

Microstructure and Flexural Strength of Hardmetals

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ABSTRACT The characteristics of various important microstructural factors of WC-base hardmetals (cemented carbides) such as the amount of Co metal binder phase, the carbide grain size, the microstructural defects acting as a fracture source, the solid solubility of tungsten in the binder phase affected by the carbon content, the precipitation of Co_3W , the domain size of binder phase, the formation of β -free layer or Co-rich layer and CVD or PVD coated layer, and the effects of these factors on the flexural strength of the hardmetals are reviewed.

1. INTRODUCTION

Hardmetals or cemented carbides such as WC-Co and WC-TiC-TaC-Co are used for cutting tools, wear-resistant parts, rock drilling bits and/or high pressure vessels.¹⁾ These hardmetals contain not only hard carbide grains but also Co metal as the component for forming ductile binder phase and/or sintering aid, and thus the mechanical properties of each hardmetal depend on (1) the amount of the metal binder phase as well as (2) the carbide grain size. The hardness of hardmetals mainly depends on these two factors. Namely, the hardness increases with decreasing the amount of metal binder phase and/or the carbide grain size, or with decreasing the mean free path (thickness) of the binder phase which is determined by these two factors.²⁾

The fracture strength, which is usually evaluated with flexural strength or transverse-rupture strength, however, largely depends on the other microstructural factors as well as the above two factors. For all hardmetals, the fracture strength is considerably affected by (3) the size of the microstructural defect which acts as a fracture source.³⁻⁵⁾ The following factors which are generated mainly owing to the addition of the metal binder are also important; (4) the solid solubility of tungsten in the metal binder phase affected by the variation of the carbon content even in the alloy free from and graphite phases,⁶⁻⁸⁾ (5) the precipitation of Co_3

W during heating at about 1070 K,⁹⁻¹²⁾ (6) the domain size of the binder phase,¹³⁾ and (7) the formation of β -free layer^{14,15)} or Co-rich layer near the surface of sintered compacts.¹⁶⁾

For hardmetals coated with hard substances, the important factors are as follows; (8) the kind and combination of coated hard substances,¹⁷⁾ (9) the type of residual stress (tension or compression) in the coated layer which depends on the kind of coating method (CVD or PVD),^{18,19)} (10) the formation of β -phase at the interface between coated layer and substrate,²⁰⁾ and (11) the properties of the substrate.²¹⁾

In this review paper, the results of the studies on both the characteristics of these factors and their effects on the fracture strength of WC-base hardmetals, which have mainly been obtained in Japan, are briefly summerized.

2. AMOUNT OF METAL BINDER, GRAIN SIZE AND FRACUTURE SOURCE

It is well known that the room temperature flexural strength of all hardmetals is affected by the amount of metal binder and the carbide grain size in the alloy.²⁾ However, it is not necessarily well known that the effects of various factors as well as these two factors on the strength should be analyzed by taking into consideration of the fracture source of the specimens. Namely, the flexural strength of hardmetals shows in general a wide

variation, when one set or one lot of plural test pieces are broken. The cause of the wide variation is in the fact that each test piece always fractures from one microstructural defect such as pore, large carbide grain or carbide aggregate, binder pool and various inclusions,³⁻⁵⁾ which are called a fracture source or fracture origin. Namely, the size of the fracture source and its location in the test pieces are different for each test piece and thus the external stress necessary for the fracture becomes different for each test piece, although the concentrated stress at the tip of the fracture source is the same for each test piece at the moment of the fracture.

The above fact that the fracture of all hardmetals always starts from one microstructural defect indicates the following.³⁻⁵⁾

- (1) The fracture strength of all hardmetals with a given chemical composition and carbide grain size can be improved by decreasing the size of microstructural defects as much as possible.
- (2) The effects of various factors on the fracture strength should be investigated, always taking into consideration of the fracture source.

