Synthesis and Evaluation of TaC:C Low-Friction Coatings

BY

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Abstract

In the large family of carbon-based coatings there are members capable of providing a rare and very desirable combination of high wear resistance and low friction. The field of application for this kind of coatings is steadily increasing which, naturally, give raise to new questions and demands.

Coatings of this type can be produced in a number of different ways, but the parameter influencing their properties most is the chemical composition. To facilitate investigations of the compositional impact on the synthesis and properties of coatings, a way to alloy magnetron-sputtered thin films was developed in this thesis. It does not involve the use of reactive gases or additional material sources; instead metallic foils are attached onto the magnetron target surface and thus sputtered alongside the target material. This co-sputtering route was later used to synthesize carbon coatings alloyed with Ta, Zr, W and Al in various amounts and configurations.

It was shown that the co-sputtering method could be used to alloy coatings in a very simple and straightforward manner, with excellent possibilities of controlling the amount of alloying elements. The process temperature could be kept as low as 70 °C.

Carbon coatings alloyed with transition metals (MeC:C) displayed polycrystalline nanocomposite structures with 5 nm metal carbide crystallites in a matrix of near-amorphous carbon. Alloying with Ta resulted in a radical 80 % reduction in friction coefficient during dry sliding in air, from 0.22 for pure carbon to 0.04 for TaC:C. This was found to be due to facilitated graphitization and the formation of lubricating surface oxides. Al additions to TaC:C resulted in a transformation of the TaC phase to a metastable, previously unreported Ta₃AlC. The coefficient of friction remained unaltered, but the oxidation rate compared to TaC:C was significantly reduced due to the formation of AlTaO₃ instead of Ta₂O₅.

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Gräset, sa Gud, ska du se på,
vandra på ängarna ut.
Asfalt är skadligt för själen,
den stelnar av den till slut.

Men gräset, sa Gud, ska du se på,
vandra på grönskande lid.
Med gräs är det annorlunda,
gräset är mullens frid.

Bernt Bergström
Enclosed papers

This thesis comprises the following papers, referred in the text by their roman numerals. Published papers are reprinted with permission from respective publisher.


VI An analytical TEM study of (Ta, Al)C:C coatings in as-deposited and oxidized states. E. Coronel, D. Nilsson, S. Csillag, U. Wiklund, in manuscript.
The author’s contributions

These are the author’s contributions to the individual papers.

I  Better part of planning and evaluation, all experimental work and writing.

II Better part of planning, experimental work and writing, part of evaluation.

III Better part of planning, experimental work and evaluation, all writing.

IV Better part of planning, experimental work and evaluation, all writing.

V  Better part of planning, experimental work and evaluation, all writing.

VI Part of planning, experimental work, evaluation and writing.

Det stod dock klart för mig redan på ett ganska tidigt stadium sedan jag kommit till Luleå att jag ville doktorera. Det stod också mer och mer klart att jag inte ville göra det i Luleå. Uppsala som stad lockade med en synnerligen attraktiv kombination av historia, kultur och vetenskap, och när möjligheten att ansluta mig till avdelningen för materialvetenskap kom, behövde jag inte lång betänketid. Nu har fem år gått under vilka jag tycker mig gjort stora framsteg, både som forskare och människa. Jag har naturligtvis många att tacka för detta, men en komplett lista skulle bli lika lång som avhandlingen den skulle innefattas i. Förutom mina hjärtligaste tack till hela avdelningen för materialvetenskap för denna tid, nöjer jag mig därför med att nämna några individer som allra mest bidragit med hjälp och stöd under dessa år.


Daniel Nilsson
Uppsala, hösten 2004
E pluribus unum.

Af flera blifva ett.
Background

Surface Engineering [1-16]

History

Man has always been forced to solve problems related to the interaction of surfaces. It was not until iron-age Greece, however, that the birth of something resembling what is today referred to as surface engineering was seen. An explanation for why this is the case stands to be found in a part of the modern definition of surface engineering:

“Surface engineering involves the application of traditional and innovative surface technologies to engineering components and materials in order to produce a composite material with properties unattainable in either the base or surface material.”

In Homero’s Odyssey, referring to the period 1400-1200 BC, the surface hardening of a sword is first described. The red-hot blade was cooled rapidly in water, producing a weapon with highly desirable characteristics; a very hard surface with the ductile interior still intact. This procedure, today called quench hardening, fits the definition of surface engineering perfectly.

As time passed, man learned that even harder surfaces could be attained by subjecting the steel to more unconventional media, like urine, decomposing soy beans, burnt hoofs and horns, bag felt, old burnt leather, tartar, and various mixtures thereof. The use of such organic compounds gave a local enrichment of carbon and/or nitrogen in the steel’s surface region, leading to the formation of hard inorganic compounds - carbides and nitrides. These processes and their relatives are now named carburizing, carbonitriding and nitriding. The largest technological achievements in surface engineering have been made in the latter part of the 20th century, i.e. quite recently from a historical perspective. Research in modern physics and chemistry gave birth to surface technologies based on atomistic phenomena earlier considered being of academic interest only.

Today surface engineering is an integral part of most manufacturing technologies imaginable and a vast portfolio of various treatments is available. Some common surface modification techniques are named and illustrated in Fig. 1.
Figure 1. Common thicknesses of engineered surface layers [1].

The coating of surfaces

The most expansive and research-intensive field in surface engineering today is that concerning the application- and production of coatings. The use of coatings to alter the surface properties of the bulk material, or substrate, is almost as interdisciplinary as surface engineering itself. Coatings can provide surfaces with unique chemical, physical, mechanical and tribological properties otherwise impossible to achieve. Large economical and environmental gains are made in applications like fuel cells, solar panels and electrical and optical components. Due to its magnitude the market showing the biggest potential today is mechanical components. These components are abundantly found in the machines and tools of the mechanical industry and in its products. Examples are cutting and forming tools, gears, pumps, compressors, etc. Coatings are utilized and introduced in all aspects of production, from the coated cutting insert used to mill or turn the component into a first crude form to the low-friction coating applied on the fine-polished surface of the final product.

Gains of utilizing coatings in the mechanical industry

There are numerous examples of great gains made by the introduction of surface coatings in the mechanical industry. One of the oldest and most mature is the area of coated metal-cutting tools. Mechanical components are machined on a large scale with highly slimmed organizations, where high productivity and short production times are vital. Compared to the late sixties, when uncoated cemented carbide was used in metal cutting, steel
machining-time has been reduced more than ten times, to a large extent due to the use of high-performing coatings; see Fig. 2(a).

A more unexplored area is low-friction coatings for mechanical components. Such coatings can result in life-time increases of more than 25000 times under certain conditions, as compared to an uncoated component, Fig. 2(b).

**Figure 2.** Major innovations in tool materials leading to reductions in machining time in steel (a) and dramatic life-time improvements by employing low-friction coatings on the vanes in a rotary-vane pump operated in additive-free hydraulic fluid (b) [6-7].

### Why coatings work

Even though modern surface coatings for mechanical applications are typically just 1-10 µm thick, or about one twentieth the diameter of a human hair, they can provide phenomenal increases in lifetime and throughput. Considering that most materials used as coatings in the mechanical industry, like titanium nitride (TiN), titanium carbide (TiC) or titanium diboride (TiB2) are quite useless in bulk form, the question is how they can be so outstanding when in the form of thin layers? The answer actually lies within their limited thicknesses. In the form of thin layers the materials possess properties partly unlike those of the bulk substance, like enhanced compliance. Some properties are preserved, however, like high hardness, high strength at elevated temperatures and often very good chemical resistance. The substrate material, be it steel, ceramics, plastics or basically any other material, then provides properties such as mechanical stability, electrical conductivity or low cost. It is possible to apply coatings with extreme properties exactly where needed in order to rid the application of
specific limitations without jeopardizing the function of the component or system on a large scale.

**Design of coatings**

So far coatings have only been discussed and viewed as being constituted of one layer of a single material, a homogenous coating as illustrated in Fig. 3(a). However, to improve one or more of the properties mentioned above most coatings today consist of several different materials in various configurations.

