Evolutional History of Coating Technologies for Cemented Carbide Inserts — Chemical Vapor Deposition and Physical Vapor Deposition

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Coated cemented carbide inserts have well-balanced wear resistance and chipping resistance compared with uncoated inserts made of other materials. Consequently, the shipment of coated cemented carbide inserts is increasing with each passing year. Coated cemented carbide inserts account for over 70% of all the inserts currently in use, and this trend seems to continue for many years to come. Sumitomo Electric Industries, Ltd. started research and development on coated materials 50 years ago, and has since been working hard to advance the innovation of chemical vapor deposition and physical vapor deposition coating technologies. This paper looks back at 50 years of history of coated materials development and introduces new materials.

Keywords: insert, coated carbide, CVD, PVD

1. Introduction

Cemented carbide^{*1,(1)} is a composite material made from ceramic and metal, the typical main ingredients of which are tungsten carbide (WC) and cobalt (Co). The principal component of cemented carbide, tungsten, is an extremely important strategic material from the military perspective. This metal is sourced mainly from China. Its price is exceptionally unstable, being subject to violent fluctuation depending on the global political climate. Because of these factors, carbide insert manufacturers have vigorously studied the use of no or a reduced amount of tungsten in cemented carbide.

One result of their efforts is the development of carbide inserts with their surfaces coated by vaporphase deposition of a thin ceramic film. Coated inserts feature both the toughness of the carbide substrate and the high resistance to heat and wear of the ceramic coating and serve as highly versatile inserts under suitable operating conditions. Accordingly, in recent years, they have been effectively used specifically in highspeed and high-feed, i.e. high-efficiency, cutting applications. Coated carbide inserts have greatly helped reduce machining cost and improved the machining accuracy of mechanical parts.

This paper looks back at the 50 years of Sumitomo Electric Industries, Ltd.'s research and development history in coating technology. It also discusses the latest technological innovations, new materials, and future developments.

2. Vapor Deposition Coating Technology for Cutting Inserts

2-1 Coated insert manufacturing methods and methodological features

Figure 1 shows a breakdown and shipping quantities of domestically produced indexable inserts by insert grade (source: statistics by Japan Cutting & Wearresistant Tool Association). This data reveals that compared with carbide, cermet and ceramic inserts, coated carbide inserts are used in a wider range of cutting applications, with their share rapidly increasing from 40% to 70% over the past 25 years, making coated carbide the most important insert material. This is a natural consequence of the recent increasingly rigorous operating conditions that cutting inserts are subject to. Coatings provided on cutting inserts include films formed by chemical vapor deposition (CVD) and physical vapor deposition (PVD).

The CVD and PVD processes both fall under the class of dry film-forming processes. One key feature of these processes is a low environmental burden compared with plating and other wet processes. Chemical vapor deposition includes various systems such as plasma CVD and photo-induced CVD. Carbide inserts are processed by the thermal CVD process, which forms films at a temperature close to 1000°C. Features of CVD are: (1) uniform coating with excellent adhesion, (2) formation of various thin films with high

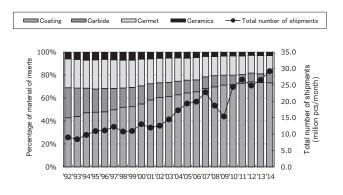


Fig. 1. Percentage of material of inserts and total number of shipments (Japan)

purity and high crystallinity, and (3) ease of achieving multi-layer or thick films.

Physical vapor deposition typically includes the film-forming processes of ion plating, which uses the plasma of a metal ion, and sputtering. Major features of PVD are: (1) formation of thin films with good adhesion at relatively low temperatures below 600°C, (2) compatibility with highly diverse kinds of substrates and coating materials, and (3) formation of thin alloy films and non-equilibrium compound films.

Table 1 shows the features of different manufacturing methods and typical applications. While each method produces residual stress in the formed thin film, the CVD process, which forms films at a high temperature, produces tensile residual stress due to the difference in thermal expansion coefficient between the carbide substrate and thin ceramic film, degrading the strength of the substrate. In contrast, the PVD process causes almost no decrease in the strength of the substrate after coating, because PVD produces compressive residual stress. Additionally, films produced by these methods differ in adhesion and thickness. Consequently, these methods are selected according to the applications suitable for their respective features.

