Inhibition Effect of Ti(C,N) Particle Dispersion on Grain Growth of WC-Co Cemented Carbide*1

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The WC-Co cemented carbides with the addition of Ti(C,N) base particles with different sizes were fabricated by liquid phase sintering and their microstructures were mainly investigated in detail comparing the microstructure of the alloys with VC and Cr3C2 addition. It was found that the WC grain growth was more strongly inhibited with increasing Ti(C,N) content and the addition of Ti(C,N) particle size. The degree of inhibition by the addition of Ti(C,N) particle with about 0.1 μm size was lower than that of VC addition and was almost same as that of Cr3C2 of addition. Considering the results about the relationship between WC grain size and Ti(C,N) particle size and the analysis of Co phase composition, it was seen that the mechanism of grain growth inhibition by the addition of Ti(C,N) particles was the pinning (Zener) effect by the second phase particle, which was different from the mechanism for the addition of VC and Cr3C2 reported previously. The case that one Ti(C,N) particle contacts plural WC grains was often observed, so that the pinning effect was considered to work by many Ti(C,N) particles neighboring one WC grain. The very important result that the pinning effect by Ti(C,N) addition enable to develop the new type of ultra-fine cemented carbide was obtained in this study. [doi:10.2320/matertrans.M2019810]

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1. Introduction

Among WC-Co based cemented carbide materials, demand for so-called “ultrafine cemented carbide materials” has increased particularly in recent years.1–3 This is attributed to the greater hardness and strength of ultrafine WC particles compared with those of larger particles, leading to tools with longer service lives and greater durability. In previous reports4–14 on ultrafine cemented carbides, it is studied for many years about the addition of VC and other carbides found to inhibit the growth of WC particles during liquid phase sintering. The VC addition has the greatest effect on grain growth inhibition. A mechanism of refinement has been proposed as follows: WC particle growth via solution-reprecipitation (i.e., Ostwald ripening) is inhibited by the formation of a V atmosphere on the WC particle surface, which is related to the fact that a large amount of V dissolves into the Co liquid phase.8,10 Transmission electron microscopy observations have revealed that V segregation occurs and a (V,W)C phase forms at both the WC/Co interface and the WC/Co interface.8,10 We have previously considered that the aforementioned V weakens the force of WC sustained by the Co phase and degrades the abrasion resistance of cemented carbides.15,16 In addition, the strength of alloys has been reported to decrease when the added VC exceeds a certain amount.15,16

The addition of Cr3C2 has the second-strongest effect of refinement after VC; the segregation behavior in this case is similar to that of VC, but its extent is smaller (milder) than that of VC. Recently reported ultrafine cemented carbides tend to involve the combined addition of VC and Cr3C2 or the addition of Cr3C2 alone.17

The addition of TaC or TiC has a small grain-growth inhibition effect on WC particles3 because TaC and TiC dissolve in the liquid phase to lesser extents than VC and Cr3C2 and because TaC and TiC form a solid solution with WC, which may lead to grain growth during sintering. TaC and TiC are not added in ultrafine cemented carbides, but TaC and TiC have long been used as additives in cemented carbides with ordinary grain sizes. In addition, segregation phenomena such as VC segregation at the WC/Co interface are not observed with these additions.11

On the other hand, in TiC based cermets, the phenomenon of atomization by addition of nitrogen is well documented and the growth of Ti(C,N) at grains during sintering is known to be more difficult than the growth of TiC.17–19 The addition of Ti(C,N) to cemented carbides of the WC base has also been reported, and Ti(C,N) is used in cemented carbides for coating base materials by addition in the form of (Ti,W)(C,N) solid solution.20,21 Because added Ti(C,N) is less dissolved in the liquid phase, and is less likely to grain growth when added to WC-Co alloy, which is similar to cermets, a new ultrafine cemented carbide could be developed in which Ti(C,N) is used to inhibit grain growth of WC grains of the cemented carbide. In other words, we propose that grain growth of WC can be inhibited by finely dispersing Ti(C,N) particles or (Ti,W)(C,N) particles. In metals or ceramics, grain growth inhibition (pinning effect or Zener effect) due to dispersed particles of a second phase is well known. However, whether grain growth during liquid phase sintering of cemented carbides can be inhibited by the presence of second phase (solid phase) particles such as Ti(C,N) particles has not been clarified.

