	$\pm S$	\bar{x}	$\pm S$	\bar{x}	$\pm S$
1	28.4	1.1	2.8	0.2	5.4	0.1	16.8	0.6	0.8	0.1	45.8	1.4
2	30.1	0.7	2.7	0.1	2.3	0.1	17.9	0.9	0.5	0.1	46.5	1.5
3	27.4	1.1	5.4	0.3	4.7	0.2	15.6	0.8	0.8	0.1	46.2	2.3
4	20.2	0.5	9.7	0.3	16.6	0.4	9.6	0.5	0.6	0.1	43.2	1.4
5	26.0	0.9	4.5	0.3	3.9	0.2	16.2	1.0	0.7	0.3	48.7	2.1
6	Raw data not available											
7	23.5	1.0	5.6	0.4	10.9	0.5	11.0	0.5	0.6	0.1	48.3	1.7
8	11.9	0.4	0.1	0.1	42.7	1.4	5.6	0.5	0.5	0.1	39.2	2.0
9	20.5	0.6	0.1	0.1	28.2	1.0	8.2	0.4	0.4	0.1	42.4	1.8
10	30.0	0.8	0	0.1	7.1	0.7	14.5	0.9	0.4	0.2	47.9	1.7
11	16.8	0.4	0	0.1	1.5	0.1	16.8	0.4	0.6	0.2	50.0	1.3
12	1.1	0.1	42.8	2.6	0.7	0.1	6.2	0.3	0.4	0.1	48.7	2.8
13	24.0	0.7	11.6	0.7	0.2	0.1	14.0	0.6	0.5	0.1	49.9	1.8
14	5.5	0.2	21.2	1.9	28.1	2.4	5.3	0.5	0.2	0.1	39.7	2.3
15	20.8	1.1	6.8	0.4	5.8	0.4	14.8	0.9	1.1	0.4	50.8	1.1

given mean metal atom content (at %) in the gamma phase and their standard deviations. These results have been converted to mole fraction of TiC, NbC, TaC, WC by assuming carbon stoichiometry and the resulting gamma phase compositions are given Table III. Standard deviations have been omitted here, but are approximately twice the standard deviations in Table II. In Table IV the gamma phase compositions in Table III have been converted to weight percent of the various carbides. In Table V are given the lattice parameters (a) of gamma phase. Also given in Table V are the densities (ρ) of the various gamma phases calculated from their measured composition and molar volume, V_m (see footnote to Table V).

Using the procedure described in the Appendix, the approximate composition of the gamma phase can be calculated from alloy composition and compared to that measured. These results are presented in Table VI together with the gamma phase volume fractions, f_γ , measured. For three of the seven grades in this table the estimated gamma phase composition is in reasonable agreement with the measured composition in Table III. For the other four grades, agreement is poor. However, it must be noted that Equation A2 is extremely sensitive to f_γ and small errors in this can yield extremely incorrect compositions.

The grades containing quaternary gamma phase are manufactured from two niobium/tantalum carbides

with different TaC/NbC ratios (1.75 and 0.82, respectively). Owing to the insolubility of TaC and NbC in WC and their low solubility in cobalt this ratio should be maintained between these carbides in the gamma phase composition. As seen from Tables I and III this is indeed so for all grades except grade 14. The reason for the discrepancy in this case is unknown.

4. Discussion

4.1. Phase diagrams

In calculating the gamma phase composition in mole fraction the assumption has been made that the gamma phase has stoichiometric carbon content. This assumption must be made due to the difficulties associated with obtaining an acceptable measurement of carbon content in the gamma phase with the microprobe. The assumption can be partially justified by the fact that all specimens contained graphite after resintering for 24 h indicating that the carbon activity was approximately unity in all specimens.

