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Practical Use of Microbeam Analysis in Development of PVD Coatings†

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Abstract:

Recently, new higher performance films produced by physical vapor deposition (PVD) coating have been expected to realize longer life of cutting tools, metal molds, machine parts and other materials. These films are expected to lead to the introduction of new working methods such dry milling for high-speed steel (HSS), mold pressing for ultra-high tensile strength steel and net shape cold forging. To commercialize such new higher performance films, JFE Precision Co. has developed PVD coatings with multi-layer and/or nanosized-layer films named the SX Series and VSX™ Series in collaboration with JFE Steel Corporation. Because precise surface analyses of worked films and sectional structural analysis of the produced films are very effective for obtaining basic data for research and development, practical use of advanced analysis technologies is essential in research and development of these films.

1. Introduction

JFE Precision Co. has performed physical vapor deposition (PVD) as an outsourcing contractor since 1987. The company performs treatment to form hard films with thicknesses on the order of several micrometers on the surfaces of cutting tools, metal molds, machine parts and other materials entrusted by customers. These films include carbonitride films such as TiAlN, CrN and others, which are produced by the ion plating method, diamond-like carbon (DLC) produced by sputtering, and others.

PVD coating has been adopted rapidly, as it realizes long life in cutting tools, metal molds and machine parts, taking advantage of features that include high hardness, high thermal resistance, etc. In addition to longer life, in recent years, higher film performance has also led to the introduction of new working methods, such as dry milling, cutting of heat-treated tool steels, high-speed steels (HSS), and other hard-to-work materials, press forming of ultra-high tensile strength steel and net shape cold forging, which were not possible with conventional techniques, and thus has further expanded the range of film applications. PVD coating treatment is an essential element in these types of working.

The methods used in ion plating are the arc ion plating method (AIP) and the hollow cathode discharge method (HCD). From the viewpoints of diversification of films and high adhesion, AIP has become the mainstream method. **Figure 1** shows the history of film development by the AIP method at JFE Precision. As can be understood from this figure, film development began from mono-composition (single metal) carbonitrides, and then evolved to binary alloy carbonitrides, ternary and higher alloy carbonitrides, multi-layer films, and further, to nanosized-layer films. In other words, aiming at higher film performance, film development has evolved from general-purpose films to high functionality films. In order to respond to increasingly sophisticated market needs, film development has aimed at higher performance by multi-composition multi-layer and/or nanosized-layer films. JFE Precision has commercialized original high performance films in the SX

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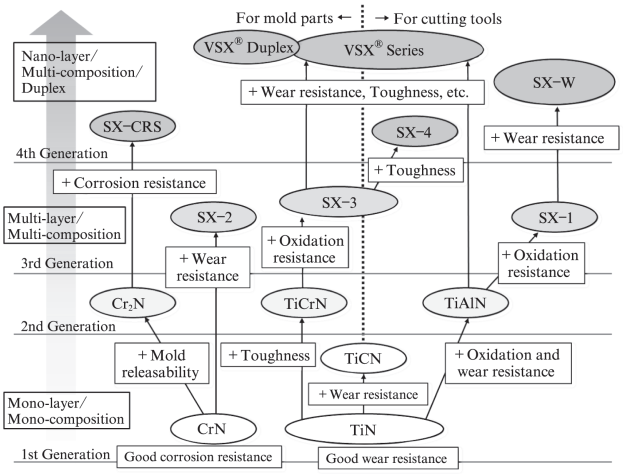

Fig. 1 History of physical vapor deposition (PVD) coating development in JFE Precision

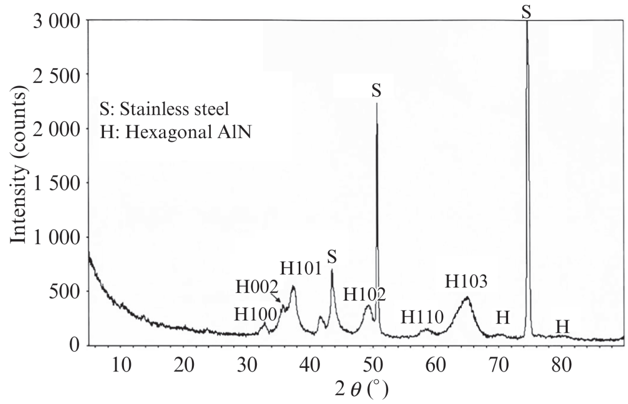

Fig. 2 X-Ray diffraction (XRD) pattern of AlCrN coating with hexagonal close-packed (hcp) structure

Series[1] and the VSX™ Series, and is continuing to devote great effort to the development of films with even high performance.

