

# THE FORMATION OF SOLID SOLUTION BAND AT THE SURFACE OF Ti(CN)-BASED CERMETS

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**SUMMARY:** Ti(CN) is a well-known substrate material for cutting tool applications. It provides attractive mechanical properties, including excellent strength, hardness, and high temperature stability. In addition, the formation of a solid solution layer at the cermet surface enhances toughness, resulting in improved cutting performance. Experiments were carried out in order to elucidate the influence of secondary carbides and various atmospheric conditions on the formation of the solid solution band. TaC and WC were used as additives to Ti(CN)-Ni-Co system, and were processed in vacuum, various nitrogen pressure (2 torr, 200 torr) and a carbon atmosphere. It was found that the addition of TaC facilitated band formation while the WC-containing system did not exhibit the band readily. Of various processing atmospheres, vacuum conditions gave rise to the band effectively by dissolving Ti(CN) near the sample surface.

**KEYWORDS:** Ti(CN), denitrification, solid solution band, material transportation

## INTRODUCTION

WC-Co cermet represents a commonly used material for metal cutting operations which has been in use since 1920's. However, tungsten and cobalt are regarded as strategic materials because of their localized production and availability. Therefore, many researchers in this field have searched for alternative materials to replace WC-Co and, as a result, a great deal of interest has developed in Ti(CN)-based cermets. Ti(CN) or TiC-based cermets are superior to WC-based hard metal alloys with respect to the properties required for cutting operations, such as hardness, strength, wear resistance, and high temperature stability for high speed machining.[1-4] Cermets based on these materials show excellent performance in final finishing steps. Recent developments in manufacturing skills, which facilitate the production of a near-net shape, justifies the use of Ti(CN) or TiC-based cermets.

The addition of nitrogen to TiC-based cermets is indispensable for these required properties. It is known, however, that the loss of nitrogen from Ti(CN) during processing causes changes in compositions, porosity,[5-7] and sometimes gives rise to a microstructurally inhomogeneous surface layer.[4,8-13] Numerous explanations have been suggested for explaining these alternations in surface microstructure, i.e., an excess or depletion of the metallic binder phase, as well as the dissolution of hard phases at the surface. The fact that the phase reactions during the sintering process are very complex explains, in part, the

reasons for many discrepancies in the interpretation of this phenomenon.

The need for hard-surfaced or toughened tools depends largely on the characteristics of the work pieces and machining steps. In fact, the microstructures at the surface and corners of cutting tools determine both the tool lifetime and efficiency. In this study the effect of TaC and WC in a Ti(CN)-Ni-Co system was studied under a variety of sintering conditions. The effects of nitrogen loss and added carbon on surface microstructure and on material transport were investigated.

## EXPERIMENTAL PROCEDURE

The sizes of powders used in these experiments, along with their manufacturers are listed in Table 1. The specified stoichiometry of Ti(CN) is  $Ti(C_{0.5}N_{0.5})$ . The powders were slurried in acetone to obtain a uniform composition prior to sintering. The starting particle size was maintained after the mixing process. Carbides such as TaC and WC were also added in order to understand the effect of each additive on the microstructure near the surface. For this study three compositions were prepared i.e., Ti(CN)-20TaC-15Ni-15Co, Ti(CN)-20WC-15Ni-15Co, and Ti(CN)-10TaC-10WC-15Ni-15Co (in wt.%). Sintering was performed at 1510. for 1h under a variety of atmospheric conditions. The vacuum level was maintained at  $10^{-2}$  torr during sintering.

The effect of nitrogen pressure on the microstructure was investigated by applying nitrogen pressure up to 200 torr. Carbon is also known to have an effect on the surface microstructure.[11] To elucidate this, some of the specimens were embedded in carbon powder during sintering in vacuum. The microstructure was observed by SEM in BSE(back scattered electron) mode and the compositional analysis was carried out with SEM EDXA(energy dispersive x-ray analysis).

## RESULTS AND DISCUSSION

### Effect of Nitrogen on the Solid-Solution Band

In this study the Ti(CN) content was set at 50wt.% and the total amount of additives such as TaC and WC were 20wt.% for the compositions of the cermets under investigation. These cermets show a typical core/rim microstructure. The cores are undissolved Ti(CN) particles which serve as precursors for the precipitation sites for the solid-solution rim. As shown in Fig. 1(a), the Ti(CN) cores having a black contrast disappeared and a band which consisted largely of (Ti,M)(CN) solid solution was observed near the surface of a sintered specimen. Fig. 1(b) is a schematic for the surface microstructure at a high magnification. In region A most of the Ti(CN) cores are depleted as compared with region C. An adjacent region (region B) is partially depleted with respect to Ti(CN) cores. The combined region A and B is referred to as the solid-solution band in this study.