The great advantage of being able to assume carbon stoichiometry for the gamma phase is that it enables the pseudo quaternary TiC-NbC-TaC-WC phase diagram to be visualized as a tetrahedron with the TiC-TaC-WC system as base (Fig. 1). To present the compositional data given in Table III use can also be made of the fact that the standard grades are

TABLE III Gamma phase composition X^{MeC} , mol fraction

	TiC	NbC	TaC	WC	TaC/NbC
1	0.532	0.052	0.101	0.315	1.94
2	0.568	0.051	0.043	0.338	0.84
3	0.516	0.102	0.089	0.294	0.87
4	0.360	0.173	0.296	0.171	1.71
5	0.514	0.089	0.077	0.320	0.87
6	0.400	0.190	0.158	0.250	0.83
7	0.461	0.110	0.214	0.216	1.95
8	0.200	0	0.709	0.093	∞
9	0.360	0	0.496	0.144	∞
10	0.581	0	0.138	0.281	∞
11	0.630	0	0.030	0.340	∞
12	0.022	0.843	0.014	0.122	0.02
13	0.484	0.234	0	0.282	0
14	0.092	0.353	0.468	0.088	1.33
15	0.432	0.141	0.120	0.307	0.85

TABLE IV Gamma phase composition (wt %)

	TiC	NbC	TaC	WC
1	26.9	4.6	16.4	52.1
2	29.9	4.7	7.3	58.1
3	26.6	9.2	14.8	49.5
4	16.6	13.9	43.8	25.7
5	26.2	7.9	12.6	53.3
6	19.4	16.2	24.7	39.7
7	22.5	9.4	33.6	34.5
8	7.2	0	81.9	10.9
9	14.8	0	65.8	19.4
10	29.9	0	22.9	47.3
11	34.3	0	5.3	60.5
12	1.1	76.0	2.3	20.5
13	26.7	22.6	0	50.8
14	3.7	24.7	60.2	11.5
15	20.9	11.9	18.7	48.5

TABLE V Lattice parameters and densities of gamma phase

Grade	Lattice parameter, a (nm)	Density* (kg m^{-3})	Density (kg m^{-3}) calculated from Eq. 10
1	0.4346	9600	9800
2	0.4338	9300	9500
3	0.4350	9400	9600
4	0.4395	10200	10300
5	0.4349	9600	9700
6	—	—	10000
7	0.4373	9700	9900
8	0.4422	12800	12800
9	0.4392	11400	11400
10	0.4345	9400	9600
11	0.4326	9030	9260
12	0.4455	8600	8700
13	0.4363	8700	8960
14	0.4440	11400	11500
15	0.4370	9870	10100

*Density has been calculated from:

$$\rho_\gamma = \frac{\sum \text{mol fraction } X^{\text{MeC}} \times \text{mol. weight MeC}}{V_m}$$

where $V_m = a^3 L/4$, L being Avogadro's number.

manufactured using (Ta, Nb)C with fixed TaC/NbC ratios. These ratios are maintained in the composition of the gamma phase formed after sintering. The compositional data can thus be presented upon pseudo-ternary sections through the quaternary tetrahedron at particular TaC/NbC ratios corresponding to the (Ta, Nb)C used. Such a section is sketched in Fig. 1. Use of such sections allows both alloy composition and corresponding gamma composition to be plotted in the same diagram. The tie-line joining them goes through the pure WC corner as none of the other carbides are soluble in WC. The one disadvantage of this method is that rather complex, but readily usable compositional axes are obtained. This approach has thus been used to plot the three pseudo-ternary diagrams TaC/NbC = ∞ (TiC-TaC-WC system), TaC/NbC = 1.75, TaC/NbC = 0.82 presented in Figs. 2, 5 and 6. Note that the TaC-NbC-TiC and TaC-NbC-WC sides of the ternary triangle now have a different length to the TiC-WC side. The correct side length is readily calculated for a given TaC/NbC ratio.