In the development of multi-composition multi-layer and/or nanosized-layer films, which is the current trend, advanced analysis technologies occupy a particularly important position. This paper introduces examples of the use of physical analysis techniques in original films developed jointly by JFE Precision and JFE Steel Corporation.

2. Analysis of Crystal Structure in Film Development

The basic properties required in films include high hardness, high thermal resistance, a low friction coefficient, high adhesion, high corrosion resistance, etc. Among these properties, high hardness, high thermal resistance and high adhesion are required in films for cemented carbide tools, which are used to cut heat-treated tool steel under a dry condition. As films for this type of cutting tool, basically, a film with high adhesion is formed on the cemented carbide base metal, and a high hardness, high thermal resistance film is formed as the top surface layer. The candidate films for a top surface layer with these properties are nitride films consisting of binary or higher alloys based on composition systems such as TiAlN, TiSiN, AlCrN, etc. **Table 1** shows the properties of the main films of this type. High hardness is achieved by solute strengthening by alloying using base materials of Ti, Al, Si and Cr, which are metals generally with high oxidation resistance. However, it is known that hardness changes greatly depending on the composition ratio of the component materials[2,3].

Among these, AlCrN has high adhesion and demonstrates a certain degree of cutting performance even as a mono-layer. **Figure 2** shows the results of an X-ray diffraction (XRD) analysis of a film formed by using a target material having the composition Al_xCr_y. Although the crystal structure predicted from the target composition should be fcc (face centered cubic lattice), deviations between the target composition and the film comparison occurred due to differences in the ionization rate, valence, mass, etc. of the Al and Cr at the time of film forming, and as a result, the crystal structure was actually an hcp (hexagonal close-packed) structure of AlN. Because the peak of film hardness is located close to the boundary where the crystal structure changes, it is important to confirm the composition deviation by XRD structural analysis, and form the film that displays the maximum hardness. **Figure 3** shows the result of XRD phase identification of a film in which this deviation in composition was corrected. The fact that the crystal structure was corrected to the targeted fcc structure of CrN system can be confirmed from this figure. **Figure 4** shows the results of cutting tests of these two types of films. It can be understood that a large difference in cutting performance has occurred. It may be noted that this

Table 1 Properties of physical vapor deposition (PVD) coatings

Coating	TiN	TiCN	TiAlN	CrN	AlCrN	TiSiN
Surface roughness	R_a=0.20 μm	R_a=0.20 μm	R_a=0.30 μm	R_a=0.15 μm	R_a=0.15 μm	R_a=0.15 μm
Critical load (by scratch test on high-speed steel (HSS))	60 N	60 N	40 N	80 N	50 N	30 N
Hardness	2 200 H_{mv}	2 800 H_{mv}	3 000 H_{mv}	1 800 H_{mv}	3 000 H_{mv}	3 700 H_{mv}
Oxidation resistance	450°C	350°C	800°C	550°C	1 100°C	1 300°C
Color	Gold	Blue gray	Violet	Gray	Dark gray	Copper

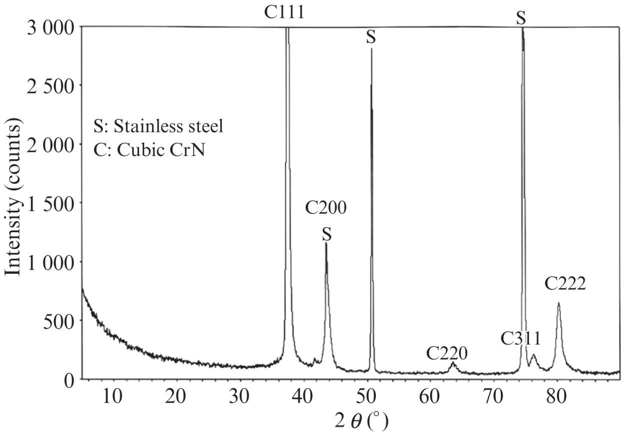

Fig. 3 X-Ray diffraction (XRD) pattern of modified AlCrN coating with face-centered cubic (fcc) structure

