CHAPTER

14

Surface Engineering and Micro-Manufacturing

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INTRODUCTION

Surface Engineering

Advanced surface technology or surface engineering is a key knowledge-based sector of great relevance for several manufacturing processes and consumer goods production. Surface engineering encompasses those technologies capable of modifying the surfaces of solids to provide them with superior performance or new functionalities.

During recent decades, part of the surface engineering sector has been devoted to the protection of the surfaces of manufacturing tools and industrial components working under severe conditions of friction, wear, oxidation or corrosion. These phenomena are usually considered as catalysts of surface degradation, and yearly they cause huge production costs mainly related to tool reshaping or replacement, as well as component rejection. It is estimated that, in developed economies, surface degradation might cause losses of up to 4% of the GDP. For the USA these features represent approximately $280 billion/year. Moreover, other studies estimate that in Germany alone, the consumption of oil-derived lubricants for wear prevention represents up to $1–2 billion/year [1] for manufacturing industries. Additional costs related to surface protection are those caused by the generation of residues derived from galvanic techniques (e.g. hexavalent chromium).

Surface engineering is facing new and exciting challenges from the advent of micro- and nano-manufacturing technologies (MNT), and surface modification processes will have a major role in enabling the industrialization of several technologies in the near future, such as micro-forming, micro-machining, or micro-nano-texturing. Moreover, new and emerging technologies need to find novel functional surfaces which could introduce new products able to outperform those already existing from classical concepts. Some examples are: (1) bio-materials, which require advanced techniques for surface bio-functionalization; or (2) renewable energy, through the engineering of functional membranes and other functional coatings for H_2 fuel cells.

Surface Contact Phenomena and Tribology

The study of tribology (friction, wear and lubrication) is a major, ongoing, priority for every manufacturing process. In fact, it is generally accepted in mechanical engineering that numerous failure cases in manufacturing are related to these surface-degradation mechanisms. Tribology addresses the contact interactions between two surfaces in relative motion, and the physical-chemical response of such surfaces against the degrading action of the environment. A deep knowledge of the basic mechanisms of friction, wear and lubrication is a major requirement to better understanding of the benefits of surface engineering and its role in improving the surface performance of tools and components. There exists an extensive amount of literature about tribology in general [2–3], and tribology in micro-manufacturing processes in particular [4–5]. A detailed revision over these studies and the reference therein will provide the reader with a better insight about surface-related failure mechanisms in manufacturing and the strategies for their prevention.

Characterization Techniques

Understanding the principles of surface functionalities and the strategies for their modification requires the utilization of purposely designed advanced characterization techniques. In fact, a good background on surface characterization enables mechanical engineers to better solve surface-related problems during prototype design, simulation or process testing. In the specific case of manufacturing tools and component surface protection, the related characterization techniques focus on the chemical composition, the mechanical properties (hardness, fracture toughness, coefficient of friction, wear rate), the thermal-chemical stability (oxidation, corrosion) and the surface topography (roughness, texturing). It is noteworthy to remark that several of the existing characterization techniques are today approved as validation standards under national and international standardization agencies, e.g. the American Society for Testing and Materials (ASTM) and the International Standards Organization (ISO) (www.astm.com and www.iso.org, respectively).

This chapter aims to provide the reader with a general and concise overview of the *surface engineering* field and its relevance for micro-manufacturing. In the first section, the fundamentals of the most extended advanced techniques for surface modification will be addressed, with special focus on those technologies which, due to their specific characteristics, might be more applicable in micro-manufacturing. The last section addresses different case studies where surface engineering plays a decisive role.

FUNDAMENTALS OF ADVANCED SURFACE ENGINEERING PROCESSES FOR TOOLING PROTECTION

In this section, different advanced surface modification processes for tooling protection will be overviewed. Surface protection technologies have been developed during recent years in order to accomplish optimal material protection, depending on the environment, the working conditions, and the compatibility between the treatment itself and the substrate material. There exists a large variety of surface treatment techniques which have demonstrated their performance for surface protection or other functionalization purposes, and therefore they are already implemented at industrial scale. In general terms, all surface treatments can be classified within three main categories: *physical–chemical functionalization*, *mechanical-structural functionalization*, and *surface coating*, as illustrated in Figs. 14-1.

In the case of micro-manufacturing, tools of sub-millimeter dimensions exhibit special features which limit the applicability of several of these techniques for surface protection. For instance, surface techniques must in this case prevent changes of the net-shape of a tool which could reduce its performance or precision. Analogously, treatments carried out at excessive temperatures might degrade the bulk mechanical properties of the tool. In this context, this section presents a series of particular techniques which have proven their effectiveness in protecting small-size manufacturing tools. These techniques are framed within the groups of *physical–chemical functionalization*, including gas and plasma nitriding, ion implantation, and *coating techniques*, including electro-deposition, chemical vapor deposition (CVD), and physical vapor deposition (PVD).

Physical–Chemical Functionalization I: Thermal and Plasma Nitriding

Nitriding is a surface technique to harden the surfaces of several types of cold- and hot-work steels for forming operations. Metal nitriding is a high

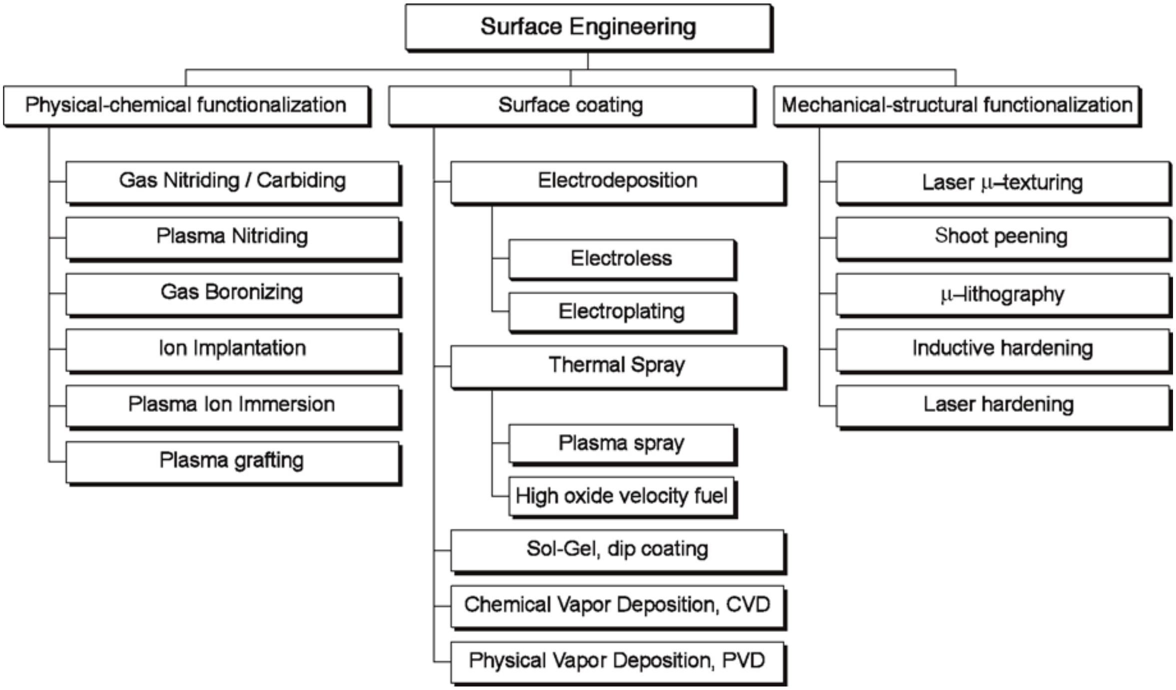


FIGURE 14-1 Classification of surface modification techniques in terms of: physical–chemical functionalization, surface coating and mechanical–structural functionalization.

temperature surface treatment based on the incorporation of nitrogen species into metallic surfaces by different mechanisms of *thermal diffusion* or *plasma-activated thermal diffusion*. The nitrogen diffusion process in steels has two main effects. On the one hand, it induces the formation of a shallow layer (2–5 microns thick) containing hard metal nitrides such as Al-N, V-N or Cr-N. The formation of small precipitates of these nitrides provides high alloyed steels with high hardness and toughness. On the other hand, nitriding produces the so-called *diffusion layer* (10–100 microns thick) in which nitrogen atoms occupy interstitial sites in the crystalline lattice of the host metal, producing an

