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Recent Development of Science and Technology of Hard Materials in Japan

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Abstract Hard materials such as hardmetal, coated hardmetal, cermet, ceramics and diamond or c-BN sintered compact are a kind of grain-dispersed alloy with high volume of hard particles. These are used for cutting tools, wear-resistant tools, rock bits, high pressure apparatus, etc. The annual production in Japan is about 1.7 billion dollars (200 billion yen). This is greatly owed to the development in science and technology which has been accomplished by applying new concepts such as fine or uniform grain microstructure, orientation of crystal grains, functionally graded material, artificial lattice and coherent bonding in recent years. In this review, the development in recent years in Japan is briefly summarized.

1. Introduction

In Japan Society of Powder and Powder Metallurgy (JSPM), there are nine research committees. The present author is the chairman of the Committee of Hard Materials among them. The Committee was founded at 1992, following the Committee of Hardmetal (or Cemented Carbide) which continued for 22 years from 1968 to 1990. There are 21 members at present, about three fourth of whom work for companies.

For my presentation in ISAPM-98, I requested all members to offer the most important recent developments in science and technology in their companies, public research center and universities, etc. Almost all members willingly offered me their good results in the form of OHP transparencies with photographs, figures and some expalnations. This paper is the summary of what they offered, including mine. Namely, the science and technology of powders, materials, working, evaluation method and simulation which have recently been developed and/or commercialized in the field of hard materials in Japan are reviewed in this report.

2. Powders

Commercial WC powders for fine grained hardmetal are in general fabricated by heating W+C mixed powders in vacuum in the same way as general type of WC powders; the mimimum mean grain size is about 0.5 μm and the size distribution is relatively wide. Instead of this general method, direct carburization method, i.e., heating of WO_3+C or WO_3+Cr_2O_3+C mixed powders in N_2+H_2 mixed gas has been developed; uniform-sized fine WC powder with mean grain size (BET size) of about 0.1~0.2 μm can be obtained. The properties of the powder are shown in Table 1.[1)] Uniform-sized fine powders of VC and Cr_3C_2 as grain growth inhibitor of WC grains in fine grained hardmetal have been produced by using similar method, i.e., heating V_2O_3+C and Cr_2O_3+C mixed powders in nitrogen gas.[2)]

TiN powders for the addivites for TiC base cermets have been produced in general by nitriding Ti metal with nitrogen gas and then crushing the product. The size distribution is wide; 0.2~6 μm for powder with the mean grain size of 1.3 μm. A new method of heating TiO_2+C in nitrogen gas has been

Table 1. Properites and chemical composition of ultra fine WC powders produced by direct carburization[1]

Grade	BET		Fsss	T.C.	F.C.	Fe	Mo	O	Inhibitor
	m^2/g	μm	μm	%	%	%	%	%	
WC02N	3.5	0.11	–	6.20	0.10	0.003	0.001	0.30	Cr_3C_2
WC04N	2.1	0.18	0.47	6.20	0.09	0.003	0.001	0.25	Cr_3C_2
WC05N	1.8	0.22	0.52	6.20	0.08	0.003	0.001	0.20	
WC04N	2.3	0.17	0.46	6.15	0.10	0.003	0.001	0.22	
WC05N	1.8	0.21	0.52	6.15	0.09	0.003	0.001	0.22	

developed.[3] The size distribution of powder with the mean grain size of 1.3 μm is very narrow (0.2~1.6 μm) and the content of Fe impurity is considerably small. The sinterability of powder itself without no sintering aid is high due to fine and uniform grain size; the relative density of the compact reaches 94% when it is sintered in nitrogen gas of mormal pressure at 2273K. This is successfully used for commercial cermet, as described later.