As for the maximum or attainable strength of a hardmetal with a given chemical composition and a given carbide grain size, it can be estimated by extrapolating the regression line between the inverse of the fracture stress (σ_d^{-1} ; σ_d is the external stress which operated on the fracture source at the moment of the fracture, and it is in general smaller than the flexural strength) and the square root of the size of the fracture source (\sqrt{a}) to the average grain size, as shown in Fig. 1,³⁾ because a linear relation can theoretically be expected between them. The attainable strength, for example, of WC-10 mass%Co high carbon alloy with the average WC grain size of 1.3 μm is about 4~5 GPa. This value is considerably higher than the measured value of ordinary hardmetal, which are in general less than 3.0 GPa.

The microstructural defects which usually act as a fracture source in WC-Co hardmetal with Co content less than about 12 mass% are pores with the size of 10~100 μm . The mechanism of pore formation is as follows,^{22,23)} (1) large cobalt particle

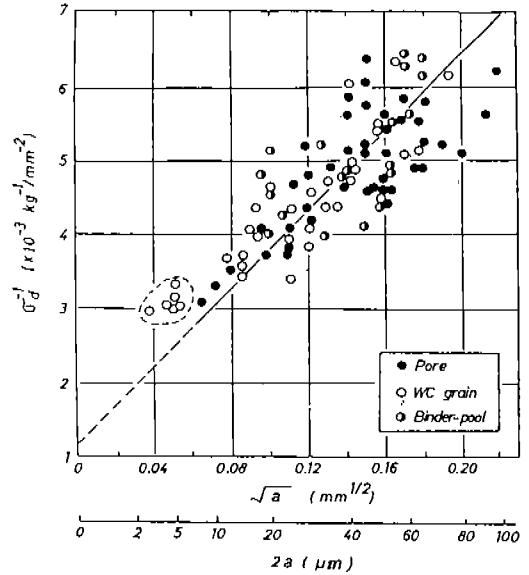


Fig. 1. Relationship between σ_d^{-1} and a for WC-10 mass%Co high carbon alloy with WC grain size of 1.7 μm . The data points encircled by a broken line are excluded in the estimation of the correlation line, because those points are assumed to be affected by residual stress due to gridding of the specimen surface.³⁾

aggregates are formed WC+Co powder mixture during ball milling, (2) the liquid generated by the melting of this cobalt aggregate in sintering flows out into the capillaries among WC grains, and pores are formed at the place where the large cobalt aggregates exist, because the skeleton of carbide grains hardly collapse in the alloy with Co content less than about 12 mass%, in contrast with the higher Co alloys. Therefore, when the Co aggregates in the powder mixture are removed or the pores in the alloy are forced to collapse by hot isostatic pressing (HIP), the strength of WC-Co hardmetal can be improved in general up about 3.3~3.5 GPa, for 10%Co alloy.^{24,25)} This value is lower than the attainable strength above mentioned. This is mainly because the fracture becomes to occur in general from a coarse WC grain or WC grain aggregate with the size of about 5~8 μm , instead of pores.

On the other hand, the effects of Co content, WC grain size and surface grinding of the test piece on the fracture strength of WC-Co hardme-

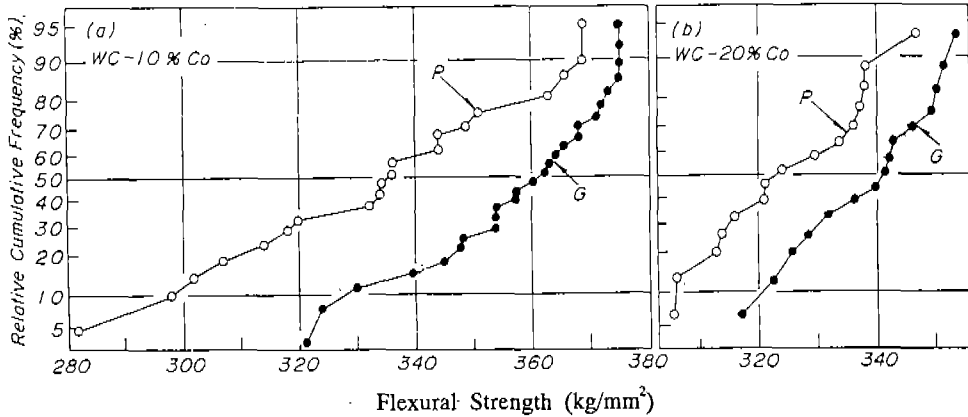


Fig. 2. Effects of surface-grinding on distribution curves of flexural strength of WC-10 and 20 mass%Co high carbon alloy with WC grain size of $1.7 \mu\text{m}$. The G-specimen is ground by using diamond wheel with diamond grain size of $150 \mu\text{m}$. The P-specimen is polished sufficiently to be almost free from residual compressive stress due to grinding.