In compositionally graded coatings, Fig. 3(b), the composition is varied seamlessly within the coatings thickness. This way the properties of the coating can be better adapted to different operating conditions than can those of a purely homogenous coating. An application requiring the combination of a hard surface and good adhesion between coating and substrate is a good example of when such a coating is suitable. For instance, it is possible to initially deposit a pure metal with excellent adhesion to the substrate and gradually vary the composition and end up with a hard compound on the surface, like a carbide, nitride or boride, thus fulfilling both needs.

Multilayered coatings are made by alternatively depositing two or more materials onto the same substrate, Fig. 3(c). By varying materials and lamellar thicknesses the properties of the constituent materials can be combined and altered in a very flexible manner. A multilayer could for instance be designed with one abrasive-resistant material, one low-friction material and one material with good oxidation resistance and that way perform very well in all three categories.

Even when disregarding the effect of varying the material, there are certain structural advantages with multilayers. One is an increased hardness due to the obstruction of dislocation movement by the increased amount of interfaces; another is an increased toughness because of crack deflection in these same interfaces. Very often an increased number of layers within a multilayered coating results in a simultaneous improvement in its mechanical properties. The newest family of multilayer coatings is the MAX-phases, where the individual lamellae consist of atomic monolayers. This nanolaminate structure gives them unparalleled properties unique within the field of ceramic materials.

The dispersion coatings, sometimes called composite coatings (Fig. 3d), consist of a matrix material containing dispersed particles of another or several other elements or compounds. The particles can inhibit dislocation movement in much the same manner as the interfaces in multilayers, which can potentially lead to a very high hardness. If the particles are small, below 100 nm in diameter, it is justified to talk about nanocomposite coatings. Such coatings have among other things been shown to possess greatly
improved ductility and toughness. All coatings studied in this thesis belong to this category.

Another example of property improvements that can be accomplished with nanocomposite coatings is a dramatically lowered coefficient of friction. In Paper II it is shown that the friction between steel and an amorphous carbon coating can be lowered by nearly 80% by the addition of small tantalum carbide particles. This makes this coating an ideal candidate for increasing life times by reducing energy losses and increasing efficiency in systems with many tribologically stressed parts, like combustion engines.

![Figure 3. Schematic view of today’s most popular structural configurations in coatings design; homogenous- (a), compositionally graded- (b), multilayered- (c) and dispersion coatings (d) [8].](image)

**Objective of the work presented in this thesis**

In the last decades there has been an increased awareness of the absolute necessity to reduce the stress that our present way of life has on the environment. The efforts to solve the problems include urging the public to recognize the problems and taking on part of the responsibility themselves, for instance by recycling, reduce excessive consumption or walking or biking instead of driving. But there is also an escalating industrial strive towards this goal. One reason is that “environmental-friendly” has become a potent means of competing for the consumers favor in many parts of the world. For example, increased pressures and working temperatures in engines can lower fuel consumption and the amount of hazardous components in the exhausts, two very attractive features today. Another reason is that taxes and regulations have made environmentally sound industrial processes more attractive; with today’s hard competition it is becoming too costly to be an environmental villain! But the most powerful driving force is still the possibility to increase revenues. Combining increased productivity, increased tooling lifetime and lower cost sounds like a contradiction in terms, but due to innovations like low-friction coatings it is well on the way of becoming a reality.

Even though already existing and commercially available carbon-based low-friction coatings perform well, naturally the features making them
successful can be improved upon. Further there are plenty of aspects on this kind of coatings that are not understood or at all investigated.

The aim of this thesis has therefore been to develop a low-friction coating based on promising and carefully chosen constituents. A major goal has been to evaluate how this coating performs from a tribological point of view, and to determine why it performs the way it does. Further objectives have been the characterization of its more basic properties and - based on the knowledge gained – improvement of those properties found to cause performance weaknesses.
Coatings Synthesis

Synthesization Basics

The basic principle behind all coatings synthesis is a controlled mass transport from a material source to a surface. In case of carbon-based low-friction coatings the most common way to accomplish this is by Physical Vapor Deposition (PVD). This process involves the following principal steps.

1. Evaporation of the material intended to constitute part of or the entire coating.
2. Transport of the evaporated material to the substrate.
3. Condensation of the vapor on the substrate surface and subsequent growth of a coating.

Because of the highly reactive nature of most elements in vapor phase, deposition is always carried out in a vacuum chamber. Inside this chamber the air is either removed or replaced by an atmosphere more suited for the coating process, most commonly the noble gas argon. Due to argon’s unwillingness to participate in chemical reactions the process becomes possible to control in great detail. The gas pressure during deposition is low, usually around $10^{-3}$ mbar. To enhance the deposition rate and resulting coating quality this gas is often partly ionized - turned into a plasma.

In chemistry and physics the concept of plasma signifies the fifth and last of the aggregate states possible for matter to exist in - the other four, in order of decreasing energy levels, are gaseous state, liquid state, solid state and Bose-Einstein condensate. Plasma in pure form, called hot plasma, is a gas where all atoms are ionized. This means that electrons in the outer orbitals of the gas atoms have been released, or excited, which results in a collection of electrons and positively charged atoms - ions. Electrons and ions are no longer bound to each other except by long-range forces. The mixture is in thermal equilibrium and, as the name implies, very hot. One example of hot plasma is the one powering fusion processes in the sun and other stars where it can reach several million degrees Celsius. However, generally when the term plasma is used cold plasma is what is intended. In cold plasmas only a small fraction of the gas is ionized. Electrons, having an extremely low mass, are accelerated by powerful electric fields to very high levels of kinetic energy or equivalently high temperatures. By means of this energy they manage to ionize part of the atoms in the gas, but the resulting ion which is tens of thousand times heavier still remains at the ambient temperature. Subsequently the ion will acquire a new electron to once again complete its orbitals, but due to the large mass difference a general surplus of positive charges will be retained. The electron acquisition, or recombination, is what
gives the plasma its beautiful, glowing appearance. As opposite to hot plasmas, cold plasmas cannot be in equilibrium processes which means that the ionization has to be retained by an energy input during operation. But it also means that the process can be readily controlled and that there is a continuous access to argon ions as long as needed.

Depending on the desired coating, argon can also be mixed with a reactive gas like nitrogen or acetylene.

**Evaporation**

Consider an example from everyday life. \( \text{H}_2\text{O} (\text{s}) \rightarrow \text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2\text{O} (\text{g}) \) is a phase transformation very common to Uppsala, especially during early spring. It visualizes the principle of evaporation perfectly and is a process anyone can master; you just melt the ice, heat the resulting water on the stove and steam will result. This course of action is in all vital parts identical to one of the two main ways available to evaporate the highly refractory materials used in coatings synthesis today – heating. In PVD the heat is not supplied by a hotplate, but through resistive heating, inductive heating, laser or a highly focused electron beam as in Fig. 4(a). Heating is a very direct and efficient approach to evaporation which yields high material fluxes. However, it also often results in substantial heat dissipation and in some cases adhesion issues. Heating induced evaporation of other than single elements is also associated with many difficulties (although solutions are available) and is thus used almost exclusively to evaporate single elements.

![Figure 4. Principle views of electron-beam evaporation (a) and sputtering (b).](image)

The idea behind the other main method of evaporation, sputtering, is somewhat more elaborate. The material to be evaporated, here called the sputtering target, is bombarded with ions as shown in Fig. 4(b). A negative potential is applied to the sputtering target which means that the positively
charged argon ions are accelerated toward the material surface. At impact they transfer kinetic energy to the surface atoms, and if this energy is higher than their binding energy they will be ejected. Thus an ion bombardment of sufficient intensity will result in a vapor of the desired material. There are a number of reasons as to why sputtering has become the most widely used vaporization technique; it is easy scalable, yields excellent coatings uniformity and show high deposition rates. Its biggest merit, however, is arguably its versatility. Sputtering is essentially a kinetic process involving momentum exchange rather than a chemical and/or thermal process. Therefore virtually any material can be deposited using a sputtering system.

