JOURNAL OF MATERIALS SCIENCE 29 (1994) 54–60

Effect of Ti(C,N) addition on sintering behaviour and properties of binder-modified WC–10Co cemented carbide

S. K. BHAUMIK, G. S. UPADHYAYA, M. L. VAIDYA
Department of Materials and Metallurgical Engineering, Indian Institute of Technology, Kanpur 208016, India

In the present investigation the microstructure and mechanical properties of WC–10Co, WC–8.3Ti(C,N)–12Co, WC–8.3Ti(C,N)–6Co–6Ni and WC–7Ti(C,N)–2Mo_2C–6Co–6Ni cemented carbides were studied. Introduction of Ti(C,N) in WC–10Co cemented carbide imposed sintering difficulties and hot isostatic pressing was required to obtain fully dense material. The modification of the binder cobalt with nickel and molybdenum did not noticeably affect the sintered microstructure. In general the mechanical properties of Ti(C,N)-containing cemented carbides were inferior to those of WC–10Co cemented carbide.

1. Introduction

WC–Co cemented carbides have a unique set of properties, namely high hardness, toughness and oxidation resistance. Because of the excellent combination of these properties, WC-based cemented carbides are extensively used as cutting tool materials and constitutes almost 70% of the cutting tools employed today. This extensive usage makes tungsten and cobalt among the strategically important materials. Many attempts have been made in the past to develop alternative cemented carbide systems which can be compatible with WC-based cemented carbides. Not much success could be achieved in this regard, and WC-based cemented carbides remain by far the major competent materials in the field of cutting and wear-resistant applications. However, some success could be achieved by substituting a portion of WC by another hard phase, e.g. TiC/TiN, to produce other grades. Addition of TiC to WC–Co has long been the practice for steel cutting grade WC-based cemented carbides to impart resistance to diffusion wear at the cost of strength. However, it is reported that with the identical addition of TiC or TiN to WC–Co cemented carbide, the TiN-containing alloy has a better strength and oxidation resistance [1, 2]. Any such replacement of a heavy and expensive transition metal like tungsten by cheaper, abundant, and specifically light metals like titanium is encouraging.

Cobalt is the most traditional binder metal used for WC-based cemented carbides, but due to its high cost and limited resources, efforts have been made to replace cobalt by other iron-group metals. It is reported in the literature [3, 4] that the same or even superior sintered properties to that of WC–Co cemented carbides can be achieved through Co–Ni binder instead of straight cobalt. On the other hand, as far as the wettability is concerned, nickel is believed to be a better binder metal with titanium carbide/nitride/carbonitride [5]. The wettability is further improved when molybdenum is also present in the nickel binder [6, 7].

In the present investigation an attempt has been made to study the sintering behaviour, microstructure and mechanical properties of WC–10Co cemented carbides containing Ti(C,N) as the hard-phase additive, with due modification of the binder cobalt by nickel and molybdenum.

2. Experimental procedure

The characteristics of the different powders used in this study are given in Table I. The starting composition of cemented carbide, i.e. WC–10Co, corresponded to approximately 16.5 vol% binder phase. All the subsequent compositions developed later were tailored so that the volume fractions of hard phases and binders remained constant at those present in the initial WC–10Co cemented carbide. The respective mass percentage additives in various cemented carbide compositions are given in Table II.

The details of processing various grades of fully dense WC–10Co-based cemented carbides and the evaluation of various sintered properties, namely sintered density, hardness, transverse rupture strength (TRS), indentation fracture and toughness, have been reported extensively elsewhere [2].

The polished samples were electroetched by using 5% HCl solution at a potential of 3 V for 10–20 s and were observed under a Jeol model 840A scanning electron microscope (SEM) in the secondary electron mode at an operating voltage of 20 kV. For each sample about ten photomicrographs were taken arbitrarily from different places at 10 000 magnification, and subsequently used for quantitative metallographic study.

0022–2461

TABLE I Characteristics of various powders

Material and source	Composition		Average particle size, FSSS (μm)
	Element	wt%	
WC (Widia India Ltd)	Total C	6.12	3.2
	Free C	0.10	
Ti(C,N) (Treibaner, Austria)	Total C	9.87	2.1
	Free C	0.04	
	Fe	0.12	
	O	0.07	
	N	11.00	
Co (Starck, Germany)	Ni	0.20	2.3
	Fe	0.04	
	O	3500 p.p.m.	
	Co	Balance	
Ni (Inco, UK) Type 123	C	0.06	3.7
	Fe	0.005	
	O	0.05	
	Co	0.0003	
	N_2	0.003	
	S	0.003	
	others	0.001	
	Ni	Balance	
Mo_2C (USSR)	—		3–4

Different microstructural parameters, namely mean linear intercept grain size, contiguity and the binder mean linear intercept distance, were measured in accordance with the method suggested by Gurland [8] using the following formulae:

(i) The carbide mean linear intercept grain size is given by

$$L_\alpha = \frac{2(V_v)_\alpha}{2(N_L)_{\alpha\alpha} + (N_L)_{\alpha\beta}}$$

where, $(V_v)_\alpha$ is the volume fraction of the carbide phase and $(N_L)_{\alpha\alpha}$ and $(N_L)_{\alpha\beta}$ are the average number of intercepts per unit length of test lines with the traces of carbide–carbide grain boundaries and carbide–binder interface, respectively.

