Magnetron Sputtering of Nanocomposite Carbide Coatings for Electrical Contacts

KRISTIAN NYGREN
Abstract

Today’s electronic society relies on the functionality of electrical contacts. To achieve good contact properties, surface coatings are normally applied. Such coatings should ideally fulfill a combination of different properties, like high electrical conductivity, high corrosion resistance, high wear resistance and low cost. A common coating strategy is to use noble metals since these do not form insulating surface oxides. However, such coatings are expensive, have poor wear resistance and they are often applied by electroplating, which poses environmental and human health hazards.

In this thesis, nanocomposite carbide-based coatings were studied and the aim was to evaluate if they could exhibit properties that were suitable for electrical contacts. Coatings in the Cr-C, Cr-C-Ag and Nb-C systems were deposited by magnetron sputtering using research-based equipment as well as industrial-based equipment designed for high-volume production. To achieve the aim, the microstructure and composition of the coatings were characterized, whereas mechanical, tribological, electrical, electrochemical and optical properties were evaluated. A method to optically measure the amount of carbon was developed.

In the Cr-C system, a variety of deposition conditions were explored and amorphous carbide/amorphous carbon (a-C) nanocomposite coatings could be obtained at substrate temperatures up to 500 °C. The amount of a-C was highly dependent on the total carbon content. By co-sputtering with Ag, coatings comprising an amorphous carbide/carbon matrix, with embedded Ag nanoclusters, were obtained. Large numbers of Ag nanoparticles were also found on the surfaces. In the Nb-C system, nanocrystalline carbide/a-C coatings could be deposited. It was found that the nanocomposite coatings formed very thin passive films, consisting of both oxide and a-C.

The Cr-C coatings exhibited low hardness and low-friction properties. In electrochemical experiments, the Cr-C coatings exhibited high oxidation resistance. For the Cr-C-Ag coatings, the Ag nanoparticles oxidized at much lower potentials than bulk Ag. Overall, electrical contact resistances for optimized samples were close to noble metal references at low contact load. Thus, the studied coatings were found to have properties that make them suitable for electrical contact applications.

Keywords: transition metal carbide, amorphous carbon, composite, contact resistance, corrosion, friction, optical properties

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Till min familj
Preface

This work has been part of an academic and industrial collaboration between Uppsala University and Impact Coatings AB,1 where I have been employed since 2010 working part-time as an industrial graduate student and part-time as an engineer in research and development.

My position was to a large extent funded by The Swedish Foundation for Strategic Research through the ProViking program via the project MaxCell 2. I was enrolled in ProViking Forskarskola, which was a national graduate school in product and production development aiming to educate doctors for activities in industry. During my final year, financial support from the VINN Excellence Centre FunMat (Functional Nanoscale Materials) is acknowledged.

In early 2010, when I was finalizing my master’s thesis, one of my co-supervisors walked into the lab and asked me what my plans were. After enthusiastically telling him about my wet chemistry experiments, he told me that he was actually asking me about my plans in life because there was a position as a graduate student available at a nearby hi-tech company. They were apparently doing things with some coating technology that I was quite clueless about at the time. Nonetheless, they had a major research project funded and ready to go. The only thing missing was a PhD student ready to serve 5 years in physics or inorganic chemistry. Since my background was in biology engineering, I was pretty unsure about this. Was this a good idea? Is that what I want to be doing? He said, “Just go over there and pay them a visit. Have a look at what they’re doing.” Sure enough, I did. What I did not expect was the three guys in formal clothing welcoming me, bringing me into a small conference room with glass walls and then starting to perform the job interview. Naturally, there had been a slight misunderstanding and I cannot really remember their questions, although 45 minutes later I walked out into the fresh air not fully realizing the consequences of what had just happened.

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1 Impact Coatings is a supplier of physical vapor deposition production technology, as well as coating services, based in Linköping, Sweden.
Most of the time, I was at Impact Coatings performing various experiments (under great freedom might be added) and writing about my findings. Occasionally, I went to Uppsala to perform depositions using research-based equipment and to use the material science analysis equipment provided by the Ångström Microstructure Laboratory. Instead of part-time teaching (which most PhD students end up doing), I was involved with industrial deposition technology, the development of materials from a practical point of view, meeting customers, attending conferences and exhibitions, intellectual property discussions, marketing, electronics and writing software. Being an industrial graduate student has given me a lot of useful experience.

As time went by, it seems that I have been doing a little bit of everything in relation to my thesis as well. A list would include deposition experiments using both research-based and industrial equipment, realizing their differences, characterizing material structure, bulk chemistry, surface chemistry, mechanical properties, electrical properties, electrochemical properties, optical properties and coming up with new models to understand my results. It has certainly been a long walk, or run. Ironically, sometimes people have asked me if going for a PhD is like running a marathon, and I guess that would be true if running a marathon means that you are initially dropped off in the middle of nowhere, without a predefined route, and it will take you several years to make it back to civilization. Seriously though, I am grateful for the opportunity and the resources that have been given to me. Moreover, I have enjoyed doing this and I also feel that I always did my best. I hope you will find interest in my thesis.

Kristian Nygren
Linköping, August 2016

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i These occasional trips were quite frequent during certain periods and eventually granted me the highest bonus level possible within the Swedish railway services, at which point I could get coffee for free. On selected departures.

iii Three times Stockholm Marathon finisher
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Influence of deposition temperature and amorphous carbon on microstructure and oxidation resistance of magnetron sputtered nanocomposite Cr–C films
Nygren, K., Andersson, M., Högström, J., Fredriksson, W., Edström, K., Nyholm, L., Jansson, U.

II Growth and characterization of chromium carbide films deposited by high rate reactive magnetron sputtering for electrical contact applications
Nygren, K., Samuelsson, M., Flink, A., Ljungcrantz, H., Kassman Rudolphi, Å., Jansson, U.
*Surface and Coatings Technology*, 260 (2014) 326-334

III Structure and properties of Cr–C/Ag films deposited by magnetron sputtering

IV The influence of nanoeffects on the oxidation of magnetron sputtered Cr-C/Ag thin films containing silver nanoparticles
Nygren, K., Folkenant, M., Jansson, U., and Nyholm, L.
Submitted

V Passive films on nanocomposite carbide coatings for electrical contact applications
Submitted

VI Optical methods to quantify amorphous carbon in carbide-based nanocomposite coatings
Nygren, K., Samuelsson, M., Arwin, H., Jansson, U.
Submitted

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My contributions

**Paper I**
I took part in planning, deposited parts of the samples and performed parts of the characterization. I took part in all discussions and wrote the main part of the manuscript.

**Paper II**
I planned the study, deposited the DCMS samples as well as took part in the deposition of the HiPIMS samples and performed parts of the characterization (excluding TEM, XRD, NRA and nanoindentation measurements). I took part in all discussions and wrote the main part of the manuscript.

**Paper III**
I characterized electrical properties. I took part in discussions and in writing of the manuscript.

**Paper IV**
I took part in planning, performed all electrochemical experiments and parts of the characterization. I took part in all discussions and wrote the main part of the manuscript.

**Paper V**
I planned the study, deposited the samples and performed the characterization (except for nanoindentation and XRD measurements). I took part in all discussions and wrote the main part of the manuscript.

**Paper VI**
I planned the study, gathered the old samples as well as data and performed the characterization (XPS when necessary) except for parts of the spectroscopic ellipsometry. I took part in all discussions and I wrote the main part of the manuscript.

This thesis includes additional results that were presented at international conferences.
• Reactively sputtered chromium carbide/carbon glasslike films for sliding electrical contact applications
  Nygren, K., Samuelsson, M., Flink, A., Ljungcrantz, H., Kassman Rudolphi, Å., Jansson, U. *Presented at the 41th International Conference on Metallurgical Coatings and Thin Films (ICMCTF), 2014, San Diego, USA*

• Reactively sputtered Cr-Ag-C coatings for electrical contact applications
  Nygren, K., Folkenant, M., Lewin, E., Ljungcrantz, H., Jansson, U. *Presented at the 16th International Conference on Thin Films (ICTF), 2014, Dubrovnik, Croatia*
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Introduction

There are many cases when surface coatings\textsuperscript{iv} provide new properties, better performance, lower cost and lower environmental impact of the tools and products that we use today. Electrical contacts are products that generally have surface coatings in order to improve contact properties. The aim is to achieve a contact member with a nearly impossible combination of high electrical conductivity, high corrosion resistance, high wear resistance and low cost [1]. Uncoated base metals do not fulfill all of the above because (a), they form insulating oxides, which require high contact loads to disrupt [2], and (b), unacceptable wear problems follow as a consequence of high contact loads [3]. Another tradeoff situation is to use coatings containing noble metals, motivated by the fact that they do not form insulating oxides. However, coatings based on noble metals are undoubtedly expensive, they are soft and they wear out easily in a sliding metal-to-metal interface [3]. In addition, they are typically applied by environmentally hostile and carcinogenic electroplating processes [4,5]. Consequently, there is a need for alternative production methods as well as new coating materials for electrical contacts.

Physical vapor deposition (PVD) is a family of dry and vacuum-based deposition methods, which are much more environmentally friendly than electroplating [6]. One such method is magnetron sputtering and the fundamental principle relies on vaporizing atoms of the desirable coating material in a vacuum chamber, followed by the atoms condensing on a substrate to form a coating [7]. The present thesis used magnetron sputtering to deposit coatings.

Regarding new materials, nanocomposite coatings based on transition metal carbide and carbon are of primary interest. In this type of material, a carbide phase is mixed up in an amorphous carbon matrix and the structural order is in the nanometer-range. The properties of these nanocomposites make them very interesting for electrical contacts, because it may be possible to combine high hardness, low friction, high corrosion resistance, good electrical conductivity, low contact resistance and low cost [8–15]. To aid the reader’s perspective, Figure 1 shows two common electrical contacts where nanocomposite coatings have been applied.

\textsuperscript{iv} In this summary and the appended papers, the deposited samples are referred to as both \textit{coatings} and \textit{thin-films}. The words are used synonymously with no intended difference in their meaning.
Figure 1. Left: I deposited a nanocomposite coating onto the partially worn-out chip on my credit card (details are blurred), which was then used to pay for dinner as a proof of concept. Right: A coated 6.5 mm audio connector. (Note that these illustrations represent purely experimental work and are in no way associated with commercial products.)

Previous studies of transition metal (Me) carbide-based nanocomposite coatings for electrical contacts have been carried out in e.g. the Ti-C [13,16] and Nb-C [17,18] systems, with the possible additions of a ternary alloying element like Si [14,19] or Ag [20]. Overall, the results have been promising, especially for the Nb-C system [18], but the Achilles heel for these materials has been poor oxidation resistance and the formation of relatively thick surface oxides. Eklund et al. reported a surface layer of 35 – 40 Å of SiO$_x$ and TiO$_x$ on nanocomposite Ti-Si-C coatings [21], and Öberg et al. acknowledged that surface oxides can hamper use in low-load contact electronics [22]. For this reason, one solution has been to add Ag since it forms a separate metallic phase, improving the contact properties [23].

However, no one has yet studied the Cr-C system in relation to electrical contacts. It is well-known that a Cr surface exposed to air forms a thin and stable passive layer of Cr$_2$O$_3$, which makes many Cr-based alloys corrosion resistant. Consequently, it is no major surprise that Cr-C coatings have been shown to exhibit high corrosion resistances in several studies [24–28]. Another very interesting property is that Cr-C coatings deposited by PVD can have a very disordered, or even completely amorphous, microstructure [29–36]. This property is in strong contrast to coatings in the Ti-C and Nb-C systems, where nanocrystalline materials are obtained [37–40]. Based on this difference in microstructure, one can expect differences in coating properties as well. In fact, a smaller grain size can improve passive-film formation as well as the protective properties of the passive film [41,42] (Paper I). As a twist, to add Ag into a highly disordered Cr-C ceramic matrix is unexplored territory. When alloying with Ag in the nanocrystalline systems, it is common to find relatively large, ∼20 – 200 nm, surface particles of Ag on the surfaces of the coatings [43–45]. For the nanocrystalline materials, Ag diffuses to the surface from the coating bulk via boundaries in the material, like grain boundaries and...
less dense regions due to columnar film growth [46]. It is not clear how Ag would behave in an otherwise largely amorphous material.

