Magnetron sputtering of binary, ternary and multicomponent thin film borides and carbides

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Abstract

Design of new thin film materials with improved properties and functionality is an important research field in materials science. In this thesis, I have used magnetron sputtering to deposit new thin film materials, which should combine high hardness and high ductility with other properties such as low friction or a good corrosion resistance. The films have been characterized with a range of techniques to determine the correlation between deposition parameters, microstructure and properties.

The first part of the thesis is focussed on binary and ternary molybdenum-containing boride thin films with potential low-friction properties. It was found that the binary Mo-B films exhibited a nanocrystalline structure of ~16 nm large MoB_{2-x} grains surrounded by an amorphous tissue phase. The special microstructure resulted in a very high hardness (29 ± 2 GPa), but limited ductility. An attempt to improve the ductility by formation of crystalline layered ternary borides such as Mo_{2}BC and Mo_{2}FeB_{2} failed due to difficulties to reach high deposition temperatures. However, the addition of carbon to the binary Mo-B films resulted initially in a reduced grain size of the MoB_{2-x} grains. For carbon concentrations >23 at.%, a completely amorphous film was formed. Transmission electron microscopy (TEM) studies revealed that these films contained Mo-rich regions surrounded by a Mo-poor amorphous BC phase and therefore best can be described an amorphous nanocomposite. The mechanical properties of the Mo-B-C films were strongly correlated to the amount of the softer amorphous BC phase. Also the Mo-Fe-B films were amorphous with a hardness ranging from 19 to 26 GPa and a limited ductility. Tribological studies of the Mo-B, Mo-B-C and Mo-Fe-B films showed very high coefficients of friction (>0.8). Molybdenum and boron oxides were identified on the surface by Raman spectroscopy, but no indication of lubricating effects from these oxides could be observed. The results suggest that Mo-based borides have limited applications in future low-friction applications.

In the second part of the thesis, a high entropy alloy (HEA) of TiCrNbTaW was studied with and without the addition of carbon. The results showed that a HEA phase with bcc structure could be deposited in a wide composition and temperature range. Small amounts of carbon were dissolved into the bcc phase, while higher carbon contents resulted in a multicomponent carbide phase. The correlation between structure and properties were studied in detail. It was found that some of the films exhibited very high hardness combined with high ductility suggesting potential application of these materials as wear-resistant coatings. Finally, the corrosion resistance of these complex alloys were investigated in a very acidic environment. They were found to exhibit excellent corrosion resistance superior to hyper-duplex stainless steels.

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List of Papers

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


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Contribution to the papers

I I planned the study, synthesized the samples and executed all the experiments. I did data analysis and wrote the main part of the manuscript. I was involved in all discussions.

II I planned the study, synthesized the samples and performed the experiments. The data analysis and writing were done by me and I was also involved in all discussions.

III I planned the study, synthesized the samples and executed the experiments. I did the data analysis and wrote the main part of the manuscript. I was also involved in all discussions.

IV I planned the study, synthesized the samples and performed the main part of the experiments. I did the data analysis and was involved in writing the manuscript. I was also involved in all discussions.

V I planned the study, synthesized the samples and executed the experiments or was actively involved in all additional experiments. I did the data analysis and wrote the main part of the manuscript. I was also involved in all discussions.

Other publications to which the author has contributed:


Disclaimer: Part of this thesis are based on my licentiate thesis entitled: Synthesis and Characterisation of Mo-B, Mo-B-C and Mo-Fe-B Thin Films Deposited by Magnetron Sputtering (Uppsala university, 2017)
Abbreviations

APT – atom probe tomography
ARXPS – angle resolved XPS
bcc – body centred cubic
ccp – cubic close packed
COF – coefficient of friction
CTF – contrast transfer function
DC – direct current
dpa – displacement per atom
EDX – Energy dispersive X-ray spectroscopy
EELS – electron energy loss spectroscopy
EM – electron microscopy
ERDA – elastic recoil detection analysis
fcc – face centred cubic
GI-XRD – grazing incidence XRD
HAADF – high angle annual dark field
HAXPES – hard X-ray photoelectron spectroscopy
HEA – high entropy alloy
HIKE – high kinetic energy XPS
HR-XPS – high resolution XPS
HT – high temperature
HVEM – high voltage electron microscopy
IBA – ion beam analysis
MS – magnetron sputtering
OCP – open circuit potential
PIPS – precision ion polishing system
PSI – phase shifting interferometry
RT – room temperature
SEM – scanning electron microscopy
STEM – scanning TEM
TEM – transmission electron microscopy
TOF – time of flight
UV – ultraviolet
VSI – vertical scanning interferometry
XPS – X-ray photoelectron spectroscopy
XRD – X-ray diffraction
Introduction

Transition metal borides and carbides have interesting mechanical and tribological properties like high hardness and wear resistance, high electrical conductivity and good oxidation resistance [1,2], which make them desirable for a number of different applications. One example is TiB₂ which is used in both bulk and thin film applications, e.g. as a hard strengthening material in armour or as coatings in cutting tool applications [1,2]. Another example is WC, which is used in cemented carbides or in coatings for cutting tools [3,4]. The high hardness of borides and carbides is an advantage in many applications but a problem is that most hard ceramic materials are also brittle. It is therefore desirable to design a material, which can combine both high hardness with high ductility. An excellent example is Mo₂BC, a nanolaminated phase which exhibit high stiffness with positive Cauchy pressure indicating a ductile behaviour [5].