There are three basic designs of sputtering devices – ion-beam systems, diode and triode systems, and magnetron systems. Of these the magnetron is by far the most popular one. We have already established that a plasma is an integral part of sputtering and that free electrons are the source of gas ionization. The magnetron is a device designed to increase ionization where it is most needed, right at the sputtering target surface. This will lead to a manifold increase in deposition rate which is the biggest reason for the popularity of magnetron sputtering. To understand how a magnetron works we first have to take a closer look at the initial stages of plasma formation. Picture a free electron accelerated by an electric field. If the gas density in the deposition chamber is too high the electron will not have time to gain sufficient energy to ionize a gas atom before hitting it and losing most of its energy. If the gas density is too low the electron will simply hit the anode without ever encountering a gas atom in the first place. Under the appropriate conditions, however, the electron will most likely hit a gas atom, ionize it and thus create an ion and a secondary electron. Each of these particles will be accelerated by the electric field; the ion towards the cathode and the original and secondary electrons toward the anode. The two electrons can then cause further ionizing collisions on their way toward the anode whilst the ion-cathode collision gives rise to both vapor and new secondary electrons. Very quickly this chain reaction leads to a condition called break-down, or plasma ignition. From this discussion it is clear that the gas pressure must be of a certain magnitude if a plasma is to be formed. At this pressure, however, less than 10% of the power input is used to form and sustain the plasma and it does not allow a very efficient deposition process. It was found, though, that the addition of a magnetic field perpendicular to the already existing electric field force the electrons to move in spiral paths instead of straight. This way the probability of electron impact increases and, together with a power increase, offer a substantial increase in the net density of ions and electrons in the plasma – an increased plasma density. Later the magnetron was constructed, where the magnetic fields were oriented so that the electrons got trapped in a closed, drifting loop near the sputter target, see Fig. 5. This resulted in even further efficiency improvements. From a theoretical point of view the geometry of
the electron drift path is not relevant, as indicated in Fig. 5 where both a circular and a rectangular magnetron cathode is shown. A multitude of other geometries are also readily available.

![Figure 5. The principle of planar magnetrons, showing the shape of the magnetic field and the resulting drift paths; circular cathode (a) and rectangular cathode (b) [20].](image)

Three of the most successful modifications to the original magnetron design are pulsed, radio-frequency (r.f.) and unbalanced magnetrons. The use of pulsing or r.f. power minimizes problems like arc discharges associated with sputtering materials with low electrical conductivity. Unbalanced magnetrons, as opposed to ordinary (or balanced) magnetrons, are designed to supply an unbalanced magnetic field. That way the plasma confinement is somewhat disrupted, expanding the ionization to include the substrate to a higher degree than in the balanced case. This leads to increased ion-bombardment of the substrate during coating growth and in many cases also to improved coating properties, as is further described in Condensation and Growth below. In the work presented in this thesis a rectangular, planar and balanced magnetron is used, with a cathode similar to the one in Fig. 5(b).

In the beginning of this section it was mentioned that heating-induced evaporation was basically limited to single elements but that sputtering could be used to vaporize just about any material. A common way to extend the field of use of the former procedure, which also is utilized in sputtering, is to introduce a reactive gas in the deposition chamber. This will cause the evaporated material and the reactive gas to immediately react and form some (hopefully) desired compound, still as vapor. This is called reactive evaporation or reactive sputtering. The reason to use this in sputtering as well is that it is much easier and certainly cheaper to produce a pure element target and a pure gas than a compound target of comparable purity.
Vapor Transport

Once vaporized the materials flux is expanding into the chamber by means of concentration gradients, temperature gradients and - in case of sputtering - momentum transfer. Because of the low pressure, evaporated species experiences a very limited amount of evaporant-to-gas collisions, resulting in a phenomenon called line-of-sight transport. This means that only the surface actually facing the vapor will be deposited. In many cases this is a disadvantage and it has led to the development of many rather ingenious substrate holders, utilizing techniques like planetary substrate motion to expose the desired surfaces to the vapor.

Condensation and Growth

Above an example on the evaporation of water was used as a familiar illustration. This can be taken even further. When the steam resulting from boiling the water hits the cooler lid covering the saucepan it will transform back into liquid water; it condenses. In the same way the vapor in PVD will condense on the substrate surface.

An atom arriving at a substrate surface loses most of its kinetic energy to the substrate lattice at impact, thereby becoming a loosely bonded adsorbed atom – an adatom. Well on the surface it will migrate, or diffuse, and combine with other adatoms or adsorbed species. This goes on until the adsorbed material comes across an energetically favorable lattice site where it may remain. How mobile the adatom will be on the surface is described by something called the homologue temperature \( T/T_m \), or the absolute substrate temperature divided by the absolute melting temperature of the adatom element in bulk form. The surface diffusion is a dangerous time for atoms as they may very well be desorbed again, by re-evaporation or re-sputtering. Supposing however that the adatom managed to find a suitable lattice site, it continues to adjust its position on a smaller scale by bulk diffusion processes.

The course of events described so far corresponds to the first fundamental step of the coating growth process as shown in Fig. 6(a)-1 and is called nucleation. It is followed by adatom-island growth (2), impingement and coalescence of islands (3), development of a continuous structure (4) and further coatings growth (5).
Adatom mobility is directly related to the homologue temperature and of the utmost importance for coatings growth characteristics. The microstructure, or morphology, of PVD coatings can be divided into four zones; zone 1, zone T, zone 2 and zone 3, see Fig. 6(b).

Zone 1 (T/T_m<0.3) morphology results when low adatom mobility, or equivalently low substrate temperature, is combined with a sufficiently rough substrate surface. In PVD high points on the surface always receive more materials flux than low points, and left unattended the high areas will grow faster. When diffusivity is too low to compensate, the resulting microstructure will be columnar with domed tops, grain boundaries with high defect-density and poor adhesion between columns as in Fig. 7(a). Metallic coatings with this structure are known to have high hardness but little lateral strength. Coatings deposited in this temperature regime are of great industrial importance due to the low thermal impact on the substrate. At higher temperatures, where chemistry and diffusion processes are able to compensate for earlier steps in the deposition route, the coating’s history becomes less important. Therefore, in the zone 1 temperature regime, the microstructure is dependent on a plethora of parameters apart from substrate temperature. This means that it is possible to produce coatings with more favorable microstructures and still not increase the temperature. Parameters able to influence the morphology include apparatus configuration, substrate surface morphology, gas pressure and degree of ion bombardment during growth.

Zone T is a transitional zone between zones 1 (T/T_m<0.3) and 2 (0.3<T/T_m<0.5) and can be described as the structure shown by zone 1 on an infinitely smooth substrate. It is characterized by a fibrous and small-scale columnar structure showing a wide distribution of grain sizes. The
intercolumnary grain boundaries are sufficiently dense to adhere well to each other, as exemplified in Fig. 7(b), and to yield excellent coating properties. When depositing low-friction coatings, temperature-sensitive materials like low-alloyed steels and aluminium alloys are commonly used as substrates. Therefore a low deposition temperature is desirable. A lot of effort has been made in the past to produce zone T microstructures at zone 1 temperatures, something readily done today by optimizing the deposition process.

In zone 2 (0.3<T/T_m<0.5) the surface diffusion is high enough to yield smooth and dense coatings. They resemble both zone 1 and zone T microstructures but compared to zone 1, zone 2 columns grow coarser and have superior inter-columnar adhesion. Similar to zone 1 but opposed to zone T their columns stretch through the entire coating, see Fig. 8(a). In zone 3 (T/T_m>0.5), Fig. 8(b), bulk diffusion becomes important which means that grains may coalesce and change growth directions during growth. The result is coatings with equiaxed grains and apparent grain boundary surface grooves.
Figure 8. Schematic illustrations of zone 2 growth (a) and zone 3 growth (b) [22].