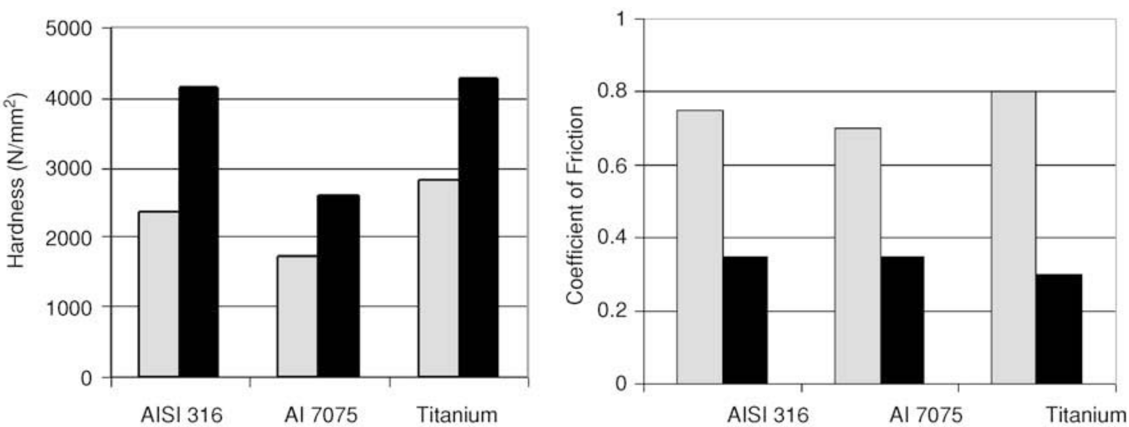


FIGURE 14-2 (left) Universal hardness. (right) COF of three different metallic compounds AISI316, Al 7075 and titanium before (gray) and after (black) nitrogen ion implantation treatment [1].

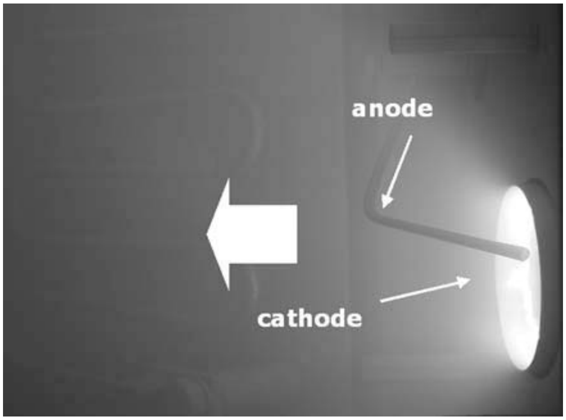


FIGURE 14-3 The reactive cathodic arc discharge PVD working. The anode tip is a high temperature resistance metal alloy rod located near the surface of the target (glowing part of the photograph). The presence of ionized nitrogen provokes the red-like glow. The arrow indicates the vapor stream direction from the cathode.

induced lattice-expansion effect. This expansion is well reported to cause compressive stresses, which leads to superior toughness and wear resistance properties. These effects have already been observed in different metallic alloys such as AISI H11-13 series steels [6], AISI-316L[7], Ti4Al6V [8], V5Ti[9] and others. The nitriding of steels often forms a shallow overlayer of iron nitrides (ε-$Fe_{2,3}N$, γ-Fe_4N, typically), denoted as *white layer*. It is usually recommended to remove such films by mechanical means (sand blasting, polishing) due to their brittleness, which can induce catastrophic crack propagation into the bulk component under normal or shear overloading.

Thermal nitriding of tool steels requires temperatures above 500°C and the use of reactive nitriding precursors such as pure N_2 or NH_3. Additionally, processing times could be of the order of 1–2 days to achieve a diffusion layer thickness of some hundreds of microns. The plasma activation permits the nitriding of tool steels at slightly lower processing temperatures (i.e. 400–500°C) due to the larger reactivity of the ionized gases to penetrate the surface-to-bulk barrier of the material.

Physical–Chemical Functionalization II: Ion Implantation

Ion implantation is a surface bombardment treatment widely implemented for tribological applications as well as for other technologies requiring special surface functionalities (e.g. microelectronics, optics, bio-materials). The technique consists of the bombardment of ionized species and their implantation into the first atomic layers of a solid. Ion implantation essentially requires an ion-generation source, an electrostatic acceleration system, and a vacuum chamber for the target housing. Ions are generated by physical means in a discharge chamber, using precursors appropriately converted to the vapor phase. There exist two main operative modes of ion implantation: *charge/mass selective mode* and *linear acceleration mode*. In *charge/mass selective mode*, the ionized species are pre-accelerated until they reach a quadrupole magnet working as a charge/mass ion filter. The filtered beam is then post-accelerated and focused onto the target component. In the *linear acceleration mode*, all ionized species produced in the discharge chamber will be accelerated towards the target component. This latter implantation mode is less accurate, as the generated beam may contain some impurities from the different process stages.

The implantation process does not modify the net-shape of sharp-edged tool features. On the other hand, ion implantation is a *line-of-sight* technique, meaning that all surfaces under treatment need to be directly exposed to the ion beam, which restricts the applicability of the technique to non-complex surface geometries. To overcome this feature, new sources of plasma immersion ion implantation (PIII) are being successfully developed. This technique allows the high energy bombardment of inhomogeneous surfaces with a variety of ionized atomic species.

For hardness-enhancement purposes on metallurgical components, nitrogen ion implantation has been found the most universal solution at industrial scale. Implanted nitrogen species (typically, N_2^+ and N^+) on transition metal surfaces form nitride phases that increase the hardness and toughness of the targeted surfaces. Some examples of hardness and coefficient of friction measurement of Aluminium Titanium an AISI 316 after Nitrogen ion implantations are depicted in Figure 14-2. In addition, implanted nitrogen induces crystalline lattice expansion at the surface of the bombarded metals. This effect is usually observable by the appearance of new diffraction peaks shifted to lower diffraction angles with respect to those of the original lattice structure. This lattice distortion provokes high compressive stress of the implanted surfaces and hence increases the hardness and toughness.

Nitrogen ion implantation increases the surface hardness of several alloyed steels, titanium or aluminum alloys [10] or even some thermoplastics such as polyethylene [11] (PE) and polycarbonate (PC). Moreover, the hardness of Ni alloys can also be increased by the implantation of metal species such as Cr, Ti or Al. Finally, the corrosion protection of some alloys is improved upon gaseous and light atomic weight metals implantation.

Coating Techniques I: Electro-deposition

Electro-deposition is a well-implemented technology in the surface treatment sector for its relatively easy installation and high performance. The technique is based on the chemical reduction of metallic precursors and the precipitation of a solid thin film onto the cathode (component) by either galvanic-induced (*electroplating*) or self-catalytic processes (*electroless*). The electroless process exhibits lower deposition rates than electroplating. Conversely, electroless coatings show larger homogeneity than electro-deposited films due to the absence of electric field lines during the process. The deposition parameters which drive the properties of electro-deposited coatings are: the electrolyte composition and its chemical stability, the deposition speed, and the surface geometry of the substrates. Hard-chromium, nickel, copper and zinc are typical materials deposited by electro-deposition methods for tooling and component protection.

Hard-chromium, produced by the galvanic reaction of CrO_3, H_2SO_4 in the presence of catalyst compounds which produce a metal Cr precipitation, leads to the formation of highly compact, porous-free films exhibiting high hardness and low COF. Hard-chromium exhibits excellent wear resistance against abrasion and a very low adhesive COF. Nickel is also a widely utilized coating for tooling and component surface protection against wear and corrosion that can be precipitated by electroplating and electroless methods. Nickel is additionally used as a base material for electro-formed tools, e.g. micro-embossing or micro-plastic injection molds. Ni-electroplated films show high hardness (see Table 14-1) and low COF, achieving efficient anti-wear properties. Moreover, this material shows excellent protection against corrosion.

Electroless nickel-M (where M can be an atomic, molecular or micro-particle additive) might show excellent anti-wear properties and low COFs. Ni-phosphor and Ni-boron exhibit a hardness between 500 HV and 1300 HV. Ni-Teflon (Ni-PTFE) exhibits a very low COF in combination with hardness values of around 500 HV.

Coating Techniques II: Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a vacuum-plating technique by the precipitation reactions of gaseous precursors onto a given surface. Depending on the temperature and the presence or absence of plasma assisting processes, CVD can be classified into *thermal CVD* and *plasma-assisted CVD* (PACVD).

