Perspective for Replacement Of Hard Chromium by PVD

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In recent years, hard chromium has been replaced for specific applications with physical vapor deposition (PVD) films that provide equivalent or superior performance. Unlike hard chromium, PVD hard chromium replacements can be tailored specifically to the application. Coatings of CrN and variants such as CrCN exhibit properties that meet or exceed the chromium they replace, as well as offer additional properties, such as reduced coefficient of friction. The family of coatings known as metal-containing diamond-like carbon (Me-DLC or Me-C:H) exhibits properties of diamond-like carbon, providing outstanding wear protection, toughness and low coefficients of friction. A survey of some proven replacement applications and their physical characteristics are discussed here.

Hard chromium is widely used in many applications. It possesses a few characteristic properties, such as relatively high hardness, good corrosion resistance and a self-leveling effect. Combinations of these properties have led to use in applications where the conditions require high hardness, low friction, low wear and corrosion resistance. Hard chromium is found in a wide range of applications, such as hydraulic parts for aerospace, automotive and offshore. Anti-wear properties of hard chromium are used in such applications as coating of piston rings and in the textile industry.

PVD is a technology that has numerous applications, such as:

- Conducting metallic layers on semiconductors,
- Reflecting Al layers on CDs,
- Selectively transmitting layers on flat glass,
- Ceramic wear-resistant layers on professional tools.

In the last few years, another group of coatings is being applied industrially as well—the anti-wear PVD coating. In principle, the PVD coating method has the flexibility to tune the coating properties by changing composition, creating multilayers, adjusting the mechanical properties and influencing the microstructure. Given the flexibility of adjusting coating properties, it is possible to engineer specific coating properties that perform better than hard chromium.

Costs of PVD coatings have been high, relative to hard chromium, but in many cases are now substantially decreasing. As the cost of hard chromium increases, the applications where PVD can be competitively applied will increase as well.

Current PVD Coatings

In Table 1, an overview is given of PVD coatings that are currently used in various applications. TiN is also shown in the table, because it is the most frequently applied PVD coating for tools.

A number of properties are shown. Not shown, however, is adhesion. Adhesion between coating and substrate is vital for a proper coating performance. As adhesion of the hard layers to the substrate is relatively low, adhesion interlayers, such as pure PVD chromium, can be used. Additionally, proper adhesion relies on proper substrate cleaning and proper substrate etching processes. Another important parameter to coating performance is internal stress. Intrinsic to PVD-grown coatings is internal stress, which may cause adhesive flaking. As the coating layer

Table 1
Industrially Applied PVD Anti-wear Coatings

	CrN	Me-C:H	a-C (pure DLC)	MoS_2	TiN
Deposition temperature (°C)	150-300	150-250	150-500	150-250	150-450
Hardness (HV 0.05)	1200-2200	800-2200	3000-7000	300-600	2000-2500
Internal stress (Gpa/µm)	0.1-1	0.1-1.5	2-6	0.1-1	1-2
Thickness (µm)	1-50	1-5	1-2	1-10	1-6
Friction coefficient	0.4-0.6	0.1-0.2	0.02-0.1	0.1-0.2	0.5-0.7
Maximum temperature (°C)	750	350	450	400	450
Abrasive wear	–	+	+++	++	–
Adhesive wear	–	+++	+++	–	–
Corrosion	+++	+	+++	+	+
Practical problems	low	low	adhesive flaking	low shear	
Industrial experience	++++	++++	–	+	++++

grows, high internal stresses are generated that limit the thickness of the coating. Table 2 indicates achievable practical thicknesses.

Chromium Nitride

Chromium nitride (CrN) is widely used as an anti-wear coating. Though having generally higher coefficients of friction than hard chromium, a great advantage of CrN is that the internal stresses are very low. Coatings with thicknesses of more than 40 µm are routinely used in automotive applications.

DLC & Metal-containing DLC

Diamond-like carbon (DLC) offers a broad potential, as it combines very high hardness with a low friction coefficient. Unfortunately, one of the major shortcomings is that the pure DLC has a very high internal stress, thereby limiting its thickness to about 1 µm. Another disadvantage is that pure DLC coatings show low electrical conductivity.

DLC coatings, however, become viable when the coating chemistry is enhanced when low concentrations of elements other than carbon are added. Examples are pure metals,[1] carbide-forming metals[2,3] (indicated with Me-C:H) and other carbide-forming elements, such as silicon[4] and boron.[5]

In principle, nanostructures are formed by addition of between 5 and 15 atomic percent of carbide-forming elements. Small carbide islands exist in a carbon matrix. The hardness is considerably less than that of pure DLC, but other properties such as internal friction and elasticity are greatly improved. These factors improve fatigue life of the coatings.