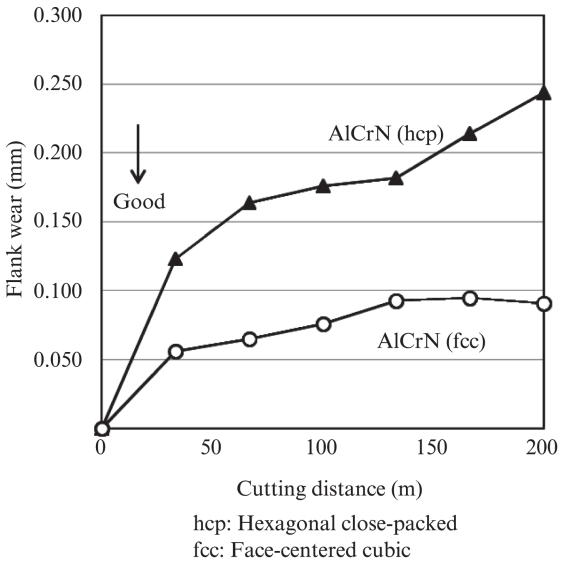

Fig. 4 Progress of flank wear with AlCrN coated tools

cutting test was performed on S50C material with the hardness of HRC 20 using an R5 ball end mill with two cemented carbide blades. The spindle speed was 5 100 rpm, feed was 1 330 mm/min, feed of cut was 0.3 mm and depth of cut was 0.1 mm. Cutting was performed without lubrication, and the cutting distance and flank wear were measured.

3. Analysis of Film Damage by SEM

In manufacturing cold forged parts, the Cold Forging Division of JFE Precision uses dies to which coatings are applied in-house. Initially, TiN was used, but later this was changed to TiCrN, which is a film that was developed independently by JFE Precision and has the effect of extending die life. Recently, however, there has been heightened demand for a further extension of die life.

When the surface condition of a TiCrN die was observed with a scanning electron microscope (SEM) after 3 000 shots, which approaches the life of the die, film wear had progressed (**Photo 1** (a)). However, a condition of point-like delamination of the film, exposing the base material of the die, was observed (Photo 1 (b)), and a condition in which metal from the workpiece had adhered to the film surface could also be seen (Photo 1 (c)). These conditions suggest that the film adhesion and metal adhesion resistance were inadequate, peeling of the film and adhesion of metal from the workpiece occurred, and as a result, this controlled the life of the die.

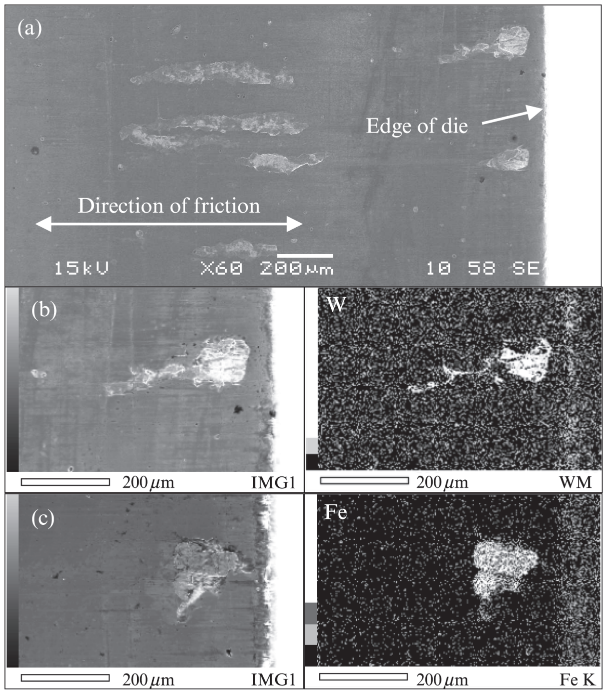

Photo 1 Scanning electron microscope (SEM) image of surface condition of TiCrN coating after 3 000 shots (a), energy dispersive X-ray spectroscopy (EDS) mappings of W (b), and Fe (c) corresponding to delamination of film and metal adhesion, respectively

The design of the film structure was reviewed based on the knowledge outlined above, and a film called VSX^{TM}-V having a combination of high adhesion, wear resistance, and resistance to metal adhesion was developed. **Figure 5** shows the basic structure of the developed VSX^{TM}-V. To obtain high film adhesion, an adhesive layer is applied directly to the base metal, and the main layer of the multi-layer structure, which displays excellent wear resistance, is applied over the adhesion layer. A layer with an anti-adhesion layer is then applied as the top surface layer. The results of life evaluation of this VSX^{TM}-V are shown in **Fig. 6**. It shows that long life greatly exceeding that of the conventional TiCrN was obtained. **Photo 2** shows the results of observation of a VSX^{TM}-V die after use for 20 000 shots. Point-like delamination of the film and adhesion of metal from the workpiece, like that seen with TiCrN, were not observed,