Ion bombardment was mentioned in the section about zone 1 growth as one way of producing better microstructures at lower temperatures. In fact, it is the single most important and widely used method and is called resputtering. The bombardment of ions and neutrals during deposition promotes increased atomic surface-mobility by providing an additional source of energy, separate from an increased temperature. This effect can be seen in Fig. 6(b) where all zones are shifted to lower $T/T_m$ as the total energy available for diffusion increases (equivalent to lower pressures). Increased ion bombardment is accomplished by applying a negative potential, a bias, to the substrate surface in the presence of positively charged ions. Higher (a more negative) bias means more energetic surface bombardment of the ionic species. Another consequence of the ion-bombardment based energy contribution is that PVD coatings can be deposited under non-equilibrium conditions. The result, metastable phases, is a possible outcome of the energy supplied by ion-bombardment is confined to the topmost atomic layers of the growing coating. Hence the deposited atoms experience a rapid energy reduction equivalent to an extremely high quench-rate, as more atoms are deposited on top. This has the potential of giving the metastable phase properties quite different from those of the same material produced under equilibrium conditions. From a chemical point-of-view they are not perfectly stable, but the transformation rate toward the equilibrium state is often too slow to be of any practical relevance. It is estimated, for instance, that the transformation from metastable cementite in steel to the equilibrium phases ferrite and carbon would take around $10^{26}$ years to complete at room temperature. More or less commonly encountered examples of materials that are metastable in room temperature include window glass, diamonds and retained austenite in steels. So quite contrary the title of the 1971 James Bond movie, diamonds are *NOT* forever - merely a measly couple of millennia!
The PVD System

A Balzers BAI 640R PVD-system, shown in Fig. 9, was used in the deposition of all coatings synthesized in this work. It is fitted with a planar, balanced d.c. magnetron sputter, an electron-beam evaporation source (E-gun) and a thermionic arc for auxiliary ionization in the chamber. The substrates were mounted with their surfaces facing the magnetron and the E-gun on a level corresponding to a 5 cm distance from the magnetron surface. All coatings were deposited by balanced d.c. magnetron sputtering. The E-gun was used to produce a titanium interlayer between substrates and coatings in Paper II. The substrate holder was rotated clockwise, passing the ion source and magnetron, in order for the coating composition to be perfectly homogenous.

Figure 9. Photograph and schematic view of the PVD equipment used throughout this thesis [27].

Sample Preparation

All substrates were carefully prepared to rule out the influence of surface roughness on test results. Three different substrate types were used; (111) single-crystal silicon wafers (Si), ball-bearing steel discs (BBS) and high-speed steel plates (HSS). The silicon substrates were chemo-mechanically polished to semiconductor standards, yielding surfaces with $R_q < 1$ nm. The BSS and HSS steel substrates were metallographically polished to $R_q \approx 5$ nm.

The most important step in ensuring good adhesion between substrate and coating is a clean substrate surface. In this work, cleaning has been performed in four steps. First the substrates were ultrasonically cleaned in an
alkali solution at 60 ºC. Then they were cleaned ultrasonically in pure ethanol, and finally mounted in the deposition chamber. After evacuation of the chamber, the substrates were heated for an extended period of time to rid the surface of adsorbed water. Time and temperature varied between three hours at 200 ºC for the temperature-sensitive BBS to one hour at 450 ºC for silicon and HSS. Lastly, ion-etching at a bias of -200 V was performed to remove residual oxides and chemisorbed species still present; 10 minutes for the silicon substrates and 15 minutes for the steel.
Coating Analysis and Evaluation Methods \[28-36\]

Fundamental coating properties

To understand why a coating behaves the way it does macroscopically, it is absolutely vital to investigate it on a more fundamental level and then try to relate those results to the large-scale behavior. In doing this a multitude of analysis methods and testing procedures are available, and it is of utmost importance to choose the one best suited to get the most information out of the performed tests.

Chemical properties

**EDX**

Energy-dispersive x-ray spectroscopy (EDX) was used throughout this thesis to quantitatively determine the amounts of elements present in the coatings. An EDAX Phoenix system was employed using a 6 kV acceleration voltage and 35 \(\mu\)s detector amplification time. Depending on the coating in question, \(\text{CK}_{\alpha}, \text{AlK}_{\alpha}, \text{ZrL}_{\alpha}, \text{TaM}_{\alpha}\) and/or \(\text{WM}_{\alpha}\) peaks were analyzed, and sintered solids of \(\text{Al}_4\text{C}_3, \text{ZrC}, \text{TaC}\) and WC served as standard materials. The use of the same instrument and parameters during all measurements combined with the use of high-quality standards make for a low estimated error in measurement, around 1%.

**GDOES**

Glow-discharge optical emission spectroscopy (GDOES) was used to do quantitative depth-profile measurements on as-deposited coatings. In doing this a Leco GDS 750A optical emission spectrometer was used. Argon plasma functioned both as sputtering- and excitation medium.

**XPS**

X-ray photoelectron spectroscopy (XPS) was used to investigate chemical bond states in coatings. The XPS equipment was a Physical Electronics Quantum 2000 Scanning ESCA Microprobe system and AlK\(_{\alpha}\) monochromatized radiation was used. The same sintered standards used for EDX were used in this analysis.
Electron-energy loss spectroscopy (EELS) was used to further study the coating chemical configuration. It was performed in an FEI Technai F30ST transmission electron microscope (TEM) with a field emission gun (FEG) operating at a 300 kV acceleration voltage.

**Phase composition**

X-ray diffraction (XRD) was used to evaluate coating phase composition and microstructural textures. Monochromatized CuKα radiation was utilized in a Siemens D 5000 x-ray diffractometer. Both the Bragg-Brentano geometry and a 3° grazing-incidence setup with a 20-120 degree detector sweep were used.

Phases and textures were also studied using selected-area electron diffractometry (SAED) in the FEI Technai F30ST TEM.

Raman spectroscopy (RAS) was used to investigate the structure and state of carbon, utilizing a Renishaw 2000 micro-Raman spectrometer equipped with a green diode laser (λ=514 nm).

**Morphology and microstructure**

Scanning electron microscopy (SEM) was used in coating thickness measurements and morphology investigations done on fracture cross-sections. A Leo 1550 SEM fitted with a FEG and an in-lens secondary electron detector was employed. Distance measurements were always performed using a magnification calibration sample, leading to an error in measurement of no more than 2%.

Cross-section TEM (XTEM) was performed using the FEI Technai F30ST TEM described in the section about SAED, above.

First estimates of crystallite sizes in the coatings were made by the Scherrer method using XRD data.
Mechanical properties

Among the most important of the mechanical properties associated with coatings are adhesion, residual stress, hardness and elastic modulus. Adhesion is perhaps the most important one since a detached coating has no chance whatsoever to fulfill its purpose. Inherent residual stresses are also important to characterize because if too high, they can decrease the practical adhesion and if too low, the coating loses a main toughness-increasing mechanism. Coating hardness is important to the extent that the coating has to be harder than the material it comes in contact with, or the counter material, to avoid abrasive wear. Since low-friction coatings often are used in combination with softer materials, the importance of hardness is not as large as one might think. The elastic modulus is also important to characterize due to the large stress gradients arising during deformation of coated components. This stress increases as the difference in elastic modulus between substrate and coating increases. The elastic modulus is also intimately connected to a material’s bond strength and thus it can be used, together with coating hardness, to qualitatively evaluate the relation between plastic and elastic properties in a coating. This can be especially valuable in today’s increasingly intricate coating designs.

Adhesion

To evaluate how well a coating adheres to the substrate, scratch testing using a CSEM Revetest scratch tester has been performed. In this procedure a 200 μm radius Rockwell C diamond stylus was moved a distance of 10 mm across a surface while the load was continuously increased from 0 to 100 N. Detection of acoustic emissions and post-scratch optical microscopy was used to determine at which load the coating showed first signs of fracture, or the critical load.

Residual stress

In measuring residual stresses, a plate-deflection technique was used as described in [35]. After proper thinning, the radius of curvature of the remaining plate was measured using a WYKO NT-2000 optical profilometer and its thickness with a micrometer caliper. The residual stress was then calculated using the Stoney equation.

Hardness and elastic modulus

To avoid that hardness measurements on coatings are influenced by the underlying substrate material the indentation depth must not surpass 10 % of the total coatings thickness. Since most coatings are very thin it is difficult to get reliable results when measuring hardness in the conventional way, by post-examination of the deformed area of an indent made on a materials surface. By considerably reducing the indentation load and continuously
recording the load- and displacement data it is possible to measure hardness on very thin coatings without risking experiencing any substrate effects. From the obtained results it is also possible to derive the material’s elastic modulus. This procedure is called nanoindentation; in the present work a NanoIndenter XP unit was utilized with a Berkovich diamond tip and an indentation depth of 100 nm. Measurements have been calibrated using a homogenous and amorphous standard sample of fused silica.

