Development of new ultrafine cemented carbide by WC-Ti(C,N)-Cr_3C_2-Co alloy

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Introduction

The demand for ultrafine-grained cemented carbide as wear-resistant tools and cutting tools is increasing due to their high hardness and strength. The addition of VC has the strongest effect on grain growth inhibition (refinement) of WC particles in ultrafine-grained cemented carbide, followed by the addition of Cr_3C_2. However, the ultrafine-grained cemented carbide with VC single addition has been rarely used in practice; VC dissolves in the liquid phase during sintering precipitates as a (W,V)C phase or a V-concentrated phase during cooling, and this phenomenon is thought to reduce the alloy properties.

Pinning (Zener) effect that the dispersed (second phase) particles inhibit grain growth of matrix phase is well known for metals or ceramics. However, it is unclear weather the grain growth during liquid phase sintering of cemented carbides can be prevented or not by the second phase (solid phase) particles such as Ti(C,N) particles. Furthermore, the combining addition of Ti(C,N) with Cr_3C_2 should more largely inhibit the grain growth than that the single addition, consequently VC-free ultrafine-grained cemented carbide can be obtained.

Fine Ti(C,N) particles were introduced to the cemented carbide with ultrafine-grained WC and sintered in this study, and whether the grain growth of WC particles could be inhibited at that time was investigated using microstructural observation. Furthermore, ultrafine-grained cemented carbide with the combined addition of Ti(C,N) and Cr_3C_2 was fabricated, and mechanical properties were investigated after microstructural examination.

***Purpose* ; VC-free ultrafine-grained cemented carbide**

Method

I. Dispersion of fine Ti(C,N) particles inhibits WC grain growth by pinning effect (Zener effect).

II. Combined addition of Cr_3C_2

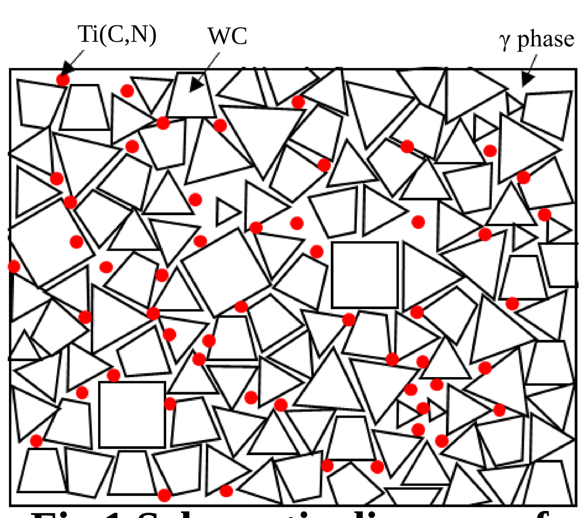

Fig.1 Schematic diagram of alloy microstructure.

Why Ti(C,N)?

1.Ti(C,N) is likely to be present as a pin because of its low solubility in the liquid phase.

2.Nano-sized TiO_2 is commercially available.

Point

TiO_2 (20 nm) is used as a starting material and carbonitrided during sintering to Ti(C,N).

Experimental Procedure

Table1 Starting powder, size and maker.

Element	Starting Powder	Size (μm)	Maker
WC	WC	0.4, 1.0	A.L.M.T
Co	Co	0.8	Umicore
TaC	TaC	1.0	Japan New Metals
Cr_3C_2	Cr_3C_2	1.0	H.C. Starck
VC	VC	1.0	Japan New Metals
Ti(C,N)	TiO_2	0.02	Nippon Aerosil

Table2 Composition of the specimens (vol%).

Signal	Ti(C,N)	TaC	Cr_3C_2	VC	Co	WC
non-addition					16.4	bal.
TaC		3			16.4	bal.
Cr_3C_2			3		16.4	bal.
VC				3	16.4	bal.
Ti(C,N)	3				16.4	bal.
VC/Cr_3C_2			1.9	1.3	16.4	bal.
Ti(C,N)/Cr_3C_2	1~5		0~2		16.4	bal.

Starting powder → **Ball mill** → **Dry & mold** → **Sinter** → **HIP** → **Evaluation**

Ball mill: 70h, in acetone

Sinter:
Temp, Time
Single addition, VC/Cr_3C_2;1653K-3.6ks
Ti(C,N)/Cr_3C_2; 1613K-3.6ks
Atmosphere
Ti(C,N) addition; N_2 gas at 2.6 kPa
Carbonitriding TiO_2 to Ti(C,N) during sintering.
Other; Vac.