Carbides, borides and silicides of all transition metals in IVa, Va and VIa groups of the Periodic Table of elements are commercially available. As for nitrides, nitrides of transition metals of IVa and Va groups and Cr of VIa group are also commercially available. However, nitrides of W and Mo in Va and VIa groups are not. Commercially available carbonitride powders are Ti(C,N), (W,Ti)(C,N) and (W,Ti,Ta)(C,N) powders at present. The preparation of W(C,N) has not been reported and the powder is not commercially available. This is due to the fact that WN is thermodynamically unstable above about 900K under nitrogen of 0.1MPa, i.e., normal pressure, although WC is stable up to 2800K. However, W(C,N) powder was found to be synthesized by heating W+C mixed powder in nitrogen gas of high pressure, although WN could not be stable at nitrogen pressure at least below 190 MPa.[4]

3. Materials and Workings

3.1. Hardmetal (Cemented Carbide)

Functionally or compositionally graded hardmetal has been commercialized as a economic substitute of coated hardmetal for cutting tools. The composition or microstructure of the sintered alloy compact, as schematically shown in Fig. 1,[5] varies from the surface to the inside as follows; a Ti(C,N) ceramic surface region → binder phase rich region free from WC grains → normal region, i.e., WC+triple carbide+binder phase. The surface region with high hardness is characterized by high compressive residual stress of 0.8 GPa, which is caused by the difference in thermal expansion coefficient among those three region. Cutting tools made from this material have higher abrasive resistance and fracture toughness than a conventional cermet with uniform composition. Because of the graded composition, the ceramic surface layer has high adhesive strength, providing longer life than CVD-coated tools, the coated layer of which tends to be spalled. The new material is produced by sintering of a green compact of uniform composition under controlled sintering atmosphere.

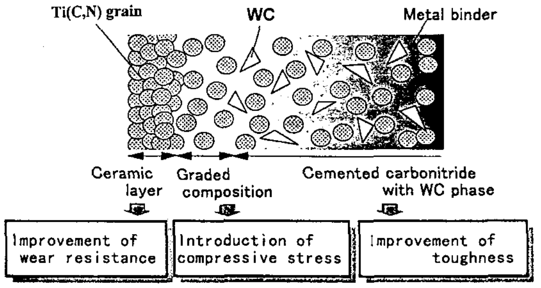


Fig. 1. Schematic microstructure of cross-section of functionally graded hardmetal.[5]

Hardmetal reinforced by disk-type WC was newly developed.[6] The (0001) crystalline plane of disk-type WC grains are preferentially oriented to almost one direction. This leads to higher hardness as well as higher fracture toughness in the perpendicular parallel

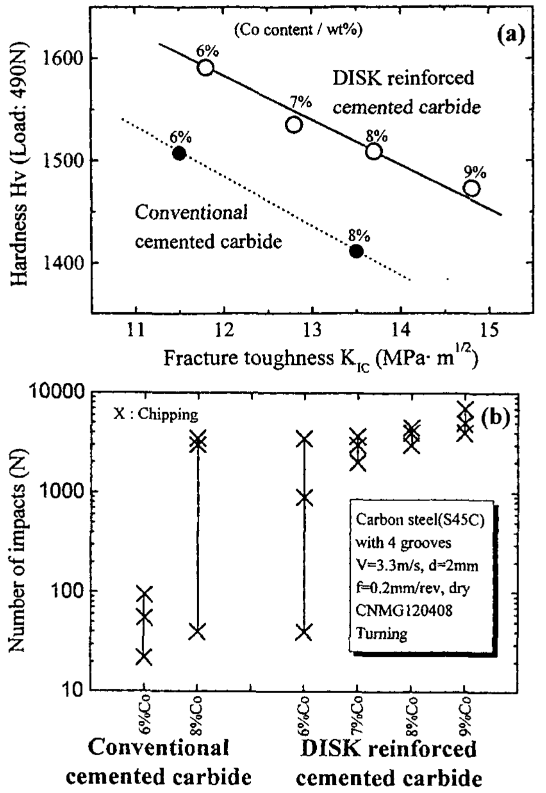


Fig. 2. **(a), (b) Relation between hardness and fracture toughness (a) and chipping resistance (b) of disk reinforced cemented carbide (hardmetal).**[6]

direction to the (0001) plane, respectively, as shown in Fig. 2(a). The material CVD-coated with Ti(C,N) has higher chipping resistance in interrupted cutting of carbon steel than conventional cemented carbides, as shown in Fig. 2(b).[6]

A new type of non-magnetic hardmetal was developed by adding a small amount of Si and Mo to WC-Ni alloy. The material is said to have high corrosion resistance and high transverse rupture strength and are used as tape cleaner and tape slitter, etc.[7]

Extremely fine hardmetal wires with diameter of 0.2~0.5 mm are widely used as pins for dot impact printers.[8]