	CVD (Chemical vapor deposition)	PVD (Physical vapor deposition)
Principle	With reactive gas at a high Temperature (thermal CVD)	Ionization of the vaporized metal atoms (Arc, Sputter, Ion beam etc.)
Coverage	Excellent	Failure
Film materials	TiC, TiN, TiCN, Al ₂ O3 (equilibrium)	TiN, TiCN, TiAIN, TiSiN, CrN (non-equilibrium)
Coating temperature	800 °C to 1000 °C	400 °C to 600 °C
Adhesion	Excellent	good
Stress	Tensile (Approx. 1 GPa)	Compressive (Approx2 GPa)
Transverse test ^{*2} (fracturing property)	Failure	good
Typical film thickness	5 ~ 20 μm	0.5 ~ 5 µm
Applications	Turning insert (contin- uous cutting, insulation efficiency), Milling insert	Milling insert, Endmill, (interrupted cutting, sharp edge), Drill

Table 1. Comparison between CVD and PVD method

2-2 Wear mechanisms in coated inserts

Coated films are usually 2 to 20 μ m thick. In sharp contrast, wear in inserts, both wear of flank face (V_B) and wear of rake face (K_T), is far larger at between 50 and 1000 μ m or more. However, thin films are effective against such large wear because they keep wear from becoming wider at Points A, B, C and D shown in Fig. 2. In particular, this effectiveness is thought to be due to the following properties of films: (1) high hardness, (2) oxidation resistance, and (3) prevention of adhesion/ reaction with iron (Fe). These features work most effec-

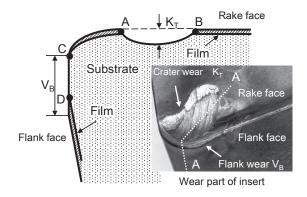
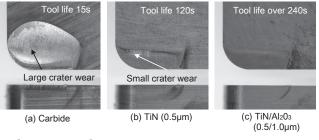


Fig. 2. Cross section A-A at the wear part of insert

tively at Points B and D to retard the removal of cemented carbide particles.

Photo 1 shows damaged inserts resulting from 15 seconds of cutting on the outside surface of an alloy steel (SCM435) at a cutting speed of Vc = 250 m/min. These results reveal that coatings as thin as several micrometers in thickness resist insert wear and extend insert life by a factor of 10 or more.



[Cutting condition] Work material: SCM435, Insert: SNGA120408 Vc=250m/min, f=0.3mm/rev, ap=1.5mm, wet, Cutiingtime: 15s

Photo 1. Comparison of tool wear after alloy steel turning

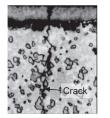
3. Developments in CVD Coating Technology

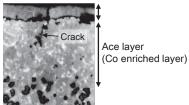
3-1 Development of carbide substrates tailored for CVD coating

Coating of cutting inserts with a thin ceramic film began in 1969 when the then West German company Krupp used thermal CVD to deposit carbide cutting inserts with a titanium carbide (TiC) film. Thereafter, carbide cutting insert manufacturers in Japan and abroad competed fiercely to develop coated cutting inserts. In 1976, Sumitomo Electric developed a cemented carbide substrate provided with the Company's proprietary tough surface layer, surpassing the earlier technology of other manufacturers. Subsequently, the use of CVD-coated inserts grew remarkably.

The notable feature of this cemented carbide was a WC-Co structure formed with a thickness of 10 to 30 μm

on the surface of the substrate immediately under the coated film as shown in Photo 2. This layer is commonly known as the cobalt (Co)-enriched layer (β phase-free layer), while Sumitomo Electric refers to it as the Ace layer. The Ace layer prevents cracks from spreading, provides a substantial improvement in the shock resistance of the substrate, and enables the cutting insert to serve in light to general and heavy cutting applications. Subsequently, Sumitomo Electric developed a zirconium (Zr)-doped carbide substrate with additionally excellent high-temperature properties. In 1994, the Company launched its general-purpose grade AC2000 for steel turning.