4.1.1. TiC-TaC-WC system

The additional experimental data show that the solubility line suggested for this system in [1] is incorrect in the vicinity of the TiC-WC axis. The new measurements indicate that the solubility line should intersect

TABLE VI Test of accuracy of analysis, use of Equations A2 and A3

Grade	f_γ	Calculated composition (mol fraction)			
		TiC	NbC	TaC	WC
1	0.77	0.59	0.07	0.12	0.22
2	0.45	0.73	0.07	0.06	0.14
3	0.47	0.60	0.13	0.11	0.16
4	0.28	0.49	0.24	0.43	-0.16
5	0.54	0.60	0.11	0.09	0.20
6	0.2	0.42	0.22	0.18	0.18
7	0.22	0.61	0.16	0.28	-0.5

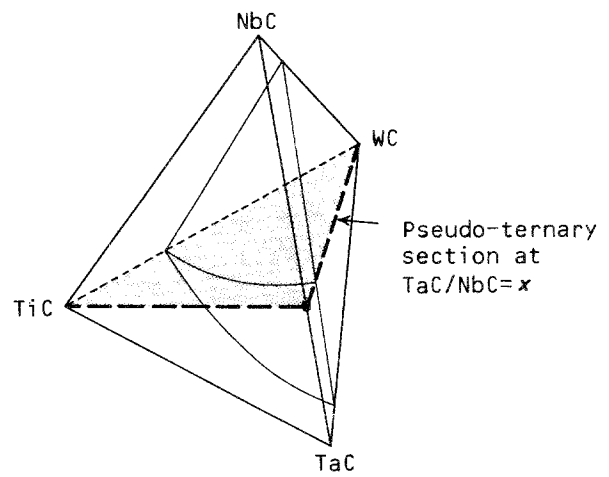


Figure 1 Illustration of a pseudo-ternary section at a given TaC/NbC ratio in the quaternary TiC-NbC-TaC-WC tetrahedron.

the TiC-WC axis at about 0.35 mol fraction WC instead of the 0.435 mol fraction WC suggested in [1]. The new value for the TiC-WC binary is the same as that evaluated for the carbon-rich side of the gamma/WC phase field by Uhrenius [3] from Rudy's [4] experimental data at 1773 K. Good agreement with the new value is also obtained by extrapolating to 1723 K the experimental measurements obtained by May [5] for the TiC-WC system over the temperature range 2173 to 1773 K.

The solubility line given in Fig. 2 is now in good agreement with that suggested by Chaporova and Cheburaeva [6] for 1773 K.

4.1.2. TiC-NbC-WC system

From the data given in Table III and the knowledge that in the TiC-WC system the gamma phase in equilibrium with WC contains 0.35 mol fraction WC the approximate position of the solubility line in the TiC-NbC-WC system can be obtained, Fig. 3.

The composition of the gamma phase in the binary NbC-WC system determined in this report is in good agreement with the extrapolation to 1723 K of Rudy's [7] experimental data for the carbon-rich side of the gamma/WC phase field in the Nb-W-C system at temperatures of 1970 K and over.

4.1.3. NbC-TaC-WC system

In this system the compositions of the gamma phase in equilibrium in the NbC-WC and TaC-WC binaries is known, see Table III and [1], respectively. Unfortunately, the "ternary specimen", grade 14, in this system was found to contain quite a high TiC content and also appears to have an incorrect TaC/NbC ratio. The experimental composition of the gamma phase in grade 14 has been "corrected" for its TiC content and is plotted in the NbC-TaC-WC phase diagram in Fig. 4 along with the compositions obtained for the two binaries. Agreement is exceptionally good considering the possible errors in the composition of grade 14. With reflection this indicates that the solubility line is virtually parallel to the NbC-TaC axis as in only such a case will errors in TaC/NbC ratio be minimized.