Many thin films have found applications in corrosive environments or at high temperatures where oxidation is a problem. Metal borides are used in corrosive environments [6], but the general corrosion properties of this group of materials are not as good. Borides immersed in aqueous environment start to corrode and form soluble species such as borate and boron oxides, which results in etching of the material [7]. In contrast, metal carbides are known to exhibit very high corrosion resistance [8–10]. For example, Nygren et al. have shown that magnetron sputtered nanocomposite of Cr-C/a-C (with a significant amount of amorphous carbon) exhibited very good corrosion resistant properties in a hot 1 mM H₂SO₄ solution [11]. A specific example where low oxidation rates are required is in electrical contacts, where low electrical contact resistance, low friction coefficients and low wear rates must be combined. Today primarily Ag and Au are used in most contact applications. However, they have severe limitations such as high friction coefficients, softness and high wear rates. In addition, they are expensive. There is therefore a need for alternative materials with a proper combination of properties. Our research group at Uppsala University has previously studied the properties of magnetron sputtered nanocomposites combining nanocrystalline (nc) and amorphous phases (a) such as nc-TiC/a-C and nc-NbC/a-C [12,13] for sliding contact applications. The results show excellent properties for some compositions but also aging problems leading to increased contact resistances with time. It is possible, that contacts based on transition metal borides may exhibit better oxidation resistance but this has not yet been investigated.
The present thesis is focussed on the design of new boride and carbide thin films, which combine high hardness, ductility and good corrosion resistance. This requires a deposition method, which allows for a good control of the composition and microstructure. Transition metal boride thin films are easily deposited by magnetron sputtering. Many binary boride systems such as Ti-B [14], Zr-B [15], Hf-B [16] and Nb-B [17] have been synthesized using this technique. However, one system studied in this thesis is the Mo-B system. This system includes a large number of possible phases (Fig. 1): MoB₄, MoB₂, MoB, Mo₃B₂ and Mo₂B. All of them differ with respect to structure and complexity.

In particular, MoB₂ has an interesting potential for sliding electric contact applications. This phase exists in at least two modifications; the hR18 and the hP3 structure. As will be described below, the hP3-MoB₂ phase has a layered structure, which should be easily formed during magnetron sputtering. Furthermore, this phase is metastable at room temperature, which suggests that it can be chemically more reactive towards e.g. oxidation, which could lead to a formation of BOₓ and MoOₓ on the surface. Molybdenum oxides have been predicted to exhibit low friction coefficients in particular at higher temperatures [18]. Also boric acid, which can form in a humid atmosphere from BOₓ is known to exhibit a very low friction [19]. Consequently, hexagonal MoB₂ may be an excellent low friction material although the formation of oxides may limit its use in an electric contacts.

The properties of a binary metal boride can also be modified by the addition of a third element. This can either lead to the formation of a ternary phase or to a composite material with a mixture of binary phases. One example is the Me-B-C systems where carbon has a strong influence on the phase composition. Magnetron sputtered Cr-B-C and Nb-B-C films have been investigated by Nedfors et al. [20,21]. They found that Cr-B-C has reduced hardness, lower wear rates and lower coefficients of friction (compared to Cr-B), but they also observed an increased electrical contact resistance as well as aging effects. The addition of C to Nb-B resulted in reduced hardness and electrical resistance, but cracking resulted in a high coefficient of friction limiting the potential use of this material in sliding electrical contact applications. The improved properties obtained by addition of carbon to a binary Me-B system suggest that Mo-B-C films may be interesting for thin film applications.

A second possibility is to add another transition metal to a binary boride system. A large number of ternary boride phases exist and may have a potential use in many applications. One example is the Mo-Fe-B system where two ternary phases, MoFe₂B₄ and Mo₂FeB₂, are known. Mo₂FeB₂ is currently used as a component in cermet coatings to increase the wear resistance and corrosion resistance in for example hot extrusion dies [22]. Recent calculations by Wang et al. suggest that Mo₂FeB₂ has a very special mechanical behaviour combining high hardness and ductility with magnetic properties [23]. Hitherto, no magnetron sputtering studies of Mo-Fe-B films have been carried out.
but it is likely that such films could have a potential use in various applications including electrical contacts.