tals, when ordinary specimens were used, had been reported as follows. The maximum strength is obtained at about 20 mass%Co and at about $2 \mu\text{m}$, respectively.²⁾ And the fracture strength was higher in the ground state than in the polished state.²⁶⁾ However, these all results are not intrinsic one; the results are considered to be affected by large microstructural defects, taking account of the low strength level of the specimens. When specimens free from large microstructural defect are used, the maximum strength is obtained at about 10 mass%Co and at about $1.0 \mu\text{m}$ respectively,²⁷⁾ and the ground specimen shows in general higher strength than the polished specimen, as shown in Fig. 2.²⁸⁾

Nowadays, most of researchers in the fields of WC-base hardmetals in Japan well recognize the importance of the fracture source in improving and analyzing the room temperature flexural strength of hard materials such as cermets and ceramics as well as WC-base hardmetals, but most of researchers in the field of ceramics even in Japan do not know the fact that the fracture of their specimens starts from a microstructural defect and thus they do not observe the fracture source of their fractured specimens.²⁹⁻³¹⁾

3. CARBON CONTENT IN NORMAL PHASE REGION

The normal phase region in WC-Co alloy, *i.e.*, the region containing only WC and binder phase (γ) or the region free from η ($\text{Co}_3\text{W}_3\text{C}$) and graphite (free carbon) phases is very narrow. For example, the range of WC-10 mass%Co alloy is only 0.18 mass%C, although the carbon content of the alloy is as high as about 5.1 mass%C. This means that the fabrication of WC-Co alloys free from η and graphite phases is not easy. The range, however, is increased with increasing additional amount of TiC or (W, Ti, Ta)C, as shown in Fig. 3.³²⁾ This is because the (W, Ti)C and (W, Ti, Ta)C phase are nonstoichiometric compounds,³³⁾ differing from WC phase. Namely, the (W, Ti)C or (W, Ti, Ta)C phase can absorb or emit carbon atoms, according to the carbon content of the alloy and thus the variation of chemical potential of carbon in Co binder phase, which is accompanied with the variation of the carbon content in the alloy, is mitigated.³²⁾

It is well known that the fracture strength of WC-Co hardmetal sharply decreases, when η or free carbon phase appears in the microstructure.³⁴⁾ However, it is not necessarily well known that the fracture strength of the alloy in the normal phase region free from those harmful phases is also affected by the carbon content.^{6-8,35)} The strength variation with the carbon content in the normal region is due to the fact that the tungsten content

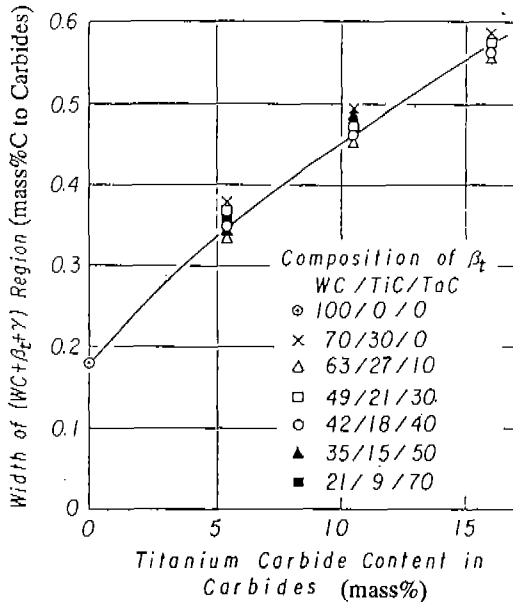


Fig. 3. Effects of titanium carbide content and composition of (W, Ti, Ta)C, i.e., β_4 , on width of (WC+ β_4 + γ) normal phase region of WC-TiC-TaC-10 mass%Co hardalloys.