In thermal CVD, the surfaces should be kept to temperatures of between 800°C and 1000°C,

TABLE 14-1 Vickers Hardness and COF for Different Electroplated Engineered Coatings

Coating	Hardness HV	COF*
Hard – chromium	1300–1500	0.15–0.25
Ni – electroplated	200–500	0.15–0.3
Electroless Ni	800–800	0.2–0.3
Ni-B	1300–1400	0.08–0.2
Ni-P	500–700	0.08–0.2
Ni-PTFE	400–500	0.05–0.1
Ni-W	900–1000	0.15–0.3

*COFs measured against chromium steels, using a ball-on-disc configuration.

hence limiting the type of materials suitable to be coated by this technique due to thermal-degradation effects. In fact, the high temperatures reached during CVD cycles often produce size distortions of the tools. A typical thickness of thermal CVD coatings for tooling protection could vary between 5 and 20 microns depending on the specific application and nature of the deposited material. Thermal CVD films exhibit very high adhesion strength, due to temperature-induced atomic diffusion at the coating/substrate interfaces. This fact converts thermal CVD into a recommended technique to be applied to tools subjected to strong normal and shear forces (cold/hot forging, metal forming). In addition, CVD coatings show low residual stresses and hence greater toughness and fatigue resistance.

The most commonly utilized coating materials for tooling protection are titanium nitride (TiN), titanium carbon nitride (TiCN), and chromium nitride (CrN). Other transition metal carbon nitrides such as hafnium or vanadium can be deposited by CVD, showing a good combination of hardness and low COF.

An alternative to thermal CVD is the plasma activation of the precursor gases, which can promote precipitation of dense thin films, even at deposition temperatures as low as 200–300°C, which limits the size distortion effects on steel tools. These processes are named *plasma activated CVD* (PACVD) [12], and represent a feasible alternative to deposit films onto a larger variety of substrate material. Other CVD activating processes can be found in the literature, such as hot-filament assisted CVD, hollow cathode CVD or microwave RF plasma-assisted CVD.

CVD is a well-implemented coating technique to deposit low friction carbon-based films containing different ratios of sp^3–sp^2 carbon-carbon bonds [13]. Highly containing sp^3 carbon films exhibit hardness values close to those of natural diamond, although they show a high tendency to brittleness and are difficult to implement in the form of thin films. Diamond-like carbon films (DLC) constitute a valid alternative as a protective coating due to their low COFs (as low as 0.1 against bearing steels) and high hardness (1500–3000 HV). DLC can be deposited even at relatively low temperatures of around 300°C with high adhesive strength using adequate bonding layers. Presently, silicon-based films produced by PACVD are pre-deposited to enhance the adhesion of DLCs on steel and hard-metal substrates.

Coating Techniques III: Physical Vapor Deposition

Physical vapor deposition (PVD) is a high vacuum coating technique used for tooling protection as well as for several technological applications (optics, photovoltaic conversion, decorative). PVD deposition is the result of producing a vapor stream in-vacuum from a solid material (usually named the *target*) by physical means (arc discharge, sputtering, heat transfer by laser or electron beams, etc). *Cathodic arc evaporation* (CAE), *magnetron sputtering* (MS) and *electron beam* (EB) at the present time constitute the core group of PVD techniques for industrial tooling protection. In fact, there exists a great variety of PVD techniques, but those of the core group alone share more than 95% of the PVD market, in terms of both equipment sales and services.

Cathodic arc evaporation (CAE) sources are probably the most widely utilized technique for industrial tooling protection. In CAE, a high electron current density is discharged onto a target material, producing a fast evaporation rate at its surface. The energy dissipated during the process sprays the evaporated atoms towards the substrate at energies of tens to some hundreds of eV (refer to Fig. 14-3). This feature, and the high ionization produced during the electron discharge (up to 90% of the evaporated species), produce uniform and dense films, with compressive residual stresses. The deposition of metal compound films can be obtained by introducing reactive gases such as N_2, O_2 or C_2H_2 during the discharge process.

Part of the energy dissipated on the target surface during CAE is able to produce micro-sized particles (*micro-droplets*) that can also be sprayed towards the substrate. In general, these micro-droplets are barely detrimental for conventional machining tools provided the net-shape of cutting edges remains unchanged upon deposition. The presence of these micro-particles, however, can be strongly detrimental for precision tools. In these cases, a surface repolishing process needs to be performed after a PVD CAE treatment. To avoid an excessive deposition of micro-particles, different arc sources design strategies are in use, such as the *lateral arc rotating cathode* (LARC) configuration, or the filtered arc.

Magnetron sputtering sources are based on the confinement of a low pressure plasma around an evaporation target by an appropriate configuration of static or alternating electric/magnetic fields. The confined plasma bombards the target material, producing the sputtering of atoms from the target towards the substrate. The energy of the sputtered atoms is usually not greater than a few eV, and their ionization rate is generally poor (below 5% of the total sputtered atoms). Both factors, low ionization and energy, make necessary the post-ionization and acceleration of the sputtered species in order to achieve sufficient impact energy during the deposition process. This can be accomplished by polarizing the substrate with a negative potential (bias potential) of some tens of volts. Under these conditions, the deposition of sputtered atoms is produced simultaneously to the bombardment of ionized inert species (typically Ar ions) onto the growing film. This combined process, so-called *ion beam assisted deposition* (IBAD), provides sufficient energy per arriving atom to form dense and well-adhered films. The ionization and energy of the sputtered atoms can also be increased using high power impulse magnetron sources (HIPIMS) [14]. HIPIMS utilizes high energetic electromagnetic mega-watts/cm^2 millisecond pulses during the sputtering process to achieve ionization rates of almost 100% of the depositing species.

Sputtering techniques are able to deposit *low friction* coatings or *solid lubricant*. This family gathers the Me:C [15] coatings, where Me is a metal and :C represent a variety of carbonaceous phases present in the film. In addition, MoS_2 or WS_2 low COF films can also be deposited in the form of thin film by sputtering techniques (see Table 14-2).

Electron beam evaporation is based on the heat generated in a target material by the bombardment of an electron beam onto its surface. The technique retains the same principles as that of CAE and sputtering, in terms of vacuum process, coating thickness, reactive deposition, etc. Electron beam deposition is, in addition, currently used in industrial applications due the surface finish properties achieved, along with good mechanical properties, such as those presented in Table 14-2. Plasma activation systems of the vapor stream are reported to contribute to the achievement of dense film growth, increasing hardness and toughness properties. A scheme of a *hollow cathode arc activated deposition* (HAD) is shown in Figs. 14-4, the trajectory of the electron beam from the source to the target, and the

TABLE 14-2 Deposition Parameters and Properties of Common PVD Coating Materials for Mechanical Engineering Applications

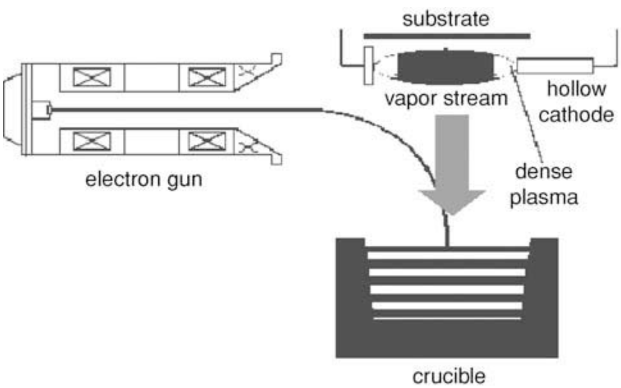
Coating	PVD Process*			Processing T°C	Hardness (GPa)	COF (ASTM G99-5)	Max Working T°C
	CA	EB	MS				
TiN	x	x	x	450–550	20–25	0.6–0.8	500
TiCN	x	x	x	450–550	25–30	0.3–0.5	300
TiAlN	x	x	x	450–550	25–30	0.6–0.8	500–700
AlTiN	x	x	x	450–550	30–35	0.6–0.8	600–800
nc-AlSiTiN**	x		x	450–550	35–40	0.6–0.8	800–1000
CrN	x	x	x	200–500	18–22	0.6–0.8	600–800
ZrN	x		x	450–550	25–28	0.5–0.7	400–500
WC/C			x	200–250	10–15	0.2–0.4	200–250
MoS_2			x		10–15	0.1–0.3	200–300
DLC***			x	200–300	10–40	0.1–0.2	200–300

*CA = cathodic arc-discharge; E-B = electron beam evaporation; MS = magnetron sputtering. **nc denotes a nano-composite phases, as produced by *Spinodal* decompositions of non-soluble phases.
***In the case of DLCs there is a large dispersion of results derived from the sp^3/sp^2 bonding relations.

plasma activation area, are indicated on the right of this figure.