(a) Conventional carbide

(b) Ace layer

Photo 2. Restraint of crack failure at the Ace layer

3-2 Development of CVD coating technology

Titanium-based compound films, such as titanium nitride (TiN) and titanium carbonitride (TiCN) coatings, were commercialized in the 1970s ahead of other CVD coatings. Subsequently, around the 1980s, κ -type alumina (Al₂O₃) coatings emerged. Sumitomo Electric launched the AC10 and AC25 (the first generation) of the Ace Coat families, which featured layering of Ti-based compound and Al_2O_3 films. These grades were widely accepted by the market and laid the foundation of the Ace Coat families today.⁽²⁾ However, the Ti-based compound coating was occasionally problematic in terms of the chipping resistance of the inserts. The reason is as follows: Ti-based compound coatings are provided on a carbide substrate at a temperature of approximately 1000°C (high-temperature (HT)-CVD method); at this temperature, substrate components such as W, C, and Co diffuse into the coatings; as a result, a brittle layer (η -layer: Co₃W₃C) forms at the substrate-coating interface, as shown in Photo 3.

As a solution to this challenge, in the 1990s, TiCN coatings, formed by the moderate-temperature (MT) CVD process at a lower coating temperature (lower by 100°C or more), and additionally thermally stable α -type Al₂O₃ coatings were developed. The results were substantially reduced formation of a brittle layer and the aforementioned AC2000 compatible with high-speed and high-efficiency cutting (the second generation). Lately, demand trends have been for improved cutting edge stability at higher operating temperatures to enable environment-friendly dry machining and increases in cutting speed for improved productivity.

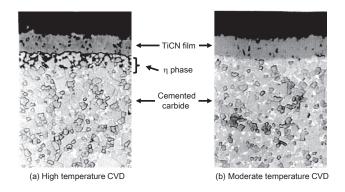


Photo 3. Comparison of cross sectional SEM image with different type of CVD method

Accordingly, it has become necessary to provide high hardness, excellent chipping resistance, adhesion resistance, and high adhesion strength. In 2006, Sumitomo Electric achieved high hardness, excellent chipping resistance and thick film formation in excess of 15 µm through success in allowing thin ceramic films to have an ultrafine crystalline structure. This was made possible by implementing equipment control at a far higher level of precision than before in the CVD gas introduction, thin film synthesis, and exhaust sections, along with optimizing film formation conditions. In addition, Sumitomo Electric achieved chipping resistance, adhesion resistance, and high adhesion strength by making the crystalline structure uniform. These properties were realized in the development of the AC800P family of steel turning grades that incorporate Super FF Coat⁽³⁾ (the third generation).

Table 2 presents observation results of the surface and cross-sectional structures of thin TiCN-based ceramic films. The observation reveals that Super FF Coat is a thin ceramic film that has a uniform, ultrasmooth and ultrafine crystalline structure in comparison with conventional thin films.

 Conventional film
 Super FF coat

 getting
 Image: Conventional film
 Image: Conventional film

 getting
 Image: Conventional film

Table 2. Structure comparison between conventional and super FF coat by using SEM

The evolution of coating technology as discussed above is summarized in Fig. 3. In sum, inserts have improved in oxidation resistance by a factor of approximately 2, in fineness of structure by a factor of 30, and in resultant cutting speed by a factor of approximately 3.

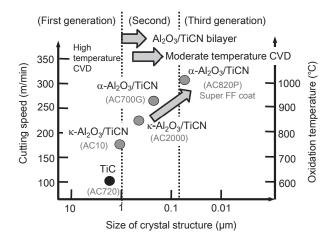


Fig. 3. Evolutional history of CVD coating technology

3-3 Development of post-coating surface treatment technology

For use under harsh cutting conditions, thin ceramic coatings need to have resistance to adhesion in addition to high hardness and chipping resistance. One recent trend is to smooth the surfaces of coated thin ceramic films. Surface smoothing was applied in 2006 to the AC600M family of stainless steel turning grades, and in 2014, as the Absotech Platinum technique⁽⁴⁾ to the AC6030M. The surfaces of coatings are smoothened in order to reduce friction between the workpiece and insert and to expose a chemically stable alumina film as the outermost surface.