HIP: 1593K-3.6ks, 40MPa, in Ar

Evaluation:
Microstructure was observed using SEM
Position of Ti(C,N) particles was confirmed using a high-resolution SEM
Hardness (HRA)
Fracture toughness (IF method)
Transverse-rupture strength(T.R.S.)
(4×8×25mm, span 20mm, 3 points bending test)
Origin of the fracture was analyzed using SEM and EDS.

Results and discussion

Microstructures

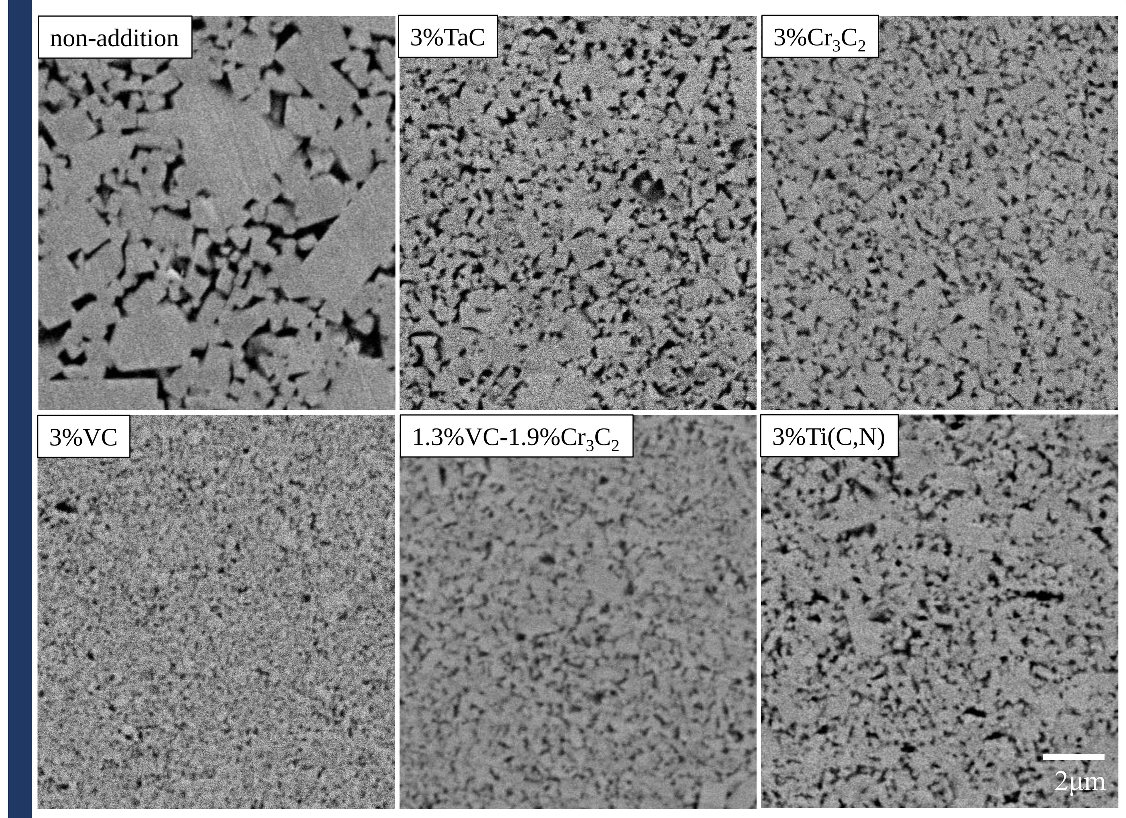

Fig.2 SEM microstructures of WC0.4μm-XC-16.4vol% Co cemented carbides.