(ii) The contiguity of the carbide phase is given by

$$C_\alpha = \frac{2(N_L)_{\alpha\alpha}}{2(N_L)_{\alpha\alpha} + (N_L)_{\alpha\beta}}$$

(iii) The binder mean linear intercept distance, i.e. the mean free path, is given by

$$L_\beta = \frac{2(V_v)_\beta}{(N_L)_{\alpha\beta}}$$

where $(V_v)_\beta$ is the volume fraction of the binder phase.

3. Results

3.1. Liquid-phase sintered alloys

3.1.1. Sintered density

Fig. 1a shows the densification behaviour of the different alloys studied, from which it is evident that WC–10Co cemented carbide achieved the full density at a sintering temperature of 1425 °C in a hydrogen atmosphere. Addition of Ti(C,N) to WC–10Co cemented carbide resulted in a relatively high sintered porosity. The maximum attainable sintered density was about 97% of the theoretical density after sintering at 1475 °C, and the value remained constant at higher temperature. Modification of binder-metal cobalt with nickel in alloy C (WC–8.3Ti (C,N)–6Co–6Ni) caused slight deterioration of the densification behaviour. A further increase in sintered porosity was observed when Mo_2C was incorporated in the system along with cobalt–nickel binder (alloy D). Even at a sintering temperature of 1500 °C the attainable density in alloy D was about 96% of the theoretical density.

3.1.2. Vickers hardness

Vickers hardness values decreased when Ti(C,N) was introduced in WC–10Co cemented carbide (Fig. 1b). A progressive decrease in hardness values was observed after the partial substitution of cobalt by nickel (alloy C) and the addition of Mo_2C (alloy D). However, the values showed an increasing trend with increase in sintering temperature for all the alloys investigated.

3.1.3. Transverse rupture strength

The TRS value obtained for any cemented carbide containing Ti(C,N) was much less than that of WC–10Co cemented carbide (Fig. 2a). A drastic drop in TRS was observed when the binder-metal cobalt was partially substituted by nickel (alloy C). The presence of molybdenum in the binder phase of alloy D marginally improved the TRS value, but it was less than that of alloy B. The TRS value of alloy B

TABLE II Nominal compositions of different alloys

Alloy	Composition (vol%)							Composition (wt %)						
	Hard phase					Binder		Hard phase					Binder	
	WC	TiC	Mo_2C	TiN	Ti(C, N)	Co	Ni	WC	TiC	Mo_2C	TiN	Ti(C,N)	Co	Ni
A	83.6	–	–	–	–	16.4	–	90.0	–	–	–	–	10	–
B	63.0	–	–	–	20.1	16.9	–	79.7	–	–	–	8.3	12	–
C	63.0	–	–	–	20.1	8.5	8.4	79.7	–	–	–	8.3	6	6
D	63.1	–	2.8	–	17.1	8.5	8.5	79.0	–	2	–	7.0	6	6