A third approach used in this thesis involves high entropy materials (HEMs). HEMs are solid solutions with at least 5 elements where the solid solution is assumed to be thermodynamically stabilized by a high entropy of mixing [24]. Most studies in this field have focussed on high entropy alloys (HEAs), which in many cases exhibit interesting chemical and physical properties (see e.g. ref. [25] for a recent review of the field). Many HEAs are high strength materials suggesting a potential use as construction material. It has also been established that many HEAs exhibit good corrosion resistance, similar or superior to those of many stainless steels [26]. Another area where HEA can be used is as radiation resistant materials [27]. HEAs exhibit exceptional structural stability and self-healing ability with very moderate displacement per atom (dpa) when exposed to ions. For example bulk AlxCoCrFeNi demonstrated no significant ordering, amorphisation or phase separation under heavy ion irradiation at room temperatures at high dpa in some composition ranges [28]. It was also observed that the reduced thermal conductivity combined with large stress in disordered high entropy alloys may promote “self-healing” effects [28]. Other authors reported a similar behaviour for a very high phase stability of CoCuCrFeNi under fast electron irradiation by high voltage electron microscopy (HVEM) [29].

The properties of a HEA can be modified by the addition of p-elements such as B, C, N and O. When the concentration of a p-element is high enough, this can lead to the formation of borides, carbides, nitrides or oxides, which can be described as high entropy materials (HEMs). In particular, the addition of carbon to a HEA is interesting, since many carbides are known to exhibit high hardness, low wear rate and low friction. Although, there are few studies of the effect of carbon in high entropy alloys, their properties should be dependent on the ability of the metals to form carbides. The transition metals can be separated into two groups: strong carbide formers represented by group 4-6 elements such as Ti, Nb, W and weak carbide-forming metals such as Fe, Co and Ni. The addition of C to strong carbide-forming metals is likely to give rise to a multicomponent carbide. The properties of such complex carbides have only been studied in a few published papers [30–32] and this is therefore to a large extent an unexplored field.

The aim of the thesis is to study magnetron sputtered films for a selected number of boride and carbide systems. In paper I, I have focussed on the synthesis and characterization of binary Mo-B films. The main purpose was to study the microstructure and phase composition and to evaluate the mechanical and tribological behaviour with respect to potential applications. The high friction coefficients observed for in these films suggest that they are unsuitable as electric sliding contacts. To improve the mechanical and tribological properties, carbon was added in paper II. An initial idea was to deposit films with the ternary phase Mo2BC which is predicted to exhibit a unique ductility, but
unfortunately, it was not possible to synthesise this material in our deposition system due to temperature limitations. I therefore focused my efforts on the study of low temperature Mo-B-C films with an amorphous structure. In paper III, I have studied low-temperature films based on the Mo-Fe-B system. Also in this case, the initial idea was to synthesise ductile ternary borides but no such phases were observed in the mainly amorphous films. Finally, multicomponent films with and without added C were studied using a high entropy alloy of TiCrNbTaW as model system. Paper IV focussed on a comparison of the HEA with small additions of C (<10 at.%), while paper V focussed on films with high carbon contents leading to the formation of carbides. The aim of these studies were to synthesize hard and yet ductile films with high corrosion resistance.
Materials systems

Mo-B

The stability of the different molybdenum boride phases has been a matter of some controversy [33–35]. In the Mo-B phase diagram (Fig. 1) several binary phases exist together with pure Mo and β-B. The most boron-rich phases described in the literature are MoB$_4$ and MoB$_3$ where the boron atoms form networks which potentially can give superhard materials [36]. Recent studies have, however, have shown that the MoB$_4$ and MoB$_3$ phases actually are identical [36]. In Fig. 1, this phase is denoted Mo$_{0.8}$B$_3$.

![Fig. 1 The binary Mo-B phase diagram [19].](image)

On the Mo-rich side, several phases such as, α and β - MoB, Mo$_3$B$_2$ and Mo$_2$B are observed. In these phases, the boron form chains and rings as the content of boron is increased [37]. The boron based coatings are used in combination with other coatings to form hard coatings on cermets (e.g. MoB/CoCr) [38] as well as a brazing materials in electrical contacts.

The phase diagram also includes two phases denoted RT-MoB$_2$ and HT-MoB$_2$, which are stable at low and high temperatures, respectively. The HT-MoB$_2$ phase is hexagonal and crystallizes in the simple AlB$_2$-type structure.
(hP3-MoB$_2$) where boron atoms form layers between Mo layers (Fig. 2a). This phase is thermodynamically stable only at high temperatures (>1517 °C), while a rhombohedral MoB$_2$-phase (hR18-MoB$_2$) with puckered boron layers is stable at lower temperatures [39,40] (Fig. 2b). Furthermore, phonon dispersion calculations have confirmed that the only stable phase at room temperature is hR18-MoB$_2$ [41]. However, recent DFT (density functional theory) calculations show that boron vacancies can increase the stability of the hP3-MoB$_2$ phase [34,42]. Therefore, a metastable formation of this phase at low temperature is favoured by substoichiometry, giving a MoB$_{2-x}$ phase with vacancies in the boron layers.