The main application of PVD coating for mechanical engineering is in machining/cutting tooling protection against wear and oxidation, this application representing almost 70% of all coating services worldwide. Forming tools, steel stamping dies, injection molds, cold- and hot-forging dies constitute another important niche sector for PVD. Finally, a smaller ratio of the PVD market is devoted to solid lubricious films, especially for the protection of bearing parts in machines or engines.

The most common industrial PVD coatings for anti-wear purposes are TiN, TiCN, AlTiN, and CrN, all deposited at processing temperatures of between 450 and 550°C, in the presence of



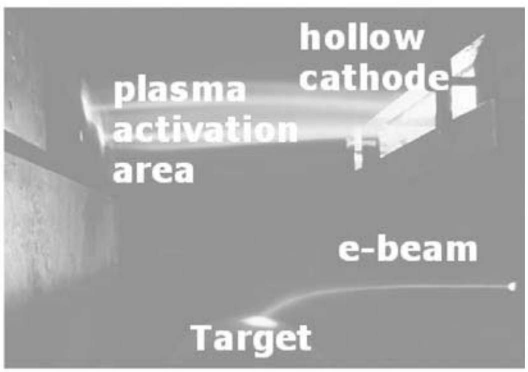


FIGURE 14-4 (right) Schematic representation of the hollow cathode arc activated electron beam deposition. (left) Picture of the running process (courtesy of Dr C. Metzner, Fraunhofer Institute for Electron Beam and Plasma Technologies).

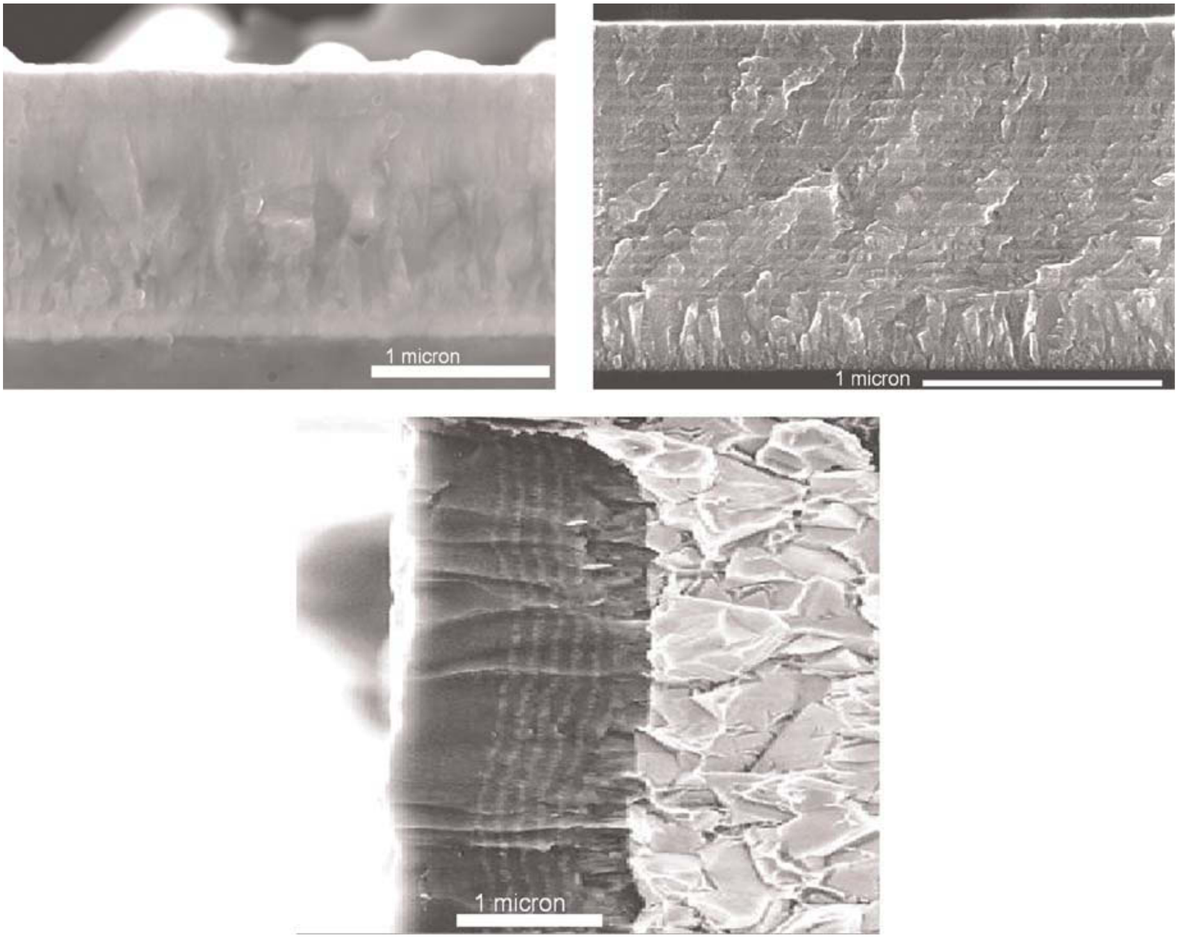


FIGURE 14-5 Different multi-layer structures developed at AIN Surface Engineering Centre using the cathodic arc PVD technique. (left) Gradient CrCN, (center) damping coating AlTiN, (right) nano multi layer TiN/CrN ($\lambda \sim 40$ nm).

gaseous precursors, N_2, O_2 or hydrocarbons (see Table 14-2). The deposition temperatures are in general compatible with those in the tempering of tool steels (HSS, cold- and hot-work steels, etc.). Powder-metallurgical tool steels additionally exhibit an excellent support to PVD hard coatings. Analogously, sintered hard-metal cutting tools show excellent load support and adhesive strength for PVD hard coatings.

Titanium nitride (TiN) [16] is the most commonly used coating for cutting and forming tools due to its high hardness, low friction coefficient and toughness. Additionally, its golden-like color makes TiN a suitable film for decoration/protection in household items and other consumer goods. Titanium carbon nitride (TiCN) shows a higher hardness and lower COF than TiN [17–18], but reduced thermal stability. In fact, this coating requires oil lubrication, especially during high speed machining operations, to avoid its premature oxidation by overheating. Aluminum titanium nitride (AlTiN) coatings [19] were implemented for industrial products in the 1990s and are used widely at the present time for high speed and dry-machining tools due to their high hardness (greater than that of TiN) and elevated thermal stability. Chromium nitride (CrN) [20] shows inferior hardness to that of TiN but very low adhesive COF, permitting its application in plastic injection molding and other forming operations where galling needs to be attenuated. This is due to the low tendency of CrN to stick to the working material during processes requiring high contact stresses at the tool/material interface. At present, recently developed CrCN [21] coatings are found to exhibit even lower adhesive COF to those of CrN when sliding on stainless steels. Zirconium nitride (ZrN) exhibits a similar hardness to that of CrN and has a very low affinity for aluminum. This characteristics enables ZrN to be a recommended coating for Al-transformation dies (extrusion, injection), as well as for the machining of non-ferrous alloys. Analogously to TiN, its brass-like color enables ZrN to be used as a decorative coating. Finally, the family of solid lubricious coatings WC-C [22–23] or MoS_2 [24] is utilized on bearing parts, as these are usually not subjected to excessively high temperatures.

PVD permits the design of a variety of film architectures with the aim to outperform the protective characteristics of single-layer configurations. Figures 14-5 show different multilayer structures developed at AIN Surf. Eng Center using the cathodie are PVD technique. A common strategy to enhance the mechanical performance of PVD films is the design of load-adaptive layers [25]. Gradient composition films containing a hard layer at the interface and a low COF outer layer is a well-developed solution for several applications in the manufacturing sector [24]. A hard nitrided layer by nitriding processes can be an excellent load support surface for a PVD coating [26–28] (duplex processes).

Nanometer scale thin films are postulated [29]. Nano-multilayered coatings made of two different compounds (usually hard ceramic-ceramic or metal-ceramic) are found to exhibit the highest hardness/toughness when the nominal bi-layer thickness ranges between 10 and 15 nm.