Therefore, in the present study, we added Ti(C,N) particles with different particle sizes and compositions to WC-Co alloy using fine WC powder and sintered it. Then, we investigated whether grain growth of WC particles were inhibited via microstructure observations and the mechanical properties of

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the cemented carbides, such as their hardness. Ultrafine cemented carbides were then prepared by addition of VC and Cr$_3$C$_2$, and their properties were compared with those of the Ti(C,N) added alloy. Consequently, we decided to investigate the feasibility of producing ultrafine cemented carbides by addition of Ti(C,N).

2. Experimental Method

2.1 Raw material powder

Table 1 shows the raw material powders used in this study. Three commercial WC powders (mean particle size 0.7, 0.4, and 10 µm, A.L.M.T. Corp.) were used as powders for cemented carbides; they are referred to hereafter as WCI, WCII, and WCIII, respectively. Co powder (0.8 µm, Umicore), TaC (Japan New Metals), Cr$_3$C$_2$ (H.C. Starck), and VC (Japan New Metals) had a mean particle size of 1.0 µm, and to be one type each. For the addition of Ti(C,N), types Ti(C,N), (Ti,W)(C,N), (Ti,Mo)(C,N) (mean particle size 1.0, 0.7, 0.5 µm, Japan New Metals), and TiO$_2$ (mean particle size 0.02 µm Aerosil Japan) are designated as Ti(C,N)I, Ti(C,N)II, Ti(C,N)III, and Ti(C,N)IV, respectively.

2.2 Alloy fabrication

Table 2 shows the characteristics of the 28 alloys prepared in this study and five kinds for binder phase analysis. First, we describe the traits common to all of the alloys. The amount of Co in the alloys was fixed at 16.4 vol%. The amount of carbon was adjusted to a medium carbon level. Mixing was carried out with a ball mill (in ethyl alcohol); then, the mixtures were vacuum dried, molded, and sintered at 1653 K for 3.6 ks. The sintering atmosphere of the alloys containing no nitrogen was vacuum, whereas that of the alloys containing nitrogen (Ti(C,N) added alloys) was N$_2$ gas at 2.6 kPa. After sintering, all of the samples were subjected to HIP treatment (1593 K, 3.6 ks, 40 MPa, in Ar).

We here describe the produced materials. The WC-Co alloy (straight) prepared with WCI powder and no other carbide is designated as ST alloy. The alloys produced with the addition of TaC, Cr$_3$C$_2$, VC, and Ti(C,N) are designated as TA alloy, CR alloy, V alloy, and TC alloys, respectively. Alloys which Ti(C,N) grain are changed are designated as TC1 to TC4 alloys. Sub-numbers were assigned to TC3 and TC4 for various amounts of additives. In addition, when WCII powder was used, F was added to each sample; these alloys are designated as STF, TAF, CRF, VF, and TCF1 to 4. Sub-numbers were assigned to TCF3 and TCF4 for various amounts of additives. Alloys prepared using coarse-grained WCIII powders are indicated by a C prefix in their sample name (CTA, CCR, CV, CTC1, and CTC4). In the case where TiO$_2$ powder was used in Ti(C,N)IV, after the addition of excess carbon to remove (reduce) oxygen at the time of compounding, N was absorbed from the sintering atmosphere to adjust the formulation to Ti(C,N).

2.3 Evaluation and analysis

To prepare a sample for analysis, a powder compact of $5.5 \times 10.5 \times 30$ mm$^3$ was sintered and each face was ground with a 0.2 mm diamond wheel. Then, the central part was cut and finished with diamond paste. After confirming that there was no difference between the ground surface and the internal structure, the WC mean particle diameter ($d$) was calculated from the photograph obtained by observing the structure by SEM using Fullman’s equation:

$$d = 4 \cdot \frac{N_l}{N_s}$$

where $N_l$ is the number of particles per unit length and $N_s$ is the number of particles per unit area. In addition, hardness
(HRA) was measured on the ground surface in a form corresponding to the particle diameter. To investigate the composition of various added Ti(C,N), the lattice constant of the surface observed by SEM was measured by X-ray diffraction, and the sample was crushed and used for nitrogen analysis. Energy-dispersive X-ray spectroscopy (EDS) was used to analyze the composition of the Co phase of coarse grained samples prepared with WCIII powder. In addition, detailed microstructures were observed by high-resolution SEM; in particular, the location of Ti(C,N) particles was examined in detail.