As can be seen in Fig. 2, the two MoB$_2$ phases exhibit a very different structural complexity. This is important in magnetron sputtered films, where the quenching rates of the incoming atoms are high. This leads to a low surface diffusion rate, which means that complex crystal structures with large unit cells rarely are formed at low deposition temperatures. The thermodynamically stable hR18-MoB$_2$ phase has a large unit cell with a c-axis of 21 Å and a very complex crystal structure (Fig. 2b). During magnetron sputtering at lower temperature, it is probably kinetically more favourable to form the structurally less complex hP3-MoB$_{2-x}$ phase with or without vacancies.

Fig. 2 Crystal structure of hP3-MoB$_2$ (a) and hR18-MoB$_2$ (b).
Mo-B-C

The other approach to tailor the properties of Mo-B films is to alloy it with something that induces a ductile behaviour and improves the tribological properties. Other studies on Me-B-C systems (Me = Nb, Cr) [20,21] indeed show that these properties can be tailored with the addition of carbon.

In the ternary Mo-B-C phase diagram (Fig. 3) we can see several binary phases: B₁₃C₂, Mo₂C, Mo₂B, MoB, MoB₂, Mo₀.₈B₃ (MoB₄) and one ternary phase: Mo₂BC. The binary Mo-B phases have already been discussed above. The boron-rich B₁₃C₂ phase has a rather complicated structure with icosahedral units bonded together with direct B-B bonds as well as other linkage units [43]. The Mo₂C phase is, on the other hand, orthorhombic with a nearly hcp array of Mo atoms with C in octahedral sites [44]. It should be noted that one of the most well-known binary Mo-C compounds is hexagonal MoC with a WC structure. This phase is, however, not stable above 1220 °C and therefore not included in the 1300 °C isothermal section in Fig. 3. The structure of ternary Mo₂BC phase is shown in Fig. 4a [5]. It consists of intermixed Mo and C layers with puckered B layers. The unit cell is complicated and has a long c-axis, which suggest that high deposition temperatures are required to form this phase in a magnetron sputtering process. As will be described below, this was also observed experimentally. In paper II, I have used a slightly substoichiometric MoB₂₋ₓ target and added C. According to the phase diagram, a mixture of MoB₂, graphite and small amounts of B₁₃C₂ should then be formed.

Fig. 3 The ternary Mo-B-C phase diagram [106].
at equilibrium. However, since magnetron sputtering involves non-equilibrium conditions, amorphous structures can be formed, especially if we take into account the complexity of the possible phases (for example $B_{13}C_2$). According to the phase diagram, the solubility of C in MoB$_2$ is small.

![Fig. 4 Crystal structures of two different phases: a) Mo$_2$BC [5] and b) Mo$_2$FeB$_2$ [23].](image)

**Mo-Fe-B**

The other possibility to modify the properties of a molybdenum boride film is to add a second metal such as Fe. As described above, several interesting ternary phases exist in the Mo-Fe-B system.

In the ternary Mo-Fe-B phase diagram (Fig. 5) we can see several binary phases: FeB, Fe$_2$B, Mo$_{5.1}$Fe$_{7.9}$, Mo$_2$B, MoB, MoB$_2$ and three ternary phases: MoFe$_2$B$_4$, Mo$_2$FeB$_2$ and Mo$_8$FeB$_{11}$. The Mo-B binary phases have been described above. The Mo$_{5.1}$Fe$_{7.9}$ phase is rhombohedral with a hR39 structure type and coordination polyhedra of Mo and Fe [45]. On the other side of the ternary diagram we find the Fe-B system with FeB and Fe$_2$B as binary phases. The FeB phase has an orthorhombic crystal structure, while Fe$_2$B adopts a body central tetragonal structure [46]. In addition to the binary phases we can also observe the ternary phases MoFe$_2$B$_4$, Mo$_3$FeB$_2$ and Mo$_8$FeB$_{11}$. As can be seen in Fig. 4b, the ternary phases have complex structures with large unit cells.

In paper III, we have deposited Mo-Fe-B films using a slightly substoichiometric MoB$_{2-x}$ target and Fe. At equilibrium, we should expect a mixture of MoB$_2$ and ternary phases as well as FeB and ternary phases with higher Fe contents (see Fig. 5). However, since the ternary phases exhibit complex crystal structures, a rather high deposition temperature is probably needed to form them. In addition, the Fe-B system is a well-known system forming metallic glasses [47,48]. Consequently, the formation of amorphous Mo-Fe-B films is
likely at reduced temperatures (<600°C). Such amorphous films are, however, likely to exhibit interesting, not yet explored properties.