The aims were to deposit and study coatings in the Cr-C (Papers I and II), Cr-C-Ag (Papers III and IV) and Nb-C (Papers V) systems for the purpose of developing new coating materials for electrical contacts. Nb-C was included because of the previous promising results [18]. Since the work was partially carried out in an industrial environment, it was important that the research results had a high possibility of being turned into commercial coating products. Therefore, studies included the deposition of coatings by both non-reactive magnetron sputtering (using research PVD systems) and high-rate reactive magnetron sputtering (using industrial PVD systems). The deposited coatings were characterized with regards to microstructure, composition and chemical bonding. Coatings properties were evaluated by performing mechanical, tribological, electrochemical, electrical and optical experiments. It was also routine to follow up on the experiments with subsequent material analyses. Finally, optical methods were used to characterize nanocomposite Me-C coatings (paper VI).

The thesis starts by introducing the materials and how the coatings were deposited. Thereafter, the methods used to characterize microstructure and coating properties are presented. A summary of the results and conclusions follow.
In this thesis, carbide-based nanocomposite coatings in the systems Cr-C (papers I, II and VI), Cr-C-Ag (papers III and IV), Nb-C (papers V and VI) and Ti-C (paper VI) were studied. The Ti-C coatings were not deposited in the present work and these coatings, as well as additional Cr-C and Nb-C coatings, were gathered from previous studies to form a large data set for studies of optical properties of nanocomposite coatings (paper VI).

**Transition metal carbides**

The transition metal carbides are known for being hard, refractory, wear resistant and good conductors of electricity [47,48] and have use in electronic applications [49]. However, depending on the metal, the properties will vary and so will the crystal structure. The presently relevant metals Ti, Nb and Cr are located in groups 4, 5 and 6, respectively, as illustrated by the partial periodic table in Figure 2.

Figure 2. Left: A limited part of the periodic table showing the transition metals of groups 4, 5 and 6. Their electron configuration is printed below. Right: Face-centered cubic (fcc) Me-C with carbon atoms in interstitial sites.

Carbides of Ti and Nb, and in fact of all the above metals in groups 4 and 5, can form a cubic close-packed structure\(^v\) with carbon interstitials in octahedral sites (illustrated to the right Figure 2, carbon in black). If all the sites are filled,

\(^v\) Nb-C can form a hexagonal Nb\(_2\)C phase as well, however this phase was not observed in the present work because of C/Nb ratios $\geq 0.8$ in all studied Nb-C coatings.
then a 1:1 atomic ratio of carbon to metal is obtained. However, within this lattice there can be empty interstitial sites with carbon vacancies, which is why the value of x can be several tenths smaller than 1. Both TiC and NbC can accommodate a significant number of carbon vacancies and thus they have wide homogeneity ranges, denoted MeCx, where x in TiCx is given by 0.47 < x < 0.99, and x in NbCx is given by 0.7 < x < 0.99 [47,48].

For the Cr-C system, Hägg’s empirical rule suggests that more complicated structures will form since the ratio of carbon to metal atom radii exceeds 0.59. In agreement, this system adopts the thermodynamically stable phases Cr23C6, Cr7C3 and Cr3C2, which are more complex than the NaCl-type structure depicted above. Note that these three Cr-C phases have large unit cells, with 116 atoms for Cr23C6, 80 atoms for Cr7C3 and 20 atoms for Cr3C2. The physical explanation is that the additional d-electrons for Cr (see Figure 2) destabilize the cubic structure due to filling of anti-bonding states [12]. However, a metastable face-centered cubic CrCx phase does exist and it is stabilized by carbon vacancies [50]. These principles had profound influence on the microstructure of the deposited coatings.

Nanocomposite coatings

The concept of cemented carbide composites is well-known and it has major technological importance in many applications. In a cemented carbide, the carbide grains are embedded in a metal matrix, which makes the material much less brittle compared to a pure carbide. For example, the wear resistance is drastically improved and the cemented carbides can be found in everyday things like tools, drill bits and studded tires.

If the grain size shrinks from micrometers to nanometers and the metal matrix is exchanged for a carbon matrix, a carbide/carbon nanocomposite is obtained. For films deposited by magnetron sputtering (introduced in the next chapter), it is common to find that the carbide grains are nanocrystalline with grain sizes ranging from a few nm up to some tens of nanometers and that the carbon matrix is amorphous. The concept is illustrated to the left in Figure 3.
Transition metal carbide nanocomposite coatings can be represented by an abbreviated form, Me-C/a-C(:H), where the prefix $a$ means amorphous and the suffix ‘(:H)’ denotes that the carbon matrix may be partially hydrogenated (which will be further discussed below). The phrasing ‘Me-C’ refers to a binary system regardless of its crystal structure, but it is common to also include a prefix in front of the carbide, e.g. ‘nc-’, which means nanocrystalline. Since many of the transition metal carbides crystallize in NaCl-type structure, e.g. TiC and NbC, it happens that the ‘nc-‘ prefix is left out and that the abbreviation is given as MeCx/a-C(:H). Here, the $x$ is used to represent carbon vacancies as discussed above. The carbide phase can also be amorphous, in which case the practice is to use the prefix ‘a-‘, e.g. a-CrC$_x$/a-C. This concept is called amorphous nanocomposite, which is illustrated to the right in Figure 3. In previous studies, Andersson et al. [29] studied the Cr-C system and showed that there can exist two separate amorphous phases, amorphous carbide (a-CrC$_x$) and amorphous carbon (a-C), and that their relative amount fluctuates on a nanoscopic scale.

Regarding the amorphous carbon phase, its chemical bonding can vary depending on how it is synthesized. The matrix can consist of mainly sp$^2$ bonds, known as graphite-like carbon, although is also possible to have mainly sp$^3$ bonds, known as diamond-like carbon. These two extremes, as well as the hydrogen content, have been used as corners to draw the ternary phase diagram in Figure 4. It illustrates that both sputtered a-C and sputtered a-C:H appear at the bottom where the sp$^2$ content is high. Associated properties are e.g. low hardness, in contrast to e.g. sp$^3$ hybridized diamond.
The fundamental advantage with the a-C(:H) phase is that it contributes with a polymeric-like character to the nanocomposite, which makes it more elastic [52]. Meanwhile, the carbide phase retains most of its typical bulk properties, like high hardness, good chemical stability and metallic electrical conductivity. In a wear situation, this concept makes the nanocomposite much less abrasive to the counterpart than a carbide [53] and it can lead to low friction and a self-lubrication mechanism based on sheets of graphite-like carbon sliding on top of each other [9,12]. It is therefore not very surprising to find that there are numerous published studies on nanocomposite coatings for wear applications [11,18,54–66].

The use of carbide-based nanocomposite coatings in electrical contact applications was suggested 10 years ago for ternary Ti-Si-C by Eklund et al. [14,67] and shortly thereafter for binary Ti-C by Lewin et al. [13]. Since then, several different studies with various twists have investigated this concept [16,17,19,22,23,68–73].

It also possible to alloy the binary systems with a noble metal like Ag. The solubility of Ag in carbide is very limited and it is therefore typical to find that Ag forms a separate metallic phase within the ceramic coating and there can also exist Ag particles on the surface [44,74,75]. The concept has mostly received interest for tribological reasons since such surface particles may reduce friction in wear applications [76–78].

These nanocomposite coatings can be deposited by physical vapor deposition (PVD) methods and one such method is magnetron sputtering. This method constitutes a common way to synthesize metallic and ceramic coatings in academic research and it is also widely utilized in industrial coating production due to tunable, robust and scalable processes. One fundamental advantage is the possibility to use low substrate temperatures, even allowing for polymers to be coated by ceramic materials from gas phase. Magnetron sputtering and practical aspects that were considered in this thesis are described in greater detail in the next chapter.
The sputtering process

The principles of magnetron sputtering are outlined in Figure 5. First of all, the process is performed in high vacuum or ultra-high vacuum. An inert sputter gas, usually argon, is introduced into the chamber and a plasma, i.e. ionized gas, is formed. Within this plasma, Ar\(^+\) ions are generated and these ions are accelerated towards a negatively charged cathode, called target, which contains the raw material that is to be deposited. When an Ar\(^+\) ion strikes the target, there will be a collision cascade from which a number of target atoms are ‘sputtered’ from the solid into gas phase. Depending on the working pressure, the sputtered atoms can travel ballistically or experience a number of scattering events. Either way, some sputtered atoms find their way to the substrate, where they condense and form a coating. Depending on deposition geometry and parameters, the amount of material that actually ends up on the substrate can range from just a fraction to nearly all of the sputtered atoms.

The target is mounted on a magnetron, which supplies the target with the negative electric potential as well as cooling (water) to keep the temperature of the target down. It also contains strong permanent magnets and these produce a magnetic field that confines the plasma in front of the target, leading to a
much higher rate of sputtering events as compared to the absence of a magnetron. In the sputtering event, the number of sputtered atoms per incident Ar⁺ ion is known as the sputter yield and it depends on the sputter gas, the target material (e.g. a metal or carbon), the energy (~0.5 keV) and the angle of incidence. In a nominal situation, Cr has a sputter yield that is about five times greater than that of C. Consequently, if a deposition process makes use of two magnetrons and two targets (called co-sputtering), and the desired stoichiometry of metal to carbon is 1:1, the current supplied to the C target needs to be about five times higher than the current supplied to the Cr target. Generally, higher currents will also lead to higher deposition rates (i.e. how much thicker the coating gets per unit of time).

As can be seen in Figure 5, the sputtered atom can collide with Ar atoms on its way forward. The mean free path between these collision events is inversely proportional to the working pressure, and in the present work, the typical mean free path was about 5 mm (1 Pa, 7.5 mTorr). Consequently, a substrate-to-target distance of 15 cm imply that the sputtered atoms should experience a number of collision events and lose nearly all of their initial kinetic energy before arriving at the substrate. This effect favors low substrate temperatures, which allow for many different types of substrate materials to be coated. However, low energy conditions inhibit surface diffusion, leading to rapid incorporation in the growing film, and the impinging atoms are unlikely to find energetically favorable sites. For this reason, magnetron sputtering can be used to deposit amorphous and metastable phases, especially if the thermodynamically stable phase of the material in question has a complex crystal structure. Hence, quenching in magnetron sputtering can be very significant. It is not uncommon to find that a deposited coating contains microscopic porosities and a density that is lower than corresponding bulk material. As an example, a cross-sectional micrograph of a Cr coating with under-dense columnar growth and characteristic vertical pillars can be seen in Figure 6.

There are different countermeasures to use in order to densify coatings. For example, it is common to use substrate heating. It is also common to apply an electrical substrate bias, typically around -50 V, which increases the kinetic energy of impinging ions. When the magnetron is operated in direct current mode, called direct current magnetron sputtering or ‘DCMS’ for short, the fraction of Me⁺ ions is only a few percent. In that situation, mainly the Ar⁺ ions will lead to resputtering (see Figure 5), which can densify the growing film by preferentially sputtering species that are in unfavorable sites. However, a too high (negative) substrate bias potential will effectively erode the deposited material and it can also lead to noble gas incorporation.