A new working method for making internal threads in cemented carbide tips (HARDTAP) has been developed and are successfully used. There are three kinds of conventional methods and their processes were as follows; (1) electric discharge machining or grinding of tips, (2) cutting of metal inserts which are brazed in cemented carbides tips, (3) cutting of Mo inserts which are sintered within cemented carbide tips. In the new method, green compacts or presintered compacts are tapped, and then sintered. There are many advantages in the new method; (1) fabrication of internal threads with high toughness is possible, (2) the time of delivery is shortened by 50%, (3) the costs is lowered more than 60%, (4) chipping and falling out which often occur in the brazed or electric discharge machined tips can be avoided, (5) machining of the internal threads in thin tips, complex formed tips and special cemented carbide tips are possible (6) machining in all directions is possible, (7) machining of tools for hot using, to which brazed tips can not be applied, are possible.[9]

MIM process was developed, although it was said to be difficult in controlling the carbon content of the alloy.[10] Systematic studies on cutting green compacts of hard materials such as hardmetal and ceramics have been made.[11]

3.2. Coated Hardmetal

The production ratio of coated hardmetal cutting tools among all kinds of cutting tools with throw-away type is about 50% in Japan. The ratio is extremely higher than that (20%) of non-coated hardmetal.

(Al,Ti)N-coated hardmetal has been developed by using PVD (physical vapor deposition) method and are widely used for end-mill (called miracle end-mill).[12] The hardness of the coated layer is 2700~2800 Hv, which is higher than those of Ti(C,N) and TiN layer (2000~2200 and 1800~2000 Hv, respectively). The adhesion of the layer is higher than that of TiN; the critical load in scratch test is 80N, compared with 60N of TiN, as shown in Fig. 3. Very high speed cutting of steel with 150 m/min is possible. The tools can be applicable to heat treated steel, stainless steel and heat resistant steel, carbon steel, pre-hardened steel, cast iron, non-ferrous materials such as

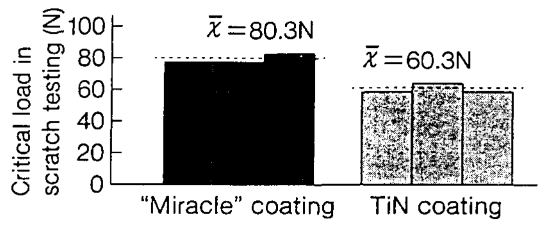


Fig. 3. Critical load in scratch test for (Al, Ti)N PVD-coated layer in miracle coating, compared with TiN coated layer. The substrate is hardmetal.[12]

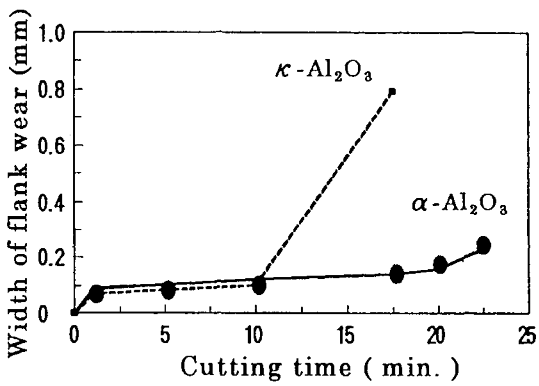


Fig. 4. Cutting performance of tools CVD-coated with high adhesive α-Al_2O_3 film, compared with conventioanl tool coated with κ-Al_2O_3 film.[13]

Al, Cu and Ti alloys, graphite and FRP. The tool life is superior to that of conventional TiN-coated hardmetal. This is considered as the in-situ formation of Al_2O_3 near the surface layer during cutting operation,[12] the concentration of which gradually varies form the surface of the tools to the inside.

The crystal structure of Al_2O_3 in Al_2O_3/Ti(C,N)-CVD (chemical vapor deposition) hardmetal is selected to be in general κ-type, although α-Al_2O_3 has higher abrasiveness than κ-Al_2O_3. This is because κ-Al_2O_3 has higher adhesive strength to Ti(C,N) than α-Al_2O_3. A company succeeded in coating good adhesive α-Al_2O_3 layer instead of usual κ-Al_2O_3 layer to Ti(C,N) layer by coating Ti(C,N,O) thin layer before depositing α-Al_2O_3. The life of the cutting tool is more than twice than that of usual κ-Al_2O_3 layer coated cemented carbide, as shown in Fig. 4.[13] The good adhesive strength of α-Al_2O_3 layer to Ti(C,N,O) layer is said to be caused by the good lattice coherency of both layer.