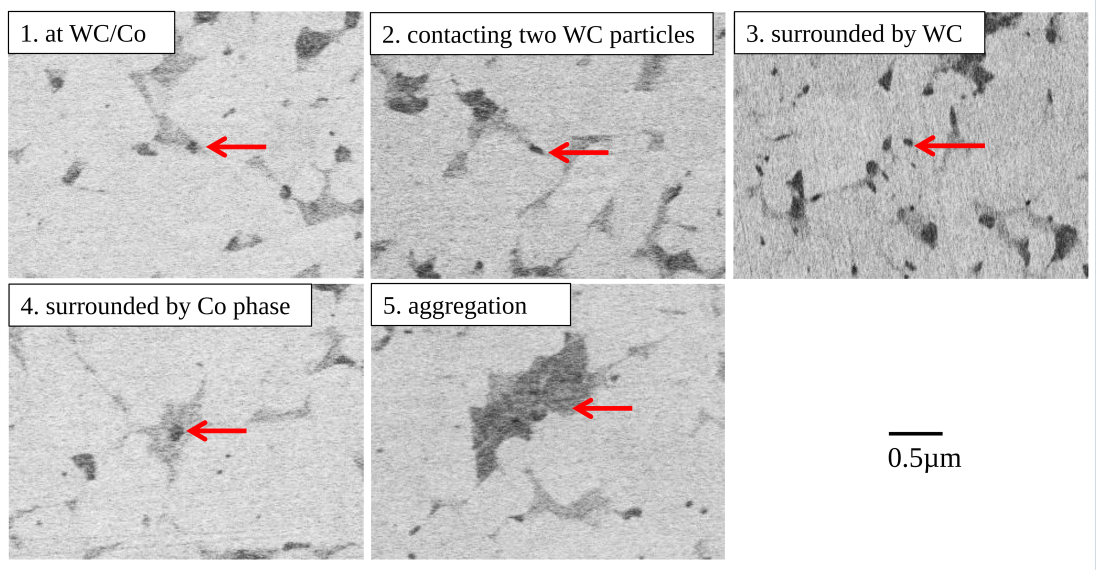

Fig.3 High Resolution SEM microstructures of WC0.4μm-Ti(C,N)-16.4vol%Co cemented carbides.

・No.1~3 contribute to grain growth inhibition.
・The most common from of Ti(C,N) present is No.1~3, No.4, 5 were rare.

・It is clear that grain growth inhibited by the pinning effect even in the presence of a liquid phase.
・Grain-growth inhibition effect is TaC<Ti(C,N) ≒Cr_3C_2≦VC/Cr_3C_2<VC.