High entropy alloys and multicomponent carbides

High entropy alloys (HEA) are multicomponent materials with equal concentrations of at least five elements (most often metals). A mixture of so many elements can lead to the formation of several intermetallic phases, but it was found that some multicomponent alloys form single phase solid solutions with a bcc or ccp structure [24] (Fig. 6a). This is explained by a high entropy of mixing, which favours solid solutions. Another parameter that highly influences the single-phase formation is the lattice distortion (Fig. 6b). Mixing of several elements with different radii will lead to lattice distortion, $\delta$, defined as:

$$\delta = \frac{\sum c_i \cdot (1 - \frac{r_i}{\bar{r}})^2}{\bar{r}}$$  (1)

where $c_i$ and $r_i$ are the atomic fraction and the atomic radii, respectively, of element $i$ and average atomic radius $\bar{r} = \sum c_i \cdot r_i$. It was observed that the formation of a HEA usually require a $\delta$-value lower than 6.6% [25]. Other factors such as kinetics are also important during the formation of HEAs [49]. Some alloys described as thermodynamically stable in the literature are in fact metastable, stabilized by kinetic factors. Upon annealing they tend to decompose and form precipitates of intermetallic compounds such as Laves phases (see e.g. ref. [50]). The phase diagrams of most HEAs are unknown but most
alloys described so far have either a ccp or bcc structure [25]). In the present thesis, I have studied the effect of C addition to a multicomponent CrNbTaTiW with a bcc structure. This alloy is assumed to be a high entropy alloy and by modifying the composition of the metal atoms, different δ-values can be obtained. The equimolar and Ta/W rich alloys studied in these thesis have the δ-values of 5 % and 3.4 %, respectively.

The structure of a HEA can be modified by the addition of a p-element such as C. The addition of large amounts of carbon to a bcc CrNbTaTiW film will lead to the formation of transition metal carbides. Nb, Ta and Ti all forms monocarbides with a B1 (NaCl) structure. In contrast, Cr and W only form this structure as metastable phases [51,52]. However, Furlan et al. [53] have shown that Ti-Cr-C films form a B1 solid solution and is therefore likely that a (CrNbTaTiW)C films also will exhibit this structure. The multicomponent carbide will include metal atoms with different radii, which can lead to a significant lattice distortion, that together with differences in the M-C bond strength, can create a driving force for element segregation and the formation of coherent or semi-coherent precipitates [54].

The addition of only small amounts of C (<10 at%) to a bcc HEA alloy should also lead to a modification of the film. The solubility of C in the early transition metals with a bcc structure is very low. For example, C has a maximum solubility of 0.3 at.% into the W at the eutectic temperature [55]. We should therefore expect that e.g. 10 at.% C is impossible to dissolve in the interstitial sites of a bcc HEA. However, the large lattice distortion in these alloys may lead to an unexpected high solubility limit.

In paper IV, I have deposited TiCrNbTaW and (TiCrNbTaW)C films with magnetron sputtering with low amount of C (< 10 at.%). The purpose of the study is to investigate if C can be dissolved into the HEA without carbide formation and also investigate the changes in the chemical and physical properties. In paper V, I have studied (TiCrNbTaW)C films with high carbon contents (~40 at%) leading to the formation of a multicomponent carbide. The main objective of this study how different metal compositions influence the structure and properties of such films.
Mechanical and tribological properties of metal boride materials and multicomponent carbides

The material systems described above are expected to exhibit interesting chemical and physical properties. In this thesis, their mechanical and tribological properties are studied in more detail and this will therefore be discussed below.

**Mechanical properties**

Boride materials exhibit high hardness and wear resistance [2]. In general, metal borides form strong Me-Me, Me-B and B-B bonds leading to materials with high hardness and high Young’s modulus but sometimes also to a significant brittleness. The hardness is related to the B/Me ratio, where strong B-B bonds play an important role. In general, a higher B/Me ratio leads to more B-B bonds and hence an increased hardness [2]. Thin films are known to often have an enhanced hardness compared to bulk materials. This can be due to several reasons such as a special microstructure or stresses introduced into the films during growth. For example, magnetron sputtered MeB₂ (Me = Ti, Nb) films are significantly harder than bulk single crystals. Mayrhofer et al. [56] have shown that overstoichiometric TiB₂ₓ films prepared by magnetron sputtering exhibit hardness values > 60 GPa, which is almost 100% harder than bulk TiB₂ [2]. This was explained by the special microstructure with oriented nanocrystalline TiB₂ grains surrounded by a B tissue phase, which hindered dislocation movements. A similar behaviour was observed by Nedfors et al. [17] for sub-stoichiometric NbB₂ₓ films. The author obtained a hardness of 42 GPa which likewise was also explained by the presence of a B tissue phase separating the boride grains. In paper I, I have studied sub-stoichiometric magnetron-sputtered MoB₂ₓ films and observed a similar microstructure with enhanced hardness.