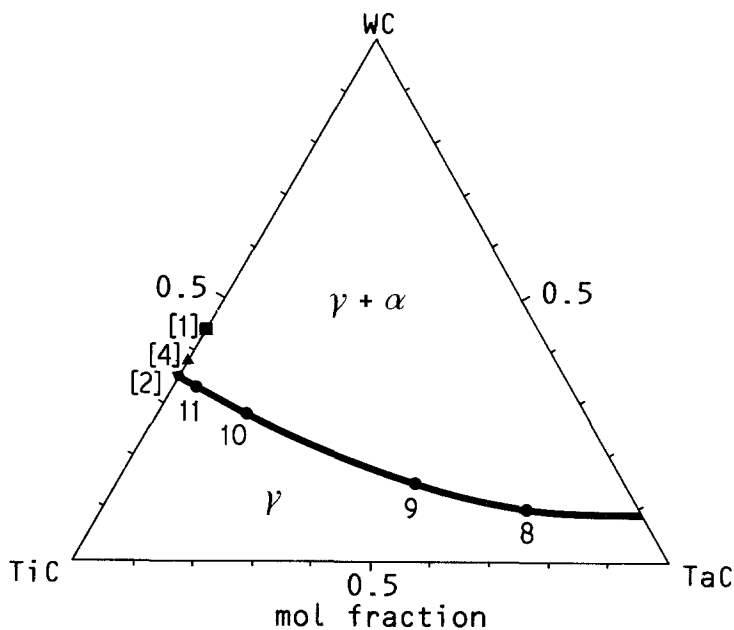


Figure 2 TiC-TaC-WC ternary phase diagram at 1723 K. Figures along the solubility line indicate grade number in the tables.

**4.1.4. TiC-NbC-TaC-WC system,
TaC/NbC = 1.75**

The experimental data are presented in Fig. 5. The composition of the gamma phase in the TiC-WC binary determined in Section 4.1.1. has been used. The value for equilibrium between gamma and WC in the NbC-TaC-WC system at TaC/NbC = 1.75 has been obtained from Fig. 4.

A solubility line has been drawn in Fig. 5 between the various experimental points and is a reasonable fit to the experimental data.

**4.1.5. TiC-NbC-TaC-WC system,
TaC/NbC = 0.82**

The experimental data are presented in Fig. 6. The compositions for the TiC-WC binary and NbC-TaC-WC end point were obtained as mentioned in the previous section.

The solubility line drawn in Fig. 6 is, once again, a reasonable fit to the experimental data.

4.2. Calculation of volume fractions of phases in cemented carbides

The phase diagrams presented in Fig. 2 to 6 can be used to calculate volume fraction of phases formed in

cemented carbides after sintering and the material has cooled to ambient temperatures.

As cemented carbides contain cobalt as well as gamma phase and WC the ternary Co-WC-gamma phase diagram sketched in Fig. 7b must be used to calculate volume fractions of phases. Note that now all compositions are in weight per cent. The base-line of the triangle in Fig. 7b is the extension of the tie-line joining alloy composition to gamma phase/WC composition of the grade in question to meet the $n\text{TaC}:(1-n)\text{NbC-TiC}$ side of the pseudoternary carbide phase diagram at, for example, A in Fig. 7a.

Following West [8] weight fractions and thus volume fractions of the three phases Co, WC and gamma phase can be calculated from the construction shown in Fig. 7b if it is assumed that all phases are essentially insoluble in one another. This is true except for WC in cobalt. However, as the solubility of WC in cobalt is less than 0.03 atom fraction [9] at temperatures below about 1300 K in specimens in which $a_c = 1$ its effect can be ignored to a first approximation.

In Fig. 7b composition X_{Co}^{all} is the weight per cent cobalt in the grade. It is also the "centre of gravity" [8] of the composition triangle $X_{Co}^1, Z_{Co}^1, Y_{Co}^1$ which represents the three phases cobalt, WC and gamma

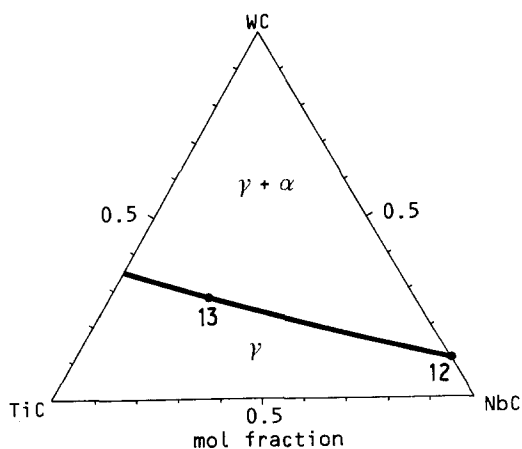


Figure 3 TiC-NbC-WC ternary phase diagram at 1723 K.