3. Results

Figure 1 shows SEM microstructures of eight comparing samples. Alloys prepared using WCI and WCII powders are arranged in the upper row and lower row, respectively. The WC grains grew large in the ST and STF alloys of other carbide-free alloys. The STF (prepared using WCII) alloy exhibits greater grain growth of the WC grains than the ST alloy (prepared using WCI). The WC grain size in alloys prepared using WCII is smaller than that in alloys prepared using WCI because the added VC, Cr3C2, and TaC inhibited grain growth. The grain-growth inhibition effect induced by the addition of these three carbides increases in the order TaC < Cr3C2 < VC, which is the same as the conventional result.4) The following sections present the results of our study of the effect of inhibiting grain growth by adding Ti(C,N) particles were investigated in detail for these comparative materials.

Figure 2 shows an SEM micrograph of the structure of the TC alloy and the TCF alloy to which four types of Ti(C,N) particles (powders) were added. In the upper row and the lower row, the cases of WCI and WCII are arranged, as in the previous figure. First, compared with the additive-free material shown in Fig. 1, grain growth inhibition is observed upon the addition of Ti(C,N) particles. Regarding the influence of the type of Ti(C,N) particles, the grain-growth

![Fig. 1 SEM microstructures of WCI,II- Co and WCI,II-(TaC, Cr3C2 or VC) -Co alloys.](image1)

![Fig. 2 SEM microstructures of WCI,II-Ti(C,N)I~IV-Co alloys.](image2)
inhibition effect tends to increase in the order of Ti(C,N) type I < II < III < IV. In other words, the finer the Ti(C,N) particles, the greater the effect of inhibiting grain growth.

Regarding the influence of the WC powders, WCII tends to be finer than WCI. In addition, in WCII, rod-like (plate-like) WC particles are observed in the structures of samples to which Ti(C,N)I, II, or III was added but not in samples to which Ti(C,N)IV was added. A comparison of the grain-growth inhibition effects of Ti(C,N)IV with those of VC, Cr3C2, and TaC reveals that the effect of inhibiting grain growth by addition of Ti(C,N)IV is not as good as VC but stronger than TaC and same degree as Cr3C2.

Figure 3 and Fig. 4 show the changes in the structure of Ti(C,N)III and IV, respectively, when the addition amount is changed. In all cases, the grain-growth inhibition effect clearly increases with increasing addition amount, WCII is finer than WCI, and in the WCII, it can be seen that rod-like WC is observed when Ti(C,N) is added in a small amount. In these micrographs, the Co phase and the Ti(C,N) particles appear black and cannot be distinguished from each other; however, when the Ti(C,N) addition amount is large, a black phase appears; we speculate that the added Ti(C,N) particles aggregated. A comparison of Ti(C,N)III and IV reveals that the grain-growth inhibition effect is stronger in Ti(C,N)IV; however, it is observed that aggregation is likely to occur.

To more quantitatively characterize the aforementioned structural changes, we decided to study the hardness of each sample and the WC particle size. Figure 5 shows the relationship between hardness and WC grain size in terms of WCI and WCII in relation to the added Ti(C,N) and carbonitrides (vol%). As a visual aid, the figures include two curves connecting the obtained points for the cases of Ti(C,N)III and IV. With increasing addition amount Ti(C,N)III and IV, the hardness increases, the WC grain size decreases, and both become saturated. When samples with the same amount of additive are compared, the hardness
increase and the atomization effect induced by Ti(C,N) addition are inferior to those induced by VC addition, better than those induced by TaC addition, and approximately the same as those induced by Cr3C2 addition. In addition, a comparison of WCI and WCII show that, regarding the hardness increase induced by increases in the added amount and the degree of atomization of the WC particles, the effect of WCII becomes more remarkable than that of WCI in the region where the addition amount is small.

Figure 6 shows the hardness and the WC grain size of the sintered body in relation to the grain size of the added Ti(C,N) powder. The particle size of Ti(C,N) is the grain size after sintering, and the particle sizes of Ti(C,N)I, II, and III were nearly equivalent to those listed in Table 1, even after sintering; however, the particle size of Ti(C,N)IV was approximately 0.1 µm. Here an attempt to connect the two lines with the type of WC powder used results in a curve. In other words, with decreasing particle size of the added Ti(C,N) powder, the hardness increases, the grain size of the WC grains of the sintered body decreases, the hardness is higher overall with WCII than with WCI, and the WC grain size of the sintered body is smaller.