The CVD process forms films at a high temperature of approximately 1000°C. When, after film formation, coated carbide is taken out and cooled, a tensile residual stress is produced in the coating due to differences in thermal expansion coefficient between the carbide and thin ceramic coating, resulting in microcracks in the coating. This is a cause of chipping or fracture of the insert cutting edge. In such cases, shotpeening^{*3} or similar surface treatment improves chipping resistance due to its effect of reducing the tensile residual stress. For these reasons, surface stress control is employed as an additional processing technique in the CVD coating process. Surface stress control was deployed for the production of the AC400K family of cast iron turning grades in 2011, of the new ACP100 and new ACK200 in 2012 as milling grades, and of the ACM200 in 2014, respectively.

4. Developments in PVD Coating Technology

4-1 World's first PVD-coated inserts

Sumitomo Electric began to apply PVD coatings on a commercial basis ahead of its competitors when in 1978 the Company produced Gold Ace GA8 by using the electron-beam ion plating process to coat the surface of high-speed tool steel with a Ti compound. The following year, Sumitomo Electric applied the process to a carbide substrate⁽⁵⁾ and developed Ace Coat AC330 (the first generation). It was an epochmaking event in that it enabled steel milling, which had conventionally been thought to be difficult with a CVD-coated insert. Thus, the range of applications of coated inserts expanded from turning to milling.

Subsequently, the Company improved the manufacturing process and developed coatings and substrates successively to deploy the technique to end mills and drills. Notably, in 1982, the Company developed Multi-drill Type P, which with a one-of-a-kind tool profile design and the use of a PVD grade, realized the Company's long-held dream of high-speed and highefficiency drilling in steel. This original milestone product from Sumitomo Electric consolidated the Company's position in the carbide drill business in the industry.

Additionally, in 1990, Sumitomo Electric applied the PVD process to cermet and developed the Z Coat families of coated cermet. These products were produced by using the PVD process to provide a substrate with a thin ceramic coating principally made of a Ti compound (TiCN). The Z Coat families featured two to six times higher wear resistance than uncoated cermet and strong adhesion of the coating, and speeded up the finishing process as well.

4-2 Super nanomultilayer coating technology

Physical vapor deposition coatings evolved in line with advances in film formation process. In the era of TiN and TiCN films, ion plating was predominant, characterized by the fusion and vaporization of raw substances in a crucible, as in electron beam and hollow cathode systems. Since the 1990s, when the arc ion plating method emerged, titanium aluminum nitride (TiAIN) coatings formed by this process have been main stream.

The arc ion plating method uses metal ions or argon (Ar) ions to clean substrate surfaces before coating, providing far better adhesion than previously used processes. This is one of the advantages of arc ion plating as a cutting insert coating process. Arc ion plating can use alloys of any composition as raw materials, if conductive. Moreover, the method achieves a coating of composition close in value to target composition. These features give an edge to arc ion plating in that the process allows for a broad range of materials for selection.

In 1994, around the same time frame as the development of ternary TiAIN coatings, Sumitomo Electric developed⁽⁶⁾ its super nanomultilayer coating technology (ZX Coat). Coatings produced by this technology are comparable to sintered CBN in hardness and highly resistant to heat. These features are achieved by

layering some 2000 alternating TiN and AIN films as thin as one nanometer (one-thousandth of a micrometer) per layer formed by arc ion plating, as shown in Photo 4. The super nanomultilayer coating technology was applied to products such as drills, end mills and indexable inserts for milling (ACZ350) (the second generation).