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vi 500 eV, Ar⁺, perpendicular geometry
Another film densification strategy is to ionize the deposition flux because ion irradiation facilitates adatom mobility [79]. The fraction of ionized material can be increased by the technique known as high-power impulse magnetron sputtering (HiPIMS), where the power to the magnetron is supplied in pulses. This method utilizes very high current densities (A/cm²) on the target surface and provides a much larger fraction of Me⁺ ions to the plasma compared to DCMS. Practical effects of HiPIMS, compared to DCMS, can be exemplified by dense sp³-bonded a-C (2.8 g/cm³ compared to 2.0 g/cm³) [80,81], no columnar growth for CrN [82] and improvements in mechanical and tribological properties for CrN and TiN [83].

Regardless of how the power to magnetron is supplied, it is possible to obtain e.g. oxides, nitrides and carbides by sputtering a metal target while introducing one or more reactive gases into the deposition chamber. This technique is called reactive magnetron sputtering. Gases like oxygen, nitrogen and hydrocarbons can be added to the process and the gas molecules will fragment within the plasma, forming highly reactive species. If for example acetylene (C₂H₂) is introduced, it will decompose into a variety of CₓHᵧ radicals and ions [84], which can react with the metal to form carbide or short hydrocarbon fragments. This reaction can take place on the target, in the plasma and on the substrate. One additional consequence is that there will be some incorporation of hydrogen in the coatings. To differentiate between non-hydrogenated and (partially) hydrogenated amorphous carbon, the suffix ‘:H’ is added to the abbreviation a-C if it is hydrogenated, i.e. a-C:H. Both abbreviations will frequently occur in the present work and the two always refer to non-reactively and reactively sputtered coatings, respectively.

The fact that the CₓHᵧ species can react with the target material can lead to a drift in the deposition process, where the chemical composition of the target changes over time. As a consequence, the composition of the coating will change as well. In principle, this effect occurs when too much of the reactive gas is introduced into the chamber. To prevent this from happening, one can monitor spectral emission lines from metal species in the plasma. By graphing the intensity as a function of time, as illustrated in Figure 7a, it is possible to evaluate if the coating process is stable. In this graph, the first seconds show high intensity, which corresponds to the deposition of a metallic adhesion
layer. Thereafter, a flow of acetylene was introduced to the chamber and the metallic intensity dropped to about one half, at which point one can expect deposition of carbide. After some time, the magnetron was switched off and the deposition process was complete. A cross-sectional micrograph of a coating deposited in this fashion is shown in Figure 7b.

Note that if the magnetron was turned on at this stage, even with no reactive gas present, the deposition flux would still initially consist of a high fraction of carbon species, as shown by the dashed curve in Figure 7a. The target is said to be ‘poisoned’, and to reset the target to its metallic state, it is pre-sputtered for some time (with substrates clear of the way). By doing this routine, the deposition chamber is also returned to a metallic state, which allows for each deposition experiment to begin in the same physical and chemical environment. If this is not done, there can be outgassing of reactive species adsorbed to the chamber walls. Pre-sputtering was performed prior to every single deposition in the present work.

![Figure 7](image.png)

*Figure 7. (a) Metallic intensity from plasma optical emission monitoring during reactive sputtering of a Cr-C coating (solid thick line) and during clean sputtering of the target (dashed line). (b) Cross-sectional micrograph of the resulting coating on a Si substrate.*

**Industrial considerations**

A large number of coatings were deposited by the industrial PVD system InlineCoater™ (Impact Coatings AB) and it can provide high deposition rates in both non-reactive and reactive mode. Photographs of this system, as well as of one of the research PVD systems at Uppsala University, are shown in Figure 8. One important aspect is the transfer of processes from research-scale equipment to industrial production. Since the sputtering process is sensitive to changes in parameters and process conditions, it is a relevant topic to study.
Figure 8. Left: The InlineCoater™ 500 system. The gray unit in the back contains power supplies, pumps and control systems. Right: The research sputter system “Svanslös”.

The InlineCoater™ has a load-lock system and short cycle times, which make it possible to transfer substrates from atmosphere to high vacuum, have them coated and then back again in ambient atmosphere in just a few minutes. This method is suitable for both academic research and industrial production. When using the research-based PVD systems, the overall throughput of coatings was low. Most notably, the deposition rate was about one hundredth of the deposition rate in the industrial PVD system. The coatings studied in this thesis had a typical thickness of 1 µm, which corresponds to a few minutes of deposition time in the industrial sputter. As such, the throughput of the industrial sputter is enormous and in addition to that, it can accommodate much larger substrates as well as greater numbers of substrates.

There are, nevertheless, many situations when the research equipment is the better choice. One reason is that it has ultra-high vacuum (< 10^{-7} Pa), which contains less residual impurities (e.g. O₂, N₂, H₂O, CO₂) compared to high-vacuum. Hence, the deposited material can in theory be of higher purity. In the present work, the research equipment also gave a better control of substrate temperature. Maintenance and cost of operation is also lower, since a relatively small chamber requires less pumping capacity. Moreover, small targets are cheaper than large ones and are generally easier to handle. From my experience, however, the larger magnetrons actually provided more stable operation and fewer issues with e.g. short-circuiting, arcing, maintaining a plasma, etc.
Characterization of the coatings

Chemical bonding and microstructure

In this thesis, one of the most heavily used methods was X-ray photoelectron spectroscopy (XPS). The principle is that a sample is irradiated with X-rays, which lead to the ejection of photoelectrons whose kinetic energies are measured under ultra-high vacuum conditions. By conservation of energy, the chemical binding energy of the electron can be calculated. Graphing the intensity as a function of binding energy gives rise to characteristic peaks, which allow for elemental identification as well as quantification. Moreover, the binding energy is affected by the local chemical environment of the species in question and can be used to study chemical bonding.

The analysis depth in XPS depends on the escape length of photoelectrons emitted from the solid without being inelastically scattered and losing energy. Hence, the analysis depth is in the nanometer range, ~1 – 10 nm. Note that the measurement spot was much larger, 200 µm, which means that the analysis probed a significant volume of material. In angle-resolved X-ray photoelectron spectroscopy (ARXPS), the angle between the sample and the detector was varied to adjust the analysis depth.

One analytical challenge was the presence of hydrocarbon contamination,\textsuperscript{vii} originating from the ambient atmosphere. The effect is illustrated in Figure 9, where two C1s spectra acquired from the same carbide coating are shown. As can be seen, the intensity from the coating was effectively masked by the hydrocarbon layer. Nevertheless, other relevant regions were studied without trouble since the hydrocarbons are merely physisorbed and do not cause shifts in the observed binding energies in e.g. Cr2p and Nb3d spectra.

\textsuperscript{vii} Also called adventitious carbon.
To remove the hydrocarbon contamination, sputter etching with Ar\textsuperscript{+} ions was used. Similar to the deposition process, bombardment by Ar\textsuperscript{+} ions will eject atoms from the sample although a difference is that the etching process uses a well-defined ion beam that is rastered across a small area (1x1 mm\textsuperscript{2}). When finished, acquiring a spectrum in this sputter-etched area will detect electrons that were previously completely attenuated. On the other hand, sputter etching can influence the measurement beyond an acceptable level due to sputter damages [85]. The situation is shown in Figure 10, where a collision cascade is schematically illustrated to depict preferential sputtering and restructuring of material in close proximity to the impingement site.

Three Nb3d spectra are plotted to the right in Figure 10. The first one (i) represents a Nb sample with a passive layer of Nb\textsubscript{2}O\textsubscript{5} and the second one (ii) shows the influences due to Ar\textsuperscript{+} sputter etching for 1 minute (500 eV). There is a broad bump of intensity, even extending beyond the Nb\textsubscript{2}O\textsubscript{5} feature at...
210.1 eV. Although NbO\textsubscript{x} suboxides exist, they are thin and should be shifted towards lower binding energies [86], indicating that the broad spectral bump was due to sputter damages. It is unwise to draw conclusions about the actual chemistry originally present based on this data. In the third spectra (iii), 10 minutes of sputter etching completely removed the oxide and the metallic Nb is found.

In the C1s region, however, the situation can be acceptable if the sputter etching is done with suitable settings [85]. One way to reduce the extent of sputter damages is to use a low ion energy, although the rate of material removal then becomes very low, making it a time-consuming process. For most nanocomposite coatings, sputter etching at 200 eV was the standard procedure to remove the passive layer (which was only 1 – 2 nm on as-deposited coatings) and to reach a depth of about 10 nm prior to the analysis of the chemical bonding in the bulk. One example of a C1 spectrum acquired from a Cr-C nanocomposite after sputter etching is shown in Figure 11. There are two visible peaks in the experimental data and they have been fitted by Lorentzian-Gaussians functions. The peak positions are typical of C-C (~284.5 eV) and C-Me bonds (~283 eV) [87] and their relative areas are then assigned as the relative contents of a-C phase and carbide phase, respectively. The explanation for the two separate peaks is that the metal adds valence charge to the carbon, causing the C1s electrons to get lower binding energy. This a general characteristic for binary transition metal carbides [88]. There is also a third peak fit, which was assigned to amorphous carbon in sp\textsuperscript{3} bonding, in agreement with the shift in binding energy of sp\textsuperscript{2} and sp\textsuperscript{3} of almost 1 eV in C1s [89]. Although this last peak is small and not experimentally resolved, it accounts for a “tail” in intensity at ~286 eV. In contrast, the peak at 284.4 eV is mainly due to the abundancy of sp\textsuperscript{2} carbon present in the a-C phase in these sputtered materials.

![Figure 11. XPS C1s spectrum acquired from a nanocomposite coating (Cr-C) obtained after sputter etching (200 eV Ar\textsuperscript{+}).](image-url)
By alternating between sputter etching and spectral acquisition, a sputter depth profile of the chemical composition can be obtained. In that case, the use of higher ion energy and lower energy resolution mean that deeper parts of the sample can be probed in reasonable time and the multiple steps allow for better statistics. Finally, the recorded intensities are multiplied by sensitive factors to get the relative atomic concentrations. These sensitivity factors were obtained from known standard samples by analyzing them using the same experimental XPS settings as for the unknown samples.

Structural information about the coatings was obtained by X-ray diffraction (XRD). When materials contain some crystallographic order, i.e. lattice planes that occur at periodically reappearing distances of a few Å, irradiation with X-rays of corresponding wavelength will get diffracted at discrete angles according to Bragg’s law. If intensity is plotted as a function of diffraction angle, a diffractogram is obtained. It is then possible to identify crystal structure and lattice parameter.

By using a low and constant incidence angle, while varying the angle of the detector, the so-called grazing incidence X-ray diffraction (GIXRD) method was performed. The purpose of this angular geometry is to get the highest possible intensity from the sample (and less from the substrate) as well as to probe lattice planes not only parallel to the surface, which is the case for θ/2θ geometry where the incoming and outgoing angles are equal.

Absence of reflections suggest that the sample is X-ray amorphous, in which case there is insufficient structural ordering to fulfill Bragg’s law. Note that even amorphous samples can have short-range order, which gives rise to broad bumps in the diffractograms [90].

In the case of nanocrystalline phases, it is typical to observe peak broadening. Based on the broadening, grain sizes can be estimated from Williamson-Hall plots [91], which rely on the principle that broadening due to grain size and broadening due to inhomogeneous strain (structural defects) have different relationships to the diffraction angle. In comparison, the well-known Scherrer equation does not account for strain broadening.