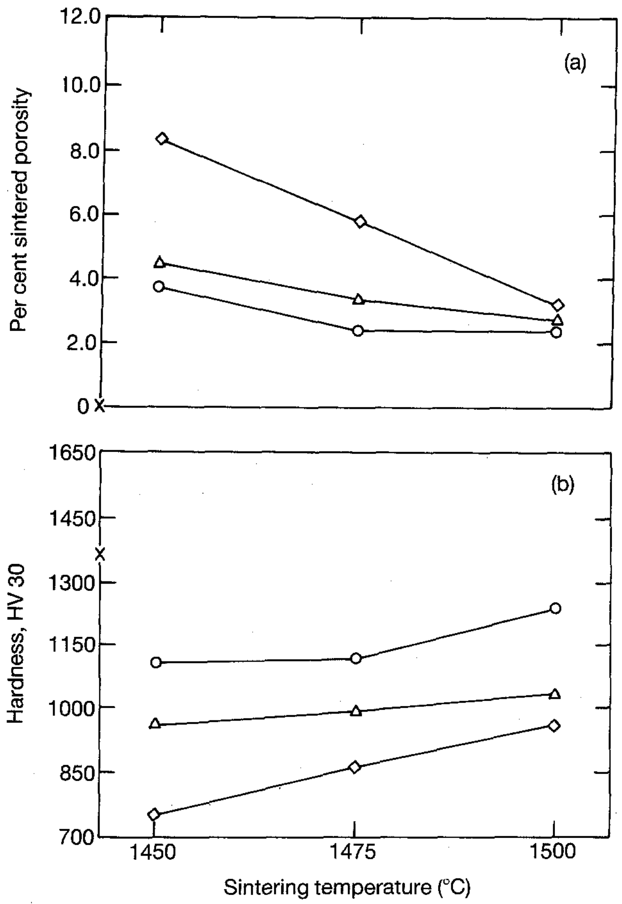


Figure 1 Effect of sintering temperature on (a) percentage sintered porosity and (b) hardness of (x) alloy A (sintered in H_2) and alloys (○) B, (△) C and (◇) D (sintered in $H_2 + N_2$).

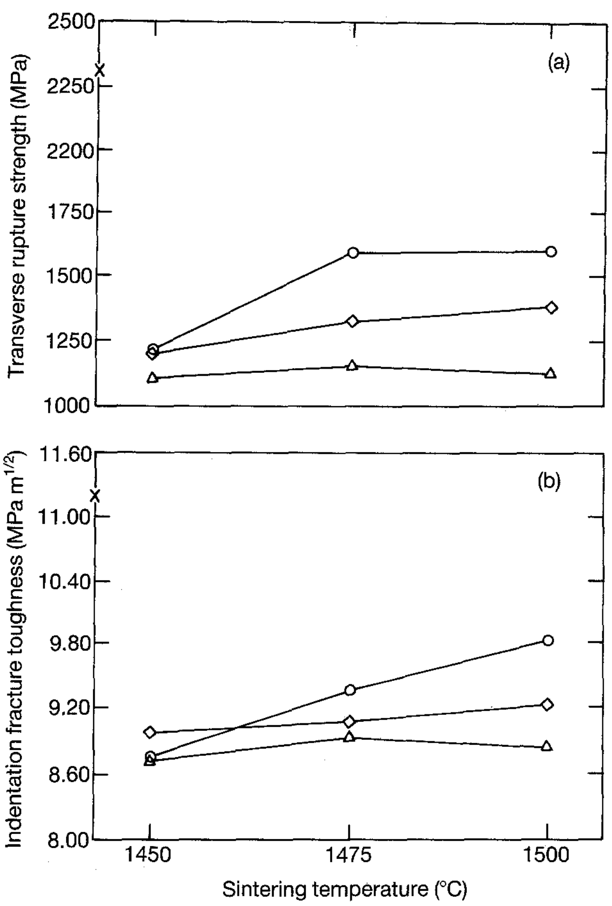


Figure 2 Effect of sintering temperature on (a) transverse rupture strength and (b) indentation fracture toughness of (x) alloy A (sintered in H_2) and alloys (○) B, (△) C and (◇) D (sintered in H_2 + N_2).

TABLE III Mean linear intercept length, $\bar{l}$, of hexagonal and cubic phases in various cemented carbides; n is the number of intercepts from which each value of $\bar{l}$ was calculated and σ is the standard deviation

Alloy	Sintering atmosphere	Temp: of HIPing (°C)	Hexagonal phase WC			Cubic phase TiC/TiN/Ti(C, N)		
			n	$\bar{l}$ (μm)	σ	n	$\bar{l}$ (μm)	σ
A	H_2	–	383	1.33	0.514	–	–	–
	Vacuum	–	332	1.30	0.507	–	–	–
B	H_2–N_2	–	176	1.27	1.26	278	1.32	1.22
	H_2–N_2	1400	261	1.28	1.26	193	1.31	1.22
C	H_2–N_2	–	284	1.27	1.26	197	1.32	1.22
	H_2–N_2	1400	267	1.26	1.26	163	1.32	1.22
D	H_2–N_2	–	249	1.26	1.26	171	1.28	1.21
	H_2–N_2	1400	221	1.26	1.26	187	1.32	1.21

increased sharply with increase in sintering temperature up to 1475 °C and thereafter remained constant, whereas it increased steadily in the case of alloy C. However, the TRS value of alloy D remained almost constant at all sintering temperatures.

3.1.4. Indentation fracture toughness

Fracture toughness results (Fig. 2b) followed more or less the same trend as that of the TRS. The introduction of Ti(C,N) into WC–10Co greatly decreased the toughness value. The toughness value of alloy B increased with increase in sintering temperature, whereas it remained almost constant for alloys C and D at all sintering temperatures.