dissolved in the Co binder phase increases with decreasing carbon content, i.e., from about 1 mass% at high carbon content to about 10 mass% at low carbon content.⁶⁻⁸⁾ When high strength specimens without large microstructural defects or HIP-ed specimens are used, the fracture strength is higher by about 5% in low carbon alloy than in high carbon alloy.³⁵⁾

The creep rupture strength at 1170~1270 K³⁶⁻³⁸⁾ and the cratering wear resistance of WC-Co hardmetal tools in cutting of steels are also affected by the carbon content or the tungsten content dissolved in the binder phase. The crystalline structure of the cobalt binder phase is f.c.c. in the as-sintered state, although the equilibrium structure at room temperature is h.c.p. The f.c.c. structure, however, transforms to h.c.p., when the alloy or the binder phase is plastically deformed.⁴⁰⁾ The transformation occurs more easily in high carbon alloy.⁴⁰⁾

4. PRECIPITATION OF Co₃W

It had been believed before that the binder

phase in sintered WC-Co and WC-TiC-TaC-Co hardmetals are thermally stable or in equilibrium state, because the thickness of the cobalt binder phase is as small as 0.1~0.9 μm ; the diffusion distance of tungsten and carbon solutes from the center of the binder phase to the surface of WC grains as homogeneous precipitation site is so small that the solutes in the liquid or solid binder phase can easily precipitate homogeneously on the surface of WC grains during the cooling after the sintering, until the alloy system becomes in equilibrium state. However, the tungsten dissolved in the binder phase, the amount of which is for example about 10 mass% in the low carbon alloy as described before, precipitates in the form of Co₃W compound until the amount of tungsten in the binder phase decreases to about 1 mass%, when the alloy is heated at about 1070 K.⁹⁻¹¹⁾ The precipitation sites are (100) crystallographic planes in the binder phase or at the interface of carbide/binder phase.¹⁰⁾ The room temperature flexural strength of the low carbon alloy decreases by about 20%, accompanied with the precipitation of Co₃W, as shown in Fig. 4.⁴¹⁾

5. DOMAIN SIZE OF BINDER PHASE

The average thickness of the binder phase in WC-Co cemented carbides is in the range of 0.1~0.9 μm , which is much smaller than the average grain size of the carbide grains (0.5~5 μm). The Co binder phase on the observed plane is surrounded by the carbide grains. Therefore, it had been believed before that the grain size of the binder phase is nearly the same as its thickness, because the growth of the Co crystal during solidification was mechanically suppressed by the carbide grains. However, the size of the binder phase grain where the crystallographic orientation of binder phase is identical, which is called the domain size of the binder phase, is as large as 100~1000 μm .¹³⁾ An example is shown in Fig. 5.¹³⁾ The domain size increases with increasing Co content, WC grain size and/or TiC content, and with decreasing carbon content and/or cooling rate from the sintering temperature. At the domain boundaries, especially at the triple point of the domain boundaries, the