Al_2O_3/Ti(C,N) CVD coated layer with fibrous structure was developed. The fibrous Ti(C,N) layer has excellent combination and balance of both crater and flank wear resistances. The micro-grain fibrous Al_2O_3 layer exhibits very good thermal resistance and chemical stability. The tool is best suited to high speed turning of materials such as steel and cast iron. The tool has far longer life than conventional grades.

A new type of PVD-coated hardmetal was de-

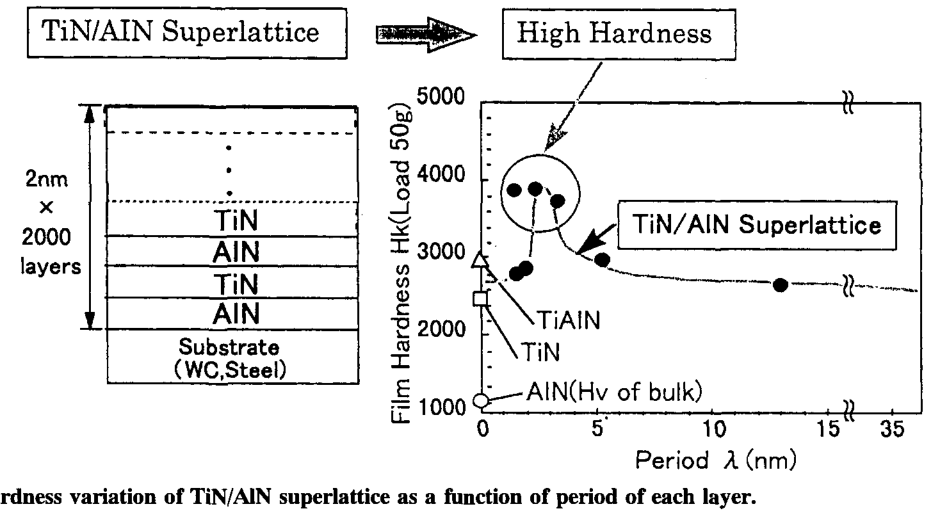


Fig. 5. Hardness variation of TiN/AlN superlattice as a function of period of each layer.

veloped by use of artificial suprer lattice. The AlN and TiN were coated alternatively by PVD method on hardmetal substrate. The hardness of the layer shows a maximum of 3800Hv at the layer period of about 2.5 nm (25 Angstrom), as shown in Fig. 5.[15] This is said to be caused by the change of crystal structure of AlN from wurzite to cubic lattice (high pressure structure) at the period of 2.5 nm. The tool life of the end-mill is said to be about 5 times than that of Ti(C,N)-coated end-mill.

Diamond coated hardmetal which had a great problem of low adhesive strength between coated diamond layer and substrate at the beginning of development becomes to be widely used for cutting high Si aluminum alloys, GFRP, CFRP, graphite, semi-sintered ceramics. This progress is owed to the continuous improvement of coated layer in composition, microstructure and adhesive strength to the substrate.