Molybdenum Disulfide

Molybdenum disulfide (MoS_2) has well-known tribological properties. A major drawback of pure MoS_2 is that the shear stress is relatively low. Coatings of pure MoS_2 are used in combination with other coatings, such as TiAlN, to produce specific sliding wear properties.[6]

Titanium Nitride

Titanium nitride (TiN) has been widely used since the late 1970s as a replacement for hard chromium. It has been used because it is generally available from various sources. Based on its specific properties, however, it is not a suitable replacement for hard chromium.

Current PVD Applications

Numerous applications have been introduced in the last five years. An overview can be seen in Table 2.

The current main application is in the automotive segment. Major applications are found in the fuel injection train. The new generation of very-high-pressure fuel injection systems has become economically feasible by use of PVD coatings. A considerable advantage of a PVD coating is that it can be made relatively thin. Because coating thickness requirements are only a few µm (±10%), allowances for coating

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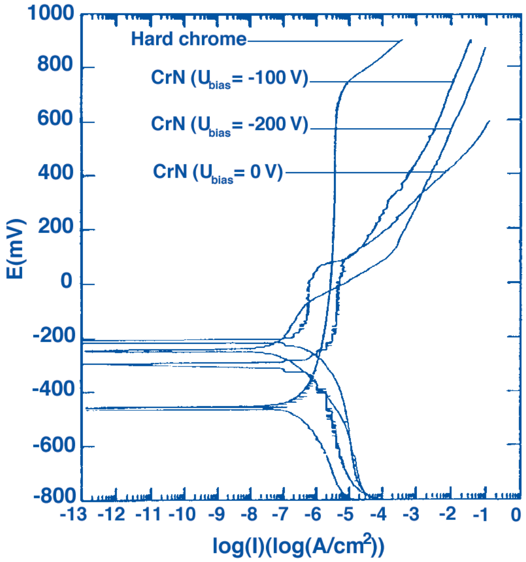

Fig. 1—Corrosion performance of approximately 3 μm CrN, deposited with bias voltages of 0 V, -100 V and -200 V, and of 25 μm hard chromium.

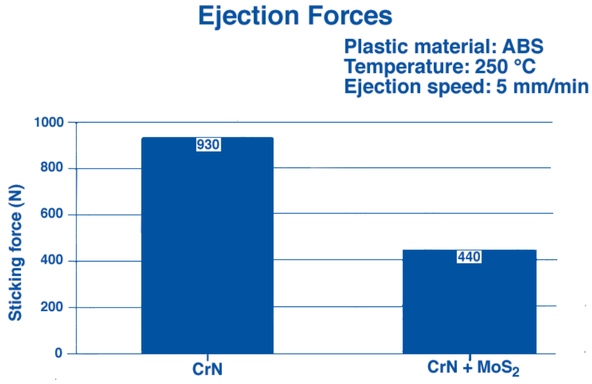

Fig. 2—Sticking forces of injection molding of ABS plastics, molds coated with CrN and CrN + MoS_2.

thickness are not required, and the part to be coated can be at final dimensions.

Another application to successfully take advantage of PVD coatings is shafts of the turbo compressor. Considerable growth for PVD is expected in the next few years in the automotive industry. Current applications are mainly for high-performance car parts. This will certainly have spin-offs for the more normal car production. The continuous drive for improved energy efficiency, weight reduction, noise reduction and volume reduction are all favorable conditions for increased use of low-friction PVD coatings.

One application that is growing rapidly is for punching and forming tools. The goal is to increase the lifetime of the forming tool and improve the surface quality of the final formed part. Coatings that provide hardness and reduce mechanical forces by adding a lubricative coating during forming are possible by PVD. To get both properties simultaneously, combinations of hard and soft coatings are used, mainly CrN, CrCN and Me-C:H.

Another application is in molds, dies and extrusion forms. Initially, CrN was widely used, but use is shifting to combinations of hard and soft coatings.

Table 2
Overview of Current & Future PVD Applications

Current Applications:				
Segment	**Substrate**	**PVD Coating**	**Thickness**	**Remarks**
Automotive	Piston ring	CrN	40 μm	Routinely used by one of the largest Japanese piston ring suppliers
	Drive rods	CrN	3 μm	Used for highly loaded race engines, such as Formula 1
	Turbo shafts	Cr/W-C:H	3 μm	For passenger car turbo engines
	Fuel injection	Cr/W-C:H DLC	3 μm	Diesel fuel pumps; fuel injectors; applied on >50% of world production
	Valve train	Cr/W-C:H	3 μm	Tappet, camshaft; starting to be used in large-scale production
	Drive train	B_4C Cr/W-C:H		Sun gears
Various	Forming tools	CrN, CrCN	2 μm	
	Molds, dies	CrN, CrCN & Cr-C:H	2 μm	
Future Applications:				
Segment	**Substrate**	**PVD Coating**	**Thickness**	**Remarks**
Hydraulics	Pistons	CrN-based multilayers	up to 20 μm	Improved field life expectancy
Cutlery	Cutting tools	CrN-based multilayers	up to 3 μm medical	Use expected in cutting, slitting,
Aeronautical	Various	Various		
Textile	Various	CrN-based multilayers	up to 10 μm	Replacement of Ni/Cr