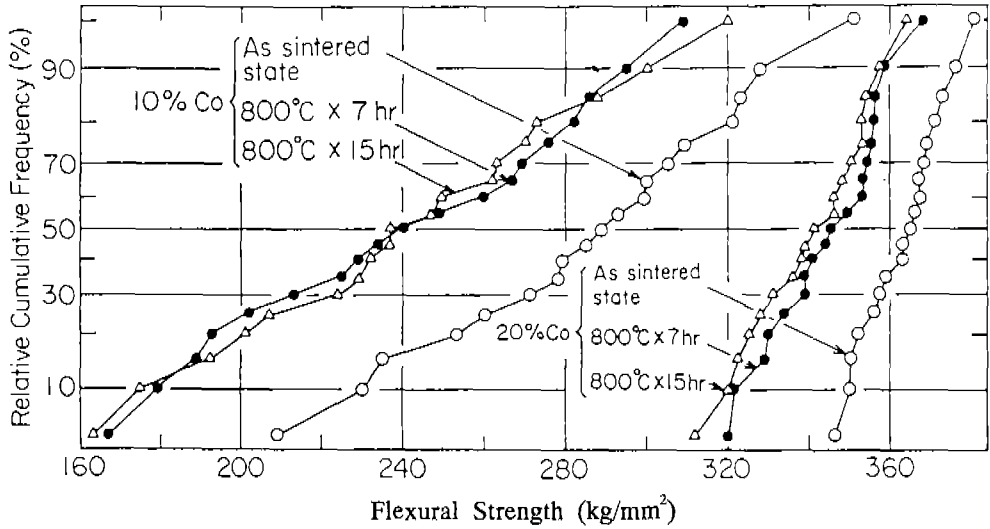


Fig. 4. Effects of Co_3W precipitation treatment (annealing at 800°C or 1073 K) on flexural strength of WC-10 mass%Co low carbon alloy with WC grain size of $1.2\ \mu\text{m}$.

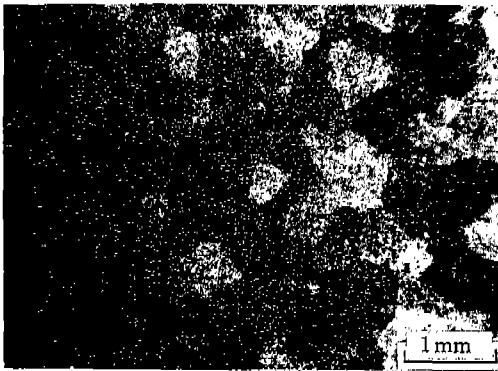


Fig. 5. Optical micrograph of domain of binder phase in WC-20 mass%Co alloy. The domain size of binder phase (about $800\ \mu\text{m}$) is considerably larger than carbide grain size ($1.2\ \mu\text{m}$) ($\times 10$).

formation of micropores and the decrease of Co content tend to occur, which are caused by the solidification shrinkage of the binder liquid. These lead to the degradation of the room temperature strength especially for high Co alloy; the flexural strength decreases with decreasing cooling rate from the sintering temperature or with increasing domain size.¹³⁾ On the other hand, the creep rupture strength or time increase with increasing domain size, on the contrary to the room tempera-

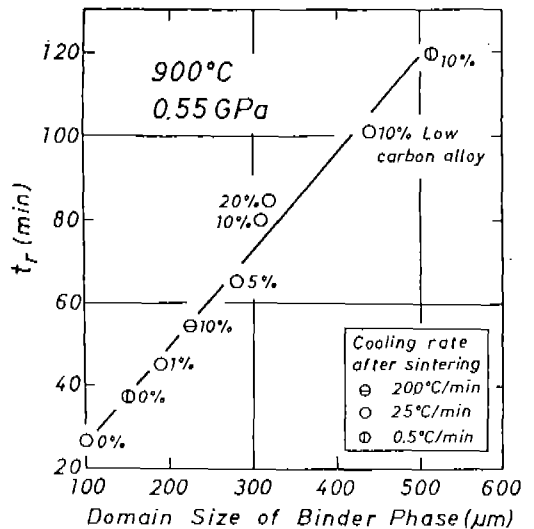


Fig. 6. Effect of domain size of binder phase on creep-rupture time (t_r) of WC-(0~20)mass%TaC-10 mass%Co high carbon alloy. The domain size is changed by the amount of TaC and/or cooling rate after sintering. Nominal creep bending stress is $0.55\ \text{GPa}$, and creep temperature is 900°C or $1173\ \text{K}$.

ture strength, as shown in Fig. 6.⁴²⁾ This is because the stable cracks causing creep-rupture tend to propagate along grain boundaries weaker than the inside of the grains, when the domain size is small.