**Tribological properties**

Tribology is the science dealing with interacting surfaces in relative motion to each other, which means that it deals with phenomena related to friction and wear. Its nature is not exact; due to the great complexity of most tribological situations it was soon realized that tribological behavior cannot be described by any kind of universal theory. Instead practical testing methods have to be designed in such a way that they simulate intended applications as well as possible.

In the testing of low-friction coatings the most common way to evaluate its tribological properties is by ball-on-plane measurements, as principally illustrated Fig. 10. This is a truly versatile test; loads can be varied, sliding speed can be changed and lubrication added. Balls of different sizes and materials can be used, coatings can be applied to plane, ball or both, test temperatures are free of choice and so is atmosphere. The proper choice of test conditions will reproduce virtually any wear mechanism found in real-life sliding situations.

![Figure 10. Schematic illustration of the principle behind the ball-on-plane test [27].](image)

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**Sliding wear**

**Ball-on-Plane**

Measurements of coefficients of friction arising between coating and ball during sliding was made using both steel and Al$_2$O$_3$ balls with a diameter of 6 mm, a load of 5 N and a sliding speed of 7 cm/s. These parameters gave a static maximum contact pressure of 1.1 GPa. All tests were performed in ambient air.

**Optical profilometry**

The amount of wear resulting from the ball-on-plane procedure was estimated by measuring the volume of the wear track on the slid coatings using the WYKO NT-2000 optical surface profilometer described above.

**SEM**

SEM was used to investigate the worn surface of the balls slid against the coating.
Contributions

Process Development I-III

In research and development of surface coatings it is often very valuable, from an experimental point-of-view, to add certain amounts of new elements to the already existing coatings recipe. However, to incorporate an additional, non-gaseous substance in a deposition process can be troublesome. This holds particularly true if the process prerequisites include flexibility, low deposition temperatures, process stability and perhaps low cost. If the scope also includes straightforward process control and the possibility to add more than one element, the number of processes at hand is very limited. On this basis it was decided to adapt an old diode sputtering method, involving the attachment of foil on a sputtering target, to better suit the more efficient magnetron sputtering technique. Since sputtering mainly is a method based on momentum transfer the foil was co-sputtered with the base target, and thus the overall chemical composition of the film was determined by the characteristics of the base target and the composition and extension of the foil used.

The base target used consisted of carbon, measuring 125×250 mm², and four different metals were used as foils; aluminium, tantalum, tungsten and zirconium. The amount of metal in the synthesized coatings was varied by changing the area covered by metal, at the expense of the carbon base target. This was done in two different ways which, in practice, always were combined. One was to alter the number of foil strips on the target surface. On the target used here, foil could be placed at a maximum of four different locations at the same time, see Fig. 11(a). Secondly, the distance between the foil and the ion-bombardment centerline was varied by varying the foil width, denoted b in the figure. This, naturally, altered the amount of foil-covered area, but it also changed the ion-bombardment intensity on the foil. By decreasing b, the foil was moved further toward the magnetron centerline where the ion-bombardment is most intense, see Fig. 11(b). This action had a large and non-linear impact on the amount of metal incorporated in the coatings.
Figure 11. Schematic drawing of the magnetron target with the four different foil positions indicated (a) and a figure illustrating the ion-bombardment intensity profile of the magnetron used in this work, viewed from the center to one of its long sides (b).

The foil temperature turned out to be the limiting factor both for the maximum amount of metal possible to incorporate in the coatings and for the maximum deposition rate attainable. The foil strips were attached to the target by means of carbon-based vacuum tape. Even though the target is water cooled, the magnetron surface may become hot during ion-bombardment. If, then, the foil extends too far towards the centerline or if the power of the magnetron is too high, the temperature will also be too high and the adhesive tape disintegrates. This will cause the foil to lift from the target surface with unpredictable process behavior as a consequence. The sweet spot, i.e. the process window showing the highest deposition rate with unimpaired process stability, was found at a magnetron power of 1.5 kW and with $b \geq 12$ mm. These results are however highly dependent on various processing parameters, like sputtering technique, magnetron set-up and pressure, which means that the parameters and limitations presented here are likely to be somewhat different in other systems. Another factor influencing the amount of metal attainable is the sputtering yield. Sputtering equally sized areas of carbon and aluminium under the same circumstances will result in the ejection of three times as many aluminium atoms as carbon atoms. This is clearly reflected in coating growth rates as shown in Table 1.

Table 1. Deposition results for all coatings synthesized in this work, as measured by SEM and EDX.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Metal content (at %)</th>
<th>Growth rate (μm / h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-</td>
<td>0.60</td>
</tr>
<tr>
<td>C / Al</td>
<td>38</td>
<td>0.95</td>
</tr>
<tr>
<td>C / Ta</td>
<td>9 – 37</td>
<td>0.65 – 0.80</td>
</tr>
<tr>
<td>C / W</td>
<td>21</td>
<td>0.75</td>
</tr>
<tr>
<td>C / Zr</td>
<td>20</td>
<td>0.70</td>
</tr>
<tr>
<td>C / Ta / Al</td>
<td>16 (15+1) – 27 (15+12)</td>
<td>0.65 – 0.75</td>
</tr>
</tbody>
</table>
It turned out that all metals could be successfully co-sputtered with carbon. Switching between different foils in an otherwise identical test setup proved very simple. The amount of metal possible to attain in the films depended on both foil layout and sputtering yield of the respective metal, and the temperature during deposition was as low as 70 °C. All in all this process makes an excellent candidate for laboratory-scale alloying of surface coatings, especially on temperature-sensitive substrates such as low-alloyed steels or low-density metals.
Microstructural Characteristics

In order to investigate the response of the synthesized coatings to various stimuli, they have been subjected to several procedures or treatments that affected their properties. Metal types and contents have been varied, process parameters altered and the coatings have been subjected to different temperatures and atmospheres. The observations made are described in the sections Microstructural Characteristics, Mechanical Properties and Tribological Properties below, divided into sections based on the stimuli in question. Coatings containing nothing but carbon and around 15 at % tantalum have been chosen objects of comparison because they are included in all papers in this thesis. They are from here on referred to as reference coatings (RC).

Coating morphology I-VI

In the RC, fracture followed the grain boundaries to a large extent, exposing the morphology; see Fig. 12(a). The coatings showed a fine fibrous structure where the columns generally did not extend all the way through the coating. It was shown that this disruption of column growth likely was the result of nanocrystallite formation, as schematized in Fig. 12(b). This gave the coating a microstructure balancing between zones 1 and T in Fig. 6(b).

Figure 12. SEM fracture-surface image showing the finely fibrous structure of the RC (a) and an illustration of crystallite-induced renucleation (b).
Metal type; coating morphology  

Carbon coatings alloyed with the carbide-forming metals Ta, W and Zr showed no differences in morphology. Aluminium additions, however, made the fracture surfaces appear clearly less columnar. This behavior is attributed to an increase in the homologous temperature, $T/T_m$, caused by the Al additions. This increase leads the deposition conditions away from zone 1 toward zone T and a more amorphous-like microstructure, as seen in Fig. 6(b).

Amount of metal; coating morphology

The metal content was the parameter found to have the strongest influence on the coating morphology. Carbon coatings without metal additions resembled coatings alloyed with aluminium but fractures went through the columns to an even greater extent, see Fig. 13(a). Those microstructures are found at very low homologous temperatures. Adding carbide-formers increased $T/T_m$ and quickly made the fracture become more fibrous and wood-like in appearance, like the coating shown in Fig. 13(b) which contains 9 at % Zr. Increasing the amount of metal reduced the column sizes and promoted intragranular fracture, like in Fig. 12(a), and at metal contents above approximately 20 at % the morphology changes to one resembling a more brittle material, see Fig. 13(c). No columnarity can be found since this is a zone T microstructure.

Figure 13. The change in coating morphology with increasing metal content; a pure carbon coating (a), a carbon coating alloyed with 9 at% Zr (b) and a carbon coating alloyed with 37 at% Ta (c).

As little as 3 at % Al added to a RC quickly transformed the fracture-surface morphology from looking like Fig. 12(a) to looking like Fig. 13(c). This indicates that Al is very powerful in increasing $T/T_m$, as expected from its low melting point. More aluminium did not further change the appearance.
Substrate bias; coating morphology

In an attempt to further stabilize the sliding properties of a RC, coatings were deposited using a changed substrate bias polarity, positive instead of negative. This had the effect on coating morphology that the amount of droplets and other large-scale defects decreased. It was contributed to increased adatom mobility and adatom diffusion time. The decreased attraction of positively charged species is also believed to contribute.