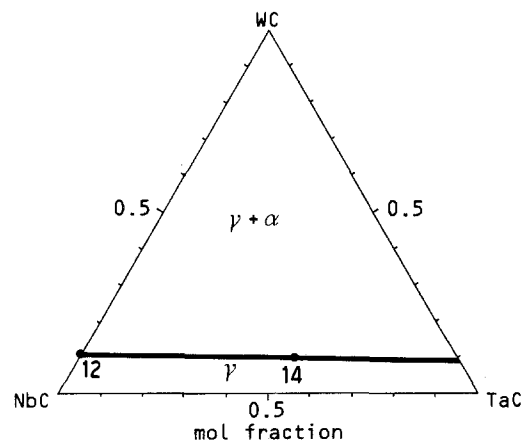


Figure 4 NbC-TaC-WC ternary phase diagram at 1723 K.

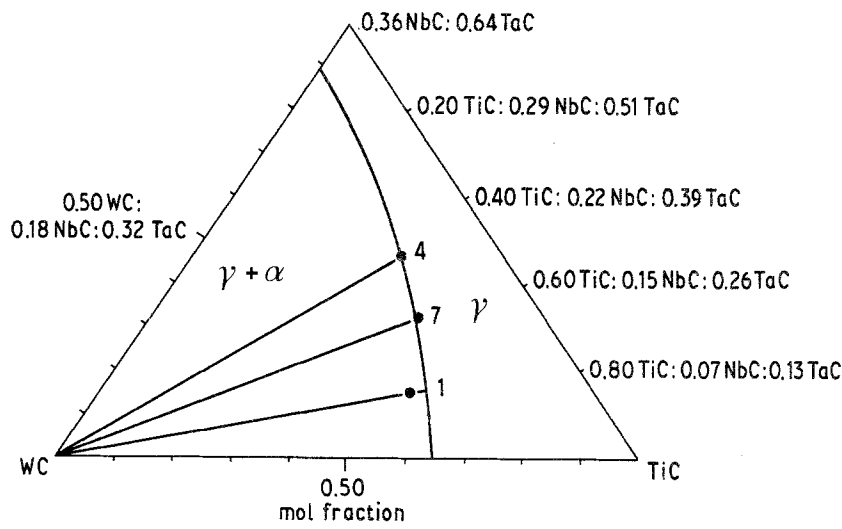


Figure 5 TiC-NbC-TaC-WC ternary phase diagram at 1723 K and TaC/NbC = 1.75.

phase (of composition equivalent to Y_{Co}^1 in Fig. 7a) respectively. Compositions X_{Co} , Y_{Co} and Z_{Co} are obtained by extrapolation of the lines joining X_{Co}^{all} to X_{Co}^1 , Y_{Co}^1 and Z_{Co}^1 . The weight fractions of the three phases of interest (W_{Co} , W_{γ} , W_{WC}) are thus:

$$W_{Co} = \frac{X_{Co}^{all} - X_{Co}}{X_{Co}^1 - X_{Co}} \quad (1)$$

$$W_{\gamma} = \frac{Y_{Co} - X_{Co}^{all}}{Y_{Co} - Y_{Co}^1} \quad (2)$$

$$W_{WC} = \frac{Z_{Co} - X_{Co}^{all}}{Z_{Co} - Z_{Co}^1} \quad (3)$$

These three equations simplify considerably as $X_{Co} = Y_{Co} = Z_{Co} = 0$ and $X_{Co}^1 = 100$.