The deposition of immiscible phases in the form of thin film can lead to the formation of finely grained coatings (denoted as *nano-composites*). This variety of coatings shows superior values of hardness and toughness than the characteristics of their single counter-phases. It is commonly found that the incorporation of silicon in TiN [30–31], or AlTiN films [32], in quantities of around 8–10 at.%, increase their hardness values by a factor of 1.5 to 2. In addition, (Al,Si)TiN nano-composites retain their mechanical properties even after annealing temperatures of above 800–900°C [33]. These outstanding properties have allowed these nano-composites to be utilized for the high speed and dry cutting of difficult-to-machine materials.

APPLICATIONS OF SURFACE-ENGINEERING PROCESSES IN MICRO-MANUFACTURING

Advanced Surface Treatments for Micro-cutting Tools

As addressed in this chapter, micro-cutting technologies are one of the most important pillars of micro-manufacturing. With regards to tool design and development, strong efforts are being focused on the investigation of new materials and design concepts [34–37]. Nevertheless, few studies focus specifically on the problem of tool surface wear, which to some extent constitutes one of the main degradation mechanisms at this scale.

Some attempts to protect diamond tools have been made using DLC films deposited by CVD methods. DLC films were tested on diamond-based micro-cutting tools with different grain refinement, from coarse- to fine-grained structures [38]. Figure 14-6 compares the appearance of the drill point for two different cases: (a) DLC on coarse-grain diamond after 1800 holes had been processed; (b) DLC on fine crystal diamond after 15,500 holes had been processed. The results provide evidence that a DLC coating deposited on fine-grained diamond single-crystal end-mills enhances the cutting performance of the system.

Yao et al. [39] investigated the wear properties and drilling precision of PVD-coated metal carbide micro-drilling tools. In particular, two different coating architectures were investigated: single hard TiN, and nano-multi-layered hard TiN/AlN coatings. The two architectures revealed different anti-wear performances under the same working conditions. The TiN/AlN nano-multi-layer exhibited greater protection against wear on both the

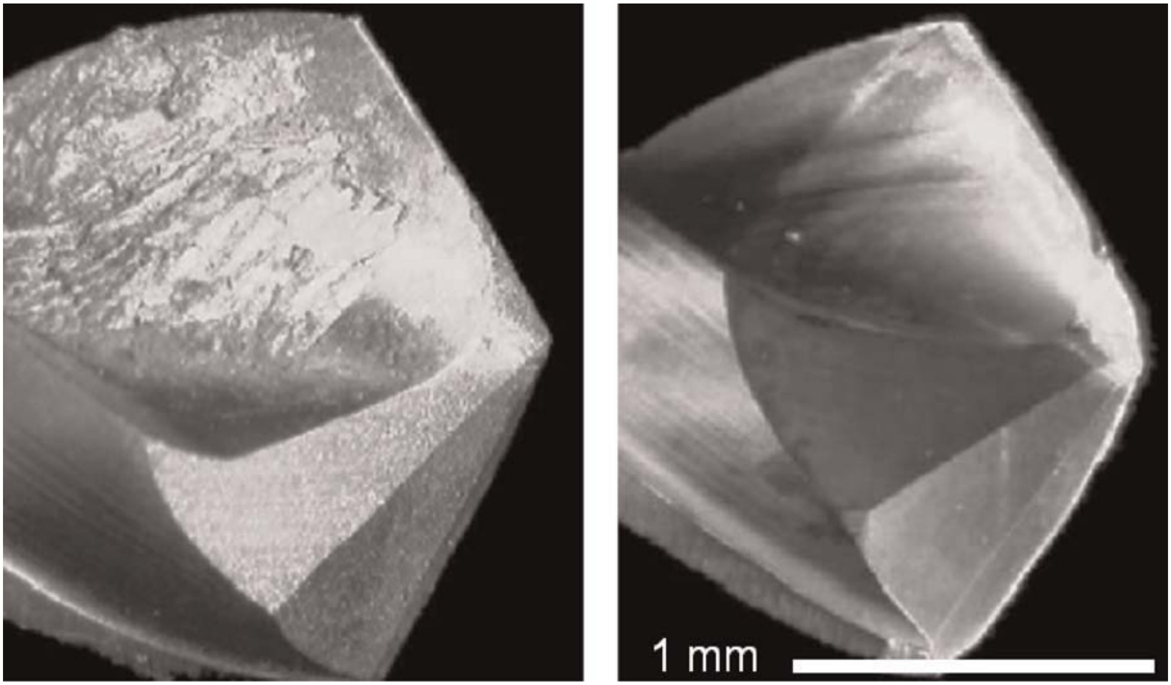


FIGURE 14-6 The appearance of drill points (width of chamfer 0.05 mm) ((a) DLC coated on coarse grain diamond after 1800 holes processed, and (b) DLC coated on fine crystal diamond after 15,500 holes processed).

tool flank and the rake faces than those shown by TiN films in the single layer configuration, as depicted in Fig. 14-7(a)–(d). Single TiN layers on the tool flank often tend to fail due to both the abrasion by hard particles and the accumulation of compressive stresses which originate from coating delamination.

Alternatively, nano-multi-layered TiAlN/TiN-coated carbide end-mills were found to outperform a single TiAlN coating, during the cutting of Cr-Mo alloyed steels. In this study, different wear mechanisms were reported, depending on the cutting speed. At low cutting speed, built-up edge (BUE) formation was identified, caused by pressure-induced welding. High cutting speeds increased the temperatures at the contact zone, resulting in the diffusion of oxygen and enhancing the oxidation of the tool surface. It was observed that a metal-nitride PVD coating prevented both premature BUE and oxidation of the tool edge under low and high cutting speed respectively [40]. Additional studies were reported on the cutting performance of different magnetron sputtering-coated carbide precision tools in terms of the flank wear resistance.

Multilayered Cr/TiAlN and Mo-doped CrTiAlN coatings as deposited by magnetron sputtering exhibited the lowest flank wear rate during the micro-cutting of NiCrMoV alloyed steels, and CrCo alloys. The low wear rate obtained by these coated tools was attributed to the magnetic field configuration utilized for their deposition process, the so-called *close-field unbalanced magnetron sputtering* [41]. Analogously, the coating thickness distribution between the tool rake and the flank faces was considered to have a significant influence on the cutting performance of carbide micro-end-mills [42]. More specifically, a lesser coating thickness on the tool rake with respect to the tool flank strongly diminishes the performance of the whole system due to uneven heat dissipation. In fact, when the coating on the rake is totally worn off during cutting, the tool base metal might come into contact with the working material, thereby increasing the COF and hence producing overheating at the tool/material interface. Thus thermal energy cannot be dissipated

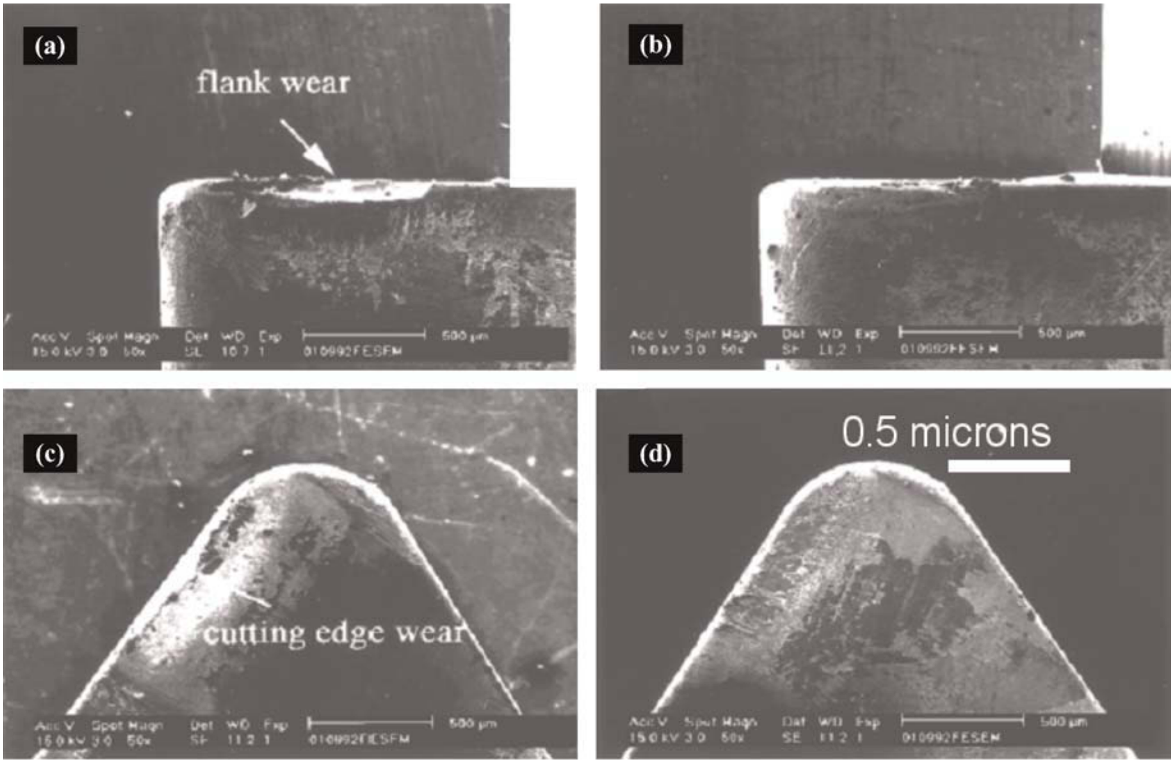


FIGURE 14-7 SEM wear morphology images of hard metal cutting tools with different coatings after running tests: flank wear for (a) single-TiN layer and (b) nano-multi-layer TiN/AlN film, and edge wear for (c) single-TiN layer and (d) nano-multi-layer TiN/AlN film.