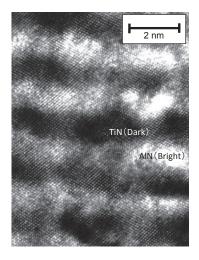
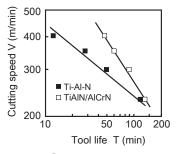


Photo 4. Cross sectional TEM image of TiN/AIN nanomultilayer film. Bright layer = AIN, Dark layer = TiN

Sumitomo Electric's original super nanomultilayer coating technology continued to evolve thereafter. One recent development is the use of chromium (Cr) and silicon (Si) as additives so as to improve the hardness and heat resistance, achieving TiAIN/AICrN super nanomultilayer coating (Super ZX Coat).⁽⁷⁾ Super ZX Coat was applied to the ACP and ACK families of milling grades and AC500U family of turning grade. These grades exhibited superiority in high-speed cutting, as shown in Fig. 4 (the third generation). Furthermore, the AITiSiN-based super nanomultilayer coatings of New



[Cutting condition] Work material: SCM435, Cutter: WGC4160R(φ160mm), Insert: SEET13T3AGSN-G fz=0.3mm/t, ap=2mm, ae=150mm, DRY

Fig. 4. V-T curves of TiAIN/AICrN nanomultilayer and TiAIN coated inserts

Super ZX Coat and Absotech Bronze have been respectively deployed on the following products (the fourth generation): the ACM family of grades for milling stainless steel and the AC6040M⁽⁴⁾ grade for turning stainless steel.

The evolution of coating technology as described above is summarized in Fig. 5. In sum, inserts have improved in hardness by a factor of approximately 3, in oxidation resistance by a factor of approximately 2, and in resultant cutting speed by a factor of approximately 3.

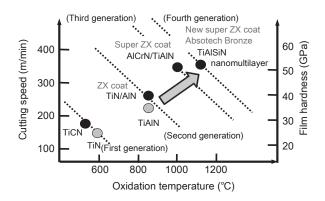


Fig. 5. Evolutional history of PVD coating technology

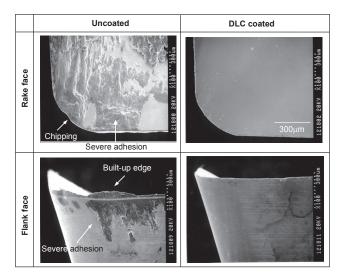
4-3 Tribological^{*4} properties improved by lubricious coating technology

Diamond-like carbon (DLC) forms three-dimensional bonds similar to diamonds and offers features such as an extremely low coefficient of friction, excellent wear resistance, and sliding properties. The exceptional sliding properties of DLC are presumably due to DLC's tendency under sliding conditions to alter to a graphite-like or organic (i.e. hydrocarbon) material and to act as a lubricant.

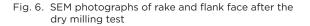
The above-mentioned sliding properties are valid with soft metals. Diamond-like carbon does not adhere even with an aluminum or copper alloy that is extremely prone to adhesion (see Fig. 6). Utilizing this effect, in 2002, Sumitomo Electric commercialized⁽⁸⁾ aluminum alloy cutting tools (indexable inserts, drill, and end mills, etc.) under the brand name Aurora Coat.

In 2012, the Company developed a coating material (Brilliant Coat) with a low reactivity towards steel and used it to commercialize the coated cermet insert T1500Z.⁽⁹⁾ Brilliant Coat is Sumitomo Electric's proprietary PVD coating, which is highly slick and exhibits extremely low reactivity towards steel, as shown in Fig. 7. Layering of such coatings on the outermost surface enabled substantial improvements in the quality of finished surfaces.

In addition to high hardness and high oxidation resistance conventionally required of coatings, improving tribological properties, such as low friction and lubricity, has become an important factor in ensuring stable cutting insert life.



[Cutting condition] Tool: WEM3032 (φ 32 mm), Insert: APET160504PDFR-S Work material: ADC12, Vc = 300 m/min, fz = 0.15 mm/t, ap = ae = 5 mm, Cutting length = 9 m, DRY



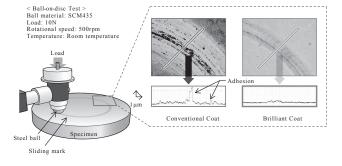


Fig. 7. Comparison of Lubrication Properties

5. Future Developments

Attempts are still presently being made to improve the cutting performance of CVD coatings, for example, by optimizing the crystal orientation and microstructure of coatings, as well as by optimizing or thickening TiCN and Al₂O₃ films. Nonetheless, no novel coating material has been produced by thermal CVD for a considerable time. However, research and development has recently begun on AlTiN films, although AlTiN films formed by PVD coating are already in general use. Expectations are high for new developments in coatings, including those other than AlTiN films.