3.1.5. Microstructural study

The SEM microstructures of alloys A, B, C and D are shown in Fig. 3. The WC phase was in general of angular shape. Ti(C,N) particles (grey phase) in alloys B, C and D are clearly distinguishable by their equiaxed nature (Fig. 3b–d). Modification of alloy chemistry in the case of alloys C and D did not

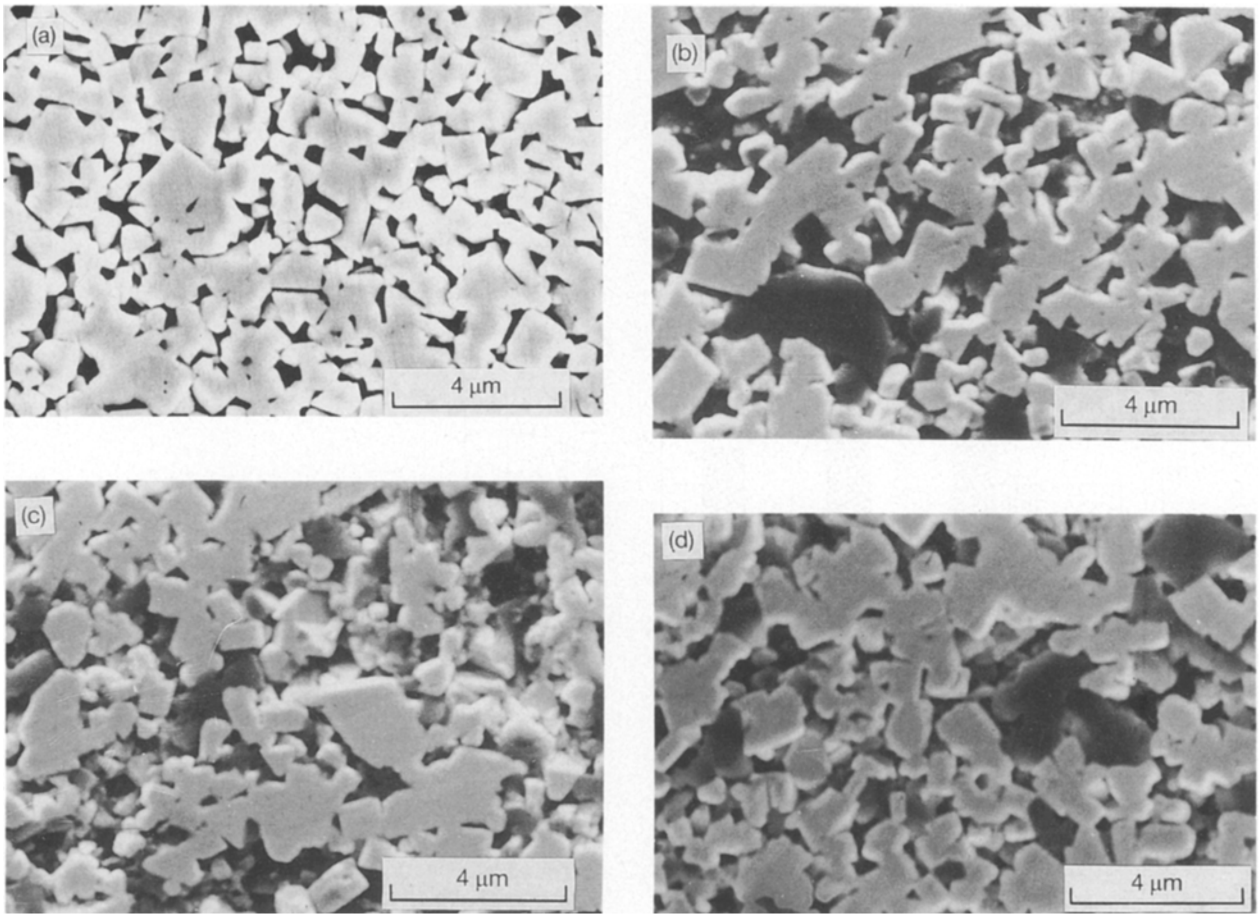
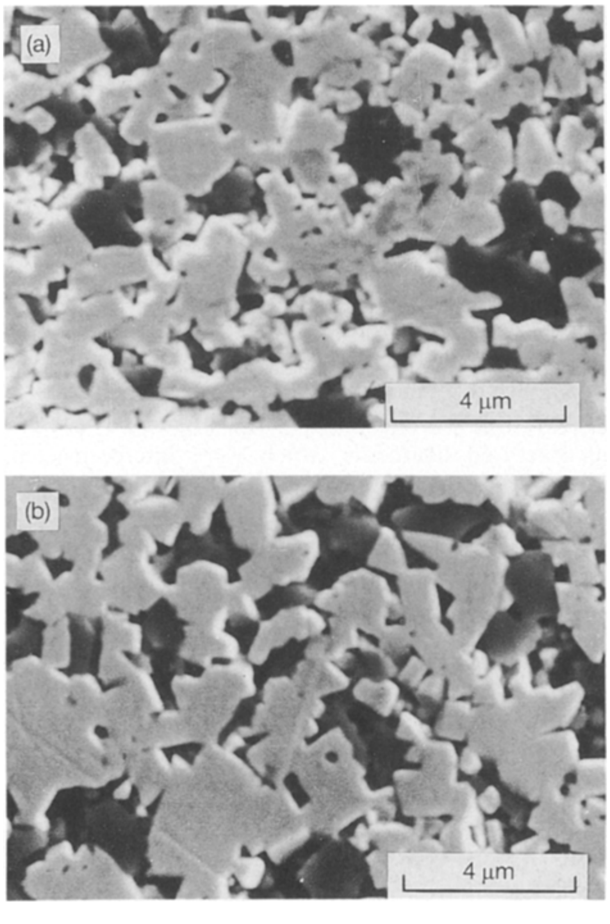