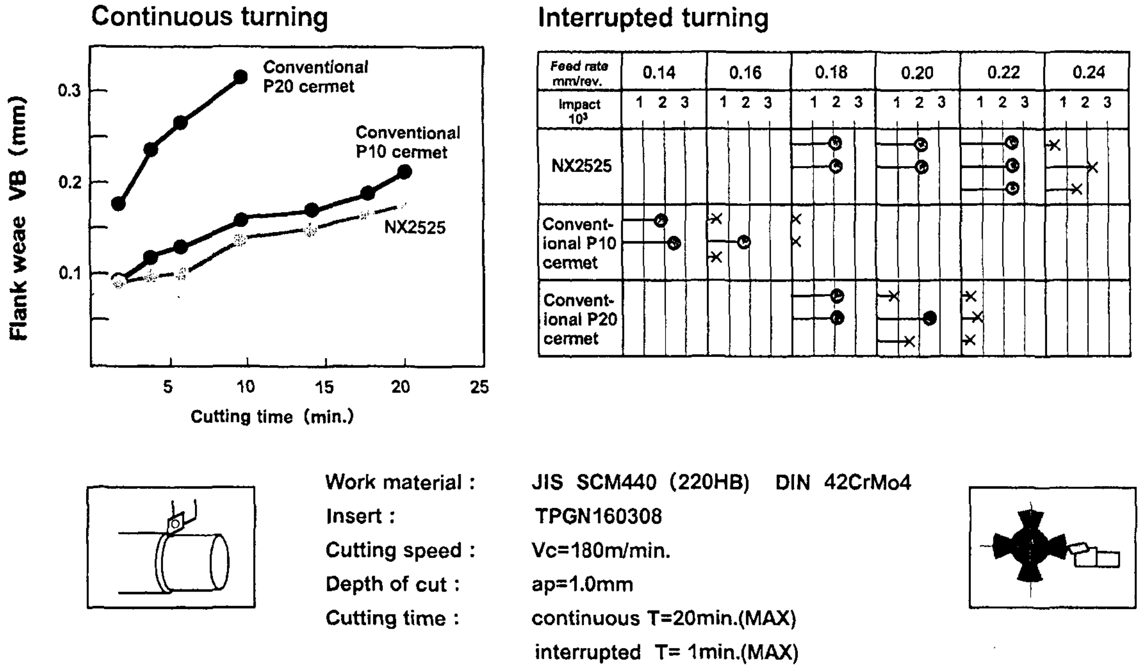
The filament for CVD deposition of diamond is usually tungsten or carburized tungsten. TaC filament was developed and was found to show longer life.[16]

3.3. Cermet

Ti(C,N) base cermet with almost uniform-sized grains was developed.[17] The alloy shows high wear resistance (hardness; 92.2 HR_A), high fracture toughness and high flexural strength and the tool shows longer life both continuous turning and iterrupted turning of steels than conventional cermet with non-uniform-sized grains, as shown in Fig. 6.

Mo_2FeB_2-Ni cermet with high heat resistance in air up to 1073K, which was invented and developed by a Japanese company,[18] was newly applied to warm forging die for carbon steel parts of automobile.[19] The material has also good corrosion resistance to molten aluminum and zinc, high wear resistance and good workability. The material can be applied also to screw parts of PIM injection machine, die parts of aluminum casting, drawing die and extrusion die of Al or Cu alloy, sliding parts used at high temperature, etc.[18,19]

TiC-Ti-Mo cermet with high corrosion- and wear-resistance was developed. The corrosion resistance



Work material : JIS SCM440 (220HB) DIN 42CrMo4
Insert : TPGN160308
Cutting speed : Vc=180m/min.
Depth of cut : ap=1.0mm
Cutting time : continuous T=20min.(MAX)
interrupted T= 1min.(MAX)

Fig. 6. Cutting performance of Ti(C,N) base cermet with almost uniform-sized grains (NX2525), compared with conventional cermets (P10 and P20).[17])

to hydrochrolic acid, sulfuric acid and NaOH aqua is excellent, compared with pure Ti and SUS304.[20] The material is widely used as sleeve for bearing of sea water pump, mold for manufacturing dry battery and electrochemical parts such as the electrode of lithium battery.

3.4. Ceramics

WC sintered compact free from binder has developed and was found to show high hardness (3200HV), high flexural strength (690 MPa) and fracture toughness (5 MPam$^{1/2}$ by IF method), compared with ceramics such as Si_3N_4, SiC and Al_2O_3, as shown in Fig.7.[21] The material shows high abrasive wear resistance, compared with WC-Co hardmetals, when it is used as compacting die for ceramic powders; the life is about three times longer than the conventional WC-Co hardmetal.