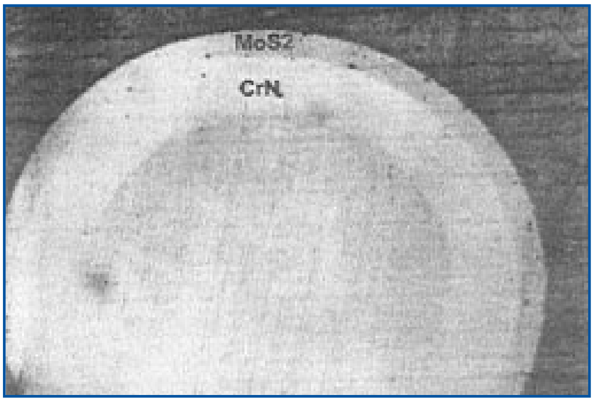

Fig. 3—Ball grind cross section by Kalo test of CrN + MoS_2 multilayer.

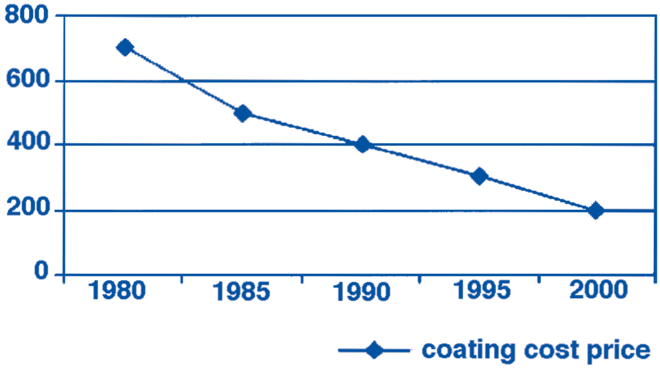

Fig. 4—Indicative cost price in USD per m^2 of 2 µm CrN growth unbalanced magnetron deposition.

PVD Coating Development

Coating development is focusing on several items:

- Corrosion resistance,
- Reduced friction,
- Proper mechanical properties, such as elasticity and hardness.

Corrosion Performance

A target of current PVD developments is to reach a corrosion performance identical or better than 20 µm of hard chromium with PVD coatings at considerably lower thicknesses.

Figure 1 shows recent results of unbalanced magnetron deposited CrN for various substrate bias voltages in comparison with 25 µm hard chromium.[7]

The figure demonstrates that 25 µm of hard chromium has better corrosion resistance than thinner PVD coatings. By tuning the deposition parameters such as bias voltage, however, a considerable improvement can be achieved.

Further developments are under way for multilayers. Promising are multilayers of CrN/NbN, such as those discussed by Munz, *et al*.[8] For these coatings, similar corrosion resistance to hard chromium is achieved for much smaller thicknesses.

Combinations of hard and soft coatings show a big improvement in molding applications. In Fig. 2, a comparison is given between performance of plastic injection molds coating with CrN and coating with CrN/MoS_2. The sticking forces are considerably reduced, resulting in lower ejection forces and, more importantly, better surface quality of ABS parts. The coating structure is shown in Fig. 3.

Further improvements are expected for multilayers. Combination layers of transition metals such as Ti, Cr and W with MoS_2 have demonstrated that the low friction coefficient of MoS_2 can be attained, but mechanical properties, such as hardness, maximum allowable shear stress and environmental stability, were considerably improved.[9]

PVD Equipment Developments

The development of PVD coating equipment has resulted in a number of improvements, such as:

- Good equipment reliability, uptimes over 95% are routinely achieved.
- Reproduction of coating processes.
- Sophisticated multilayers with individual thicknesses of 2 µm are possible.
- Reject levels acceptable for the automotive industry have been achieved.
- PVD coating cost price has been decreased by an order of magnitude.

In Fig. 4, the PVD coating cost price is shown for a typical 2 µm CrN coating. For the calculations, it is assumed that the coating volume fills the capacity of that one typical PVD machine. The price decrease can be attributed to a combination of matters, such as:

- Availability of much larger equipment
- Shorter cycle times
- Utilization of large magnetron sources

The cost price can come down further, provided that product quantities are sufficiently high to fully utilize large, dedicated equipment.

Conclusion

Applications of PVD coatings for parts traditionally coated with hard chromium is still a small activity as compared with electroplated hard chromium.

For specific applications requiring not only a hard and corrosion-resistant surface but also a low friction, however, PVD coatings are now replacing hard chromium routinely. It is expected that the coating performance will increase with a resultant decrease in the cost price. As a result, future growth is expected in applications where PVD will replace hard chromium. P&SF

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