Figs. 2 and 3 are the microstructures of Ti(CN)-20TaC-15Ni-15Co and Ti(CN)-20WC-15Ni-15Co (in wt. %) in the vicinity of the sample surface. These were sintered at 1510. for 1h at a variety of atmospheric conditions. The formation tendency of the solid-solution band is found to be different, depending on the types of carbide additives used and the nitrogen pressure to a large extent. In general, the thickness of the solid-solution band increases as nitrogen pressure decreases regardless of the types of carbides. The Ti(CN)-20TaC-15Ni-15Co system, however, exhibited a stronger tendency for band formation than the other

system. The band size of the system reached 50. in  $10^{-2}$  torr vacuum (Fig. 2(a)). On the other hand, the Ti(CN)-20WC-15Ni-15Co system shows a weaker tendency to form a band. By sintering at 200 torr of nitrogen pressure, a microstructure which did not contain the band was obtained in both cases(Figs.2(c) and 3(c)). The EDXA analysis, described in the following section proves this trend which becomes obvious in microstructure with an increase in temperature.

The microstructure of Ti(CN)-TaC-Ni-Co shows more heavy elements at a higher magnification within the gray solid-solution band (Fig. 2). The phase is noticeable by its white contrast and a moderate angular shape. Considering the small amount of TaC, 20wt.% (5.7 mol. %), the high volume percent of white particles suggests that they are Ta-rich, i.e., (Ti,Ta)(CN) or (Ta,Ti)(CN), solid solutions. It has been reported that the TaC phase dissolves and precipitates first on the surface of base phases such as Ti(CN) or TiC during the stage of liquid forming ( $<1370^{\circ}\text{C}$ ).[14] Interestingly, the Ta-rich solid-solution phase in this study was found abundantly as cores near the surface when it is processed in a vacuum or low nitrogen pressure( $<6$  torr). The active precipitation of the Ta-rich solid solution is associated with the increase in the amount of Ta in the liquid binder near the surface.

In contrast to TaC addition, the W-rich solid solution band was not frequently observed in Ti(CN)-WC-Ni-Co. Instead, the undissolved Ti(CN) cores are distributed even at the edge of the sample (Fig. 3). This agrees with previous results that the formation of a W- containing solid solution is less favorable than that of a Ta-containing solid solution due to the poor affinity between W and N.[15-18] This reduces the dissolution of the Ti(CN) phase significantly. The fact that a large amount of W is present in the binder phase for the central part of the cermets [16,19-21] is in accord with this observation. Ta is not normally detected in the binder phase and most of the dissolved TaC is precipitated in the form of a solid solution. In the case of the Ti(CN)-WC-Ni-Co system, the rim growth around the Ti(CN) cores was found to be greatly suppressed near the central part of the specimen. Among various carbide additives WC is known for its superior effect for grain refinement.[17]

In order to understand the combined effect of the two carbides, Ti(CN)-10TaC-10WC-15Ni-15Co (in wt. %) system was cermets were prepared at various nitrogen pressures. The typical microstructure of the cermet is not significantly different from those of the WC-containing systems. It suggests that there is no synergy effect in the formation of the solid-solution band with the simultaneous use of carbides of different nitrogen affinity. Rather, as the nitrogen pressure increases it begins to form a segregated layer of TiC or Ti(CN) at the very edge of the surface which is evidenced by the Ti(CN)-TaC-Ni-Co system of this study (Fig.2(b)). This issue will be discussed in a subsequent paper.