Almost uniform fine grained Si_3N_4 ceramics with high flexural strength of about 1.5 GPa was developed and becomes to be used as cutting tool for cast iron, roller of rolling machine, squeeze roll, guide roll of steel hot drawing process, etc.[22,23]

3.5. Diamond Sintered Compact

The sintering aid or binder material for diamond Compax has been cobalt, nickel or iron metal, since diamond sintered compact (Compax) was developed about 25 years ago by G.E.Company. Recently, diamond sintered compact with sintering aid binder of $MgCO_3$, which was developed together with Japanese Inorganic Material Research Institute about 10 years ago, is commercialized by a Japanese company. The sintered compact is produced at 7.7 GPa and 2300℃, which are higher than those (5.5 GPa and 1500℃) for conventional Co-bonded compacts. The cutting tool of the compact has about two times longer life in cutting of WC base hardmetal than conventional compact.[24]

The diamond sintered compact with thickness of about 1 mm was applied to the chuck part of race center, instead of hardmetal. The life was found to be longer over 100 times than that of the hardmetal.[25]

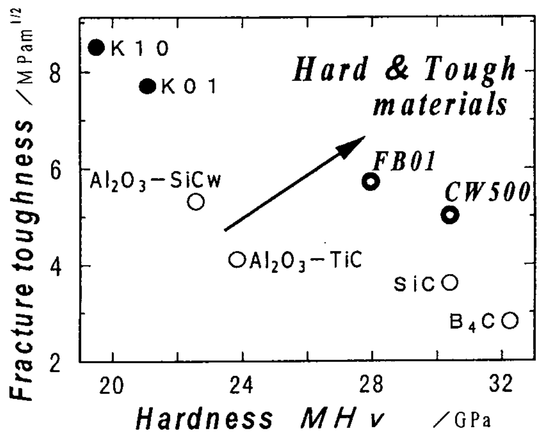


Fig. 7. Relation between hardness and fracture toughness for WC ceramics (FB01 and CW500), hardmetal (K10 and K01), Al_2O_3-SiC, Al_2O_3-TiC, SiC and B_4C.[21]

4. Evaluation Method

Usual measuring method for fracture toughness K_{IC} of hard materials is SEPB (Single Edge Precracked Beam) method; (1) introduction of semicircular pre-crack in test piece by Vickers hardness indentation, (2) extension of the circular-crack to a rectangular pre-crack by Bridge Indentation Method, (3) measurement of flexural strength σ_f of the precracked test piece by bending fracture test, (4) measurement of the size of rectangular pre-crack on the fracture surface, and (5) calculation of K_{IC} with the equation $K_{IC}=\phi\sigma_f C^{1/2}$, where the value of ϕ depends on the rectangular pre-crack size (C) and specimen size.

Abuout six years ago, an entirely new method for evaluating fracture toughness K_{IC} of hard materials has been developed.[26] The value can be evaluated from the macroscopic fracture surface area S_{mf} and flexural strength σ_m of normal test piece without special pre-crack or notch, by using the following semi-theoretical equation.

$$\sigma_m = \psi K_{IC} S_{mf}^{1/2}$$

where ψ is a factor including the volume of stressed part of test piece, the shape and size of microstructural defect which acted as the fracture source, and the ratio

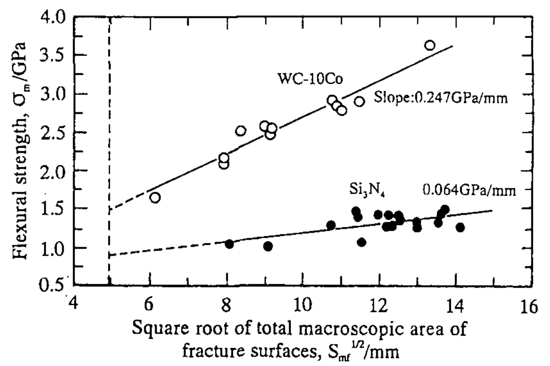


Fig. 8. Relation between σ_m and $S_{mf}^{1/2}$ of fractured test piece. The ratio of slopes (ψK_{IC}) of two regression lines for WC-10mass%Co hardmetal and Si_3N_4 ceramics is 3.9, which coincides well with the ratio (3.7) of K_{IC} of both materials, indicationg that the value of ψ is nearly the same for both materials.[26]

of kinetic and vibrational energies of flying fragments to elastic strain energy stored in test piece just before the fracture.[26,27] The equation suggests that there is a linear correlation between σ_m and $S_{mf}^{1/2}$ and that the slope of the correlation line is proportional to K_{IC}, if the value of ψ is nearly the same for all kinds of hard materials. This suggestion was verified for WC-10 mass%Co hardmetal and Si_3N_4 ceramics, as shown in Fig. 8.[26]