Hardness usually comes with brittleness or low ductility. The ductility of a boride material can be improved in several ways. One of approaches is to add an element like carbon. This can lead to the formation of a ternary compound such as Mo₂BC. This phase exhibits a layered structure (Fig. 4a) and DFT
calculations by Emmerlich et al. [5] showed a B/G (bulk over shear modulus) value of around 1.72 for this phase and a positive Cauchy pressure ($c_{12} - c_{44}$). This suggests that Mo$_2$BC could combine high stiffness and ductility. Recent experimental studies on Mo$_2$BC films have confirmed this assumption [57].

It should be noted, however, that no ternary compounds are known in most Me-B-C systems. Due to a low solid solubility, carbon is not alloyed into the boride structure, but modifies the microstructure. The mechanical properties of magnetron sputtered Me-B-C (Me = Ti, Nb, Cr) have been studied by several authors [2,20,58,59]. In general, the addition of carbon leads to a nanocrystalline structure with metal boride grains surrounded by a BC$_x$ matrix. However, Nedfors et al. [20] have demonstrated that Cr-B-C films are completely amorphous. In general, the addition to carbon leads to softer and more ductile films. For example in the Mo-B-C system, the hardness is reduced from 29 GPa to 22 GPa with 37 at.% C [paper II]. This can be explained by a softer carbon-containing matrix in the films. Experimentally, it is possible to study ductility trends by measuring the H/E or the $H^2/E^2$ ratios [60]. It is generally accepted that $H/E \geq 0.1$ is typical for a ductile material. For example, sputtered superhard Ti-B films exhibit a H/E ratio of around 0.13 [61], which can be considered ductile.

The mechanical properties can also be modified by the addition of a second metal. One example is the Mo-Fe-B system where several ternary phases are known. Wang et al. demonstrated that Mo-Fe-B forms an amorphous phase with 10-30 at.% B and becomes crystalline only at higher growth temperatures than $\sim$500 °C [62].

Mo$_2$FeB$_2$ is a well-known hard and wear-resistant material in cermets (see e.g. [63]). A recent theoretical study by He et al. [23] showed that the B/G ratio for ferromagnetic or antiferromagnetic Mo$_2$FeB$_2$ phases is close to 1.5, suggesting a high degree of ductility [23]. The hardness was estimated to be around 25 GPa.

As is shown in paper III, also our sputtered Mo-Fe-B films are also amorphous at lower deposition temperatures. The mechanical properties of such films will then be similar to those observed for metallic glasses. It is well known that metallic glasses are rather soft and brittle. Upon deformation they form so-called shear bands leading to a limited ductility.

HEAs also have interesting mechanical properties. An increased hardness compared to the pure elements due to solid solution hardening and lattice distortion [25]. A hardening can also be caused by spinodal decomposition forming a mixture of coherent regions influencing the plastic deformation of the alloys [64]. The same is true if there are precipitations of other intermetallic phases (e.g. σ-phases or Laves phase) [25]. The formation of such intermetallic phases is known to reduce the ductility of e.g. steels. However, Al$_{0.5}$CrFeNi-Ti$_{0.25}$ are found to have maximum compressive strength and ductility in the presence of precipitates of ordered bcc (B2 structure) [65].
There are only a few studies on mechanical properties of multicomponent carbides based on carbide-forming transition metals. These carbides can have a significant lattice distortion and can therefore exhibit quite different mechanical properties compared to binary compounds. One example is (TiZrNbHfTa)C films which show higher hardness and lower wear rate than that of the binary carbides [31]. Gorban’ et al. showed similar results for (TiZrHfVNbTa)C films with (mainly) a NaCl Fm-3m structure [32]. They observed a hardness of 43-48 GPa. In papers IV and V, the mechanical properties of carbon-containing films based on TiCrNbTaW were studied by nanoindentation. It was found that multicomponent carbides grow epitaxially with a B1 structure on α-Al2O3(001) at 300°C. Much harder films (36 GPa) with a distorted cubic structure is formed at 600°C and a non-equimolar composition. It was also found that TiCrNbTaW films with 8 at% C exhibited a special combination of high hardness (20 GPa, higher than the HEA) and high ductility.

Tribological properties

Tribological properties include friction behaviour, lubrication and wear. The friction coefficient of a material versus a counter surface is important if the two surfaces are in contact and in motion relative to each other. For example, if we search for sliding electric contacts materials, a low friction and low wear together with a low contact resistance are desired to keep the film functional as long as possible. Since a material in a tribological contact often is chemically reactive, it is important that the formed products on the sliding surface also have a low contact resistance.

Boron compounds are used in some low friction applications, such as solid lubricants, liquid lubricants, lubricant additives and coatings [66]. Boric acid and hexagonal boron nitride are used as solid lubricants at extreme temperatures where liquid lubricants cannot be applied [18]. Metal borides are hard and rather brittle with rigid crystal structures, and can therefore be expected to exhibit high friction coefficients. More important, however, are the properties of the tribofilms which can be formed on the surface. Metal borides in a sliding electric contact can form boron oxides, BOx, and metal oxide in a tribological contact. BOx can in a humid atmosphere form boric acid which has a layered structure known to reduce friction [67]. Furthermore, many metal oxides are known to exhibit low friction coefficients [67]. Consequently, metal borides should have a potential as low friction materials. In paper I, we have studied the tribological properties of the metastable hP3-MoB2 phase. This phase may form lubricating BOx and MoOx tribolayers, but as will be demonstrated in paper I, formation of brittle materials in the tribocontact results in crack and debris formation, leading to a high friction coefficient.