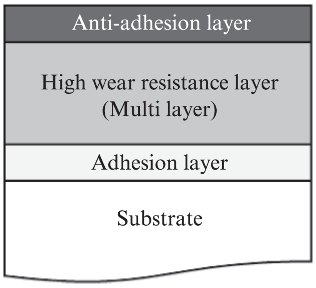

Fig. 5 Schematic structure of VSX®-V

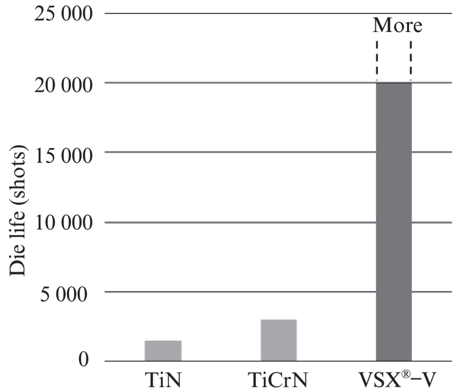

Fig. 6 Die life of cold forging die coated with TiN, TiCrN, and VSX®-V

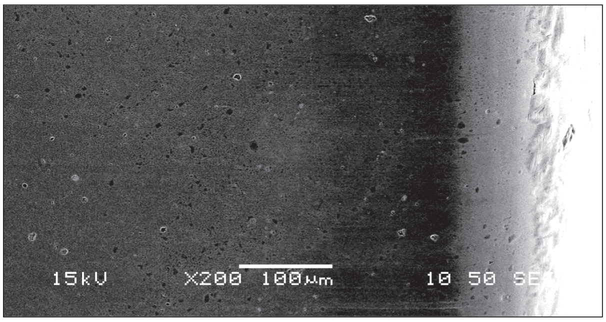

Photo 2 Scanning electron microscope (SEM) image of surface condition of VSX®-V after 20 000 shots

and the fact that film properties were obtained as targeted could be confirmed.

It is possible to obtain films which have a combination of multiple excellent properties as a whole by using a multi-layer structure and dividing the required functions among the various layers. However, in order to obtain targeted properties, it is important to carry out a detailed surface analysis of the film, understand the mechanism of film damage, and reflect that understanding in film design.

4. Film Structural Analysis at Nanometer Level by TEM

In dies for press forming and forging, machining is performed after heat treatment in order to improve

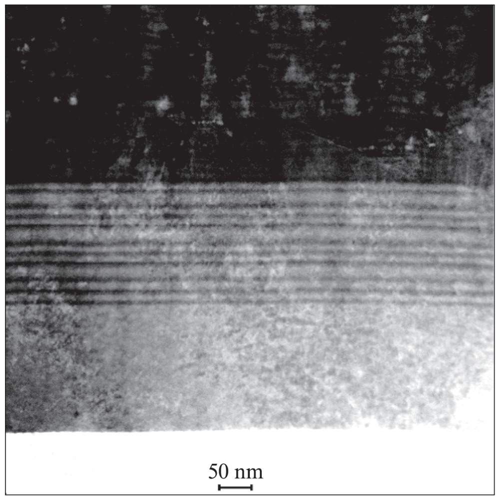

Photo 3 High-angle annular dark-field (HAADF) image of the cross-section of nano-layer

dimensional accuracy and productivity. For this, cutting tools which enable machining of high hardness dies of HRC 60 and higher are necessary. In order to cut high hardness materials, high thermal resistance, high adhesion and a low friction coefficient have been required in films higher than conventional materials. However, it has become impossible to satisfy these requirements completely with only nitride films of binary alloy systems or higher and simple layers of those films. In response to this difficulty, higher performance has been achieved by alternating deposition of multiple films with thicknesses of the nanometer level[4,5]. Because these multi-layer films must have a distinctive structure at the nanometer level and must also form a consistent continuum in order to demonstrate their performance, it is necessary to confirm the structure of the formed film. However, due to the extremely thin thickness of the layers, observation at the magnification of SEM is extremely difficult. Therefore, observation is performed by transmission electron microscopy (TEM). **Photo 3** shows a high-angle annular dark-field (HAADF) image of the cross section of a film that was developed for use in cutting high hardness materials, and **Fig. 7** shows line profiles of the elements obtained by energy dispersive X-ray spectroscopy (EDS) by scanning with a nanoprobe. It can be understood that a regular layer structure at the nanometer level was obtained.