Oxidation; coating morphology

During investigations of the oxidation resistance of the RC, coating samples were annealed in air in a chamber furnace. The samples were unaffected up to 350 °C, where a new phase was found to develop on their surface. There was a very sharp interface between transformed and non-transformed material, as seen in Fig. 14(a), and increased temperatures increased the thickness of this new phase. At 500 °C the RC was completely transformed. Not surprisingly this new phase was found to consist purely of tantalum oxide, Ta$_2$O$_5$.

In trying to improve the oxidation properties of the RC, increasing amounts of aluminium was added at the expense of carbon. When annealed in air, initial oxidation of the Al-alloyed coatings started at 350 °C, just as it did for the unalloyed RC. The oxidation rate was however strongly reduced, see Figs. 14(b) and 15(a), and found to be highly dependent on aluminium content. The aluminium additions were found to improve the oxidation behavior due to two factors; the formation of a more stable surface oxide, AlTaO$_4$, and a structural densification in the oxide phase arising from the formation of this new oxide. The amount of AlTaO$_4$ was increased at the expense of Ta$_2$O$_5$ as the aluminium content increased, see Fig. 15(b), and subsequently the slowest oxidation rate was shown by the coating with the highest aluminium content.
Figure 14. A RC (a) and a RC alloyed with 12 at % Al (b) annealed for one hour at 400 °C. Observe the shift in appearance of (the unaffected lower part of) the coating brought about by the aluminium addition.

Figure 15. Decreased oxidation rate accomplished by adding aluminium to a RC, as measured by SEM (a) and the change in AlTaO₅-to-Ta₂O₅ ratio with increasing aluminium content as concluded by XPS and chemical calculations (b). The different curves should merely be considered a guide for the eye.
Phases, textures and bonds I-VI

Intercolumnary, the RC showed a nanocomposite structure with two distinct features; tantalum carbide (TaC) precipitates and a carbon matrix. The TaC particles were less than 5 nm in size, polycrystalline and stoichiometric, as shown in Fig. 16. Their crystal structure is best described as consisting of a face-centered cubic tantalum lattice with all octahedral holes occupied by carbon atoms.

The carbon in the matrix exclusively showed graphitic sp²-bonds, as concluded by RAS studies, but no larger continuous graphite layers of any kind were found. Instead the structure consisted of small clusters, featuring strong graphitic interlayer bonds, oriented in a random fashion.

Metal type; phases, textures and bonds I-IV, V-VI

The change of incorporated metal from tantalum to one of the other transition metals naturally resulted in other phases; see Fig. 17(a). Tungsten incorporation resulted in an understoichiometric tungsten carbide phase, WC_{1-x}, and zirconium additions resulted in the stoichiometric ZrC. The carbide precipitates were polycrystalline, just as in the TaC case, and equal in size. Aluminium combined with pure carbon did not result in any detectable crystalline phases whatsoever. Aluminium added to the RC, however, formed a metastable solid solution with the TaC phase, as shown by EDX, XPS, XRD and SAED. This resulted in a Ta_{1-x}Al_xC in which
aluminium atoms were incorporated by substituting for Ta in the cubic TaC crystal lattice; see Fig. 18.

**Amount of metal; phases, textures and bonds**

Increasing the amount of transition metals in the coatings increased the amount of carbide phase as well; see Fig. 17(b) for tantalum. No phase changes could be observed and the grain size was unchanged.

**Figure 17.** XRD patterns of carbon coatings incorporated with Ta, W, Zr and Al, respectively (a) and illustration of how increasing amounts of Ta increases the coating crystallinity (b). For the Ta, W and Zr-alloyed coatings all allowed reflections are present in the coatings, indicating polycrystallinity.

Increasing the amount of Al in the RC altered the Ta$_{1-x}$Al$_x$C stoichiometry. $x$ was varied between 0 (0 at % Al) and 0.44 (12 at % Al), as shown by calculations based on EDX measurements, XPS analysis and XRD results; see Table 2. Throughout this range complete solid solution was retained.

**Table 2. Changes in carbide-phase composition with increased amounts of incorporated aluminium.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ta / Al (at %)</th>
<th>$x_{Ta}$</th>
<th>$x_{Al}$</th>
<th>Compound formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Al</td>
<td>15 / 0</td>
<td>1</td>
<td>0</td>
<td>TaC</td>
</tr>
<tr>
<td>1Al</td>
<td>15 / 1</td>
<td>0.94</td>
<td>0.06</td>
<td>(Ta$<em>{0.94}$Al$</em>{0.06}$)C</td>
</tr>
<tr>
<td>3Al</td>
<td>15 / 3</td>
<td>0.83</td>
<td>0.17</td>
<td>(Ta$<em>{0.83}$Al$</em>{0.17}$)C</td>
</tr>
<tr>
<td>6Al</td>
<td>15 / 6</td>
<td>0.71</td>
<td>0.29</td>
<td>(Ta$<em>{0.71}$Al$</em>{0.29}$)C</td>
</tr>
<tr>
<td>7Al</td>
<td>15 / 7</td>
<td>0.68</td>
<td>0.32</td>
<td>(Ta$<em>{0.68}$Al$</em>{0.32}$)C</td>
</tr>
<tr>
<td>12Al</td>
<td>15 / 12</td>
<td>0.56</td>
<td>0.44</td>
<td>(Ta$<em>{0.56}$Al$</em>{0.44}$)C</td>
</tr>
</tbody>
</table>
Oxidation: phases, textures and bonds IV–V

As mentioned earlier, oxidation of the RC resulted in the transformation of TaC:C into Ta2O5. Aluminium additions resulted in a mixture of Ta2O5 and AlTaO4, and increased amounts of Al increased the amount of the latter at the expense of the former. This indicates that AlTaO4 is the more stable oxide. Using EDX, XPS and XRD results the AlTaO4-to-Ta2O5 ratio was calculated, as shown in Fig. 15(b) and Table 3.

Table 3. Calculations of the amount of AlTaO4 resulting from oxidation of reference coatings incorporated with different amounts of aluminium.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Suggested oxidation path</th>
<th>AlTaO4 fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Al</td>
<td>2 TaC → 1 Ta2O5</td>
<td>0</td>
</tr>
<tr>
<td>1Al</td>
<td>16 (Ta0.94Al0.06) C → 7 Ta2O5 · 1 AlTaO4</td>
<td>0.13</td>
</tr>
<tr>
<td>3Al</td>
<td>6 (Ta0.83Al0.17) C → 2 Ta2O5 · 1 AlTaO4</td>
<td>0.33</td>
</tr>
<tr>
<td>6Al</td>
<td>14 (Ta0.71Al0.29) C → 3 Ta2O5 · 4 AlTaO4</td>
<td>0.57</td>
</tr>
<tr>
<td>7Al</td>
<td>22 (Ta0.68Al0.32) C → 4 Ta2O5 · 7 AlTaO4</td>
<td>0.64</td>
</tr>
<tr>
<td>12Al</td>
<td>18 (Ta0.56Al0.44) C → 1 Ta2O5 · 8 AlTaO4</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Mechanical Properties

Adhesion II-III

The critical load of all tested coatings was 25-30 N, independently of coatings composition, substrate material and whether or not a metallic interlayer was present. These rather low values are attributed partly to intentionally moderate but apparently insufficient heating prior to coatings synthesis and partly to low deposition temperatures and the lack of ion-bombardment during coatings growth, leading to low surface activity. Unpublished results show considerable improvements when correcting these factors.

Residual Stress III

Residual stresses were found to be very low. When depositing reference coatings at -50V and +50V respectively, the residual stresses decreased from already low -0.8 GPa to 0 GPa. The low level of stress in the -50V coating is contributed to the low deposition temperature, and the decrease when switching bias polarity is contributed to lowered ion-bombardment during coatings growth.