The following discussion details our study of the structure of the material (sintered body) obtained in this research. Figure 7 shows the lattice constants of powdered Ti(C,N)I, Ti(C,N)II, TI, TiN, and (Ti0.5W0.5)C on the pseudo-ternary phase diagram (schematic) of WC–TiC–TiN and the lattice constants of the sintered bodies of Ti(C,N)IV. Because TiC and TiN are full-rate solid solutions and C+N approximately 1, we considered that the lattice constant of Ti(C,N) was established as a simple mixture rule of TiC and TiN (Vegard’s law). Furthermore, using a carbon/nitrogen analyzer to carry out C/N analyses of a sintered body containing Ti(C,N)IV, we found the C/N ratio to be approximately 5/5. This figure shows that the change in lattice constant is small even if W dissolves extensively in Ti(C0.6N0.4). The Ti/W ratio of (Ti,W)(C0.5N0.5) with Ti(C,N)IV added cannot be determined from lattice constant measurements; thus, the Ti/W ratio is likely close to that of (Ti0.8W0.2)(C0.5N0.5) of the Ti(C,N)II added sample. In this study, we estimated the value of the composition of Ti(C,N); a more detailed analysis is needed in a future study.

Table 3 shows the EDS analysis results for the Co phase for materials prepared using coarse grained WCIII. The table also shows the conventional results related to the solubility...
of WC and carbides in the liquid phase when each carbide (or carbonitride) is added. The EDS analysis of the Co phase also shows the conventional results \(^{11}\) (TiC addition).

Accordingly, in the case of Ti(C,N) addition, the amount of Ti solid solution is substantially smaller than in samples of V with VC added or Cr with Cr\(_2\)C\(_2\) added and is approximately the same as the amount of Ti solid solution in TiC added cemented carbide. The W solid solution amount is approximately the same as that indicated in the conventional EDS analysis results. The solubility of Ti(C,N) in the liquid phase during liquid phase sintering was not investigated in this study, but its solubility is likely the same as that of TiC and remarkably smaller than that of VC or Cr\(_2\)C\(_2\).

The object of the present study is the inhibition of grain growth by the addition (dispersion) of Ti(C,N) particles. The effects of grain growth inhibition by addition of VC or Cr\(_2\)C\(_2\), which is a conventional technique for obtaining ultrafine cemented carbides, differ dramatically from each other. Analysis of the Co phase showed that the solid solution amount of Ti when Ti(C,N) particles were added was substantially smaller than that of V when VC was added and that of Cr when Cr\(_2\)C\(_2\) was added; in addition, the Ti solid solution amount of TiC added cemented carbide was almost the same. The solubility of Ti(C,N) in the liquid phase during liquid phase sintering in the case where Ti(C,N) particles were added was not investigated in this study; however, its solubility is likely the same as that of TiC and remarkably smaller than that of VC or Cr\(_2\)C\(_2\). The mechanism of the V atmosphere at the interface between the WC particles and the liquid phase, as considered in the case of addition of VC or Cr\(_2\)C\(_2\), is considered not to be applicable in the case of adding Ti(C,N) particles.

Figure 8 shows the results (a to e) of our examination of the form of Ti(C,N) particles in the Ti(C,N)IV added alloy by high resolution SEM. Schematics corresponding to the images are shown in (a' to e'). In Fig. 8(a), one Ti(C,N) particle is present in the Co phase adjacent to one WC particle. In Fig. 8(b), one Ti(C,N) particle is present in the Co phase adjacent to the plurality of WC particles. In Fig. 8(c), one Ti(C,N) particle is observed at the WC/Co interface. In Fig. 8(d), one Ti(C,N) particle exists in the Co phase apart from the WC particle. In Fig. 8(e), because of agglomeration, the Ti(C,N) particles appear to be classified into five forms. Details of the ratios of these forms are not clear here; however, the ratio in (b) appears to be the largest, whereas that in (d) appears to be the smallest; thus, the ratios in (a), (c), and (e) are intermediate.