Figure 3 SEM microstructures of (a) alloy A, (b) alloy B, (c) alloy C and (d) alloy D sintered at 1425, 1475, 1475 and 1500 °C, respectively (alloy A sintered in H_2 and alloys B, C and D sintered in $H_2 + N_2$).



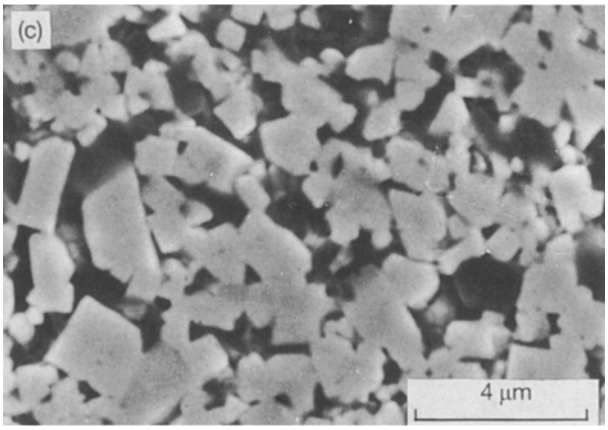


Figure 4 SEM microstructures of (a) alloy B, (b) alloy C and (c) alloy D after HIPing at 1400 °C.

apparently result in any change in microstructure from that of alloy B (Fig. 3b–d). However, quantitative metallographic study showed that the average grain sizes of WC and Ti(C,N) increased marginally (Table III).

3.2. Hot isostatically pressed alloys

3.2.1. Metallographic study

Almost full density with residual porosity in the range 0.06 to 0.15% was obtained after hot iso-static press-

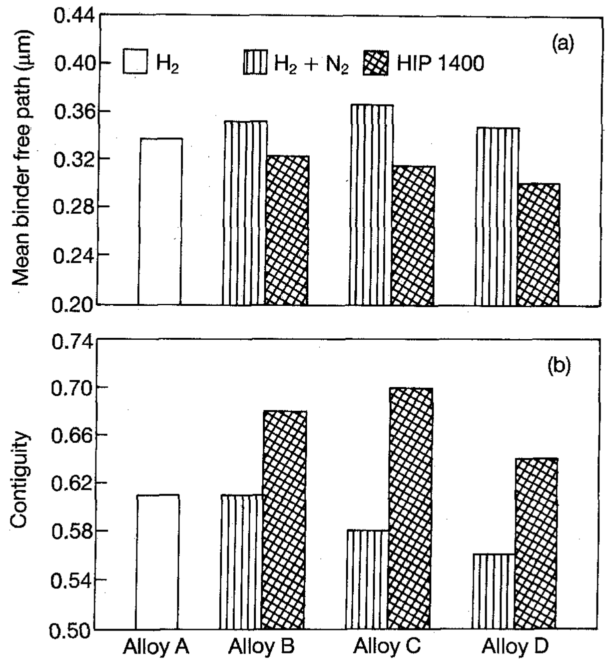


Figure 5 (a) mean binder free path and (b) contiguity in alloys A, B, C and D.