Figure 8 shows the results of a cutting test with a VSX™-V film, in which this layer structure was introduced. The cutting test was performed on the alloy tool steel SKD11 material with the hardness of HRC 60 using an R5 ball end mill with two cemented carbide blades. The spindle speed was 3 000 rpm, feed was 800 mm/min, feed of cut was 0.3 mm and depth of cut was 0.1 mm, and cutting was performed without lubrication. The cutting distance and flank wear width were

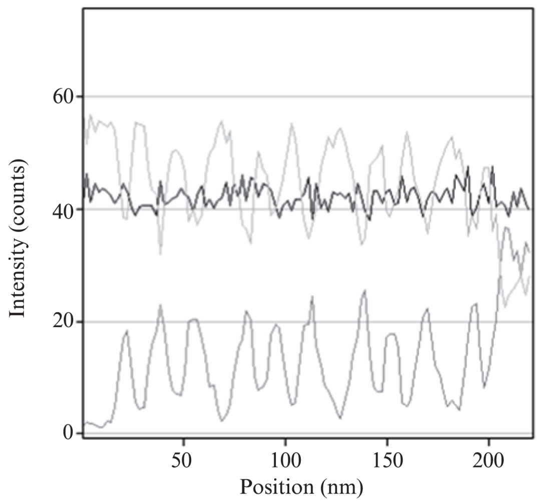

Fig. 7 Line profiles of nano-layer measured by energy dispersive X-ray spectroscopy (EDS)

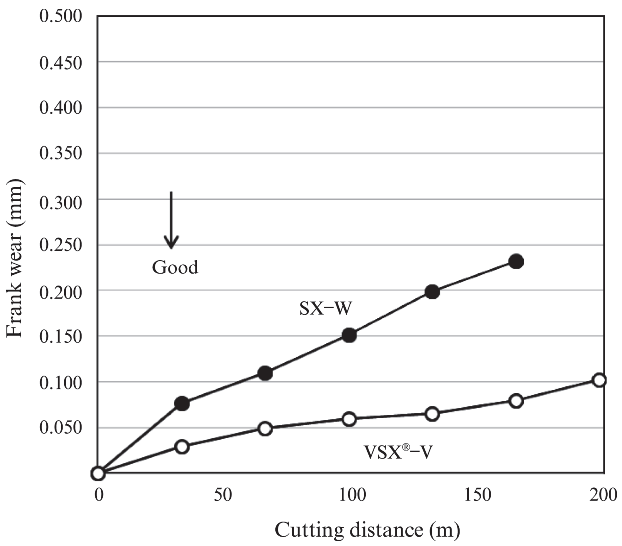

Fig. 8 Flank wear of tools with SX-W and VSX®-V coating

measured. As a result of the layer structure, a tool with an SX-W film has excellent life with materials having hardness up to about HRC 55, but at HRC 60, adequate life could not be obtained even with this tool. However, with VSX™-V, in which the above-mentioned layer structure was adopted, wear is reduced and life exceeding that of SX-W for cutting high hardness materials could be obtained. This cutting performance exceeds that of the film which is considered to provide the highest performance in the industry at the present time.

5. Conclusion

(1) In recent years, the improved performance of PVD films not only achieves the conventional aim of tool longer life, but can also realize new working methods that were not possible in the past, such as press forming of high tensile strength steel. JFE Precision, in joint development work with JFE Steel, commercialized the SX Series and the VSX™ Series, which improve film performance, including film wear resistance, thermal resistance, adhesion and other properties.

(2) In the development of high performance films, it is necessary to incorporate multi-layer structures consisting of layers of different types and/or nanosized-layer structures. For this, nano level physical analysis techniques are necessary in order to confirm that the formed layers are as designed.

(3) Analysis of the condition of films after use and elucidation of the mechanism of damage are also important for film design, and analytical techniques are also indispensable for these purposes.

(4) Use of advanced analytical techniques is increasingly important in film development. In the future, JFE Precision will continue to make the fullest possible use of the strengths of the JFE Group, namely, the fact that the JFE Group possess both advanced coating technologies and state-of-the-art analytical techniques, in order to promote the development of new Only 1 and No. 1 films.

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