out of the tool due to the thermal-barrier effect of the remaining unworn coating at the flank, causing rapid tool degradation. The optimal situation was identified when the coating thickness distribution was similar on the tool rake and the tool flank.

A new generation of nano-structured PVD coatings was attempted in micro-end-mills for hardened steel precision cutting. Figure 14-8(a)–(b) shows SEM pictures of a PVD-coated micro-tool (coating trade name nACRO®): (a) as coated and (b) after 14,000 holes had been drilled on PCB plates. The tool-blank total wear during the drilling tests for uncoated, PVD-nACO® coated and PVD-nACRO® coated is presented in Fig. 14.8 (c) in the form of blank diameter evolution as a function of the number of drillings. The horizontal line represents the size tolerance of the tool. Figure 14.8(c) shows how the wear rates of PVD coated micro-drills decrease significantly with respect to those of uncoated tools. Thus, whereas uncoated tool blank wear reaches the size tolerance limit after 5000 drillings, nACO- and nACRO-coated tools reached the size tolerance limit after a number of drillings of around 10,000 and 15,000, respectively, indicating an increase of tool life by a factor of 3 with respect to that of untreated tools (courtesy of Metalestalki – PLATIT ACS Ltd).

Anti-adhesion and Wear Resistance Coatings on Micro-molding Tools

The adhesion of the surface-forming materials (plastics, ductile metals, etc.) to the surface of the molding tool during demolding is a common feature in manufacturing which causes several problems of tool adhesive wear and workpiece quality. Additionally, waste production due to

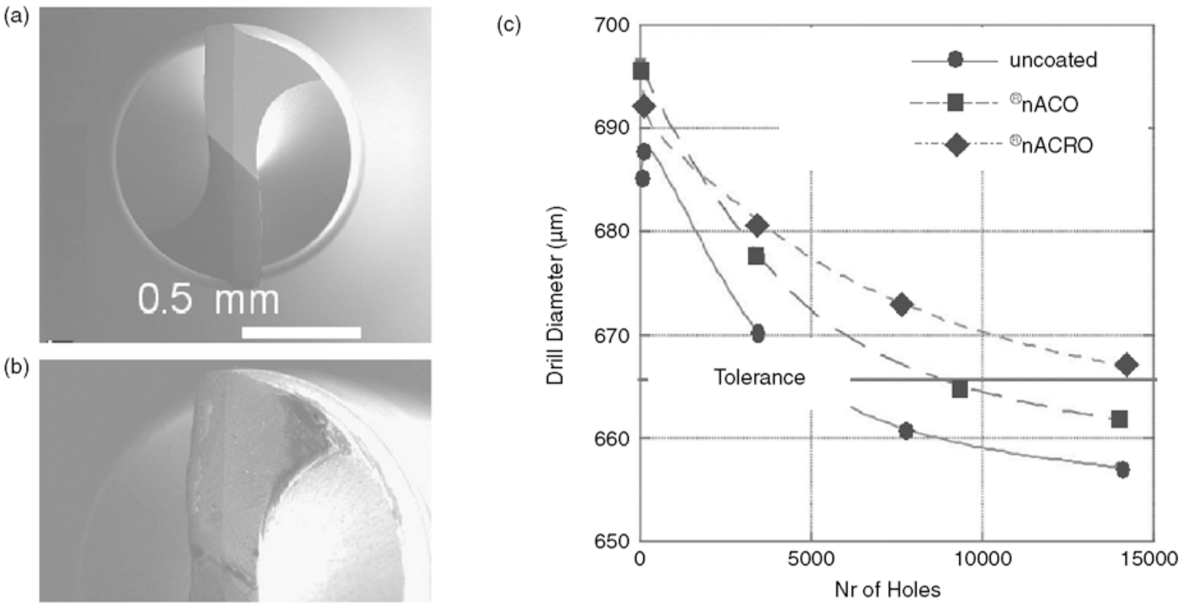


FIGURE 14-8 SEM pictures of a PVD-coated micro-tool blank (coating trade name nACRO®), (a) as coated and (b) after 14,000 drills on PCB plates. Figure 14.8(c) represents the tool wear during the drilling tests for uncoated, PVD-nACO® and PVD-nACRO® in the form of blank diameter, as a function of the number of drills. The horizontal line represents the tolerance of the tool (courtesy of Dr Ibon Azcona, Metalestalki – PLATIT ACS Ltd).

the use of oil lubricants or other wet demolding products is a common drawback associated with this surface-interface problem [43–44].

The reduction of the specific tool/material contact area in sub-millimeter micro-forming processes implies the loss of effective lubrication caused by a small lubricant retention capacity in the so-called closed valleys of the tool surface [5,45–46]. This fact leads sub-millimeter-scale contact interfaces to register COFs of up to one order of magnitude greater with respect to the same interface systems scaled at macroscopic level. Micro-stamping, micro-embossing, and sub-millimeter metal bulk forming are a few examples where a high COF may provoke surface failures during component plastic deformation or workpiece demolding.

Different solutions are currently under development in this area. Polytetrafluoroethylene [47] (PTFE or Teflon) coatings are a standard solution for anti-adhesive purposes in plastic injection molding. Silane and fluorinated silane were proposed as anti-adhesive single films on electroplated Ni micro-featured molds for embossing or imprint operations. Different chemical formulations are able to produce self-assembled monolayers of silane derivatives which exhibit extremely low surface energy, therefore preventing the adhesion of plastic during demolding operations. The mechanical stability of silane-based films can be enhanced by depositing support SiO_2, NiO or TiO_2 films [48–49] by vacuum plasma techniques such as plasma enhanced CVD.

Teflon- or silane-based films, however, have poor mechanical stability and high wear rates, making them unable to support mass production. In order to design mechanically stable surfaces on Ni-based micro-molds, other approaches are required. Ion beam-assisted DLC and SiO_x doped coatings are proposed due to their self-lubricious properties, low surface energy, mechanical stability and mimicking ability to replicate complex surfaces [50].

Chromium nitride-based PVD coatings with different stoichiometries and lattice structures have been investigated for their application in high precision plastic injection molding. It was found that the hexagonal Cr_2N phase deposited by magnetron sputtering exhibited the lowest surface energy among the most common transition metal nitrides [51], and therefore this film is proposed as an anti-adhesive coating for Ni-based micro-embossing tools and other shape micro-replication processes.

Nano-multi-layer coatings TiAlN/ZrN deposited by the magnetron sputtering technique have been applied on silicon micro-featured molds for the production of glass-based optical components. The tested coatings replicated well the original surface micro-pattern of the molds, and exhibited an excellent thermal stability during the stamping of molten glass at 700°C. Additionally, their good anti-oxidation behavior retarded the sticking of glass onto the coated Si molds [52].

Low friction coatings such as MoS_2, amorphous carbon (a-C:H) and WC-C deposited by magnetron sputtering were tested on Ni-electroplated tools providing different wear rates under sliding against steels [53]. In general, low friction coatings improve the wear rate of Ni molds for plastic micro-embossing, imprinting or other surface-replication purposes.

DLC coatings deposited by PECVD techniques were reported to prevent the sticking of aluminum to the surfaces of hard-metal molds during sliding in a ball-on-disc configuration at temperatures of between RT and 150°C [54]. While the sticking of aluminum to the uncoated mold is found to occur at very early stages of the sliding contact, DLC inhibited the galling of aluminum on the surface of the hard-metal tool even for temperatures greater than 120°C.