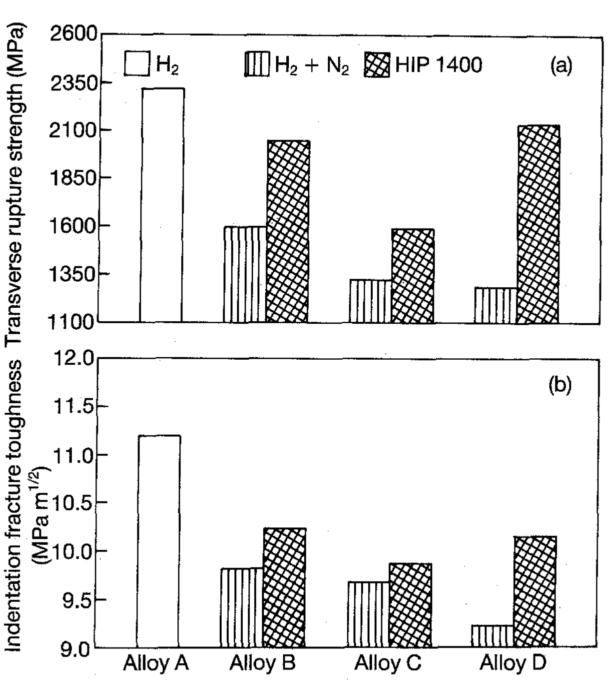


Figure 7 (a) Transverse rupture strength, and (b) indentation fracture toughness in alloys B, C and D.

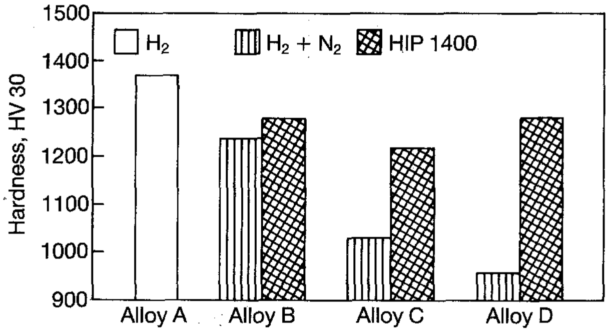


Figure 6 Hardness variations in alloys A, B, C and D.

ing (HIPing) of the liquid-phase sintered alloys at 1400 °C. Large pores in the originally sintered compacts were completely eliminated by HIP treatment. However, some micropores were still present in the HIP'ed alloys. Though alloy D had a greater sintered porosity than alloy C, it had less residual porosity than alloy C after HIP treatment.

SEM microstructures of HIP'ed alloys (Fig. 4) did not show any difference from those of the liquid-phase sintered ones (Fig. 3) except for the pores. In fact, all the Ti(C, N)-containing cemented carbides showed similar microstructures. Apparently no grain coarsening with respect to liquid-phase sintered alloy was observed after HIPing (Table III). Quantitative metallographic study showed that HIPing resulted in a decrease in mean binder free path (Fig. 5a), but the contiguity value increased to a great extent (Fig. 5b).

3.2.2. Mechanical properties

It is evident from Figs 6 and 7 that HIPing resulted in an enhancement of different mechanical properties, namely hardness, TRS and indentation fracture toughness. In general, the addition of Ti(C, N) to WC–10Co cemented carbide caused deterioration of the hardness, TRS and indentation fracture toughness. A comparison between HIP'ed alloys B and C indicated that the change in binder-phase chemistry led to inferior properties, the deterioration being more in the TRS value. On the other hand, among all the Ti(C, N)-containing cemented carbides, namely alloys B, C and D, alloy D had the best combination of properties (Figs. 6 and 7).

3.2.3. Fractographic study

The typical fracture surfaces of all the alloys are shown in Fig. 8. The basic modes of local fracture were the same in all the alloys as explained elsewhere in detail [9]. Fig. 8b reveals that the binder phase in alloy B was present as a mixture of ruptured ligaments and dimpled structure, of which a large proportion consisted of the former. The predominant local fracture mode was crack initiation at the contiguous boundaries followed by transgranular fracture of the hard phases. Modification of the binder phase led to a distinctive difference in the binder-phase fracturing of alloy C (Fig. 8c). The binder phase was mostly present as fractured ligaments which were interconnected, forming a net-like appearance on the fracture surface. Addition of Mo_2C resulted in an important change in the fracturing of the binder phase, such that it was present as a dimpled structure on the fracture surface (Fig. 8d). The binder phase in alloy C fractured mainly by rupture of the ligaments, which was more or less absent in alloy D.

4. Discussion

4.1. Liquid-phase sintered alloys

From the results obtained it is apparent that the sintered properties of WC–10Co cemented carbide are comparable to those available in the literature [10].