Further structural information was obtained by transmission electron microscopy (TEM). In TEM, a meticulously prepared thin (< 100 nm) slice of a given coating is irradiated by a high-energy beam of electrons (200 – 300 keV) and detectors are used to construct an image based on the transmission and interactions of the electrons with the sample. Owing to the short wavelength of the electrons, high resolution micrographs can be obtained (HRTEM). Diffraction of electrons can also be detected and this is used to create a selected area electron diffraction (SAED) pattern, which can be evaluated to get distances between lattice planes. These techniques only probe a very small fraction of a sample; however, they are valuable tools when it is important to more accurately discern the structure of X-ray amorphous coatings.
Scanning electron microscopy (SEM) was used to study cross-sections and surfaces of coatings. Micrographs are obtained by rastering a beam of electrons on the area of interest, where the electrons will interact with a volume of the material and experience scattering events. Detectors are used to construct an image from the emission of secondary electrons (ionization events) and from the scattering of beam electrons. The obtained micrographs provided information about coating thickness, thin-film growth and surface properties (related to e.g. tribological and electrochemical experiments).

Energy dispersive X-ray spectroscopy (abbreviated both EDX and EDS) was used to get elemental information about the materials investigated in SEM and TEM based on the emission of characteristic X-rays.

Raman spectroscopy was used to detect and study the chemical structure of the a-C(:H) phase. The principle is that a surface is illuminated by monochromatic laser and the photons will experience a shift in energy due to interactions with the vibrational modes in the material. The method is highly sensitive to differences in carbon bonds and can be used to study carbon hybridization. Relevant literature on amorphous carbons can be used as reference material [51,92–94].

Coating properties
Mechanical properties
Hardness and elastic modulus are important properties since they will strongly influence the electrical contact area due to plastic and elastic deformation. In this thesis, hardness and elastic modulus were measured using nanoindentation, which is a technique where a small diamond tip with known geometry is pressed into the material. Meanwhile, the load and displacement are recorded and presented as load-displacement curves. The hardness as well as the elastic modulus can then be obtained using the procedures given by Oliver and Pharr [95].

Tribological properties
Friction and wear are important when considering properties of a sliding electrical contact. Two setups were used to study coefficients of friction and the first one was a reciprocating sliding setup and the second one was a ball-on-disc setup with rotating geometry. In both cases, an uncoated ball bearing steel ball was used as counterpart and there was no lubrication. The ball-on-disc setup is illustrated in Figure 12. The resulting wear tracks were studied e.g. by SEM.
Electrical properties

Obviously, the electrical properties of the coating are critical for the performance of the electrical contact. When electrical current flows from one contact member to another via an interface, the addition to the total resistance due to this interface is the contact resistance. Important parameters for the contact resistance include the chemistry in the interface, the applied load and contact mechanics. Following contact resistance theory [96], the contact resistance for conductive bulk-sized connectors with a thin coating can be approximately given by the equation

\[ R = \frac{\rho d}{A_c} \]  \hspace{1cm} (1)

where \( R \) is the contact resistance, \( \rho \) is the resistivity of the coating, \( d \) is the coating thickness and \( A_c \) is the conductive contact area. (In the present work, constriction resistance can be neglected [96]). The conductive area is strongly related to the applied contact load.

Electrical resistivity was obtained by measuring the sheet resistance using a 4-point probe and multiplying by coating thickness. The setup used to measure contact resistance, which is not a material property and it depends on the system, is described in Figure 13. A counterpart with Au coating and hemispherical geometry was pressed against a sample. Meanwhile, the contact load was measured by a force gauge and the voltage drop across the junction was measured while applying a small current.

*Figure 12.* Ball-on-disc setup. The coefficient of friction is determined from the ratio of the normal load to the frictional force \((F_N/F_F)\). Counterpart was a ball bearing steel ball with a diameter of 6 mm. Load was 2 N. Sliding speed was 0.1 m s\(^{-1}\). See paper III for details.
Figure 13. Setup to measure contact resistance. A low contact load (typically 1 N) was applied via a spring-loaded test probe featuring a hemispherical tip with Au coating. Contact resistance $R$ was obtained by measuring the voltage drop across the junction when a low current was applied. The diameter of the tip was typically 1.2 mm ($d = 1.4$ mm in paper IV). Larger tips ($d = 3.2$ mm) were used in sliding contact resistance experiments. (Adopted from Paper V.)

Electrochemical properties

Many metals form passive films, which are thin oxide films of a few nanometers in thickness that protect the underlying material from corrosion (i.e. loss of material). Stainless steel is such a material and it is passivated by a thin layer of Cr$_2$O$_3$. However, passive films can fail and problems due to corrosion may follow. In the presence of an electrolyte, it gets especially problematic if the corrosion process is localized to pits, which can be initiated by a local disruption of the passive film by e.g. chloride ions. In that case, the situation can spiral downwards, where the pit gets highly acidic and enriched in anions, leading to active and localized corrosion. An example is shown in Figure 14a, where localized corrosion created holes in stainless steel.

Figure 14b shows a micrograph depicting grains boundaries of stainless steel. In those boundaries, there can be loss of passivity due to depletion of chromium. In contrast, Figure 14c shows a high-magnification micrograph of 316L
steel coated with an a-CrC/a-C:H coating and note that there are no grain boundaries in an amorphous material. The promising properties of this concept can be understood from Ralston and Birbilis [42], who concluded that a refinement in structure, and an increase in grain boundary density, improve both the formation of the passive film as well as its adhesion. However, a magnetron sputtered coating does not flatten uneven substrate topography. If there are valleys present on the uncoated substrate, the valleys will remain after coating and this effect is illustrated in Figure 14d. Here, a grain boundary region after coating is shown in great magnification.

Electrochemical properties of the coatings were studied by voltammetry and chronoamperometry using a three-electrode setup. Different potentials, relative to a Ag/AgCl reference electrode, were applied to the working electrode, in this case a coated sample, and the current was measured. The counter electrode was made of Pt. In the voltammetric experiments, the potential was swept at a rate of 5 mV s⁻¹, normally covering both the passive and transpassive regions of Cr. In the chronoamperometric experiments, a single step to a given potential was used and it was maintained from 5 up to 60 minutes. Two amperograms, representing uncoated 316L and 316L with a sputtered Cr-C coating, are shown as examples in Figure 15. As evidenced by the lower current density, Cr-C can improve the corrosion resistance of stainless steel, as was concluded in previous studies [29,97].

![Figure 15](image_url)

*Figure 15.* Amperograms for uncoated stainless steel (316L) and stainless steel with a magnetron sputtered Cr-C coating (46 at.% C). Potential was +0.64 V vs. Ag/AgCl. Electrolyte was 1 mM H₂SO₄, 80 °C.

All experiments were performed in an electrolyte containing sulfuric acid, which was historically bound to previous studies within our group related to the passive behavior of uncoated, as well as coated, stainless steel electrodes with possible functionality in renewable energy applications e.g. batteries and
fuel cells [29,97,98]. In a sense, such electrodes are also electrical connectors, although in an electrolyte.

Photographs taken of one of the two electrochemical setups that were used in the present work are shown in Figure 16. The second electrochemical setup featured an analogous concept (paper I). Details can be found in Högström [99].

![Diagram of electrochemical cell](image)

*Figure 16. Photographs with labels describing the electrochemical cell used in paper IV.*

**Optical properties**

Reflectance spectrophotometry and spectroscopic ellipsometry were used to measure optical properties of Ti-C, Cr-C and Nb-C nanocomposites. In the reflectance spectrophotometry measurements, the coatings were illuminated by light in the visible range and the reflectance (%) as a function of wavelength was recorded. In spectroscopic ellipsometry measurements, the change in polarization of light (245 – 1690 nm), as it was reflected from the coatings, was measured at different angles. The signal will depend on materials properties, but to actually find material constants (e.g. resistivity) requires complicated modelling and simulations to find a physical model that describes the data. In the present work, the primary data was only used to find empirical trends.
Results and discussion

Microstructure

The Cr-C system

**Non-reactive magnetron sputtering**

It is known that the substrate temperature during deposition of Cr-C coatings has major influence on the microstructure, which can be crystalline, nanocrystalline and amorphous [29,32,34–36,100–103]. However, it was unclear how the structure and chemical bonding of Cr-C nanocomposites would be affected by changes in deposition temperature and composition. Therefore, a study with the aim to investigate those parameters was conducted (Paper I). Deposition experiments were performed in the research PVD system using non-reactive deposition to have maximum control over the experimental conditions.

Two series of Cr-C coatings, with high carbon content (HC, ~70 at.% C) and low carbon content (LC, ~40 at.% C), were co-sputtered at substrate temperatures of 20, 300, 500 and 700 °C. Results from GIXRD are shown in Figure 17a. The HC coatings deposited at temperatures up to 500 °C were X-ray amorphous and at 700 °C, the diffractogram corresponds to Cr$_3$C$_2$, Cr$_7$C$_3$ and X-ray amorphous Cr$_x$C. The diffractograms for the LC coatings correspond to an X-ray amorphous microstructure up to 300 °C. At 500 °C, the Cr$_7$C$_3$ phase was formed and at 700 °C, there was a mixture of Cr$_7$C$_3$ and Cr$_3$C$_2$. Overall, this result indicates that it was easier for the system to form Cr$_7$C$_3$ compared to Cr$_3$C$_2$. 
Figure 17. (a) Diffractograms (GIXRD, 1°) for non-reactively sputtered Cr-C coatings with high and low carbon content (HC and LC, ~70 at.% C and ~40 at.% C, respectively). The Cr reflections are due to an adhesion layer. (b) XPS C1s spectra for the HC and LC coatings. The carbon content is printed (in at.%) above each spectrum. (Adopted from paper I.)

One question is if the X-ray amorphous CrCₓ coatings contained some nanocrystalline order that was undetectable by XRD. A previous study on Cr-C coatings, deposited in the same sputter system, suggested that such coatings were amorphous based on TEM results [29]. However, a follow-up study on coatings with a broader range in composition found that small amounts of metastable cubic nc-CrCₓ phase were present when the C/Cr ratio was close to 1 [104]. Later, another study revealed that the electron beam in TEM could induce crystallization of amorphous carbide-based nanocomposites and it is
therefore unclear if the observed nanocrystallites were formed during the deposition process or if they were a beam-induced artefact [105]. In the present work, the possible presence of small amounts of medium-range order (< few nm) in an otherwise mainly amorphous matrix is not that important for the discussion on coating properties. Therefore, these “X-ray amorphous” coatings will be referred to as amorphous a-CrCx. The formation of amorphous Cr-C (at low substrate temperatures) will be further discussed below.

Composition and chemical bonding were studied by XPS and results from the C1s region are shown in Figure 17b. There are two main peaks visible, which have been attributed to carbide (C-Cr) and a-C (C-C). The a-C phase was fitted by functions corresponding to sp² and sp³ bonds. The carbide carbon, however, can in this case be separated into two separate contributions, related to carbon in the Cr:C; and Cr:Cr phases, in correspondence with the diffractograms (Figure 17a). By evaluating the area of the peak fits, it was established that the HC series contained 79 (± 5) % of a-C phase and the LC series contained 19 (± 4) % of a-C phase. Moreover, the carbon content in the a-CrCx phase was, on average for all coatings, 35 ± 2 at.% (a-CrC0.54), which is just between that of Cr:C; (30 at.% C) and Cr:Cr (40 at.% C). This is in good agreement with the findings in XRD. Thus, the addition of carbon to the coatings resulted in formation of additional a-C phase, while the carbon content in the carbide phase remained close to constant. In conclusion, different Cr-C coatings that were amorphous, nanocomposite or crystalline were obtained. These results will be compared to reactively sputtered Cr-C coatings below.