In paper II, we have studied the influence of C on the tribological properties of Mo-B films. Carbon is well known to form lubricating graphitic surface
layers, which can reduce the friction coefficient substantially [68]. In addition, the added carbon can modify the tribochemistry and also reduce the brittleness which can further reduce the friction coefficient. Alloying a second metal into a binary metal boride system is also expected to change the tribological properties. Depending on the metal, we can expect a modified tribochemistry with other oxides in the tribocontact. Furthermore, the mechanical properties and brittleness can also be modified in such a way that the friction coefficient is reduced or increased. In paper III, we have studied the effect of Fe on the tribological properties.

High entropy alloys exhibit tribological properties from high dry friction to low friction with self-lubricating layers. Most metallic HEAs studied so far exhibit high dry coefficient of friction (COF) of around 0.8 [69–71] (here the discussion is limited to dry friction only). A mixture of several tribologically active materials (oxides, free carbon, friction resulting compounds etc.) can reduce the friction. An example is AlCrCuFeNi2, which exhibit a COF of around 0.3 [72]. Another approach is to design a composite structure with a HEA (CoCrFeNi) as matrix combined with other phases such as Ni and C, which reduce the friction coefficient [73]. Although the friction coefficient in these examples reaches moderate values, it is not enough for most applications. One way to further reduce the COF is to alloy HEA with C or to form a multicomponent carbide. The increase of carbon content can reduce the dry friction coefficient to a value as low as 0.05 [69]. A similar effect of carbon was also shown in references [70] and [74]. Other authors report highly C saturated samples of TiZrHfVNbTa exhibiting a COF of around 0.15 [32]. The examples above show a dry COF of around 0.1-0.2, which matches the value for diamond like carbon (DLC) films [75]. Therefore, most authors agree that the low COF comes from a graphite-like lubricating tribolayer. The thin films in paper IV and V have no or very small amounts of free carbon available to form such a tribolayer and they are therefore not expected to exhibit extremely low friction coefficients.
Methods

The films studied in this thesis are deposited with non-reactive magnetron sputtering (MS) and characterized using a wide range of techniques such as XRD, XPS, ERDA, SEM, TEM, nanoindentation, ball-on-disk method, electrochemical method (corrosion), Raman spectroscopy and optical profilometry. In this section, these methods and techniques are briefly described.

Magnetron sputtering

Sputtering is the process where ionised atoms (in our case Ar⁺) are accelerated towards a desired target via an electromagnetic (EM) field to knock-out material from the target. The atoms from the target are transported to the substrate where they are adsorbed. The adsorbed atoms diffuse on the surface and are finally incorporated into a growing film (Fig. 7). All this is done in a closed vacuum system with Ar gas. There is a wide variety of sputtering techniques.
One of the most employed techniques, used in this thesis, is non-reactive DC magnetron sputtering where no reactive gases are introduced into the chamber. Here DC stands for direct current – that means the power on the targets is kept constant. Magnetron simply means that the targets are in a magnetic field, so the Ar$^+$ ions could be more efficiently ionised. Different targets (single element or compound) can be used and by varying the power on each target, different compositions in the films can be obtained. An alternative technique is reactive magnetron sputtering, where a reactive gas such as N$_2$ or a hydrocarbon is added to deposit a nitride or carbide film. An advantage with reactive sputtering is that one can deposit insulating compounds that cannot be sputtered from a metallic target and have better control of the growth by tuning the reactive gas flow rate. A disadvantage with reactive sputtering can be that the reactive gases may poison the targets and form insulating layers on the chamber walls, resulting in a so called “disappearing anode” effect. To further control the microstructure of the film, a bias can be applied to the substrate. The bias can help to attract the ions to the substrate, hence increasing the energy of the ions and the surface diffusion rates. This leads to better adhesion, denser and in some cases also more crystalline films.

The MoB$_{2+x}$, Mo-B-C and Mo-Fe-B thin films discussed in this thesis were deposited by non-reactive DC-magnetron sputtering using a MoB$_2$ (99.5% claimed purity) and C (99.9% claimed purity) or Fe (99.5% claimed purity) targets in an ultra-high vacuum chamber (base pressure $\sim$ 10$^{-10}$ Torr). The total pressure was 3 mTorr in all experiments using a 42 sccm Ar gas flow rate. The MoB$_2$ target current was kept constant at 150 mA in all experiments while the C and Fe currents were tuned to obtain the desired concentrations film composition. All depositions were performed with -50 V bias voltage on the substrate holder. The films were deposited on Si (001), $\alpha$-Al$_2$O$_3$ (001) and 316L stainless steel for structural properties, stress measurements, mechanical properties and tribological analysis. The substrates were pre-heated (to 300 °C) and pre-sputtered with Ar$^+$ ions prior to the deposition and a thin layer (around 30 nm) of Mo or Nb was sputter-deposited on the substrates (at exactly the same conditions as the films) to improve the adhesion of the boride films. The deposition temperature in all experiments was 300 °C. The films thickness was about 600-1000 nm with a deposition rate of about 2 nm/min.