### **Effect of Carbon on the Band Formation**

Such a solid-solution band also forms in nitrogen-free compositions. Thus, the influence of carbon was investigated as one of the possible factors for these phenomena. In order to elucidate the effect on the microstructure near the surface, sintering was performed with green compacts embedded in carbon powder. Other conditions for sintering were the same as before. As can be seen in Figs. 4 and 5, the samples which were embedded in the carbon powder exhibited an intermediate microstructure between vacuum and 6 torr nitrogen process at  $1510^{\circ}\text{C}$ .(Figs. 2 and 3)

In the case of Ti(CN)-TaC-Ni-Co, the band-like structure extended to 500. or more. This is more clear from the EDXA results in the following section. At a high magnification, a

remarkable increase in TaC-rich (white) phase is apparent near the surface. The cores of the solid solution are Ta-rich phase in appearance while Ti(CN) has no rim structure. The growth of the Ta-rich rim phase and their angular shapes can be noted from Fig. 4(b). It was also shown in a separate experiment that the application of nitrogen pressure did not appear to affect the microstructure under the carbon atmosphere. This suggests that the nitrogen pressure does not play a major role in the formation of the solid-solution band, as influenced by carbon.

Fig. 5 shows the microstructure of Ti(CN)-WC-Ni-Co which was sintered in carbon powder. No essential difference in microstructure is observable between Figs. 3 and 5. A relatively small quantity of W-rich solid solution in white contrast was found at higher magnifications. While flake-shaped carbon precipitates in the TaC-added system could be seen, no phase like  $W_6C$ ,  $W_{12}C$ , WC, or carbon precipitate were observed in Ti(CN)-WC-Ni-Co.

When the sintering temperature was increased to 1650°C, the change in the microstructure of Ti(CN)-TaC-Ni-Co due to the presence of saturated carbon became more obvious as shown in Fig. 6(a). The morphology of the Ta-rich phase at the surface is definitely affected by the presence of a high carbon content in the surface liquid. The addition of carbon appears to cause the surface energy between the solid solution and liquid binder to be more anisotropic than before, resulting in a more faceted shape. In addition, the process at a higher temperature greatly enhanced the growth of the solid solution phase. In Fig. 6(a) flake-like precipitates of carbon was seen which is evidence of carbon saturation in the liquid. The extension of the carbon-saturated region provides a larger area of uniform microstructure near the surface. For Ti(CN)-WC-Ni-Co system, the carbon addition at a higher temperature improved the tendency to form a uniform solid solution near the edge. However, the band formation was not clearly seen.

### **Compositional Analysis of the Band Structure**

Figs. 7 and 8 are the EDXA results obtained by using SEM line scanning. The changes in the Ti, W, and Ta concentrations were plotted as a function of distance from the surface for various sintering atmospheres. The W concentration decreases rapidly even at 6 torr of nitrogen pressure. In contrast the application of nitrogen pressure raised the Ta content near the surface in the Ti(CN)-20TaC-15Ni-15Co sample, compared to the average composition. The reverse responses were observed in Ti contents from both systems. The compositional changes associated with nitrogen were not readily noticeable, as mentioned, in the microstructures shown in Figs. 2 and 3.

The decrease in the W content with nitrogen content, in Ti(CN)-WC-Ni-Co, is indicative of a reduction in the amount of the (Ti,W)(CN) and WC phases. This suggests that the formation of the solid solution band appears to be less favorable in this system and/or the WC phase tends to move away from this region after dissolution. This stems from the intrinsic characteristics of W, i.e., a weaker affinity with N than Ti. It also shows that there is no significant difference in the W concentration from 6 torr- and 200 torr-nitrogen pressure. It can be said that 6 torr of nitrogen pressure is sufficient to cause the same effect as 200 torr on the band formation. The influence reaches a depth of 500-600 $\mu$ m from the surface for this WC-containing system.

In the case of Ti(CN)-TaC-Ni-Co nitrogen has a better affinity for Ta than for Ti, resulting in an increase in Ta content. Fig. 2 reveals the influence of nitrogen pressure on Ta concentration. More Ta tends to move near the surface, forming (Ti,Ta)(CN) or (Ta,Ti)(CN). Therefore, it is difficult to expect a synergy effect in the formation of the band structure.

Band formation was not observed for the case of Ti(CN)-WC-TaC-Ni-Co

In addition, the increase in the carbon concentration causes the W or Ta concentration to increase dramatically. This implies that Ta and W have an excellent affinity with carbon. This is more obvious with Ta than with W. The effect of carbon extends to more than ~1000  $\mu\text{m}$  from the sample surface in the case of the Ti(CN)-TaC-Ni-Co system while that of nitrogen is limited to 2~300  $\mu\text{m}$ . Note the moderate difference in the microstructures shown in Figs. 2 and 4. The addition of carbon to the liquid phase appears to change the activities of other elements significantly, depending on their affinity for carbon.