Reactive magnetron sputtering

Since nanocomposite Cr-C coatings for use in electrical contact applications were not previously reported in literature, the aim was to investigate the microstructure of reactively sputtered Cr-C coatings with different chemical composition and their properties in relation to electrical contacts (Paper II). Coatings were deposited by high-rate DCMS and high-rate HiPIMS, since the latter may provide denser coatings with better functional properties [106]. Cr-C coatings with different carbon contents, in the range 19 – 69 at.%, were deposited by sputtering Cr in Ar/C2H2 discharges, which provided deposition rates of about 200 nm min⁻¹ and 50 nm min⁻¹ for DCMS and HiPIMS, respectively, in reactive mode. Substrate temperatures were in the range 100 – 150 °C, which is low in comparison to the much higher melting point of Cr-C, ~1800 °C [107].

Diffractograms for the coatings are shown in Figure 18a (below). As can be seen, there are no clear crystalline reflections in any of the diffractograms and there is a broad bump at around about 2Θ = 40 °. This bump suggests that...

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*Deposition rates in metallic mode were 150 % higher.*
the films are mainly amorphous [29,104]. However, there are also weak features present, which correspond to lattice planes in metastable fcc CrCₙ [108]. The lattice parameter for this phase was determined to 4.08 Å.

Two high-resolution TEM micrographs, corresponding to one DCMS coating and one HiPIMS coating, both with 56 at.% C, are shown in Figure 18b (below). Note that areas rich in carbon have bright contrast and areas rich in chromium have dark contrast. These micrographs, as well as additional ones, strongly indicated that a vast majority of the material was indeed amorphous. Nevertheless, one fcc CrCₙ grain, 3 nm in size, is marked in the HiPIMS micrograph. Selected area electron diffraction (SAED) patterns, shown as insets in Figure 18b, typically consisted of diffuse rings, merely indicating an average distance between neighboring atoms (and not ordered lattice planes). In the SAED pattern presented for the HiPIMS coating, there are more distinct rings and the distances correspond to the fcc CrCₙ phase observed in XRD. Overall, however, the nanocrystalline content was estimated to be less than 10%.

If the diffractograms in Figure 18a are compared to the ones in Figure 17a, for non-reactively sputtered coatings at temperatures ≤ 300 °C, it can be concluded that the reactive sputtering process resulted in more crystalline material (albeit still highly amorphous) than the non-reactive process. This is unlikely to be a coincidence. A review of literature on this topic reported in ref. [29] indicate that this is a systematic trend in the Cr-C system. However, the difficulties to accurately analyze the microstructure by XRD and TEM mean that a lot of literature should be critically assed. Still, from a physical and chemical standpoint, CₓHᵧ species physisorbed on the surface of the growing film should exhibit greater surface diffusion than neutral carbon atoms. The plasma chemistry in the reactive process contains hydrogen, which can interact with C-containing species and chemically sputter them. Furthermore, charged radicals (e.g. CH⁺ [84]) may lead to densification based on the general effects of ion-assisted deposition. In fact, it has been reported that carbon ionization in magnetron sputtering can greatly enhance the density of carbon coatings [81]. Still, in the present work these effects were insufficient to result in significant amounts of crystalline carbide phases. One explanation is the high deposition rate, which was two orders of magnitude higher compared to relevant literature [29–31,34,36,109]. Higher deposition rates mean less time for physisorbed species to find favorable sites for nucleation, leading to mainly amorphous Cr-C.
Figure 18. (a) GIXRD diffractograms (1°) for reactively sputtered Cr-C coatings. Coatings were deposited at a substrate bias potential of -50 V (alternatively -150 V, as marked). (b) TEM micrographs for two of the coatings with 56 at.% C. Areas rich in carbon have bright contrast and areas rich in chromium have dark contrast. The insets are SAED patterns. (Adopted from paper II.)
In the introduction, it was mentioned that stable phases for Cr-C are the Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_3$C$_2$ phases, whereas a stable Cr-C phase with NaCl-type structure would violate Hägg’s rule. The experimental results show that the stable phases were not obtained (unless the coatings were deposited at substrate temperatures of 500 °C and above) and instead, there was formation of the metastable nc-CrCx phase with NaCl-type structure. This can be explained by the high quenching rate in magnetron sputtering carried out at low substrate temperature, effectively inhibiting surface diffusion and formation of complex crystal structures. Simpler structures are therefore favored. In addition, quenching is enhanced by ion-bombardment and it can be concluded, based on refs. [50,110,111], that formation of fcc CrC$_x$ is facilitated by ionized deposition. It can also be noted that this phase decomposes above 250 °C [50,112].

The amount of a-C:H phase that was formed as a function of the total carbon content was evaluated from XPS C1s spectra. Results are shown in Figure 19. As the carbon content increased from 19 up to 69 at.% C, the a-C:H phase content increased as well, from practically zero up to 84 %. Thus, the deposited coatings can be described as a-CrC$_x$/a-C:H nanocomposites (neglecting the minority of nc-CrC$_x$ phase). Note that the different deposition methods (DCMS or HiPIMS) and substrate bias potentials (-50 V or -150 V) did not result in any clear difference.

![Figure 19](image-url)  
Figure 19. The a-C:H phase content as a function of total carbon content for Cr-C/a-C:H coatings deposited by DCMS and HiPIMS. Substrate bias was -50 V (alternatively -150 V, as marked). Results for Ti-C, Zr-C and Nb-C have been added from refs. [13,17,61]. (Adopted from paper II.)

The non-reactively sputtered coatings (Fig. 17b) basically obey the same trend as shown in Figure 19, e.g. 79 % a-C for a carbon content of 70 at.%. In this figure, there are also markers for related Me-C systems (Me = Ti, Zr, Nb). As seen, all the systems principally exhibit the same trend as well albeit with
slightly different offsets. This trend is further discussed on p. 59, where a much larger data set is considered.

Further information on the chemical bonding of the carbon matrix was obtained by Raman spectroscopy. Based on suitable reference data in ref. [93], the a-C:H phase was concluded to be similar to sp²-rich hydrogenated graphite-like amorphous carbon (GLCH). Since XPS cannot detect hydrogen, two coatings were analyzed by ion beam analysis and the atomic ratio of H:C was found to be 2:3. It can be expected that the hydrogen was mainly present as C-H groups, i.e. within the a-C:H phase, and hence depended on the total carbon content. This trend has been shown for nc-TiCₓ/a-C:H [12,113].

A final important conclusion is that there was not any significant difference in coating microstructure or phase content related to the use of DCMS or HiPIMS. However, coatings deposited by HiPIMS appeared to be denser compared to coatings deposited by DCMS when evaluating SEM micrographs (not shown).

The Cr-C-Ag system

The Cr-C-Ag system was previously uninvestigated and fundamental studies of structure and chemical bonding were therefore motivated. The deposition experiments were made by non-reactive magnetron sputtering using a research-based sputter and high purity targets. To strengthen the industrial relevance, coatings were also deposited in the industrial sputter by reactive magnetron sputtering. ix

Non-reactive magnetron sputtering

By co-sputtering elemental targets of Cr, C and Ag, it was possible to form novel nanocomposite coatings containing Ag nanoclusters, 2-5 nm in size, embedded inside an a-CrCₓ=0.41-0.47/a-C matrix. The formation of a separate metallic Ag phase can be expected from the very low solubility of Ag in carbide. The Ag content ranged from 0 – 14 at.% and peak fits of C1s spectra suggested that the fraction of a-C phase was 28 – 42 %, which was also found to be linearly proportional to the Ag content.

One challenge with this material system was to get dense coatings. In fact, deposition at a substrate temperature of 300 °C resulted in very porous coatings, which did not exhibit satisfactory functionality in e.g. tribological experiments. By not using any intentional substrate heating, it was possible to obtain denser coatings that had practical usability, leading to the conclusion that the mobility of the Ag was significant during deposition and that this behavior must be quenched by using proper deposition conditions.

ix This study was presented at an international conference and it is not included in the appended papers.
These coatings also had very large numbers of Ag nanoparticles, hereafter called NPs, on their surfaces and one such surface is illustrated in Figure 20. The enrichment of Ag on the surfaces is due to Ag diffusion from the bulk, preferentially via boundary regions, e.g. between grains as well as less dense regions due to columnar growth [46]. To be able to explain coating properties, it was necessary to evaluate the sizes of the NPs, which was very cumbersome to do manually. Therefore, image processing techniques were used and computer automation made it possible to approximately separate the NPs from the ceramic matrix, count them and evaluate their sizes. Results revealed that the surfaces contained from $5 \times 10^8$ up to $5 \times 10^{10}$ NPs per cm$^2$ and that the particle sizes ranged from 4 – 14 nm in radius.

![Figure 20. SEM micrograph depicting the surface of an a-CrC$_x$/a-C/Ag nanocomposite. The white clusters are Ag nanoparticles, which were formed due to diffusion of Ag from the bulk of the film where smaller clusters of Ag were present. (Adopted from paper IV.)](image)

**Reactive magnetron sputtering**

It was possible to deposit coatings in the Cr-C-Ag system by high-rate reactive magnetron sputtering as well. The basic concept was to use a Cr target and then put a small strip of Ag on the Cr target to cover a small part. Consequently, a fraction of the Cr was replaced by Ag in the deposition flux and this change was reflected in the coating composition as well.

The reactively sputtered coatings were found to have a similar microstructure as the non-reactively sputtered ones. Results showed that the coatings comprised a-CrC$_x$, a-C:H and surface Ag NPs. GIXRD diffractograms showed no signs of crystalline phases and the diffractograms were similar to ones obtained for the non-reactively sputtered coatings with low Ag content (see paper III, c.f. Fig. 1a). Although the structure within the bulk was not further studied by TEM, the presence of small nanoclusters of Ag should be expected.

Table 1 lists process parameters that were found to yield coatings of apparent good quality, allowing for experimental studies of their properties. Cross-sectional micrographs, illustrating one a-CrC$_x$/a-C:H coating (deposited without the Ag strip) and one a-CrC$_x$/a-C:H/Ag$_5$ coating, are shown in Figure 21a.
and Figure 21b, respectively. As can be seen, the coatings were 1 µm thick and exhibited broken columnar growth. It was also found that the surfaces were smooth and appeared to be featureless, even when using relatively high magnification in the SEM, as shown in Figure 21c. This latter micrograph depicts the a-CrCₓ/a-C:H/Ag₅ coating deposited on polished high speed steel.

Table 1. Process parameters used for reactive magnetron sputtering of Cr-C-Ag coatings.

<table>
<thead>
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<tr>
<td>Target</td>
<td>Cr + Ag strip (purity 99.9 %)</td>
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<td>Substrate bias</td>
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<td>Working pressure</td>
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<tr>
<td>Deposition rate</td>
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Figure 21. Cross-sectional micrographs of (a) a-CrCₓ/a-C:H and (b) a-CrCₓ/a-C:H/Ag₅. The micrograph in (c) depicts the surface of polished high speed steel with the coating in (b). The two faint lines are microscopic scratches left behind by polishing.

However, even higher magnification actually confirmed the presence of Ag NPs. Surface micrographs of non-reactively and reactively sputtered a-CrCₓ/a-C(:H)/Ag₅ coatings can be compared side by side in Figure 22a and Figure 22b, respectively. Clearly, the NPs on the reactively sputtered coating were, on average, much smaller compared to those on the non-reactively sputtered coating. Two explanations can be given for this difference. The first one is that the high deposition rate inhibited diffusion of the otherwise highly mobile Ag species. The second one is that a slightly more refined structure allowed for less Ag to reach the surface via columnar boundaries.
The Nb-C system

The previous studies on Nb-C in refs. [17,18] demonstrated a successful transfer from non-reactive magnetron sputtering using research sputter equipment, to industrial-scale reactive magnetron sputtering. Moreover, promising properties for electrical contacts were demonstrated, although it was unclear how and why the contact resistance could vary several orders of magnitude. Therefore, the industrial PVD equipment was used to deposit coatings for a new study, in which the coating microstructure and most notably the surface chemistry were investigated in order to explain the variations in contact resistance.