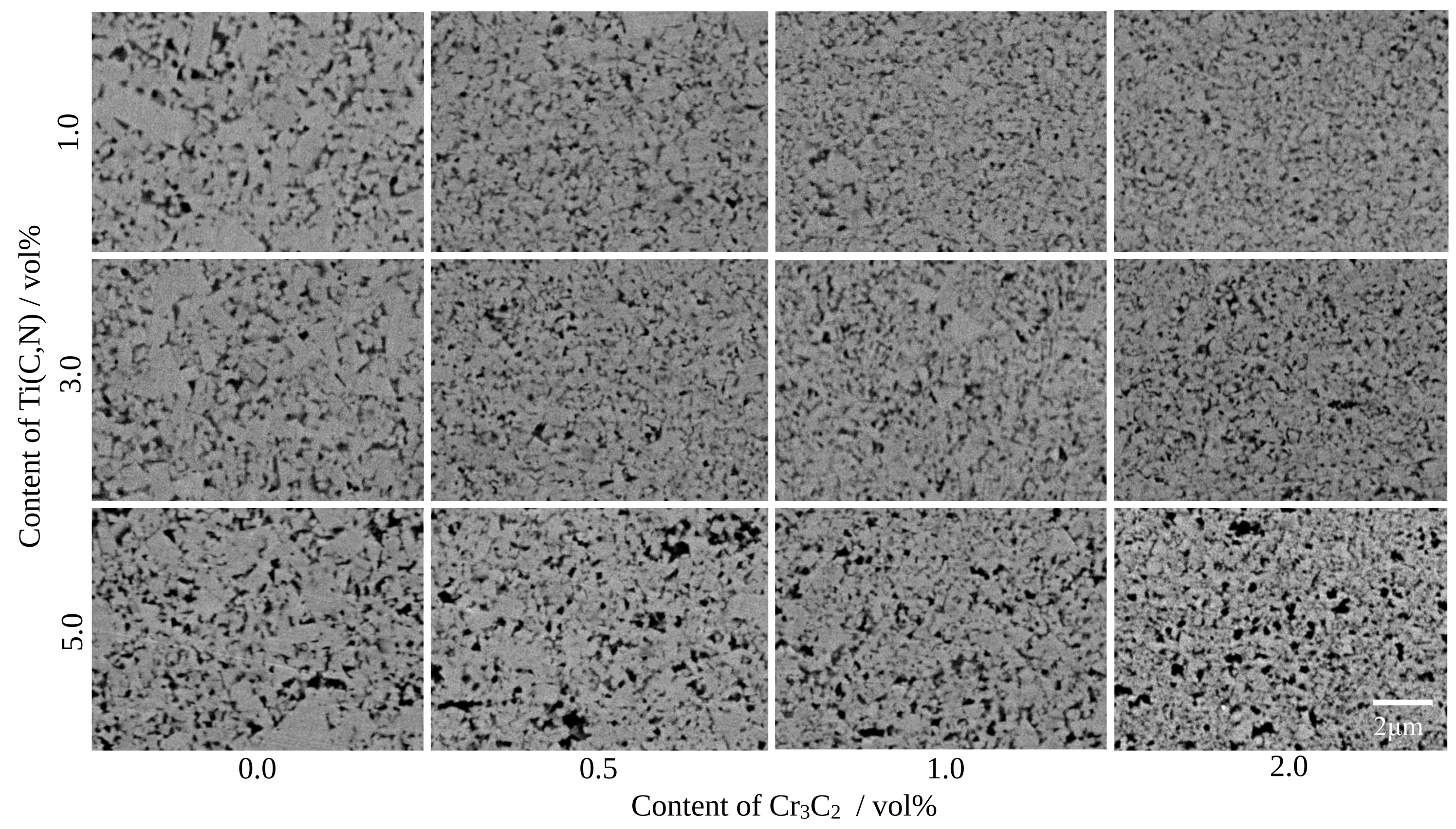

Fig.4 SEM microstructures of WC0.4μm-Ti(C,N)-Cr_3C_2-Co cemented carbides.

・The microstructures become finer with increasing additions of Ti(C,N) or Cr_3C_2.

・Ti(C,N)/Cr_3C_2 composite, the WC particles become much finer and the microstructures becomes more homogeneous than Ti(C,N).

・ Ti(C,N) particles tend to aggregate at the addition of 5% of Ti(C,N).

Mechanical properties

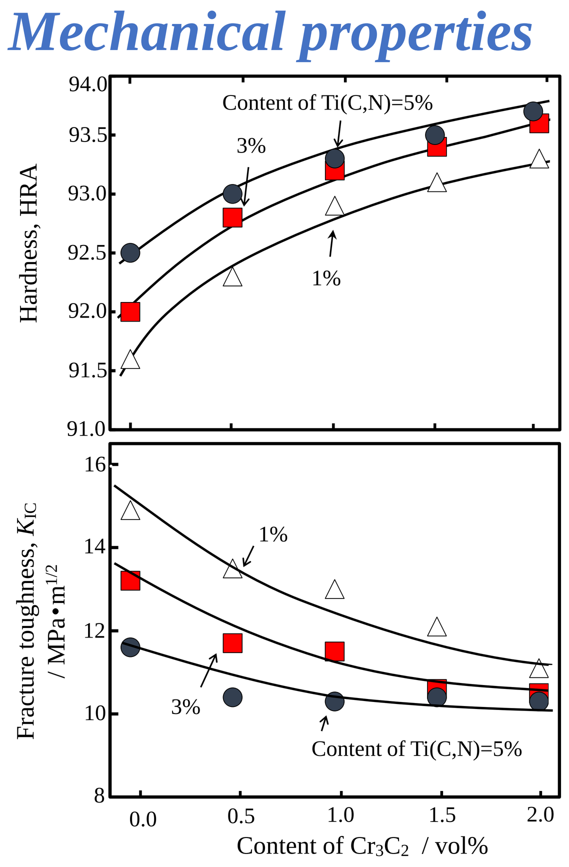

Fig.5 Relationship between HRA or K_{IC} and content.

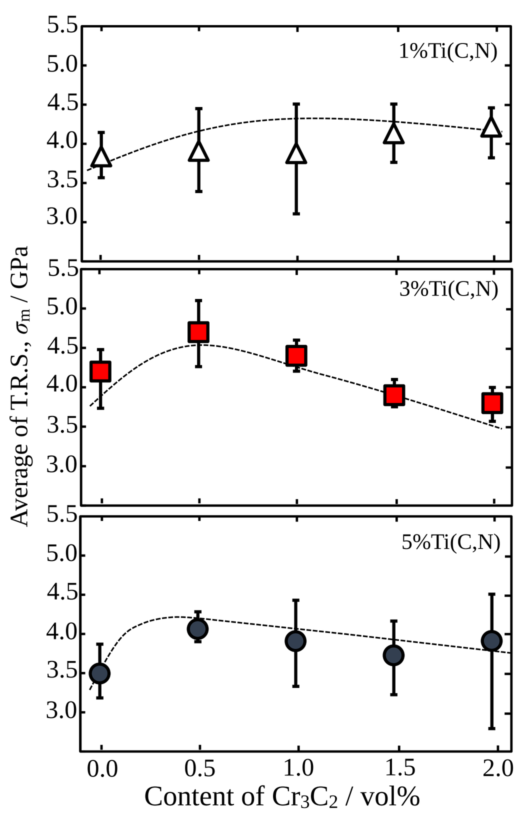

Fig.6 Relationship between average of T.R.S. and content.