Assuming 100 g of material, then from definition of density:

$$V_{Co} = \frac{100W_{Co}}{\rho_{Co}} \quad (4)$$

$$V_{\gamma} = \frac{100W_{\gamma}}{\rho_{\gamma}} \quad (5)$$

$$V_{WC} = \frac{100W_{WC}}{\rho_{WC}} \quad (6)$$

where V_{Co} is the volume of cobalt, etc.

Volume fractions are thus

$$f_{Co} = \frac{V_{Co}}{V_{Co} + V_{\gamma} + V_{WC}} = \frac{V_{Co}}{\sum V_i} \quad (7)$$

$$f_{\gamma} = \frac{V_{\gamma}}{\sum V_i} \quad (8)$$

$$f_{WC} = \frac{V_{WC}}{\sum V_i} \quad (9)$$

Volume fractions have been calculated using these equations for a number of the samples studied. Values are given in Table VII and compared to measured volume fractions. Agreement is generally good.

In Equation 5 values of ρ_{γ} can be estimated for compositions lying between those measured. It has been found that by assuming that the density of the gamma phase is a linear function of the densities of the pure carbides in proportion to their mol fractions (MeC), i.e.

$$\rho_{\gamma} = M_{TiC}\rho_{TiC} + M_{NbC}\rho_{NbC} + M_{TaC}\rho_{TaC} + M_{WC}\rho_{WC} \quad (10)$$

then reasonable agreement is obtained with densities calculated from lattice parameters, see Table V. In Equation 10 the following values for the densities of

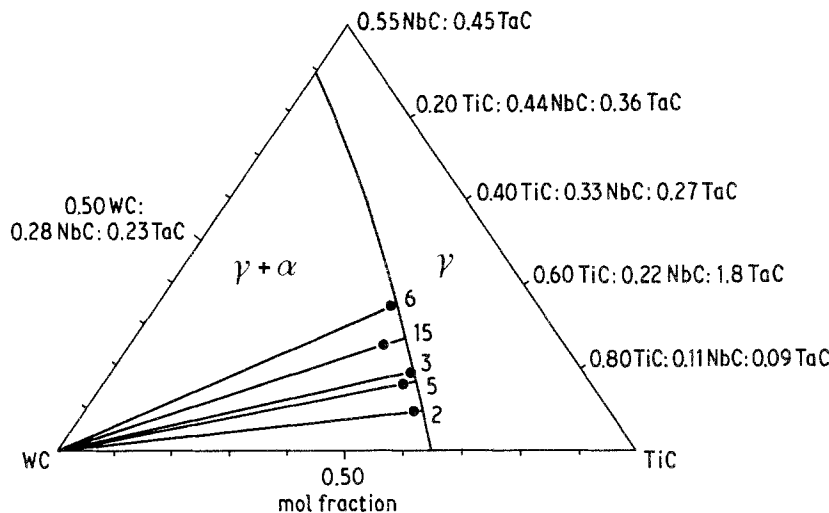


Figure 6 TiC-NbC-TaC-WC ternary phase diagram at 1723 K and TaC/NbC = 0.82.