6. β -FREE OR Co-RICH LAYER NEAR COMPACT SURFACE

When WC-TiC-Co or WC-TiC-TaC-Co hardmetal containing a small amount of nitrogen are sintered in vacuum, β , *i.e.*, (W, Ti)C or β , *i.e.*, (W, Ti, Ta)C grains disappear near the surface of the sintered compact,^{14,15} as shown in Fig. 7.¹⁴ This layer is called in general β -free layer. The Co content is increased, accompanied with the disappearance of β phase. The formation of β -free layer results in the softening of the compact surface and the strengthening of the compact. The mechanism of the formation of the β -free layer are as follows;^{14,15} (1) During vacuum sintering, nitrogen atoms near the compact surface escape to the sintering atmosphere, *i.e.*, vacuum. (2) Then, the total content of nitrogen and carbon which determines the solubilities of W, Ti and Ta in the liquid binder phase decrease near the surface, resulting in the increase of the solubility of β phase (strictly speaking, β phase containing a small amount of nitrogen) in the liquid phase. (3) Then, the elements of β phase such as W, Ti and Ta diffuse from the surface to the inside of the sintered compact and precipitate on the surface of β grains in the inside of the sintered compact. (4) Through the repetition of these processes, β grains near the compact surface continue to decay and/or disappear, and β grains in the inside of the sintered compact continue to grow. Balancing with the volume of the β phase, the elements of which diffused to the inside of the compact, Co content near the compact surface increases. The rate determining step of the β -free layer formation is the diffusing-in of W, Ti or Ta atoms in the liquid phase.

A Co-rich layer where β grains remain can be generated in WC-TiC-Co and WC-TiC-TaC-Co hardmetals containing no nitrogen by the following process,¹⁶ (1) The high carbon alloy is sintered in vacuum, (2) In the final stage of the sintering, the sintering atmosphere is changed from vacuum to decarburizing one for a short time, and (3) The compact is cooled. The mechanism of the formation of the Co-rich layer is as follows.⁴³ (1) The carbon content near the compact surface decreases

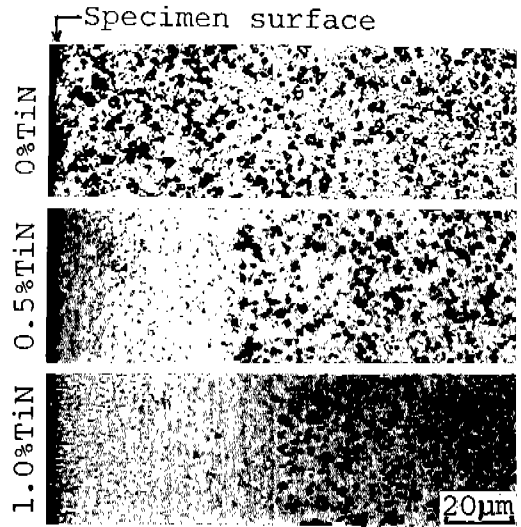


Fig. 7. β -free layer formed near the specimen surface of WC-11.5 mass% β (WC-30 mass%TiC solid solution)-(0.5, 1.0)mass%TiN-16.8 vol%Co alloy, sintered in vacuum at 1673 K for 10.8 ks ($\times 400$).

by changing the sintering atmosphere from vacuum to decarburising one, resulting in the increase of the solidus temperature, (2) The solidification of the liquid phase near the compact surface occur, before the liquid phase in the inside of compact solidifies, (3) Accompanying with the solidification shrinkage of the liquid near the compact surface, a tensile stress is formed near the surface because the inside of the compact does not shrink, (4) The liquid phase, which has high flowability differing from carbide grains with skeleton structure, flows from the compact inside to the compact surface so that the tensile stress in the surface layer is released, resulting in the increase of Co content near the compact surface.

Accompanying with the formation of the β -free layer or the Co-rich layer, the room temperature strength increases, whereas the hardness decreases.^{14,16}

7. KIND AND COMBINATION OF COATED HARD SUBSTANCE

The wear resistance of WC-TiC-TaC-Co hardmetal for steel-cutting tools are greatly improved

by the coating of hard surface by the process of chemical vapor deposition (CVD)¹⁷ or physical vapor deposition (PVD).¹⁸ The CVD coated tools are used in general for turning of steels, and PVD coated tools are used for milling of steels. The hard substances are in general TiC, TiN, Ti(C, N) and Al₂O₃ for CVD coating, and TiN and TiC for PVD coating. TiC has high hardness and high wear resistance and Al₂O₃ has superior high temperature hardness, high oxidation resistance and high adhesion resistance. However, TiC and Al₂O₃ has low fracture strength. TiN has the average hardness and chemical properties between TiC and Al₂O₃, but higher fracture strength. Ti(C, N) has the average properties between TiC and TiN. Thus, each substance has advantages and disadvantages. Therefore, these substances are coated together layer by layer in general.