The role of vacuum during the sintering process has often been explained by an extrapolation of low nitrogen pressure. The effect of vacuum ( $10^{-2}$  torr) processing on the material transport is in agreement with this assertion based on the results shown in Figs. 7 and 8. It is much stronger than those of carbon and nitrogen in both systems and it is even more clear with the TaC-containing system. This might be related to the carbon gradient established at the surface region during vacuum sintering as well.

Often the segregation of metallic species such as Ti near the surface results in a TiC-type hard phase, providing an extremely hard surface[22]. This suggests that the carbon concentration near the surface is already sufficiently high to form a carbide phase. Since vacuum processing reduces the nitrogen concentration at the surface, the formation of a TiC-type hard phase indicates that the carbon concentration is near the saturation point in the liquid binder phase and inversely proportional to that of nitrogen. As a result, the carbon addition by embedding the sample in the carbon powder simply extends the region of carbon saturation inward, causing a widened band.

Based on the overall observations made in this study it can be said that the concentration gradient of nitrogen always initiates the transport of other species such as Ti, W, Ta, and C. The nitrogen concentration determines the dissolution of Ti(CN) due to the limited solubility of nitrogen in the liquid binder. That is, if the concentration exceeds a limit, it retards the dissolution of Ti(CN) significantly during vacuum sintering. For WC-containing systems the nitrogen pressure in the 2-6 torr range is already high enough to maintain the same dissolution rate for Ti(CN) as inside the bulk without resulting in the solid solution band.

## SUMMARY AND CONCLUSIONS

The carbonitride solid solution formed around Ti(CN) cores is the equilibrium phase at the sintering temperature involving a liquid binder phase. The findings show that the surface microstructure depends strongly on the carbides added and the sintering atmosphere. The conclusions of this study are;

- (1) Vacuum processing is the most essential condition for the formation of the solid solution band. In addition, the band can be formed in the samples embedded in the carbon powders under a vacuum. The hard phase Ti(CN) actively dissolves at the surface under vacuum or a low pressure of nitrogen and the super-saturation of solutes at the surface promotes the formation of a solid solution phase. This reaction provides a need for the material transport in the direction of from the interior to the surface.
- (2) The TaC phase added to a Ti(CN)-based cermet behaves as a vehicle which forms active solid solution and enables a solid solution band to form near the surface. On the other hand, WC in the cermet system exhibits a significantly reduced tendency to form

the band due to its weak affinity for nitrogen. The addition of both TaC and WC to Ti(CN)-Ni-Co cermet did not provide a synergy effect in forming the band.

- (3) The nitrogen concentration appears to significantly affect the carbon concentration in the liquid binder phase; the carbon concentration varies inversely proportional to that of nitrogen. The metalloids appear to limit total solubility even in the liquid state of the binder phases so long as the binder phases do not form carbides or nitrides. The fact that a TiC-type hard phase forms near the surface in Ti(CN)-WC-TaC-Ni-Co during vacuum sintering supports this conclusion.

### ACKNOWLEDGMENT

This research was sponsored through the Korean Ministry of Education Research Fund for Advanced Materials (1997) and the HAN Project of STEPI (1997).

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*Table 1 The size and manufacturers of the powders used in the study.*

	Ti(CN)	TaC	WC	Ni	Co
Average size (um)	2.97	0.9	1.9	3.7	1.35
Maker	Kennametal	H.C.Stark	KTC	INCO	H.C.Stark
stoichiometry	Ti(C <sub>0.5</sub> N <sub>0.5</sub> )				