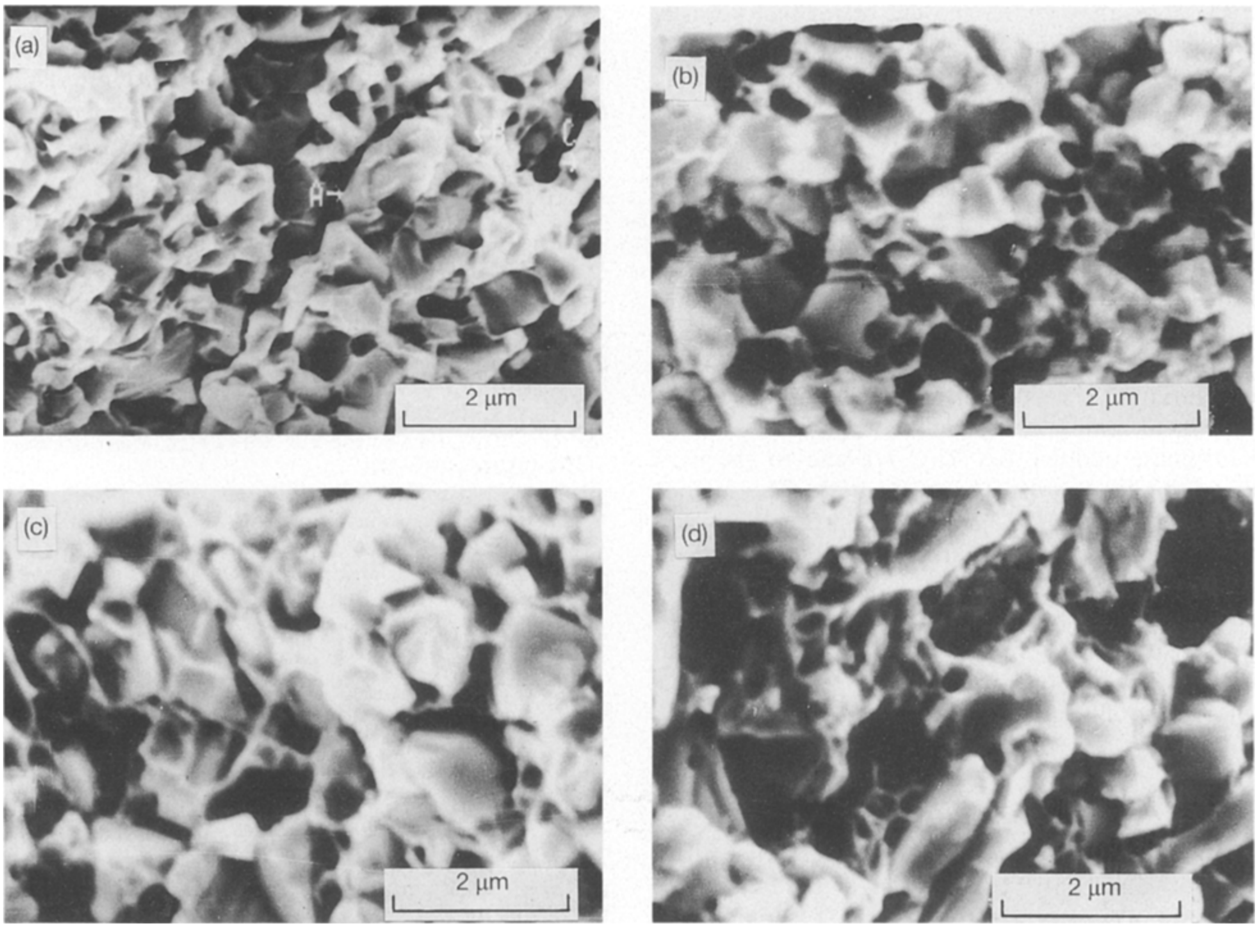


Figure 8 SEM fractographs of (a) alloy A, (b) alloy B, (c) alloy C and (d) alloy D.

It appears from the present results that Ti(C,N) addition to WC–10Co cemented carbide imposed processing difficulties such that full density was not achieved even at a sintering temperature of 1500 °C by normal liquid-phase sintering, which may be related to the poor wettability of Ti(C,N) with cobalt. As far as the effects of binder phase compositions are concerned, partial substitution of cobalt by nickel did not improve the densification behaviour for alloy C. Ti(C,N) has a better wettability in nickel than in cobalt, whereas it is the other way round for WC. It appears from the present results related to densification, pore morphology and its distribution that the overall wettability deteriorates due to the binder-phase modification. Based on the literature [6, 7] and earlier work of the authors [2] on WC-based cemented carbides containing TiC/TiN, an attempt has been made to improve the wettability of both WC and Ti(C, N) in the cobalt–nickel binder by adding Mo_2C. However, a higher sintering temperature was required for alloy D to achieve even the same density level as that of alloy B, which is unexpected. The reason for such deterioration in densification behaviour after Mo_2C addition to alloy C is not clear.

Though the overall wettability and solubility of Ti(C, N)-containing cemented carbides are inferior to those of WC–10Co, in contrast to TiC addition [11], no noticeable non-uniformity in the microstructure was observed after Ti(C, N) addition. The present results agree with those of Suzuki [12] who suggests that addition of nitrogen to WC–TiC-based cemented carbide promotes fine microstructure. The binder phase compositions do not seem to have any noticeable effects on the microstructural development during sintering, such that the grain sizes and their distribution in all the alloys follow almost similar trends (Table III).