### 4. Discussion

The object of the present study is the inhibition of grain growth by the addition (dispersion) of Ti(C,N) particles. The effects of grain growth inhibition by addition of VC or Cr\(_2\)C\(_2\), which is a conventional technique for obtaining ultrafine cemented carbides, differ dramatically from each other. Analysis of the Co phase showed that the solid solution amount of Ti when Ti(C,N) particles were added was substantially smaller than that of V when VC was added and that of Cr when Cr\(_2\)C\(_2\) was added; in addition, the Ti solid solution amount of TiC added cemented carbide was almost the same. The solubility of Ti(C,N) in the liquid phase during liquid phase sintering in the case where Ti(C,N) particles were added was not investigated in this study; however, its solubility is likely the same as that of TiC and remarkably smaller than that of VC or Cr\(_2\)C\(_2\). The mechanism of the V atmosphere at the interface between the WC particles and the liquid phase, as considered in the case of addition of VC or Cr\(_2\)C\(_2\), is considered not to be applicable in the case of adding Ti(C,N) particles.

As Fig. 6 shows, the growth of WC particles was inhibited as the added Ti(C,N) particles became fine, which we consider the most important result related to the grain growth mechanism. In other words, this result appears to support the idea that the grain-growth inhibition effect of adding Ti(C,N) particles is essentially different from that of VC and similar carbides. This difference is attributed to the grain-growth inhibition effect of WC particles not changing greatly when VC or Cr\(_2\)C\(_2\) is added, even if the particle diameter of added carbide is changed. As mentioned in the introduction, VC and similar carbides are strongly related to the mechanism of the
grain-growth inhibition effect (i.e., the V atmosphere theory) because they dissolve in large amounts in the liquid phase.\textsuperscript{10} In this context, the findings in the present study are reasonable. In addition, in the case of the Ti(C,N) particle added alloy in the present study, segregation of Ti is almost not observed on the WC surface. We speculate that this scenario is the same situation reported by Kawakami et al.\textsuperscript{11}

We here consider further the effect of inhibiting grain growth of WC particles in the alloys with Ti(C,N) particles added. As Fig. 8 shows, Ti(C,N) particles surrounded by the Co phase exist in part of the sample, although most of the Ti(C,N) particles are contacting (adhering) to the WC particles and one Ti(C,N) particle is adhered to multiple WC particles. Ti(C,N) particles were also observed at the WC/WC interface. Here, for a more quantitative discussion of the relationship between Ti(C,N) particles and WC particles, we compare the mean free path $\lambda$ of the Co phase with the size of the second-solid-phase particle:

$$\lambda = \frac{2}{3} \frac{f_{\text{Co}}}{1 - f_{\text{Co}}} d$$

where $f_{\text{Co}}$ is the volume fraction of the binder phase and $d$ is the mean particle size of WC. If we assume that the volume fraction of the Co phase in this study is approximately 20\% and that the particle size of WC is 0.4 $\mu$m, $\lambda$ is approximately 0.07 $\mu$m. The particle-size range of Ti(C,N) particles added in this study is 0.1–1 $\mu$m, which is larger than $\lambda = 0.07 \mu$m even for the finest Ti(C,N) sample (i.e., Ti(C,N)IV). This large particle size of Ti(C,N) increases the likelihood that Ti(C,N) particles will adhere to WC particles.

In addition, if we assume that the particle sizes of the WC particles and the Ti(C,N) particles are 0.4 $\mu$m and 0.1 $\mu$m, respectively, and that their volume ratios are 77\% and 3\%, respectively, then, the ratio between the number of WC particles and the number of Ti(C,N) particles is calculated as 1/2.5. The particle diameter of the Ti(C,N) particles may be smaller than 0.1 $\mu$m, for example, 0.05 $\mu$m; in this case, the ratio between the number of WC particles and the number of Ti(C,N) particles is calculated as 1/20. If we consider that the number of Ti(C,N) particles is between 3 and 20 particles per WC particle, and given the aforementioned value for $\lambda$, the WC particles would be in contact with a substantial number of Ti(C,N) particles and would likely be surrounded by them.

Figure 9 shows a schematic of the second-solid-phase particles in the (a) solid phase structure and (b, c) liquid phase structure. The inhibition effect of dispersed particles on the grain growth of a solid phase is called the pinning effect or Zener effect. It has long been a topic of study and is actually used in the development of metal and ceramic materials.