Hardness and Elastic Modulus I-V

The RC showed a hardness of approximately 17 GPa and an elastic modulus of 210 GPa. Compared to the pure carbon coating this is an increase in hardness of 21 % and 27 % in elastic modulus. These are rather high values and were explained by the introduction of hard and stiff tantalum carbide particles.

Metal type and amount of metal; hardness and elastic modulus I-II, V

Increasing the Ta content from zero to the maximum amount attainable with the sputtering method used in this thesis, 37 at %, resulted in very even increases in hardness and elastic modulus, see Fig. 19. This was attributed to a simultaneous increase in tantalum carbide phase. Exchanging Ta for W or Zr revealed a different behavior. Zr additions gave a curve resembling that of Ta but with an initial decrease. W additions gave a larger initial increase than Ta but this trend diminished or even reversed at higher metal contents. This is believed to be caused by the less perfect bond states generally shown by understoichiometric carbon coatings.
Figure 19. Increases in hardness (a) and elastic modulus (b) with increasing amounts of incorporated tantalum. The lines are meant to guide the eye.

The addition of aluminium to the RC decreased the hardness by 15% but did not affect the elastic modulus at all.

Oxidation; hardness and elastic modulus IV

Annealing of the RC in an oxygen-depleted atmosphere showed that the hardness and elastic modulus are retained to at least 700 °C, as long as the oxygen levels are low.
Tribological Properties

Friction II-III, V

The addition of 15 at % Ta to a pure carbon coating leads to a remarkable 82 % reduction of the friction coefficient in air, from 0.22 to 0.04 in dry sliding against steel or Al₂O₃ balls; see Fig. 20(a). Compared to steel slid against steel (0.6), TiN (0.5) or commercial low-friction coatings (0.15-0.25) this must be considered extremely low. This large improvement was found to be due to a combination of two mechanisms. One was facilitated graphitization of the near-amorphous carbon matrix induced by the presence of nanometersized TaC crystallites. The other was the in-situ formation of a very thin surface oxide during sliding, acting as a solid lubricant; see Fig. 20(b).

Figure 20. Reduction of the friction coefficient during dry ball-on-plane sliding between a coated plane and a steel ball, upon the addition of 15 at % Ta to a pure amorphous carbon coating (a) and lubricating tantalum oxide filling a pore in the wear track on a RC, thus healing a potentially detrimental coating damage (b). The identification of the oxide was made by EELS.
Metal type; friction II, V

Exchanging Ta for W or Zr gave noticeable changes in the friction levels. Zr additions gave a friction coefficient of 0.07, around 40% higher than the RC. For W the coefficient of friction was 0.09, 80% higher than for the RC. These higher friction values were coupled to the shift in properties of the lubricating oxide resulting from the metal change. It should be noted, though, that these are still very low coefficients of friction compared to commercially available coatings.

Amount of metal; friction II, V

When the amount of transition metal is increased from zero and up, the coefficient of friction varies, as exemplified in Fig. 21(a). It was hypothesized that low metal contents provided insufficient amounts of lubricating oxide for low friction, and that high metal contents reduced the amount of free carbon to such an extent that there was insufficient raw material left for the graphitization process. The release of abrasive carbide particles were also thought to increase with decreasing matrix carbon, disrupting the sliding process. Moderate amounts of metal (8-20 at %) reduced the friction for the thermochemically more stable carbides ZrC and TaC, whereas more metal (around 30 at %) was needed for the less stable carbide WC_{1-x}. The same behavior was found when adding aluminium to reference coatings. Al additions of less than 12 at % Al, corresponding to a total Ta+Al content of 27 at %, did not affect the coefficient of friction. 12 at % Al, however, gave an unpredictable sliding behavior; see Fig. 21(b).

Figure 21. Variations of friction levels on the amount of incorporated tungsten in an amorphous carbon coating (a) and the change in sliding behavior when increasing the amount of incorporated aluminium from 6 at % to 12 at %. The line in (a) is only meant to guide the eye.
Atmosphere; friction
As yet unpublished results show that the amount of moisture in the air has a profound impact on the RC friction levels. The absence of water increases the friction coefficient to levels equal to those of pure carbon. The mechanism behind the water-induced reduction of the friction coefficient of these coatings is believed to be a combination of a massive termination of strong bonds by water molecules and water-induced facilitation of the shearing of surface oxides.

Wear II, V
The same mechanisms lowering friction upon metal additions - facilitated graphitization and formation of a surface oxide - inherently give higher coating-material consumption during sliding. The RC showed a 200 % increase in wear rate compared to the unalloyed carbon coating. However, a transfer layer was formed on the counter surface which provided it with an efficient protection; an imperative trait when using reactive, sensitive or expensive counter materials. The mechanism wearing down the coating was a combination of mild polishing and chemical wear.

Amount of metal; wear II, V
Coating wear during sliding was shown to increase with increasing metal content, regardless of metal used. This was explained by the increased release of abrasive carbide particles due to a decreased amount of matrix carbon, adding an abrasive wear component to the graphitization and oxidation processes. Graphitization and oxidation are somewhat sympathetic wear mechanism, giving lowered friction parallel to the wear rate increase. Abrasive wear, however, is a bad-to-the-bone wear mechanism which both increases the materials consumption of the coating and destroys the transfer film vital for good sliding behavior. At moderate metal contents the release (and possibly also the size) of carbide particles is increasing but still rather low, raising coating wear to a certain extent but still allowing for a good sliding behavior. The somewhat vague metal content limit between acceptable and non-acceptable wear behavior, η, was found to be in the interval 20<η<30 at % for Zr, 22<η<27 at % for Ta+Al, 30<η<40 at % for W and η≈35 at % for additions of pure Ta.
Summary of Contributions

The following major conclusions can be drawn from this doctoral thesis.

- A co-sputtering method was developed which make possible alloying of thin films and coatings on a laboratory scale, without having to use gases or employ additional equipment. It is flexible, stable and simple to use, and high-quality films can synthesized at temperatures as low as 70 °C.

- Carbon coatings alloyed with different transition metals (MeC:C) can be synthesized and found to have a microstructure consisting of nanometersized metal carbide crystallites embedded in a matrix of highly disordered carbon – a nanocomposite structure. Increased amounts of metal gives corresponding increases in the amount of metal carbide, resulting in an increased coating hardness and elastic modulus.

- The alloying of a pure carbon coating with transition metals can result in heavily reduced friction levels. An addition of 15 at % Ta reduces the coefficient of friction during dry sliding against steel in air by 80 %, to \( \mu = 0.04 \). This improvement is attributed to two factors. One is facilitation of the low-friction mechanism already present in the pure carbon coating, graphitization, by the introduction of small TaC crystallites which disrupted the carbon structure. The other is the appearance of a second low-friction mechanism – the formation of a lubricating surface oxide from the decomposition of metal carbide. These processes interact and protect the counter surface by the formation of a very stable transfer film, in which subsequent sliding takes place.

- Sliding friction of sputtered MeC:C coatings is highly dependent on the amount of metal incorporated in the coating. Low amounts of metal are not able to disrupt the carbon matrix enough or provide enough lubricating oxide to reach the lowest friction levels. High amounts of metal leave too little carbon to the matrix for enough graphitization to take place. For low friction the optimum metal content is 10-20 at % for Ta or Zr, forming stable and stoichiometric carbides, and around 30 at % for W, forming a less stable and understoichiometric carbide.
Increases in coating metal content not only lower the friction, it also increases coating wear. This is attributed to the very same mechanisms yielding low friction, since they are both material-consuming processes. Moreover, above the metal contents optimal for low friction the wear rate increased dramatically. This is due to the increased release of unconsumed carbide particles during sliding, following the decreased amount of matrix carbon, and it added an abrasive wear component to the two mechanisms already at work. While graphitization and oxidative wear give lowered friction simultaneous an the increased wear rate, abrasion only impairs a good sliding behavior by further increasing the material consumption and destroying the transfer film vital for optimal tribological performance.

Al added to a TaC:C coating with 15 at % Ta, at the expense of carbon, is believed to form a complete solid solution with the TaC phase through substitution for Ta. This leads to the formation of Ta_{1-χ}Al_χC, where χ increases with increasing Al content.