4.2. Hot isostatically pressed alloys

It is virtually impossible by normal liquid-phase sintering to achieve a fully dense product out of TiN/Ti(C, N)-based hard metals, irrespective of any variation in the sintering atmosphere. This may arise from the fact that pores containing nitrogen gas arising out of denitrification or the sintering atmosphere are difficult to remove during sintering and invariably give rise to large pores in the sintered compacts [5, 13, 14]. These pores are the origin of fractures and are responsible for the low strength of such cemented carbides. HIPing of such liquid-phase sintered compacts seems an obvious way of eliminating such defects and achieving increased strength.

The relatively higher amount of residual porosity in alloy C compared with either alloy B or alloy D may be attributed to the fact that the hard phases, namely WC and Ti(C, N), as a whole have inferior interaction with cobalt–nickel as compared with cobalt alone. On the other hand, though alloy D required a relatively higher sintering temperature to achieve the same density level as alloy C, the amount of residual porosity after HIPing was much less in the former. This suggests that an improvement in wettability did take place in the presence of Mo_2C in the alloy.

The important change in microstructure that could be observed after HIPing is the increase in contiguity value in all the alloys. This may be due to the substantial pressure during HIPing which results in the liquid binder melt squeezing out from the intergranular region of the hard phases to fill the voids, thus establishing a direct hard phase–hard phase contact.

Since the microstructures in all the alloys were more or less similar, the mechanical properties obtained can be related mainly to the intrinsic properties of the hard-phase additive (i.e. Ti(C, N)) and to the hard phase–binder interface bond strength. The inferior TRS and toughness of alloys B, C and D as compared to those of WC–10Co cemented carbide may therefore, be attributed to the inferior WC–Ti(C, N)/binder bond strength and more brittle nature of Ti(C, N) than that of WC. In addition. the relatively high contiguity values of the hard phase are also responsible for low TRS and toughness.

5. Conclusions

1. It is possible to substitute a reasonable amount of WC by Ti(C, N) in WC–10Co cemented carbide without much sacrifice in strength and toughness. However, a greater control over the sintering atmosphere and post-sintering treatment such as HIPing are required.

2. The modification of binder cobalt with nickel and molybdenum does not have any major effect on microstructural development during sintering.

3. The fracture modes of alloys were dependent on the binder composition: nickel addition favoured binder-phase fracturing, while Mo_2C addition improved the hard phase–binder interfacial strength.

References

1. N. TSCHIYA, O. TERADA, A. SASAKI and H. SUZUKI, *J. Jap. Soc. Powd. Powd. Met.* **37** (1990) 80.
2. S. K. BHAUMIK, G. S. UPADHYAYA and M. L. VAIDYA, *J. Mater. Sci.* **27** (1992) 1947.
3. W. PRECHT, R. K. VISWANADHAM and J. D. VENABLES, in “Science of Hard Materials”, edited by R. K. Viswanadham, D. J. Rowcliffe and J. Gurland (Plenum, New York, 1983) p. 649.
4. G. S. UPADHYAYA and S. K. BHAUMIK, *Mater. Sci. Eng. A* **105/106** (1988) 249.
5. R. KIEFFER, P. ETTMAYER and M. FREUDHOFMEIR, in “Modern Developments in P/M”, Vol. 5, edited by H. H. Hausner (Plenum, New York, 1971), p. 201.
6. H. E. EXNER, *Int. Met. Rev.* **24** (1979) 149.
7. J. M. BARRANCO and R. A. WARENCHAK, *Int. J. Refrac. Mater. Hard Met.* **8** (June 1989) 102.
8. J. GURLAND, in “Practical Application of Quantitative Metallography”, STP 839, edited by J. L. McCall and J. H Steele Jr (ASTM, Philadelphia, 1984) p. 65.
9. S. K. BHAUMIK, G. S. UPADHYAYA and M. L. VAIDYA, *Pract. Metallogr.* **28** (1991) 238.
10. V. K. SARIN, in “Advances in Powder Technology”, edited by G. Y. Chin (ASM, Ohio, 1982) p. 253.
11. S. K. BHAUMIK, G. S. UPADHYAYA and M. L. VAIDYA, *Mater. Sci. Tech.* **7** (1991) 723.
12. H. SUZUKI, *J. Jap. Soc. Powd. Powd. Met.* **29** (1982) 25.
13. P. S. KISLY and M. A. KUZENKOVA, *Powd. Met. Int.* **4** (1972) 67.
14. P. ETTMAYER, H. KOLASKA and K. DREYER, *ibid.* **23** (1991) 224.

Received 13 May 1992
and accepted 3 February 1993