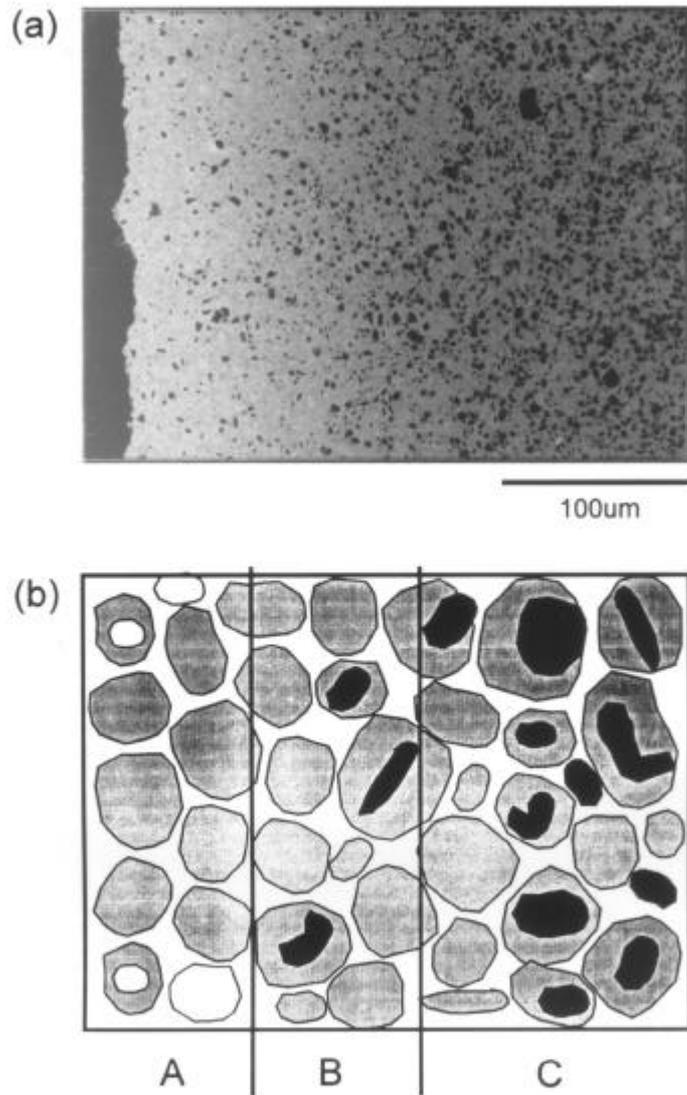


Fig.1. A typical solid solution band formed at the cermet surface: (a) SEM micrograph (x250) and (b) schematic illustration.