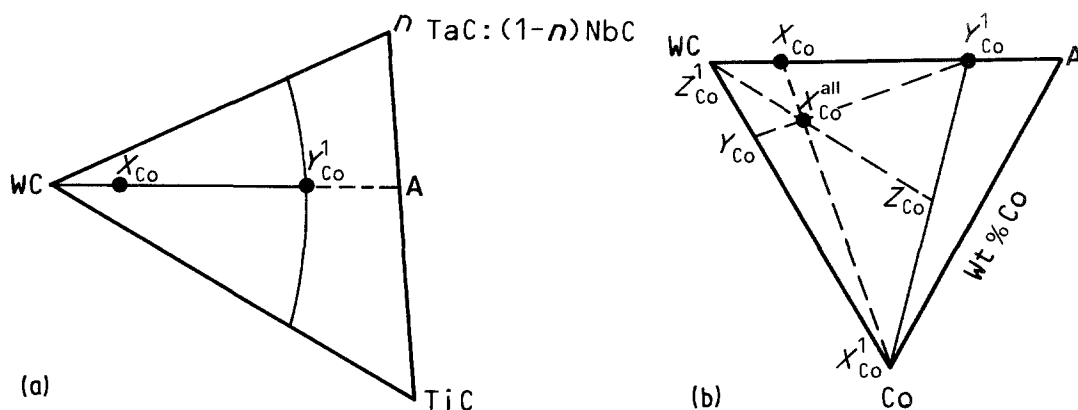


Figure 7 This sketch illustrates how the ternary Co-gamma-WC diagram can be constructed to calculate volume fractions of component phases. (a) A WC-TiC- n TaC: $(1-n)$ NbC diagram. The tie line extending from WC to A defines the base of the triangle in Fig. 7b. (b) A Co-gamma-WC ternary diagram for a particular gamma phase composition. X_{Co}^{all} is the centre of gravity of the triangle $X_{Co}^1 - Y_{Co}^1 - Z_{Co}^1$. X_{Co} , Y_{Co} , Z_{Co} are extrapolations of X_{Co}^1 , Y_{Co}^1 , Z_{Co}^1 through X_{Co}^{all} .

carbides (calculated from XRD) are: $\rho_{TiC} = 4910$, $\rho_{NbC} = 7800$, $\rho_{TaC} = 14470$, $\rho_{WC} = 16860$ (all values are in $kg\ m^{-3}$). The latter density is that of fcc (B1) form of WC [10]. The densities of cobalt and hexagonal WC used were 8900 and $15770\ kg\ m^{-3}$, respectively.

5. Comments

The experimentally determined phase diagram for mixtures of WC and gamma phase seems to be self-consistent. The volume fractions of gamma phase calculated from the experimentally determined phase diagrams are in good agreement with volume fractions obtained by stereological analysis. It must be emphasized that the solubility surface defined in this article corresponds to that expected at carbon activities close to unity. Changes in gamma phase composition will occur at lower activities. Some idea of the magnitude of changes expected can be obtained from Rudy's work in the Ti-W-C system [4].

The various pseudo-ternary diagrams presented in this article represent a reasonable first approximation to the quaternary system even at lower activities and at deviations from sintering temperatures of $\pm 100\ K$. The diagrams presented can be used with confidence for the design of new cemented carbide grades.

Appendix

Knowing the volume fraction, f_y , of the various phases in a sample it is possible, using the equations below, to obtain an approximate value for the composition of the gamma phase to provide an independent check of the measured composition.

It has been shown [11] that TiC, NbC and TaC are

TABLE VII Comparison between measured and calculated volume fractions of phases

Grade	Volume fractions calculated using Equations 6 to 14			Volume fraction measured, f_y
	f_{Co}	f_γ	f_{WC}	
1	0.11	0.78	0.12	0.77
2	0.11	0.51	0.38	0.45
3	0.14	0.47	0.38	0.47
4	0.15	0.34	0.52	0.28
5	0.12	0.56	0.32	0.54
6	0.09	0.22	0.70	0.20
7	0.16	0.25	0.59	0.22

insoluble in WC. It can also be assumed that they have low solubilities in the binder phase, then:

$$\text{mol fraction MeC}^{alloy} = f_\gamma \times \text{MeC}^{gamma/WC} \quad (A1)$$

and thus

$$\text{MeC}^{gamma/WC} = \text{MeC}^{alloy} / f_\gamma \quad (A2)$$

where MeC^{alloy} and $\text{MeC}^{gamma/WC}$ refer to mol fraction of a given carbide (MeC) in the grade mixture and in the gamma phase in equilibrium with WC. For completeness we note

$$\begin{aligned} \text{mol fraction WC}^{gamma/WC} \\ = 1 - \sum \text{mol fraction MeC} \end{aligned} \quad (A3)$$

However, experience shows that this rarely gives good agreement with the measured WC content of the gamma phase due to small errors in the other compositions.

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