Regarding PVD coatings, it has been reported⁽¹⁰⁾ that the nc-MeN/Si₃N₄ film (Me: Ti, W and vanadium (V)), which features a nanocrystal-amorphous composite film structure (nanocomposite structure), has a hardness of 105 GPa, at a level similar to diamond. This material has aroused great hopes in the area of development of high-hardness materials. Moreover, if magnetron sputtering is combined with a high-frequency or pulse power supply, it has become possible to form nonconductive coatings

of oxides (e.g. alumina), although it is difficult with the conventional PVD process. It is quite probable that this coating will be applied to inserts. Furthermore, a novel film forming process of high-power impulse magnetron sputtering (HIPIMS) is currently the focus of attention. Using this technology, it is possible to render the smoothcharacteristics of magnetron sputtering and to form a dense film with good adhesion owing to the high ionization rate characteristics of arc ion plating. Therefore, great hopes are placed on HIPIMS as a next-generation PVD process.

6. Conclusion

In the 1970s, the CVD process combined with dedicated carbide substrates performed well as a forerunner in commercializing coated inserts. Subsequently, the PVD process came into use in a wider range of applications along with the widespread use of arc ion plating in the 1990s. Since then, both processes have evolved greatly. Currently, it is increasingly important to select suitable insert materials according to the intended use. As a tool manufacturer, Sumitomo Electric intends to provide solutions for market needs or challenges in the area of machining, such as environmentally sound measures, improved accuracy, improved efficiency, reduced tool cost (extended tool life), and adaptation to hard-to-cut materials, by working on the development of novel ceramic coating materials and coating processes.

 Ace Coat, Super FF Coat, Absotech, Absotech Platinum, Absotech Bronze, Gold Ace, Multi-drill, Z Coat, ZX Coat, Super ZX Coat, New Super ZX Coat, Aurora Coat, Brilliant Coat are trademarks or registered trademarks of Sumitomo Electric Industries, Ltd.

Technical Terms

- *1 Cemented carbide: A ceramic-metal composite material, the main ingredients of which is tungsten carbide (WC) and cobalt (Co).
- *2 Transverse rupture strength (TRS): A bending strength index determined by the three-point bending test; Test method: CIS 026 (JIS R 1601/ ISO 3327).
- *3 Shot peening: A process intended to harden and give a compressive residual stress layer to the surface of a workpiece through plastic deformation by impacting the surface with many small ball-like particles at a high speed.
- *4 Tribology: The science and engineering of all phenomena that occur between two interacting surfaces in relative motion, including lubrication, friction, wear and adhesion.

References

- (1) H. Gotou, SEI TECHNICAL REVIEW, 68 (2009) pp4
- (2) M. Chudou et al., SEI TECHNICAL REVIEW, 128 (1986) pp100 in Japanese
- (3) Y. Okada et al., SEI TECHNICAL REVIEW, 64 (2007) pp68
- (4) H. Takeshita et al., SEI TECHNICAL REVIEW, 80 (2015) pp91
- (5) M. Kobayashi et al., Thin Solid Films, 54 (1978) pp67
- M. Setoyama et al., SEI TECHNICAL REVIEW, 146 (1995) pp92 in Japanese
- (7) H. Fukui et al., SEI TECHNICAL REVIEW, 169 (2006) pp.60 in Japanese
- (8) Y. Kagiya et al., SEI TECHNICAL REVIEW, 55 (2003) pp89
- (9) S. Koike et al., SEI TECHNICAL REVIEW, 78 (2014) pp90
- (10) S. Veprek, J. Vac. Sci. Technol., A17(5), Sep/Oct (1999) pp2401

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