Following the previous studies [17,18], it was possible to deposit nc-NbCx=0.7-1.0/a-C:H nanocomposites. Grain sizes were estimated from the broadening of diffraction peaks (see Figure 23a) and lower bound estimates were 12, 4 and 2 nm for coatings with C/Nb ratios of 1.6, 1.0 and 0.8, respectively, while the a-C:H phase fractions were determined to be 44, 24 and 11 %, respectively, by XPS analysis. By assuming a rudimentary cube model [12,88], where all the carbide grains are approximated by equiaxed and evenly distributed cubes embedded in a carbon matrix, the mean matrix thickness separating the carbide grains was calculated to be 0.24 nm. This value can be interpreted as the presence of a single monolayer of carbon, on average, between the carbide grains. A thin matrix thickness has been shown to be beneficial for the contact properties, at least a high contact loads [13].
Surface chemistries of the Nb-C coatings were studied by XPS. Angle-resolved XPS N3d spectra for one Nb coating and for one NbC_{0.8}/a-C_{24}:H coating are shown in Figure 23b. The subscript ‘24’ (i.e. a-C_{24}:H) is the a-C:H phase fraction obtained from C1s spectra (not shown). What should be noted is that the nanocomposite coating exhibited a significant contribution from Nb-C bonds even at grazing angles (15°), in contrast to metallic Nb where the intensity mainly can be ascribed to Nb-O bonds. Calculations of oxide thicknesses resulted in a mean oxide thickness of 1 nm for the nanocomposites, whereas the metallic Nb exhibited a thicker mean oxide of 4 nm.

Additional XPS analyses of the nanocomposites revealed that their surfaces not only consisted of Nb_{2}O_{5}, but they also contained a-C:H and C expelled from the Nb-C when it was oxidized to Nb-O. To eliminate possible influences from hydrocarbon contamination in XPS C1s, gentle Ar⁺ sputter etching was used to probe different depths. Key results are shown in Figure 24, which contains a surface plot that illustrates how the carbon chemistry, as observed in the C1s region, changed as a function of depth near the surface for a NbC_{1.0}/a-C_{44}:H coating. This sample featured a more oxidized surface layer (due to oxidation in air at 200 °C) and its mean oxide thickness was 4 nm (based on the Nb3d region). However, in Figure 24, the dark red regions represent maximum intensity and the blue regions represent background. Close to the surface, the binding energy where the intensity has its maximum corresponds to C-C.
bonds. At a depth of about 3 – 4 nm, it transitions into a majority of C-Nb bonds, corresponding to the bulk chemistry of the coating. In conclusion, the passive films formed on the nanocomposite coatings are more complex than a traditional oxide overlayer and this effect should be taken into consideration when studying surface properties of nanocomposites.

![Figure 24](image)

Figure 24. Surface plot of intensity (= color) in the XPS C1s region as a function of binding energy and sputter depth (reached by sputtering etching, 500 eV Ar⁺). This plot was interpolated from five C1s spectra. All hydrocarbon contamination was eliminated right away by a short Ar⁺ sputter etch. Dotted lines at 282.8 eV and 284.4 eV correspond to C-Nb and C-C bonds, respectively. (Adopted from paper V.)

The Ti-C system

Additional coatings, in the Ti-C system, were also studied in this thesis (paper VI). However, those samples were not deposited in the present work and were studied by Samuelsson et al. [79,114]. In brief, the samples were deposited by both DCMS and HiPIMS and can be described as nc-TiCₓ/a-C:H. The use of HiPIMS lead to more stoichiometric carbide, i.e. fewer carbon vacancies.

Properties

Mechanical properties

In general, the contact mechanics are important for the properties of an electrical contact since the mechanical response to the contact load, applied via the counterpart, will determine the mechanical contact area. In this area, the penetration or removal of oxides can occur, giving rise to a smaller electrical contact area. Although it seems much more common to discuss hardness rather than elastic modulus in relation to electrical contacts [2,72,115,116], the elastic properties of a nanocomposite can have a strong positive influence on the wear resistance as discussed by Leyland and Matthews [117].
Hardness and elastic modulus were obtained by nanoindentation and results for a-CrC<sub>x</sub>/a-C:H coatings are shown in Figure 25a and Figure 25b, respectively. Here, the horizontal axis represents the a-C:H phase content obtained from XPS C1s spectra. It can be seen that the hardness values range from ~12 GPa without a-C:H and then decrease linearly to ~6 GPa at ~80 % a-C:H phase. Meanwhile, the elastic modulus follows a similar trend. It starts at ~200 GPa without a-C:H and then it decreases to ~70 GPa at ~80 % a-C:H phase.

![Figure 25. Nanoindentation (a) hardness and (b) elastic modulus for a-CrC<sub>x</sub>/a-C:H coatings. Results from literature for a-CrC<sub>x</sub>/a-C [29] and nc-NbC<sub>x</sub>/a-C:H [18] have been added as well. Dashed lines are linear regressions intended as guides for the eye. Standard deviations were, on average, 9 % for hardness and 5 % for elastic modulus. (Rearranged figures from paper II.)](image)

Literature data for non-reactively sputtered a-CrC<sub>x</sub>/a-C [29] and nc-NbC<sub>x</sub>/a-C:H [18] coatings have been added to Figure 25a and Figure 25b as well. Starting with the nc-NbC<sub>x</sub>/a-C:H coatings, they mainly had much higher hardness, in the range 16 – 23 GPa. In literature, a lower hardness for amorphous carbide, compared to crystalline carbide, has been demonstrated for the Cr-C system [33]. Thus, the higher hardness of the Nb-C coatings is expected. The decrease in hardness with an increase in a-C:H content (leading to smaller NbC<sub>x</sub> grains) can be explained by that the volume fraction of grain boundaries determines the plastic deformation via grain boundary sliding. Therefore, the hardness decreases for an increase in a-C:H. Moving on to the a-CrC<sub>x</sub>/a-C coatings, it can be seen that they were of similar hardness as the a-CrC<sub>x</sub>/a-C:H coatings, although the decrease as a function of a-C(:H) phase was not as

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*Note that the nc-NbC<sub>x</sub>/a-C:H coatings in ref. [18] were deposited in the same PVD system using very similar deposition conditions as the a-CrC<sub>x</sub>/a-C:H coatings.*
was not as strong. Hence, at ~80 % a-C(:H) phase the a-CrC_x/a-C:H coatings were softer than the a-CrC_x/a-C coatings and in addition, the a-CrC_x/a-C:H coatings had lower elastic moduli for the whole range in a-C(:H) content. Since the carbide phase was mainly amorphous, and that there was no significant difference in the amount of a-C(:H) phase between the series of coatings, the differences in hardness and mainly in elastic modulus can be attributed to the incorporation of hydrogen. In fact, hydrogen-terminated ends of carbon groups imply the presence of very weak van der Waals interactions in the material, adding a polymeric-like character [118]. Hence, it is very reasonable to observe lower hardness and lower elastic modulus when the carbon is (partially) hydrogenated compared to when it is not hydrogenated.

The Figure 25 does not include coatings in the Cr-C-Ag system, because the mechanical properties of those coatings were chiefly governed by the Ag content. Nanoindentation showed that the hardness and elastic modulus of the CrC_x/a-C/Ag coatings were in the range 8 – 12 GPa and 167 – 267 GPa, respectively. In conjunction with XPS data, it was found that both parameters decreased in a linear fashion with an increase the Ag content (0 – 14 at.%). Overall, it can be expected that the addition of a soft metallic Ag phase should lead to a decrease in hardness as well as in elastic modulus.

**Tribological properties**

The tribological properties are important for an electrical contact, especially when the contact is in a sliding configuration. Uncoated base metals are avoided because the high contact loads required to penetrate the oxides can result in major wear [3]. On the other hand, noble metal coatings are soft and coatings can easily wear out even at low loads. To demonstrate this issue in an actual contact situation, Figure 26 shows SEM results obtained for an Ag/Ni coated 316L contact member after reciprocating sliding against a counterpart with Au plating at 1 N load. There is a clearly visible wear track and the SEM-EDX maps show that the Ag coating was completely worn away. There was also transfer of Ag to the counterpart (not shown in Figure 26). Thus, it was important to study the tribological properties of the nanocomposite coatings.
In Figure 27, the coefficients of friction obtained during 2 000 reciprocating dry-sliding cycles for a-CrC/a-C:H coatings are shown. The counterpart was a ball bearing steel ball and a normal load of 5 N was applied. For coatings with a high amount of a-C:H phase, the coefficient of friction was as low as 0.13 based on averages of 500 continuous cycles. In general, the coefficient of friction decreased with an increase in the amount of a-C:H phase. It is known that this reduction in friction is due to formation of a lubricating tribo-layer of graphite-like carbon and the effect is observed in many Me-C systems [53,61,119,120]. As also can be seen, there was no difference between DCMS and HiPIMS and this is not surprising considering the similar coating microstructure.

Although a low coefficient of friction is principally desirable, a too high amount of a-C:H phase did not constitute optimal conditions for the electrical
contact resistance, which will be discussed below. Therefore, it was interesting to study if the addition of Ag to the Cr-C coatings could reduce the coefficient of friction at more moderate a-C contents. The main hypothesis was that a counterpart would shear the surface particles of Ag and form a smear layer, which would reduce friction.

In contrast to the hypothesis, the experimental results suggested no improvement in friction properties for the a-CrC\textsubscript{x}/a-C/Ag coatings compared to Ag-free coatings. On the other hand, results for reactively sputtered CrC\textsubscript{x}/a-C:H/Ag indicated a minor improvement.\textsuperscript{x1} In Figure 28a, coefficients of friction obtained from dry-sliding experiments performed in the ball-on-disc setup (see p. 30) are shown. Three coatings are represented: Cr, a-CrC\textsubscript{x}/a-C:H (43 at.% C) and a-CrC\textsubscript{x}/a-C:H/Ag\textsubscript{5} (39 at.% C). As can be seen, the Cr coating did not perform very well and exhibited a coefficient of friction of 0.9. For the other two coatings, there was no significant difference during the first 700 revolutions. Thereafter, however, the coefficient increased for the Ag-free coating and this effect was not observed for the Ag-containing coating.

![Figure 28](image.png)

**Figure 28.** Coefficients of friction from ball-on-disc experiments using Cr, a-CrC\textsubscript{x}/a-C:H (43 at.% C) and a-CrC\textsubscript{x}/a-C:H/Ag\textsubscript{5} (39 at.% C) coatings deposited on polished high speed steel. To the right are SEM micrographs, obtained using the SE2 (topographical contrast only) and in-lens detectors, for the a-CrC\textsubscript{x}/a-C:H/Ag\textsubscript{5} coating. Experimental details on the ball-on-disc experiments can be found on p.30.

The wear track that was formed on the a-CrC\textsubscript{x}/a-C:H/Ag\textsubscript{5} coating is illustrated by the SEM micrographs in Figure 28b. When using the SE2 detector (topographical information), there was very limited contrast from the wear track,

\textsuperscript{x1} Results were presented at conference (ICTF-16).
indicating only minor wear. With the in-lens detector (topographical + work function), the wear track was more clearly resolved and it was found to have a quite smooth appearance, indicating a carbon-rich film. In high-magnification micrographs, it was possible to identify very small Ag particles in the wear track as well. These findings are in good agreement with Wang et al. [121], who studied tribological properties of TiC/a-C:H/Ag coatings and suggested that Ag particles diffused from the bulk to the carbon-rich wear track and reduced friction. However, further studies are required to draw definite conclusions about the tribological properties of the a-CrCx/a-C:H/Ag coatings although the results are encouraging.