Me-C:H PVD coatings have been used to enhance the tooling service of EDM-produced micro-compression molds for imprinting applications on aluminum surfaces [55]. Figure 14-9(a) shows an SEM image of a coated compression Ni-based micro-mold containing a series of parallel inserts in the form of cylinders. The applied coating was a hybrid CVD/PVD Ti-C:H film (2.5 microns thick). Figure 14-9(b) shows the imprinted hole produced in a one-step stamping stroke.

The results of the Al-imprinting tests at different temperatures showed that the as-fabricated Ni

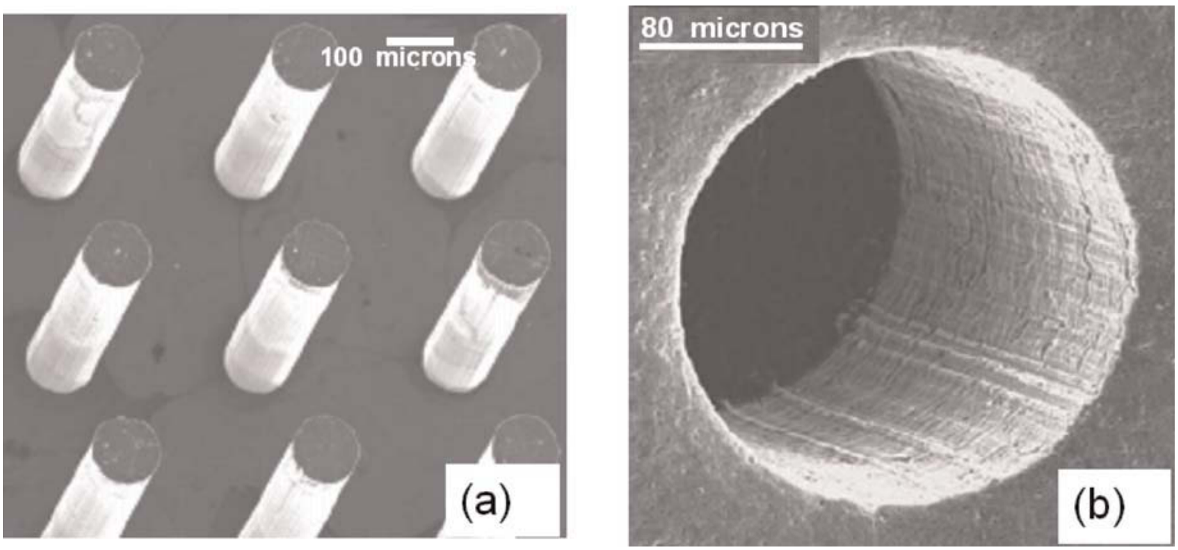


FIGURE 14-9 (a) SEM image of compression Ni micro-molds containing a series of parallel inserts in the form of cylinders, and (b) imprinted hole produced by one-step stamping insert on aluminum plates at 450°C. The inserts are coated with a hybrid CVD/PVD Ti-C:H overlayer (2–3 microns thick).

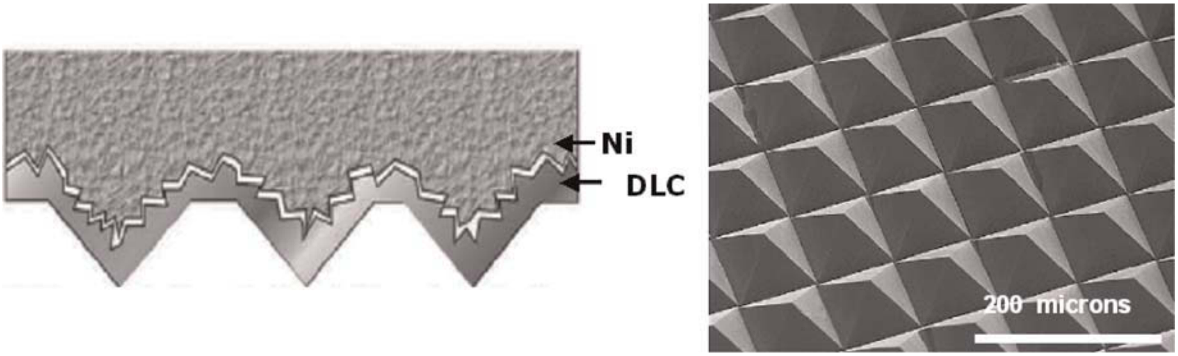


FIGURE 14-10 (top) Scheme of the design of a DLC-deposited Ni mold. (bottom) SEM image of micro-textured molds encompassing a well-defined pattern of indenter pyramids of 100 microns base side (courtesy of U. Petterson et al. Tribology International 39 (2006) 695).

inserts were not suitable for Al micro-molding due to strong abrasive surface wear. On the other hand, Ti-C:H deposition over Ni inserts enabled the Al micro-molding process to be carried out with near 100% shape replication.

Micro-forming Tool Fabrication using Surface-engineering Processes

Micro-manufacturing tool production at large scale represents a technological challenge due to the inherent difficulties found in the replication of sub-millimeter features in a reproducible manner. In this context, the increasing demand for smaller micro-components or micro-patterned surface textures has led researchers to explore new alternatives in the design and production of higher precision tool systems where such precision cannot be achieved by traditional manufacturing processes.

Downscaling traditional tool production methods is a well-known approach to achieve micro-tools, e.g. micro-cutting or micro-erosion by electro-discharge machining (EDM) techniques. However, mechanical removal processes by cutting often cause excessive burr formation, especially when the cutting process is made at sub-millimeter scale. On the other hand, the surface finishing of micro-forming molds as produced by micro-cutting or EDM is often too poor, and usually electro-polishing post-treatments are required. Surface engineering has recently been emerging as a feasible method to fabricate custom-designed ultra-precision tools both for mass manufacturing as well as for flexible production systems.

Surface patterning by photolithography and electro-forming are well-developed techniques within the family of surface engineering. Traditionally employed for the production of plates for ICs, these technologies offer a great potential for the production of ultra-high precision micro-tools, e.g. molds for micro-embossing, micro-stamping, and end-mills for micro-cutting. Moreover, the combination of photolithography, in its different resolution ranges, visible light, UV, or X-ray, with electro-forming is well suited for manufacturing with a high degree of repetitivity and rapidity, thus permitting its scalability to industrial production. As a drawback, photolithography technologies generate large amounts of residuals, which might compromise environmental regulations on waste production. Analogously, electro-forming is limited to a small set of materials, often with low to medium hardness, having high wear rates in some applications. To overcome this problem, further engineered coatings might provide appropriate hardness values in combination with low coefficients of friction.

The production of Ni-based micro-embossing molds by using surface engineering methods [56] has been proposed, in which hard micro-textured DLC deposited Ni plates are produced following a six-step chain according to Fig. 14-10. In steps 1 to 3 a pattern of oxidized Si is produced by photolithography and chemical etching, leaving sharp cavities, of which each shape depends on the different etching speed of each family of crystalline planes. In step 4, the patterned Si surfaces are coated with a DLC hard film of 1–2 microns thickness, the DLC replicating accurately the original texture formed. In step 5, an electro-deposited Ni film of 1 to 2 millimeters thickness is deposited on top of the DLC. Interface-bonding films such as Ti could eventually enhance the adhesion strength between the DLC and the electroplated Ni film. Finally, the Si template is removed, and the Ni surfaces polished, leading to a master DLC-coated Ni-embossing tool.

These prototype embossing masters are successfully applied for texturing purposes on thermoplastics such as polymethylmethacrylate (PMMA), polyethylene-terephthalate (PET) or polystyrene (PS). Additionally, the hardness and toughness provided by the DLC film enables these masters to perform well on certain steels.

Figure 14-11 illustrates the result of stamping the DLC-Ni-embossing tool on steel plates. The grooves imprinted on the steel plates resemble those of a Vickers indenter (Fig. 14-11 left). The presence of prominent ridges is caused by the plastic flow of material during the indentation process. Such ridges are easily eliminated by a smooth polishing (Fig. 14-11 right). On the other hand, industrially scalable molds should eventually work over non-planar surfaces. In consequence, the mechanical performance of the molds depends strongly on the appropriate optimization of the Ni electro-deposition method and the adhesion and mechanical stability of the coating, in order to avoid premature crack failure under tool deflections.