Internal friction study on hard material such as Mo_2FeB_2-Cr-Ni cermet was found to be useful to detect micro-plasticity of the alloy.[27]

5. Simulation

WC-Co base fine grained hardmetals where a small amount of VC are mainly added as the grain growth inhibitors during sintering are being used as materials of tools such as drills, shear blade and end-mill. The mean grain size of the fine grained hardmetals on the market are ordinarily set above 0.5 μm, although the wear resistance tends to increase further with decreasing mean grain size below 0.5 μm and the finer WC powders are commercially available. This is said to be because the fracture strength of the alloy tends to considerably drops with decreasing mean grain size below 0.2~0.3 μm, due to the appearance of large WC grains which are generated by abnormal grain growth and act as the fracture source.

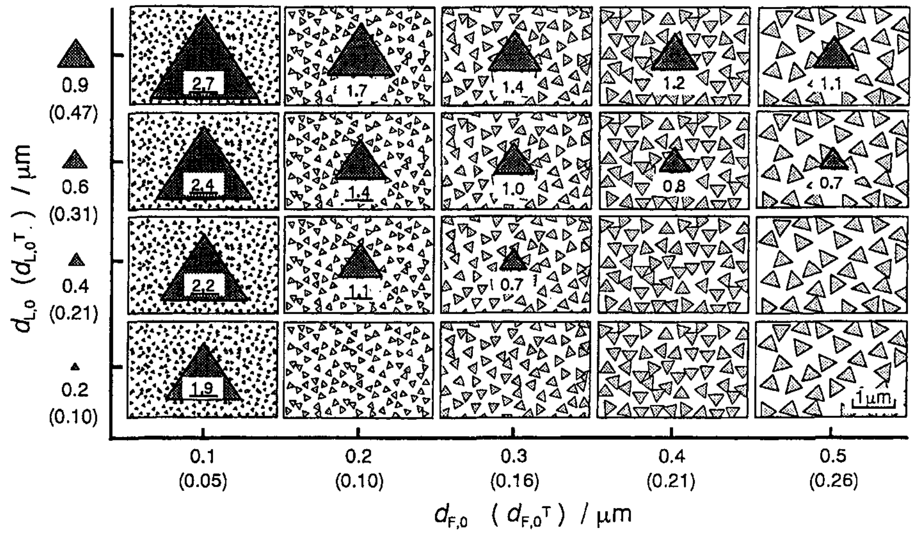


Fig. 9. Simulated microstructure which shows the size of large grains after sintering for 3.6ks at 1673k as a function of initial fine grain size ($d_{F,0}$) and initial large grain size ($d_{L,0}$) for WC-o.5 mass %VC-10 mass%Co hardmetal. The numerals inside or near large grains are the values of dL,3.6 [μm]. The figure shows that abnormal grain growth indicated with a underline substantially occurs when $d_{F,0}$ becomes less than 0.1 μm.[28])

The cause or mechanism for the abnormal grain growth of WC grains in fine grained hardmetal had not been clear. A simulation based on two kinds of grain size alloy model where a large amount of uniform small grains and a little amount of uniform large grains exist in WC-Co hardmetal suggested that the abnormal grain growth of large grains substantially occurs when the grain size of small grain size or the mean grain size becomes below about 0.1~0.2 μm, as far as VC (5 mass% in binder) is used as grain growth inhibitor and sintering condition is 1673K-3.6ks, as shown in Fig. 9.[28]

Computer simulation by Monte Carlo method for the grain growth in liquid phase sintering of grain-dispersed alloy was made as a function of contact angle, binder content, etc.[29]

6. Future of Hard Materials

The hard materials have continulously been studied and developed, since the study of carbide phase in tool steels at the beginning of 20th century, which fruitfully resulted in the invention of WC-Co hardmetal. This is caused by the following.

(1) The endless demands for working tools such as cutting, drilling, drawing, forging, rolling, compacting, piercing, etc., in industries such as automobile, machine, mine and construction.

(2) The birth of new type of materials which require new working tools with different properties.

(3) The continuous demands for high speed working, longer tool life, higher reliability of tools, etc.

(4) The continuous demands for lowering of tool cost, recycle of raw materials or inverse manufacturing of tools,[31] etc.

These have no limitation. This means that the study and development of hard materials will continue also in the future.

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