Electrical properties

Resistivity
The conduction mechanism in the nanocomposite coatings is metallic although the conductivity is reduced by scattering effects from the small grains and short mean free conduction paths [122]. There can also be electron tunneling through thin layers of carbon matrix [123,124]. Thus, resistivities of transition metal carbide nanocomposites are generally a bit higher than the corresponding bulk carbides. However, Lewin [125] showed that low resistivity was actually not necessary in order to obtain low contact resistance for nanocomposite coatings. Either way, present results from measurements on a-CrCx/a-C/Ag coatings ranged from 172 to 217 µΩ cm for Ag contents of 0 – 14 at.%. For nc-NbCx/a-C:H coatings, the resistivities were in the range 310 – 940 µΩ cm for C/Nb ratios of 0.8 – 1.6.

Static contact resistance
Nanocomposite Me-C/a-C(:H) coatings have been shown to exhibit excellent electrical contact properties in several studies [13,14,16,18,22]. However, the contact resistance is known to vary several orders of magnitude depending on the deposition conditions. To understand why this is, Nb-C was chosen as a model system to study different factors that could affect the contact resistance (paper V).

By annealing samples at different temperatures, up to 260 °C, and performing XPS analysis as well as contact resistance measurements, the trends in Figure 29 were obtained. It illustrates that the contact resistance was exponentially dependent on the mean oxide thickness for a given coating composition. In fact, the contact resistance covered four orders of magnitude despite a maximum mean oxide thickness of only 8 nm. Note that the contact resistance of the NbC1.0/a-C44:H series was much lower than that of the NbC0.9/a-C44:H series. This difference can be explained by a substrate temperature of 200 °C during deposition (compared to unheated for the other series) and that the contact resistance was measured only a few hours after deposition. However, even
for very similar oxide thickness (e.g. 1 nm) there were differences in contact resistance of up to two orders of magnitude. Therefore, additional factors, apart from the mean oxide thickness, must have influenced the contact resistance.

![Figure 29. The contact resistance at 1 N contact load vs. the mean oxide thickness. (Figure from paper V.)](image)

As can be conceived from the trends in Figure 29, the amount of a-C:H phase is important and it induces differences in the contact mechanics. A general model explaining contact resistance of nc-Me/a-C(:H) nanocomposites was designed. It consists of three structurally different coatings in an electrical contact junction with a noble metal counterpart. Three corresponding schematic cross-sectional views are illustrated in Figure 30. In Figure 30a, the coating is coarse-grained and is practically without a-C(:H) phase. In Figure 30b, the coating has grains of medium-size and a medium amount of a-C(:H) phase. In Figure 30c, the coating has very small grains and a high amount of a-C(:H) phase. As can be seen, the carbide grains get covered by an increasingly thick layer of a-C(:H) when going from (a) to (c). Numbers in Figure 30, from 1 to 7, are areas in the contacting process. In area (1), an insulating oxide layer covers the surface and the counterpart cannot easily penetrate this layer apart from in a few areas (2). Oxidation of carbide is accompanied by the release of carbon in the surrounding region. This oxide, in conjunction with the carbon, give rise to high electrical contact resistance (see e.g. NbC$_{0.7}$/a-C$_{11}$:H in Figure 29). Moving on to the second coating (Figure 30b), the grains are smaller and become covered by a-C(:H), shielding the grains from oxygen (3). Upon mating to the counterpart, the superficial a-C(:H) layer gives way and a
still oxidize (4). In the last case (Figure 30c), the situations in areas (5) and (6) are just like in areas (3) and (4). However, in area (7) the a-C(:H) layer has become too thick and the counterpart cannot establish electrical contact to the carbide grain below, leading to a higher contact resistance. Note that the mean oxide thickness, obtained by XPS, is the same for the three different cases.

In conclusion, there is an optimum amount of a-C(:H) phase, in relation to the grain size, that will provide the lowest contact resistance. Such minima have been reported for nc-TiC/a-C [13], nc-VC/a-C [125] and nc-NbC/a-C(:H) [17,18]. A similar minimum was found for the a-CrCx/a-C:H coatings as well (paper II, c.f. Fig. 10), however, it is difficult to model amorphous materials and further studies are needed to explain those results in detail.

For the other material systems, this type of surface modeling was not performed. However, for the a-CrCx/a-C:H coatings, the lowest static contact resistance was about five times greater than that of a Ag reference at 1 N load. By the small addition of 9 at.% Ag, to form a-CrCx/a-C/Ag, the contact resistance was reduced to about twice that of a Ag reference sample. XPS analysis showed that the Ag nanoparticles were in metallic state, which explains the low contact resistance. Obviously, the cost of a carbide-based coating with noble-metal-like properties, while only containing 10% of noble metal, could be greatly reduced compared to that of a pure noble metal coating.
Sliding contact resistance

Experiments were performed to evaluate the contact resistance of Cr-C coatings under sliding conditions. The experimental sliding setup, schematically drawn in Figure 31a, provided a reciprocating horizontal motion and consisted of principally the same contact resistance setup as previously described (p. 31). Note though that the counterpart had a larger hemispherical tip with a diameter of \( d = 3.2 \) mm.

![Figure 31](image)

Figure 31. (a) Reciprocating sliding contact resistance measurements. Counterpart was a hemispherical tip (\( d = 3.2 \) mm) with Au plating. Applied load was 1 N. Stroke length was 1.5 mm. Peak velocity was 1.35 mm s\(^{-1}\). Peak acceleration was 10 mm s\(^{-2}\). Measured frequency was 0.22 – 0.28 Hz. Contact resistance was measured as previously described (p. 31) and continuously recorded. (b) Experimental results for uncoated 316L and 316L coated with a-CrC\(_x\)/a-C:H (49 % a-C:H).

Experimental results for two samples, uncoated 316L steel and 316L steel coated with a-CrC\(_x\)/a-C:H (49 % a-C:H), are shown in Figure 31b. While both samples started off with relatively low contact resistance, the performance of the uncoated 316L then degraded as the number of sliding cycles increased. Thus, it was found that the contact properties of 316L could be improved by applying the a-CrC\(_x\)/a-C:H coating because of the low and more stable contact resistance. Coatings with about 30 – 60 % a-C:H provided the best results, whereas other compositions resulted in contact resistances that were similar to that of the uncoated 316L.

Both the coated sample and the counterpart from the above experiment were studied by SEM-EDX and the results are shown in Figure 32. To the left is the wear track formed on the coating and to the right is the counterpart. As can be seen, there was no major change in the chemistry of the wear track compared to the surrounding material. No Au was observed in the wear track.

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\(^{xii}\) Presented at conference.

\(^{xiii}\) Upon initial contact (before sliding commenced), the contact resistance for 316L was 1000 m\(\Omega\) and for coated 316L it was 44 m\(\Omega\).
The counterpart revealed an area affected by wear that was about 100 µm in diameter, in correspondence with the wear track observed on the sample, so clearly the diameter of the tip is very misleading when it comes to defining the actual contact area. In the EDX map representing Au, it can be seen that there was no decrease in intensity within the wear area, although there appeared to be less intensity in the peripheral area. In the EDX maps representing Cr and O, there is strong intensity in the corresponding peripheral area and it suggests that Cr (oxide) was transferred from the coating to the counterpart during sliding. In literature, André et al. [73] analyzed Ti-Ni-C coatings that had been sliding against a counterpart made of Ag. Their results, based on XPS and Raman spectroscopy, indicated that metal oxide was removed from the coating and adhered to the counterpart. Although further studies are required to draw certain conclusions, there are now (at least) two different and independently performed sets of experiments that show a similar trend. If these results are compared to the wear track for the Ag coating shown above (p. 48), the very promising properties of the a-CrC\textsubscript{x}/a-C:H coatings can be understood. The nanocomposite has much better tribological properties, and given that the nanocomposite does not wear out as easily, it should provide good durability as well as corrosion protection.

![SEM-EDX results](image)

*Figure 32. SEM-EDX results for the coated sample and the counterpart from the reciprocating sliding contact resistance experiment in Figure 31.*

**Electrochemical properties**

The oxidation resistance of contact materials is important because growth of thick passive layers can impair the electrical contact properties. On the other hand, a dense oxide will reduce corrosion and these two aspects suggest a trade-off situation. Based on a review of literature, it can be established that Cr-C, in general, provides excellent corrosion resistance in many applications due to the formation of a thin surface layer of Cr-O [126–132]. Thus, it was interesting to study the electrochemical properties of nanocomposite Cr-C coatings.
Cr-C

Two series of Cr-C/a-C coatings with high and low carbon content were subjected to chronoamperometric experiments and linear sweep voltammetric experiments, both in 1 mM H₂SO₄ at 80 °C. The chronoamperometric experiments were evaluated by considering the total oxidation charges, shown in Figure 33. After 1 hour of polarization at +0.64 V, as well as at +0.45 V, (vs. Ag/AgCl), the coatings with high carbon (HC) content resulted in lower oxidation charges compared to the coatings with low carbon (LC) content. Overall, a higher substrate temperature during deposition resulted in lower charges as well.

![Figure 33](image_url)

*Figure 33. The total oxidation charge obtained after chronoamperometric experiments for Cr-C films with high and low carbon content, HC (~70 at.% C) and LC (~40 at.% C), respectively. Time was 60 minutes and two potentials were used: +0.45 and +0.64 V (vs. Ag/AgCl). Three different deposition temperatures: 20, 300 and 500 °C. (Adopted from paper I.)*

XPS Cr2p spectra of the oxidized surfaces showed that the HC samples contained a lower fraction of Cr-O bonds than the LC samples. Hence, the lower oxidation charges may partially be attributed to less Cr available for oxidation. However, evaluation of the charge ratios of the LC/HC series revealed a value of 1.3, which was significantly smaller than the ratio in Cr content for the two series of 2.0. XPS C1s spectra revealed higher concentrations of C on the surfaces after oxidation, suggesting that carbon previously in Cr-C phase was released on the surface upon the oxidation of Cr-C. Furthermore, there was an increase in oxidized carbon groups on the surfaces (C-O, C=O), indicating that carbon oxidation contributed to the oxidation charges. These findings are in agreement with results in related studies [29,97].
In the linear sweep voltammetric experiments, the potential was scanned from -0.5 to +1.5 V (vs. Ag/AgCl), i.e. well into the transpassive region. Linear sweep voltammograms, obtained for one crystalline Cr$_7$C$_3$/a-C (41 at.% C) coating and for one a-CrC$_x$/a-C coating (71 at.% C), both deposited at 500 °C, are shown in Figure 34a. As is seen, the two samples exhibited very low and similar current densities in the passive region. However, in the transpassive region the current densities increased rapidly. Here, the a-CrC$_x$/a-C coating exhibited lower current densities than the Cr$_7$C$_3$/a-C coating. SEM micrographs of the surfaces, as-deposited and after oxidation, are shown in Figure 34b. The Cr$_7$C$_3$ coating experienced localized etching of Cr, while the a-CrC$_x$/a-C coating appeared significantly less affected. Still, the slightly darker and smoother appearance of the latter indicates that there was loss of material albeit more evenly distributed across the surface. A combination of high carbon content and a high deposition temperature (500 °C) exhibited the highest oxidation resistance, which was due to the formation of a thin but dense passive film composed of Cr$_2$O$_3$ and C.

![Figure 34](image)

Figure 34. (a) Linear sweep voltammograms for Cr-C coatings with 41 and 71 at.% C. Scan rate was 5 mV s$^{-1}$. Electrolyte was 1 mM H$_2$SO$_4$, 80 °C. (b) Micrographs of the two coatings; as-deposited and after the voltammetric experiments. (Replots of polarization curves and adopted SEM micrographs, paper I.)