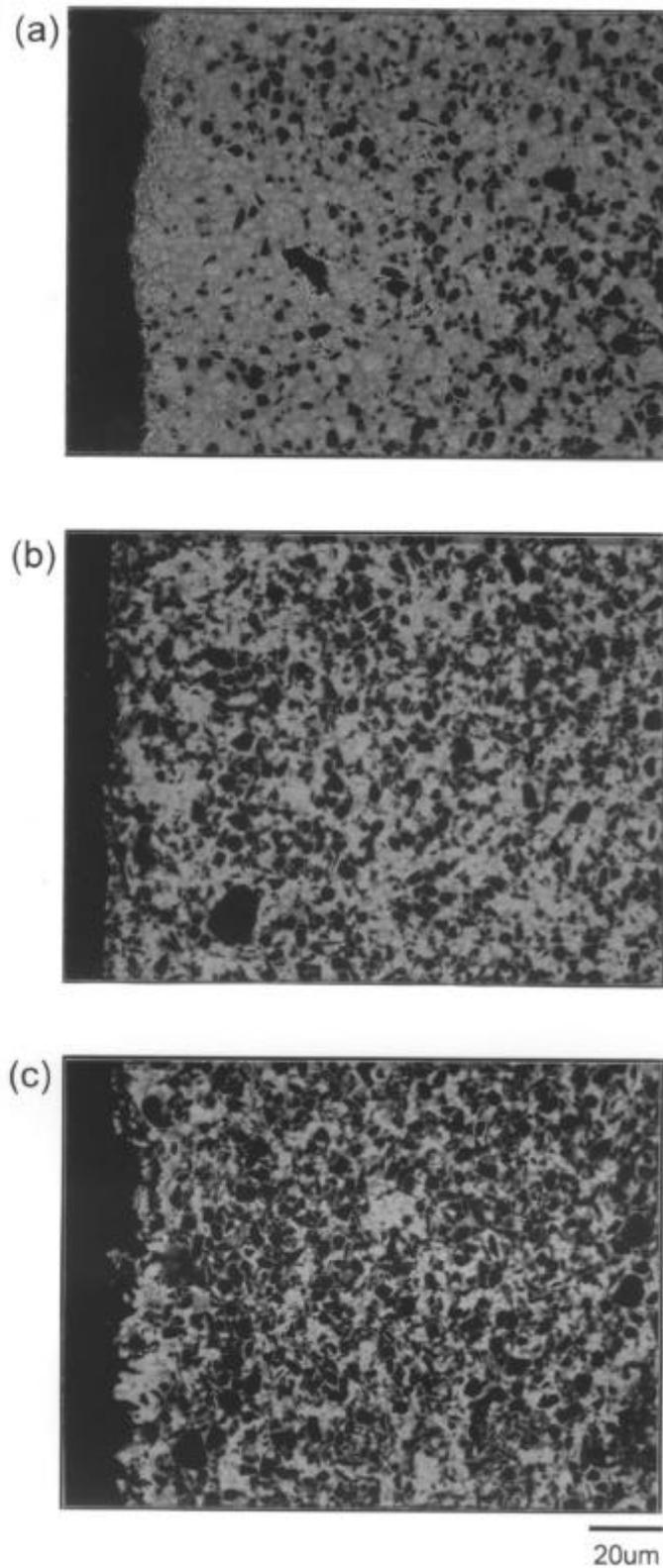


Fig.2. Microstructure of Ti(CN)-20wt%TaC-15wt%Ni-15wt%Co sintered at 1510°C for 1h in (a) vac., (b) N<sub>2</sub> at 6 torr, and (c) N<sub>2</sub> at 200 torr. (x500)