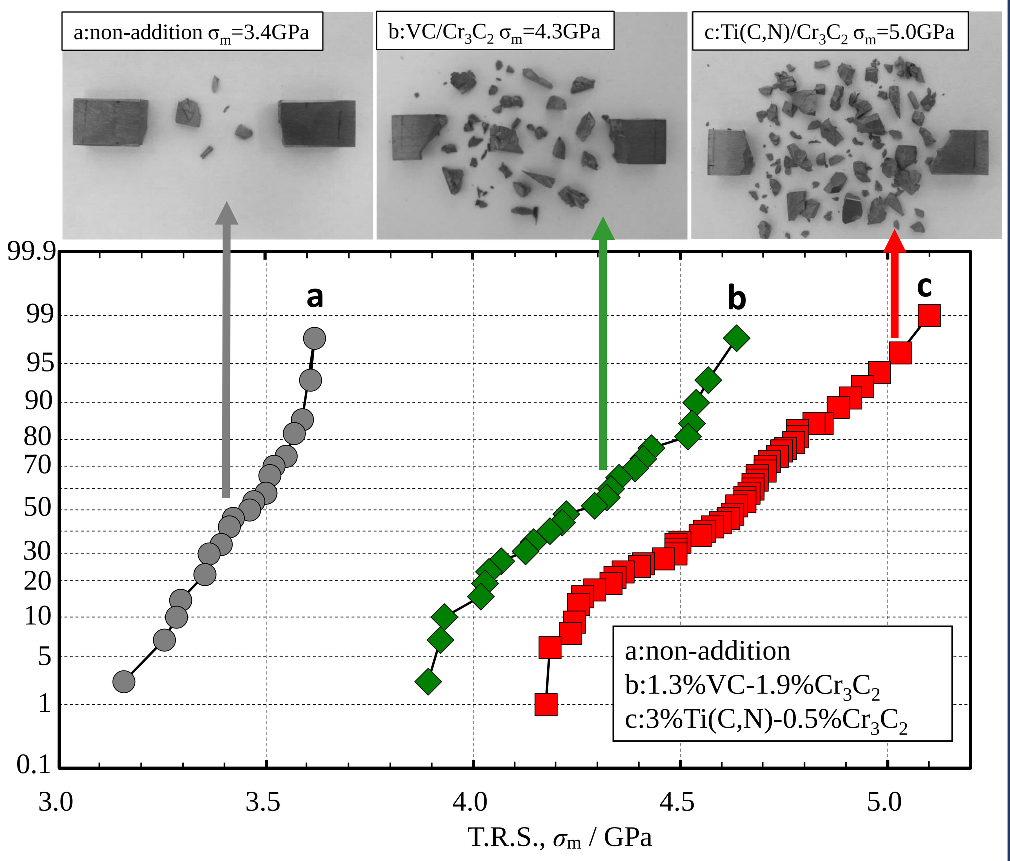

Fig.7 Relative cumulative frequency of T.R.S.

・Hardness increased with amount of both Ti(C,N) and Cr_3C_2, but toughness decreases.
・The average strength in 3%Ti(C,N)-0.5%Cr_3C_2 alloy is **extremely high at 4.7GPa**. This alloy exhibits a **maximum strength of 5.1GPa.**
・Ti(C,N)/Cr_3C_2 composite additives showed higher strength than those non-addition or VC/Cr_3C_2 composite additives.
・The number of broken pieces increases in the order of (a)→(b)→(c). The higher strength, the greater number of fragments.