**Cr-C-Ag**

Although the a-CrC$_x$/a-C coatings did show promising resilience to oxidation, it was unclear how the addition of a noble Ag phase would affect this property. For this reason, coatings in Cr-C-Ag system were subjected to similar experiments as the Cr-C coatings.
The large numbers of nanometer-sized surface Ag NPs exhibited significant nanoeffects. In linear sweep voltammetric experiments, the NPs exhibited oxidation potentials that were 0.4 V more negative than the standard reduction potential for the Ag⁺/Ag redox couple at 1.0 M Ag⁺ (0.59 V vs. Ag/AgCl). The effect is shown in the voltammogram in Figure 35, where the NPs can be seen to oxidize at +0.15 V. (There was no oxidation peak for Ag-free Cr-C reference.) Total oxidation charges were found to correlate to the amount of nanoparticles observed in SEM, and in addition, post-experimental XPS and SEM analyses revealed that the nanoparticles were stripped away by the oxidation. One practical consequence is that the coatings would lose the advantageous properties related to the NPs.

![Figure 35](image)

*Figure 35. Linear sweep voltammogram obtained for an a-CrC₅/a-C/Ag coating with 9 at.% Ag in the bulk and large numbers of surface nanoparticles of Ag. Electrolyte was 1 mM H₂SO₄ at room temperature. Scan rate was 5 mV s⁻¹. (Replot of data in paper IV.)*

The major part of the negative shift in oxidation potential was caused by the low Ag⁺ concentration in the electrolyte. Nonetheless, the small radii of the nanoparticles accounted for about 60 mV of the shift, according to the Plieth equation [133]. Both of these effects are in good agreement with literature [134,135]. However, the degree of surface oxidation of the carbide/carbon matrix were also found to influence the oxidation potentials of the NPs. Therefore, the chemistry of the supporting matrix should be considered in studies on electrochemical properties of NPs. If the concept with surface NPs on a ceramic surface is further developed, it may be useful for electrodes in e.g. catalytic applications.

**Optical properties**

The conventional method used to quantify the carbon content and the amount of a-C phase in nanocomposites is XPS. From an industrial perspective, XPS
has several disadvantages: it is expensive, complicated, it takes long time to analyze even a small set of samples and the substrates can typically not be larger than a few centimeters in size. In coating production, more suitable analysis methods are required to meet demands from quality and control. In that sense, optical methods are promising since they offer fast and non-contact analysis (paper VI).

About 100 different coatings\textsuperscript{xiv} in the Ti-C, Cr-C and Nb-C systems were studied by XPS, reflectance spectrophotometry and spectroscopic ellipsometry. First of all, XPS was used to established the a-C(:H) fraction as a function of the carbon content for each coating. These results are shown in Figure 36a-c. The dashed lines correspond to stable phases in the three Me-C systems and a variable amount of a-C(:H) phase. In general, the a-C fraction increases as the total carbon content increases and as can be seen, most data markers are found within the areas enclosed by the dashed lines. From results in the Ti-C system (Figure 36a), it can be understood that oxygen contamination (c.f. marker size) can shift the trend, leading to higher amounts of a-C than expected for a given carbon content.

From a thermodynamic point of view, all the Me-C/a-C coatings should end up on the dashed line to the far right for each system. This effect was not observed and instead, the a-C fraction can be seen to rise at much lower carbon contents. As was previously discussed, the stable chromium carbide crystal structures are too complex to form under low energy conditions, leading to the formation of a-CrCx phase. In the Ti-C and Nb-C systems, a-C phase forms despite available interstitial sites in the carbide lattice. This effect can be found in literature as well \cite{37,79}.

\textsuperscript{xiv} All of the Ti-C coatings as well as parts of the Cr-C and Nb-C coatings were provided by colleagues \cite{1,15,30,42,55}.
Figure 36. The a-C(:H) phase fraction versus the total carbon content for (a) Ti-C, (b) Cr-C and (c) Nb-C coatings. Non-reactive and reactive sputtering are represented by unfilled and cyan markers, respectively. Samples deposited by HiPIMS have a black dot inside their markers. Dashed lines represent one stable crystal structure and a variable amount of a-C. Markers scale in size to oxygen content. (d) Average reflectance (wavelength range 400 – 740 nm) for all coatings vs. the total carbon content. (Adopted from paper VI.)

In Figure 36d, the average reflectance in the visible range (400 – 740 nm) as a function of the total carbon content is shown. In this case, all the Ti-C, Cr-C and Nb-C samples have been merged into a single plot. Regardless of metal and deposition method, all samples exhibit the same general trend and that is
a decrease in reflectance with an increase in carbon content. Thus, it should be possible to estimate the carbon content (and the a-C phase fraction) of unknown samples by measuring their spectral reflectance and by comparing results to known reference samples. From a practical point of view, the device used to measure the reflectance was a handheld spectrophotometer, normally used for measuring the color of objects, and the time required for each measurement was not longer than a few seconds. Analogous trends were also obtained by spectroscopic ellipsometry (not shown here). It is concluded that the studied optical methods can be used to fulfill an industrial need.
Conclusions

Nanocomposite coatings, consisting of transition metal carbide, carbon and silver, were studied as alternative materials for electrical contact applications, where noble metal coatings are commonly used today. Coatings in the systems Cr-C, Cr-C-Ag and Nb-C were deposited by magnetron sputtering and their microstructure, composition and chemical bonding were studied. To evaluate the functionality of the deposited materials, studies of mechanical, tribological, electrical, electrochemical and optical properties were also made.

In the Cr-C system, the deposited coatings were mainly amorphous nanocomposites (a-CrCx/a-C). Stable crystalline phases were obtained if the substrate temperature during deposition was at least 500 °C. In the Cr-C-Ag system, the additional co-sputtering of Ag resulted in a-CrCx/a-C(:H)/Ag coatings, in which the Ag formed metallic nanoclusters within the ceramic matrix. Large numbers of Ag nanoparticles were also formed on the surfaces. In the Nb-C system, the coatings were nc-NbCx/a-C:H, featuring nanocrystalline NbCx grains with sizes of 2 – 12 nm. The presence of thin native passive films of Nb2O5 and a-C was demonstrated.

Regarding properties, the a-CrCx/a-C:H coatings were unusually soft for being carbide-based nanocomposites and exhibited a nanoindentation hardness from 5.5 – 12 GPa. Friction experiments showed that an unlubricated coefficient of friction of 0.13 could be obtained when the coating was sliding against uncoated ball bearing steel. Electrical resistivity was a couple of hundreds of μΩ cm for most samples. The electrical contact resistances for the Cr-C and Nb-C systems were low, although typically still higher when compared to noble coatings. Nevertheless, Cr-C coatings improved the sliding contact resistance of 316L. For the coatings alloyed with Ag (a-CrCx/a-C/Ag), the contact resistance was lower and the best sample resulted in a value that was only twice that of a Ag reference coating at 1 N contact load. Electrochemical experiments showed that dense a-CrCx/a-C coatings were resilient to oxidation in hot sulphuric acid due to a self-passivation mechanism, where both chromium oxide and carbon could protect the underlying material from further oxidation. For the a-CrCx/a-C/Ag coatings, the Ag nanoparticles were less noble than bulk Ag due to the presence of nanoeffects. The addition of Ag decreased the corrosion resistance of Cr-C coatings. Overall, the studied nanocomposites have properties that make them promising candidates for use as surface coatings in electrical contact applications.
Finally, it was demonstrated how optical methods can be used to quantify the carbon content and the a-C(:H) fraction in coatings in the Cr-C and Nb-C systems, as well as in the Ti-C system which was also included.

In a future outlook, the following ideas might be interesting for additional studies.

- Study passive films in related Me-C nanocomposite systems to obtain systematic knowledge. The results may lead to new tailored multifunctional materials.
- The concept of alloying a carbide-based nanocomposite with a noble metal should receive further attention.
  a. Add Ag to Nb-C. Two good things may give even better properties for electrical contacts.
  b. If Ag nanoparticles are lost from the coating surface, e.g. due to corrosion, it would be nice to have a self-replenishing mechanism in place, but in deep-sleep, and a way to activate such a mechanism (perhaps by moderate heat).
  c. Replace Ag with Pt.
  d. Densify the coatings in controllable ways by adding things that can lead to weak interactions between the elements in the ceramic matrix and Ag.
- Study the coatings under fretting conditions (i.e. vibrational wear).
Populärvetenskaplig sammanfattning på svenska


Målet med studien var i huvudsak att ta fram nya material för elektriska kontakter med förbättrade mekaniska, elektriska och kemiska egenskaper samtidigt som det skulle gå att producera materialen på ett industriellt, kommersiellt och miljömässigt relevant sätt. I dagsläget används ofta beläggningar av ädelmetaller och dessa är dyra, har dåligt motstånd mot mekanisk nötning och produceras alltför ofta med miljöfarlig våtkemisk plätering. Det sist nämnda är bildligt talat ett badkar fullt med flytande miljögifter. I denna avhandling deponerades materialen med vakuumteknik där källmaterialen förångas i en vakuumkammare för att sedan kondensera på det objekt som ska beläggas. Detta är en torr metod som inte skapar miljöfarligt avfall.

De material som studerades bestod av kol, titan, krom, niob och silver i olika varianter. När dessa grundämnen förångades med vakuumteknik erhölls så kallade nanokompositer som består av mycket små karbidkorn omringade av en matris bestående av amorft (oordnat) kol\textsuperscript{xv}. En liknelse till den makroskopiska världen är att blanda upp smågrus med snö och packa det riktigt tätt. Storleken på dessa karbidkorn är i storleksordningen 0 – 20 nanometer (miljarddels meter) och kornen kan endast ses med elektronmikroskop. Nere på nanonivå beter sig material annorlunda och nya materialegenskaper uppträder ofta. När vi förstår hur materialen ser ut på atomnivå, varför de uppvisar vissa egenskaper och hur dessa material kan produceras på ett bra sätt skapar vi

\textsuperscript{xv} Andra former av kol som är mer kända är diamant, grafit och på sistone även grafen och kolnanorör.


Elektrokemiska experiment visade att nanokompositerna förbättrade korrosionsskyddet på rostfritt stål. Ytkenin studerades då med röntgenfotoelektronspektroskopi, vilken är en kraftfull metod för att analysera sammanläggning och kemisk bindning i tunna skikt. Förutom att det bildades en tunn skyddande oxid på beläggningens yta, lik den som bildas på rostfritt stål, uppstod anrikning av kol som gjorde materialet ännu bättre.

När materialen legerades med silver upptäcktes med elektronmikroskopi att det hade bildats upp till 10 miljarder små nanopartiklar per kvadratcentimeter på beläggningens yta. Förutom att detta ger goda elektriska kontakt-egenskaper, kan det på sikt leda till material med katalytiska egenskaper som kan reparera sig själva vid till exempel korrosion. Vid förlust av det katalytiska ytskiktet kan nytt material komma upp underifrån, ungefär som kantreller i skogen. Det finns massor av svamprådar under markytan som inte går att se, men när svampen dyker upp ovanför marken kan du få stor glädje och nytta av detta. Om någon annan plockar svamparna kanske du blir lite missnöjd, men nya svampar förväntas växa upp inom sinom tid.

Därmed hoppas jag att du som läsare har fått en inblick i området rörande karbidbaserade nanokompositer och deras intressanta egenskaper. Att läsa de vetenskapliga artiklar som ligger till grund för denna populärvetenskapliga sammanfattning kan vara nog så komplicerat även för en insatt person. För den intresserade finns alla artiklar i sin helhet i den tryckta versionen av avhandlingen som finns tillgänglig via Uppsala universitetsbibliotek.
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References


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