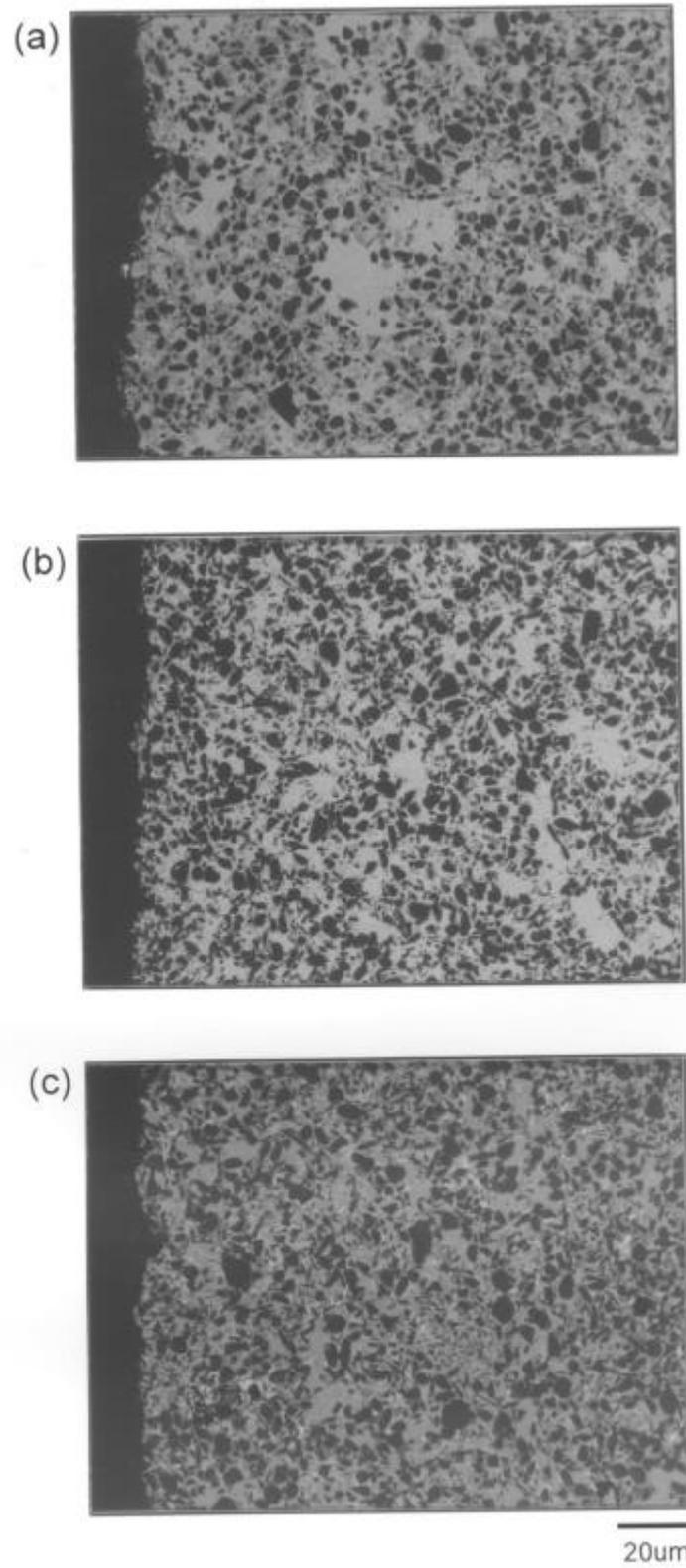


Fig.3. Microstructure of Ti(CN)-20wt%WC-15wt%Ni-15wt%Co sintered at 1510°C for 1h in (a) vac., (b) N<sub>2</sub> at 6 torr, and (c) N<sub>2</sub> at 200 torr. (x500)

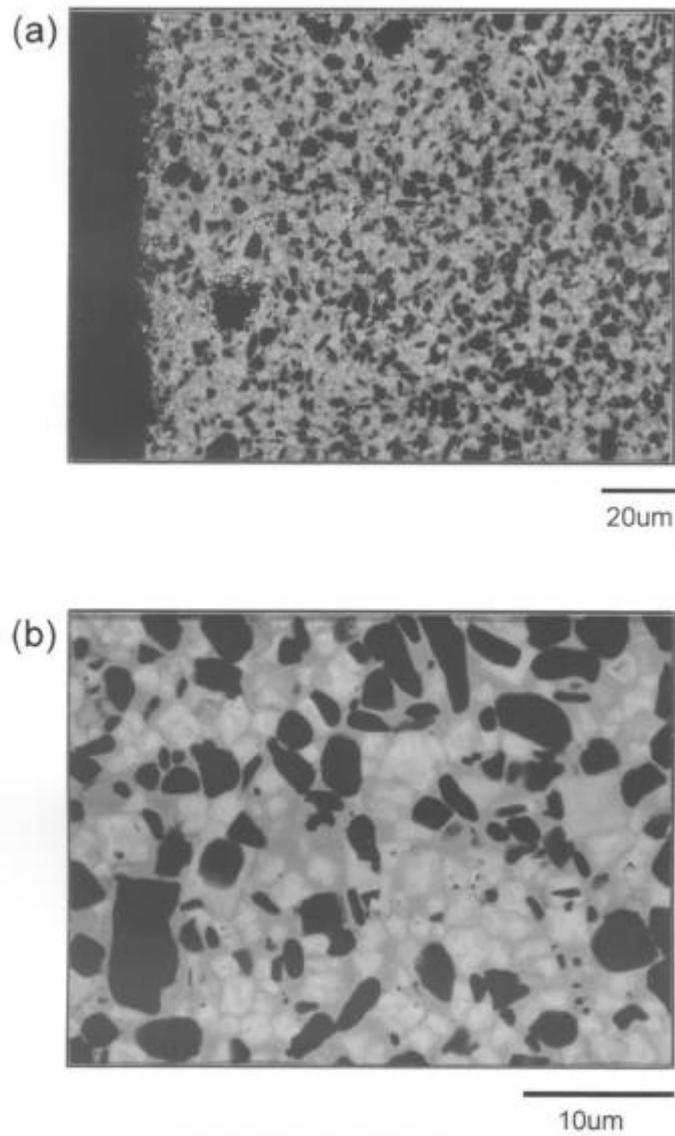


Fig.4. Microstructure of Ti(CN)-20wt%TaC-15wt%Ni-15wt%Co embedded in carbon powder and sintered at 1510°C for 1h at (a) x500 and (b) x2000.