Under the condition that the grain growth of the base phase is stopped (saturated) by the presence of the second-solid-phase particle, the pinning effect is considered using the following equation\textsuperscript{22–24} known as the Zener relationship:

$$R = \frac{\beta r}{f}$$

where $R$ is the mean particle size of the base phase, $r$ is the dispersed particle size, $f$ is the volume fraction of the dispersed particles, and $\beta$ is the coefficient ($= 4/3$).\textsuperscript{25,26} This equation shows that, when the dispersed particle size is small and the volume ratio of the dispersed particles is large, the particle diameter of the base phase decreases, consistent with the results of the present study. Here, if the values of $R$, $r$, and $f$ are 0.4 $\mu$m, 0.1 $\mu$m, and 3\%, respectively, $\beta$ is calculated to be 0.12. The $\beta$ in actual systems is often smaller than 4/3.\textsuperscript{26}

In this study, it is considered that grain growth (pinning effect) is not saturated, and that pinning effect in this system is large. However, further detailed examination is necessary. Furthermore, future studies are needed to determine whether the pinning effect will be weakened when the volume fraction of the Co phase (liquid phase) and $\lambda$ both become large.

As emphasized in the introduction, regarding grain growth during sintering in the presence of a liquid phase such as a cemented carbide, no experimental evidence suggesting a pinning effect due to the presence of the second-solid-phase particles has been reported. Grain growth during liquid phase sintering, which occurs in cemented carbides, is thought to proceed via a solution-reprecipitation mechanism of solid phase particles in the liquid phase, so-called Ostwald ripening. If the WC particles and the Ti(C,N) particles are similarly surrounded by the liquid phase, if the WC particles and the Ti(C,N) particles are separated from each other in the liquid phase pinning should not occur.

We consider this point with Fig. 9(b), (c), where (c) shows the relationship of each interface energy that is important in considering inhibition of grain growth due to dispersed particles in the presence of a liquid phase. Given that the interfacial energies of Ti(C,N)/WC, Ti(C,N)/liquid, and WC/liquid are $\gamma_{\text{TW}}$, $\gamma_{\text{TL}}$, and $\gamma_{\text{WL}}$, respectively, we assume that the following equilibrium equations hold between them:

$$\gamma_{\text{TW}} = \gamma_{\text{WL}} + \gamma_{\text{TL}} \cos \theta$$

where $\theta$ is the angle between $\gamma_{\text{TL}}$ and $\gamma_{\text{WL}}$. This relational expression is similar to that of the wetting angle or dihedral angle but is applied to interfacial energy for the first time in
the present study. Applying this equation leads to the following interpretation. As noted, for Ti(C,N) particles to pin the growth of WC particles, the Ti(C,N) particles must be in contact with the WC particles. Equation (4) can be considered to express the ease of contact (difficulty). In other words, it indicates that Ti(C,N) particles tend to contact WC particles. From this point forward, research from the viewpoint of interfacial energy is also necessary. Furthermore, analysis by comparison of simulated and experimental results will be informative. We plan to conduct such studies in the future.

5. Conclusions

We examined the base structure of the WC-Co alloy obtained by liquid phase sintering with the addition of Ti(C,N) particles with different particle sizes and compositions, and compared it to that of the alloys containing VC or Cr3C2. We deduced the following conclusions.

1) The growth of WC grains during sintering can be inhibited by adding Ti(C,N); in addition, with increasing amount of Ti(C,N) added, the smaller the grain size and the greater the grain-growth inhibition effect.

2) When fine TiO2 is added, it is changed to (Ti,W)(C,N) with a particle size of approximately 0.1 µm via the reaction at the time of sintering. In this case, the atomization effect was smaller than with WC addition but was approximately equivalent to that with Cr3C2 addition.

3) The WC particle size/Ti(C,N) particle size relationship and results of the composition analysis of the Co phase indicated that the mechanism of grain growth inhibition by addition of Ti(C,N) based particles was the pinning effect (Zener effect) of the second-phase particles. This mechanism differs from that associated with the addition of VC or Cr3C2.

4) The form of Ti(C,N) is often such that one Ti(C,N) particle is adjacent to multiple WC particles in many cases; in other words, many Ti(C,N) particles were judged to be in contact with an individual WC particle.

5) In summary, this study revealed that a new type of ultrafine cemented carbide can be prepared via the pinning effect of Ti(C,N) particles.

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