The order of coating of these substances in multi-coating are selected, according to the use of the coated tools or the kind of work material.^{17,18} For example, TiC/Al₂O₃/substrate, TiC/TiN/substrate, TiC/Al₂O₃/TiN/substrate, Ti(C, N)/Al₂O₃/TiN/substrate, *etc.*, are usual for CVD coating. TiN/substrate, TiN/Ti(C, N)/TiN/substrate, TiN/TiC/Ti(C, N)/TiN/substrate, *etc.*, are usual for PVD coating. The total thickness of coated layer is in general about 7 μm for CVD coating, and about 4 μm for PVD coating. The thickness of each layer is widely varied in the range of 2 nm to 3 μm , depending on the use of the tools. The flexural strength of the coated hardmetal depends mainly on the total thickness of the layer, irrespective of the kind of the hard substance, when the coating method is the same.¹⁸ The adherence of CVD coated layer to the substrate and the wear resistance of the layer are superior to those of PVD coated layer.

8. TYPE OF RESIDUAL STRESS IN THE COATED LAYER

The largest difference between CVD and PVD coatings is the strength level of coated tools. The flexural strength is considerably decreased about 30~70% by CVD coating, as shown in Fig. 8(a),⁴⁴

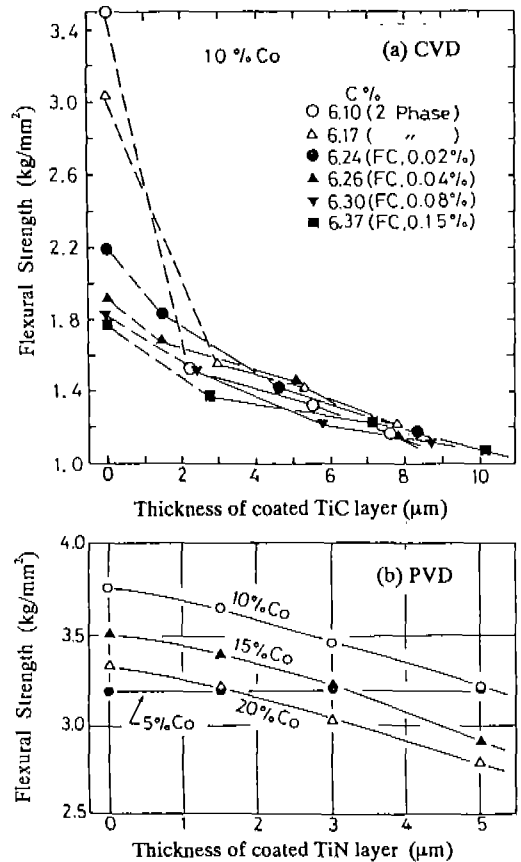


Fig. 8. Effects of thickness of coated layer on flexural strength of WC-(5~20)mass%Co hardmetals coated by CVD process (a) and PVD process (b). "FC" in figure (a) means "Free carbon phase".

which is ascribed to the existence of residual tensile stress of 0.15~0.8 GPa⁴⁴) in the coated layer which is generated by the difference in the thermal shrinkage between the coated layer and the substrate, after the coating at about 1270 K. Namely, cracks are generated in the coated layer during cooling, or cracks are further generated during the loading before the fracture, and the cracks act as the notch of the fracture, resulting in the considerable decrease of the flexural strength. On the other hand, the degradation of the flexural strength of the alloy by PVD coating is small, compared with that by CVD coating, as shown in Fig. 8(b).⁴⁵ This is attributed to the facts that there are no cracks in the coated layer and also the formation of cracks in the layer during loading

is difficult due to the existence of the large residual compressive stress of 2.3~4.8 GPa⁴⁶⁾ in the coated layer. The residual compressive stress is considered to be generated by the bombardment of hard substance ions, which are accelerated by application of voltage during coating, onto the layer. Therefore, the fracture of PVD coated alloy occurs at the moment when a crack is formed in the coated layer during loading and immediately propagates into the substrate.⁴⁶⁾

9. FORMATION OF η -PHASE AT INTERFACE BETWEEN CVD COATED LAYER AND SUBSTRATE

During CVD coating of TiC on hardmetal substrate, η -phase layer with the thickness of 0.5~3 μm tend to form at the interface between TiC coated layer and WC-TiC-TaC-Co substrate,²⁰⁾ because the carbon atoms in the substrate diffuse out to the TiC coated layer and then the carbon content of the substrate becomes lower. The η -phase acts as the notch to the fracture of the substrate and thus degrade the flexural strength of the coated hardmetal, together with the coated layer itself.²⁰⁾ And the η phase has lower wear resistance than the coated hard substances. Therefore, the formation of the η -phase should be avoided as much as possible. The methods for suppressing the formation of the η -phase at the interface are as follows.