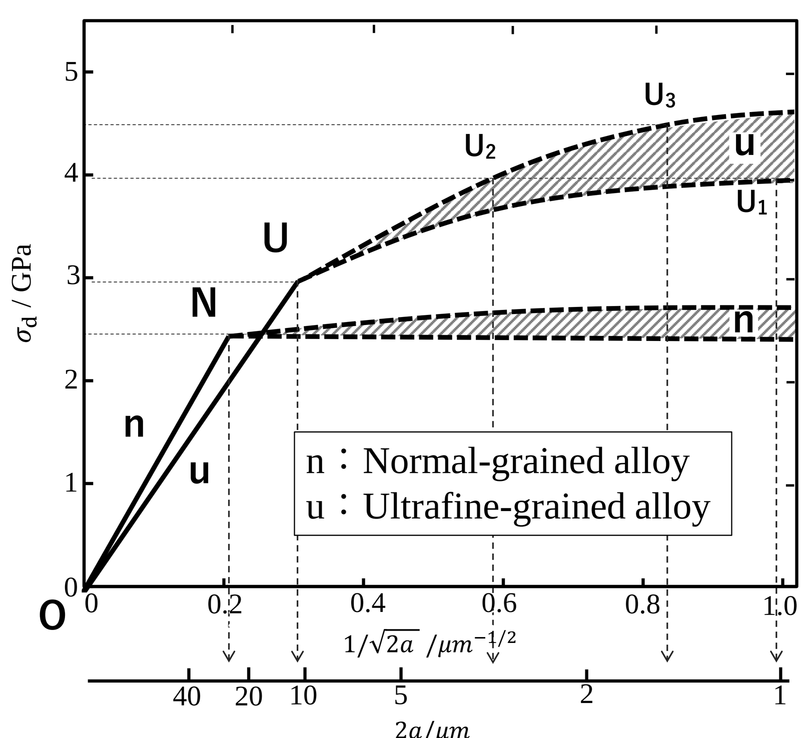

Fig.8 Schematic drawing of relationship of σ_d and $1/\sqrt{2a}$.

1.Limiting strength exists in normal-grained alloys.
2.Ultrafine-grained alloys have higher limiting strength than normal-grained alloys.
3.Limiting strength of even ultrafine-grained alloys varies depending on composition.

Cutting Condition

Drill: ϕ 6mm
Coating: PVD-TiAlN
Work material: S50C
Cutting speed: 88.5[m/min]
Feed speed: f=0.13[mm/rev]
Hole depth: 20mm(Blind hole)
Cutting fluid: water-soluble

Composition of the drills

Category	Composition	Hardness (HRA)	TRS (GPa)
Ti(C,N)/Cr_3C_2	WC(0.4μm)-Ti(C,N)-Cr_3C_2-Co	92.8	4.6
VC/Cr_3C_2	WC(0.4μm)-VC-Cr_3C_2-Co	93.4	3.6
Cr_3C_2	WC(1.0μm)-Cr_3C_2-Co	91.7	3.9
Straight	WC(2.0μm)-Co	90.0	3.3

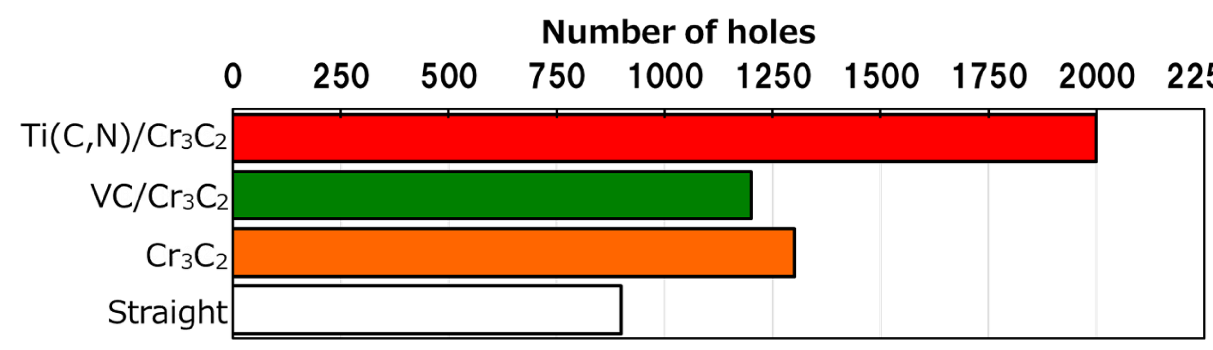

Fig.9 Number of holes to be machined until lifetime.

Ti(C,N)/Cr_3C_2 composite added alloys can generate longer-life tool comparing conventional alloys.

Conclusions

Ti(C,N)/Cr_3C_2 composite is the VC-free ultrafine-grained cemented carbide with **very high strength, making it a very promising tool material.**