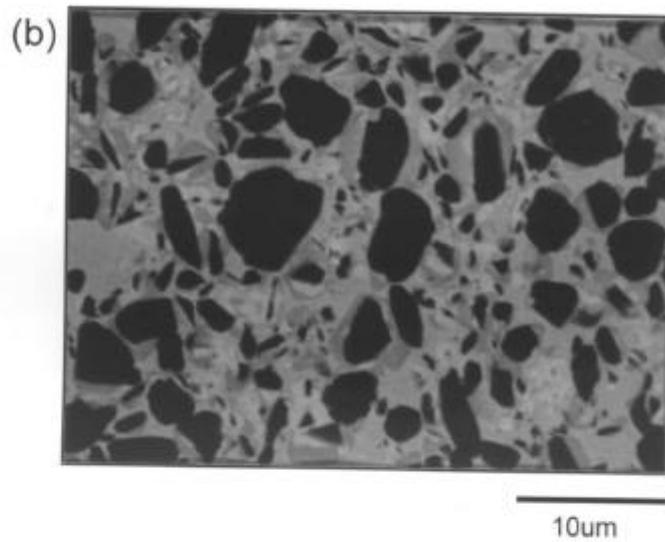
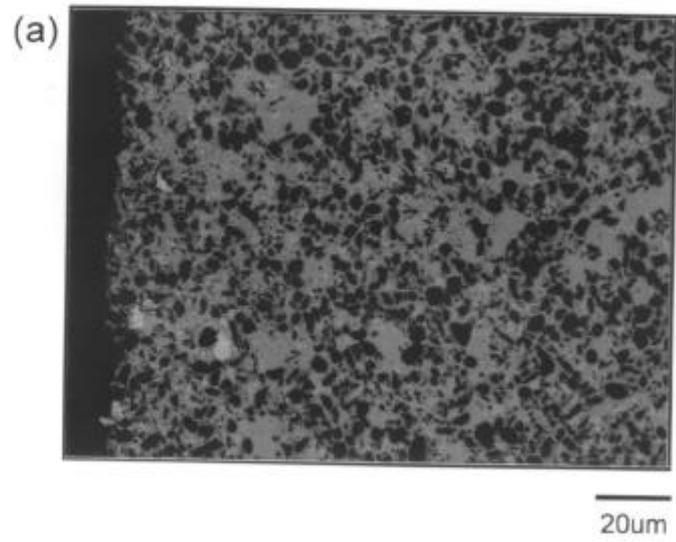


Fig.5. Microstructure of Ti(CN)-20wt%WC-15wt%Ni-15wt%Co embedded in carbon powder and sintered at 1510°C for 1h at (a) x500 and (b) x2000.

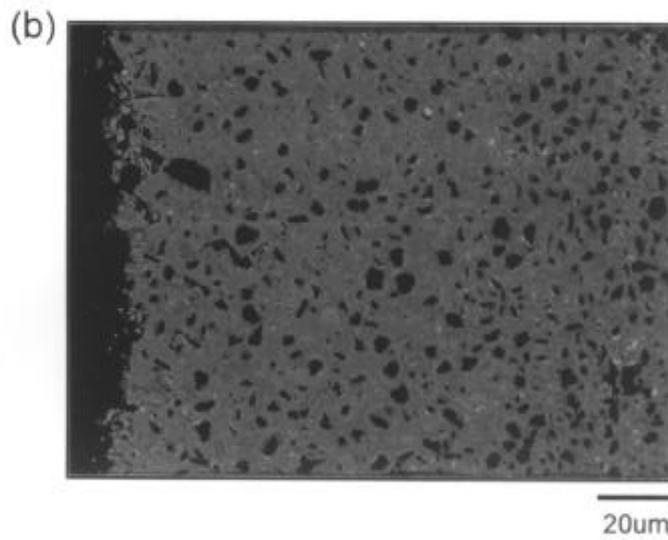
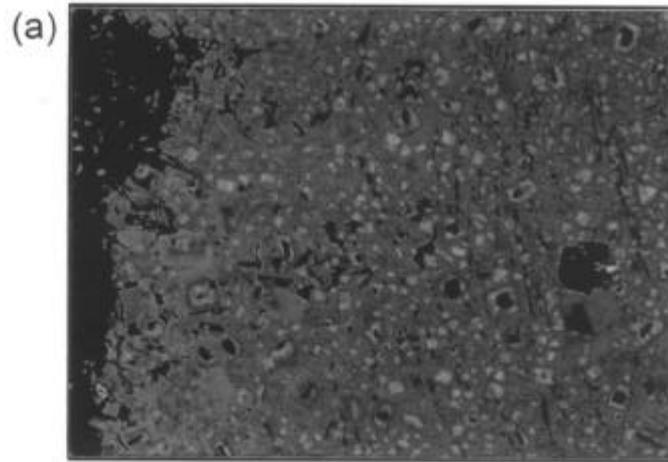


Fig.6. Microstructure of  $\text{Ti(CN)-20wt\%MeC-15wt\%Ni-15wt\%Co}$  embedded in carbon powder and sintered at  $1650^\circ\text{C}$  for 1h in vacuum. (x500) : (a) TaC (b) WC for MeC