Oxidation resistance is heavily dependent on coating metal content and microstructure. The TaC:C coating with 15 at % Ta starts to oxidize between 300 and 350 °C and is completely consumed at 500 °C. Upon oxidation the TaC:C is transformed to pure Ta_2O_5. The addition of Al at the expense of C greatly reduces the oxidation rate due to a gradual shift from Ta_2O_5 to AlTaO_4 with increasing amounts of Al. The latter oxide is more stable and its structure is denser than that of the former, which make oxygen diffusion more difficult.

As Al is incorporated into the TaC crystal lattice, there is no difference in sliding behavior of Ta+Al-alloyed coatings as compared to coatings alloyed with transition metals only. A compositional window at around 6-7 at % Al is established, where extremely low friction, low oxidation rate and a moderate increase in wear rate is combined.

The flexibility demonstrated by the co-sputtering method coupled with the large variations in mechanical, tribological and oxidation properties seen when changing the coating metal content, makes this a very suitable method for experimental alloying of thin films and coatings.
Sammanfattning på svenska

Bakgrund

Att belägga ytor med tunna skikt är en företeelse som är på stadig frammarsch, och har så varit sedan tidigt sjuttiotal. Anledningen är enkel; genom att förse en yta med en beläggning kan man ge detaljen ytan tillhör egenskaper som vare sig grundmaterialet etter beläggningsmaterialet klarar av att göra var för sig. I vissa fall är användandet av ytsskikt en förutsättning för att applikationen i fråga skall kunna fungera, som i bränsleceller eller tunnfilmsolceller. I andra fall är användandet styrt av marknadskrafter eller politiska ställningstaganden. De största vinsterna med ett ökat användande av ytbeläggningar står dock förmodligen att finna inom den mycket resurskrävande och kapitalintensiva mekaniska tillverknings- och förändlingsindustrin. Ett bra exempel där införandet av skikt givit stora ekonomiska och miljömässiga fördelar finns inom vissa företag i plåtformningsindustrin. Användandet av lågfriktionsskikt har där inneburit att den miljöfarliga smörjmedelsanvändningen avsevärt kunnat minskas samtidigt som bearbetningshastigheten ökat och verktygsslitaget minskat. Betänker man därtill att ytfinhet och toleranser hos de formade varorna förbättrats förstår man varför intresset för att implementera skikt i produktionsprocesser ökar.

Införandet av lågfriktionsbeläggningar ger alltså ofta ekonomiska och/eller miljömässiga fördelar. Den undergrupp av sådana beläggningar som visar upp den bästa kombinationen av mekaniska egenskaper (t.ex. hårdhet och elasticitetsmodul) och tribologiska dito (friktion och slitagemotstånd) anses generellt vara de kolbaserade lågfriktionsbeläggningarna. De ger en låg friktion tack vare ett glidlager av smörjande grafit bildas i slitytan under processens gång. Det finns sedan länge ett antal väl fungerande skikt av denna typ på marknaden, men utveckling pågår naturligtvis för att ytterligare förbättra de egenskaper som ursprungligen gjort skikten framgångsrika.

Resultat och bidrag

Egenskaperna hos dessa skikt är starkt beroende av deras kemiska sammansättning. För att på experimentskala smidigt kunna undersöka inverkan av förändringar i skiktsammansättning presenteras i denna avhandling en metod att legera sputtrade skikt. Metoden är okomplicerad,
mycket flexibel och ger goda möjligheter att kontrollera mängden tillsatt legeringsämne på ett bra sätt. Belägningstemperaturen kan hållas på en såpass låg nivå som 70 °C och dessutom finns inget behov av vare sig reaktiva gaser eller ytterligare materialkällor i processen.

Det visade sig att legering av rena kolskikt med övergångsmetaller går utmärkt. Skikten består av nanometerstora metallkarbidpartiklar i en matris bestående av rent kol, en nanokompositstruktur. När metallinnehållet ökas, ökar också mängden metallkarbid, vilket resulterar i en kraftig hårdhets- och elasticitetsmodulökning. Därtill påverkas dessutom friktionskoefficienten kraftigt av metalltillsatserna; 15 at % Ta i en ren kolbeläggning sänker friktionen mellan skiktet och en stålkula i osmord glidande kontakt i vanlig luft med över 80 % till 0.04. Detta är en extremt låg friktionskoefficient, jämfört med stål mot stål (0.6), stål mot TiN (0.4) eller stål mot kommersiellt tillgängliga lågfriktionsbeläggningar beläggningar (0.15-0.25). Denna förbättring beror på två saker. En är att grafitisering av oordnat kol underlättas på grund av - eller tack vare - att de mycket små karbidpartiklarna som bildades vid legeringen stör kontinuiteten i skiktens kolstruktur. Den andra anledningen är att ytterligare en smörjningsmekanism aktiveras. Under glidning bryts nämligen metallkarbiden ned och bildar en smörjande metalloxid. Genom samverkan mellan dessa två mekanismer bildas en skyddande tribofilm på motytan, i detta fall stålkulans, och vidare glidning sker mellan denna film och skiktet. Detta innebär att motytan skyddas på ett ypperligt sätt och ger densamma en mycket låg förslitningstakt.

De allra lägsta friktionsnivåerna uppträder bara vid fördelaktiga förhållanden mellan grafitisering och oxidation, dvs vid vissa metallinnehåll. För låga metallhalter resulterar i en otillräcklig mängd karbider, vilket leder till att grafitiseringen inte går så lätt som den gör vid "rätt" halter och att den oxidativa smörjningen blir dålig. För höga metallhalter innebär att nästan allt kol binds i karbidform och att grafitiseringen därför inte blir tillräckligt omfattande. För metallerna Ta och Zr, som bildar stabila och stökiometriska karbider, är 10-20 at % metall lämpliga mängder. För den mindre stabila och understökiometriska wolframkarbiden WC_{1-x} är den lämpligaste metallhalten högre, omkring 30 at %.

Legering med metall för inte bara med sig sänkt friktion utan tyvärr också ökad nötningshastighet. Det beror på att just de två mekanismer som ger låg friktion också är ansvariga för den ökande nötningsstaken, eftersom både grafitiseringen och oxidationen är av naturen materialavverkande processer. Vid metallhalter som ligger över de optimala för låg friktion ökar nötningsstaken dramatiskt. Detta på grund av att ooxiderade och abrasiva karbidpartiklar lättare frigörs ur matrisen när denna innehåller låga halter fritt kol. Vid högre metallhalter dyker alltså en abrasiv nötningskomponent upp och ansluter sig till de två som redan verkar i slitytan. Men medan grafitisering och oxidation är ganska sympatiska nötningsmekanismer, som
också ger låg friktion, är abrasion en mycket otrevlig slitagemekanism som ökar den materialavverkningen och förstör den, för låg nötning och låg friktion, så viktiga tribofilmen.

Kolskikt legerade både med 15 at % Ta och 1-12 at % aluminium bildar en blandning av fritt kol och en hittills opåvisad fast lösning av aluminium i tantalkarbik, Ta₁₋₂AlₓC. Detta sker medelst Al-substitution av Ta i det kubiska Ta₃C-gitteret. \( \chi \) ökar med ökade aluminiumtillsatser.

Oxidationshastigheten hos sputtrade kolskikt beror i stor utsträckning på mängden metall och hur tät mikrostruktur skiktet besitter. En kolbeläggning med 15 at % Ta börjar oxidera mellan 300 och 350 °C, och vid 500 °C är den helt omvandlad till porös Ta₂O₅. Tillsatser av Al gör att oxidationshastigheten minskar kraftigt, vilket beror på bildandet av den tätare och mer stabila oxiden AlTaO₄ som effektivt bromsar syrediffusionen och därmed oxidationsprocessen. Ökad aluminiumhalt ger mer AlTaO₄ på bekostnad av Ta₂O₅ och följdaktligen sänkt oxidationstakt. En sammansättning som ger åtskilligt sänkt oxidationstakt med oförändrat låg friktion och bara en mättlig slitageökning innehåller 15 at % Ta, 6-7 at % Al och resten kol.

Mycket stora variationer i mekaniska, tribologiska och oxidationsegenskaper följde på de ändringar som gjordes i skiktens sammansättningar under arbetet med denna avhandling. Detta tillsammans med den goda flexibiliteten hos beläggningsmetoden gör densamma ytterligt lämpad för legering av tunna ytskikt i experimentella syften.
References

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