(1) High carbon hardmetals are used as the substrate.

(2) The volume ratio of CH_4 or C_2H_4 gas as the carbon source to the carrier gas of H_2 is set at a higher value.

However, these methods tend to cause the appearance of graphite phase in the coated layer, which decrease the wear-resistance and strength of the coated layer. Recently, the following new method began to be employed.

(3) Thin TiN layer is deposited on the substrate before TiC layer, so that the absorption of carbon by TiC layer from the substrate successfully suppressed.

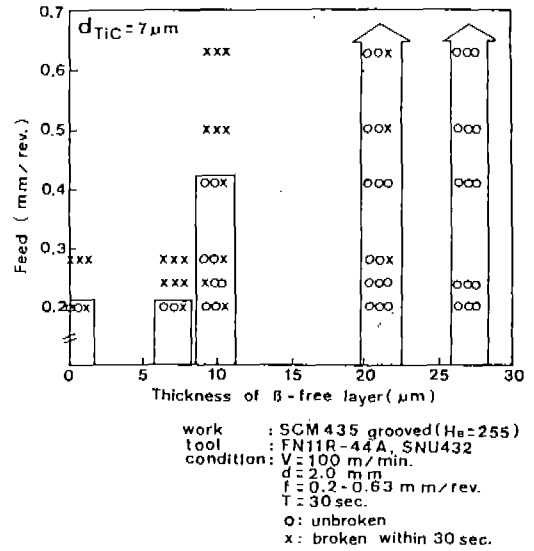


Fig. 9. Effects of thickness of β -free layer on life of coated hardmetal tool in intermittent cutting. The tool is WC-9 mass%(W, Ti, Ta, Nb)(C, N)-5.6 mass% Co alloy coated with TiC by CVD process.

10. SUBSTRATE FOR CVD COATING

The cracks in the coated layer formed by CVD process act as the notch and sharply decrease the room temperature strength of the coated hardmetal, as described above. The methods for suppressing this notch effect are as follows.

(1) WC-TiC-TiN-TaC-Co hardmetals having β -free layer or Co-rich layer near the surface of the sintered compact (a kind of functionally gradient material), which has higher fracture toughness or strength than normal sintered compact, are used as the substrate.⁴⁷⁾

The life of coated hardmetal tools in milling or intermittent cutting is fairly increased by using these alloys, as shown in Fig. 9.⁴⁷⁾

(2) Shot pinning is done on the coated hardmetals.⁴⁸⁾ By this process, compressive residual stress yields in the substrate, which suppresses the propagation of the cracks to the substrate.

11. SUMMARY

As mentioned above, there are many factors

which affect the flexural strength of WC-base hardmetals. These principles for improving the flexural strength by controlling of these factors are of course applicable to other hard materials such as cermets and ceramics. For example, by decreasing the size of the microstructural defects as well as the grain size of hard phase, the flexural strength have already been improved from 1.8 GPa to about 3.2 GPa for TiC-base cermet,⁴⁹⁾ and from 0.6 GPa to 1.2 GPa for Al₂O₃,⁵⁰⁾ and from 0.8 GPa to 1.5 GPa for Si₃N₄.⁵¹⁾ Therefore, for the further improvement of the flexural strength as well as hardness of hard materials, entirely new alloy systems such as borides base cermets⁵²⁾ and C₃N₄,⁵³⁾ and also the use of whisker,⁵⁴⁾ and/or innovative principles such as stacking of ultra thin layers (superlattice)⁵⁵⁾ and functionally gradient materials¹⁴⁻¹⁶⁾ are needed to devise.

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