Micro-textured DLC-based films where also produced by plasma-based ion implantation [57]. The procedure encompassed the imprinting of micro-patterns on a sacrificial aluminum foil, which is coated afterwards by a thin DLC coating. The aluminum foil is then eliminated by chemical methods, leaving a free-standing DLC-textured

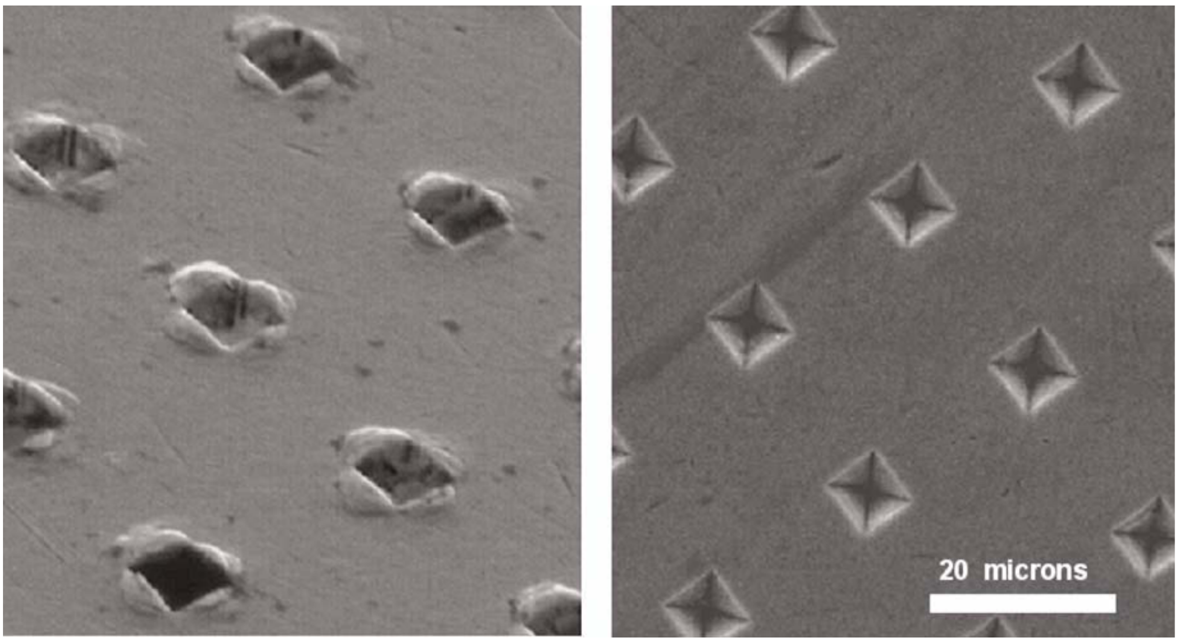


FIGURE 14-11 SEM images of flat steel plate grooves produced by DLC-coated Ni embossing tool molds – (left) ridges caused by the plastic flow of material during the indentation process and (right) ridges can be removed by a smooth polishing process.

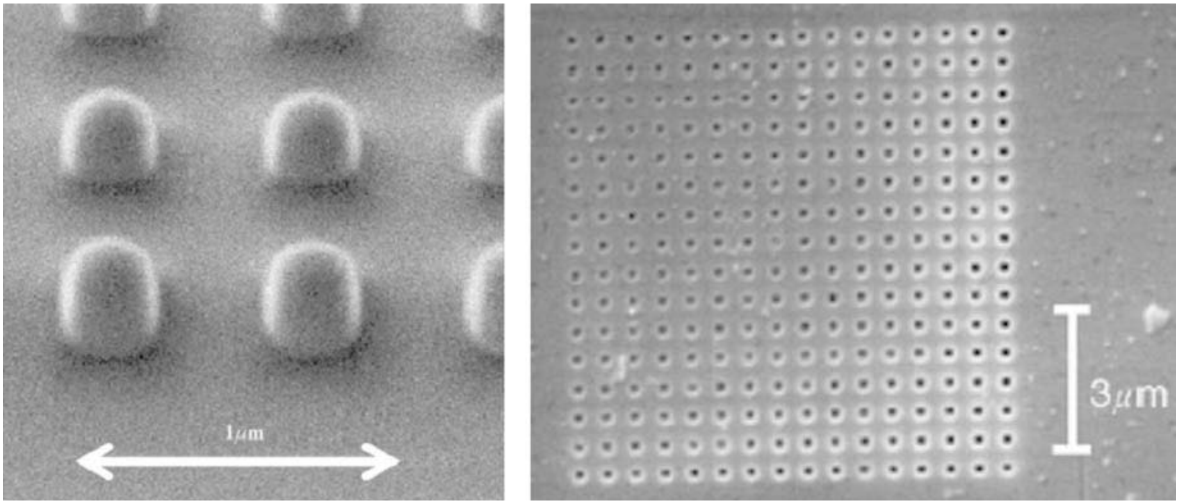


FIGURE 14-12 SEM images of: (left) nano-structured diamond tool produced by FIBs techniques, and (right) imprinted pattern on glass by the prototyped micro-molding tool.

film. The process provides the rapid production of these films, thus enabling mass production upscaling.

Ion beam bombardment methods are under development for the production of extremely fine precision micro-cutting and molding tools. The process of ion beam etching provides excellent precision in the design of micrometer-sharp structures by the so-called focused ion beam (FIB) techniques. Conversely, the process is slow and somewhat expensive as it requires advanced vacuum facilities and ion-acceleration sources, presently available within research laboratories. Ultra-precision diamond micro-shaped end-mills for glass micro-cutting were produced by focused ion beam etching for the prototyping of a new micro-array chip for DNA assembly [58]. Micro-structured glass surfaces were produced using micro-embossing tools previously prototyped by FIB techniques (Fig. 14-12). The textured surfaces provided the micro-array chip with the functional properties required for their performance: low surface energy, low COF, and high transparency.

Micro-featured punches for sheet micro-forming tools have been semi-finished by FIBs methods and finally coated with low friction DLC films deposited using ion beam-assisted deposition [59] (see Fig. 14-13 for 0.15 mm diameter punches, after different ion beam regrinding cycles). Micro-forming tool finishing is a complex process which requires non-conventional polishing techniques, such as electrochemical etching,

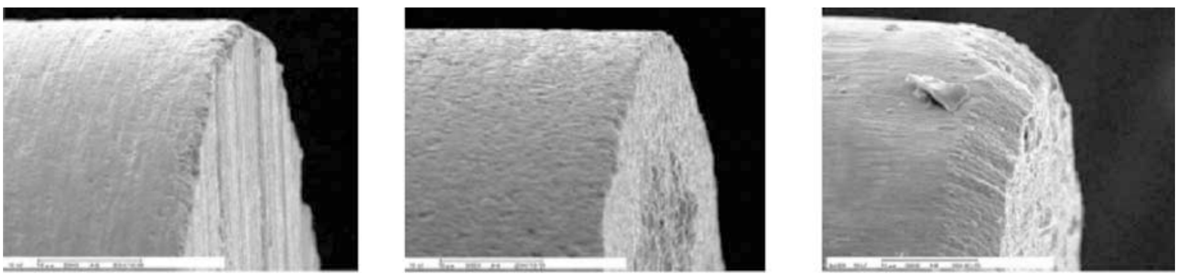


FIGURE 14-13 Surface finish of micro-dies by ion irradiation – (left) before ion irradiation, (center) ion irradiation with 45° beam incidence, and (right) ion irradiation with 10° beam incidence with respect to the tool parallel axis.

which become difficult to control at the micrometer scale, and is strongly dependent on the properties of the tool material. Contrarily, net-shape finishing by FIB mostly depends on the ion beam properties and less on the intrinsic properties of the tool material.

SUMMARY

In this chapter a concise review of recent progress in surface engineering for tooling protection has been presented, with particular focus on applications in micro- and nano-production technologies. As a general conclusion, it can be stated that surface engineering has the potential for great impact in the further development of miniature and micro-manufacturing. In this context, research and development in this field should focus on new concepts of flexible surface modification systems, in order to achieve an optimal performance on non-standard tooling elements. Moreover, the implementation of reliable testing tools and standards needs to be addressed in detail. The development of surface/interface modeling tools is envisaged to help in the integration of both process design and surface engineering for micro-manufacturing. Substantial integrative endeavors need to be undertaken between the scientific community and the relevant industrial stakeholders to obtain the full potential of surface engineering and to convert it in a true enabling technology for micro-manufacturing.

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