The (TiCrNbTaW)C carbides and low carbon content thin films were deposited by non-reactive DC-magnetron sputtering using a Nb (99.9% claimed purity), Ti/Cr (composition 1:1 and 99.9% claimed purity), segmented Ta/W (composition 1:1, claimed purity 99.9%) and C (99.9% claimed purity) targets in an ultra-high vacuum chamber (with a base pressure of $\sim$ 10$^{-9}$ Torr). The total pressure was 4.5 mTorr in all experiments using a 42 sccm Ar gas flow rate. The C target current was kept constant at 150 mA in all experiments while the metal target currents were tuned to obtain the desired film compositions. All depositions were performed with a -100 V bias voltage on the substrate holder. The films were deposited on Si (001), $\alpha$-Al$_2$O$_3$ (001), a-SiO$_2$ and
316L stainless steel for structural properties, mechanical properties, corrosion studies and tribological analysis. The substrates were mounted on a rotational table with an integrated heater, preheated (for 1h) before deposition and kept at constant temperature of 600 °C, 450 °C, 300 °C and RT respectively as measured by thermocouple. To attain a coating thickness of around 600 nm the deposition times for the HEC coatings were 360 minutes.

**X-ray diffraction (XRD)**

X-ray diffraction (XRD) is based on coherent scattering of the X-ray radiation with a wavelength close to the lattice plane distance in the crystalline structure. Different geometries can be used in the XRD analysis, which give different information. The traditional and mostly commonly used mode is the so called θ-2θ scan where the incident and exit angles are coupled. This results in a setup where diffraction is observed only from lattice planes parallel to the surface. For a thin film a θ-2θ scan gives important texture information. A problem, however, is that diffraction peaks from the substrate can overlap with the film peaks.

XRD measurements can also be carried out with a fixed incident angle while the escape angle is scanned. For small incident angles, this will give several benefits; first of all, it will decrease the penetration depth of the X-rays and result in an enhancement of the intensity for the thin film peaks. This type of measurement is called GI-XRD (grazing incidence XRD). Another benefit with GI-XRD is that it gives signal from all grains with different orientation, which may make it easier to determine the structure of an oriented film.

![XRD diffractogram of Mo-B-C samples grown at room temperature (RT) and at high temperature HT (550 °C). The literature data for cubic MoC phase with NaCl structure is marked with dashed lines (unpublished results).](image)

Fig. 8 XRD diffractogram of Mo-B-C samples grown at room temperature (RT) and at high temperature HT (550 °C). The literature data for cubic MoC phase with NaCl structure is marked with dashed lines (unpublished results).
The position and shape of the peaks can also give additional information. This can be seen in Fig. 8, which shows diffractograms recorded in an attempt to synthesize Mo$_2$BC (see results and discussion). As can be seen, the film deposited at room temperature (RT) showed no diffraction peaks suggesting that the film is X-ray amorphous. In contrast, the film deposited at 550 °C (HT) showed four peaks, which can be fitted to a cubic MoC phase with a NaCl structure. However, the peaks are much broader than expected and slightly shifted compared to literature data. The shift can be due to stresses or a change in the composition resulting in changed unit cell parameters of MoC with incorporation of B atoms, where the unit cell is distorted in one direction (e.g. c-axis) more than in other (a-axis). The broadening can be due to the smaller grain size or crystal lattice distortion. If the stresses are negligible or not present, the Scherrer’s equation can be used to calculate the crystalline size from the peak broadening [76]. Scherrer’s equation is, however, a rough approximation and a better approach is to use the Williamson-Hall method, which separates the strain and size contributions, but which requires at least three peaks to yield reliable results [76]. All calculated grain sizes in this study were obtained with the Scherrer’s equation. The grain sizes calculated with Scherrer’s equation must be handled with care but the method can still be used to show trends within a series of samples. The grain size in Fig. 8 was determined to around 5 nm, which indicates that the peak broadening is mostly due to size effects only.

In this thesis, the XRD experiments were performed with a Philips X’Pert MRD diffractometer with Cu Kα radiation and a parallel beam geometry. The grazing incidence XRD (GI-XRD) experiments were performed on the same instrument using a fixed 2θ-incident angle.

A pole figure is a form of stereographic projection of the orientation distribution of the crystallographic lattice planes in e.g. XRD analysis. Pole figure measurements were performed using a Philips X’Pert MRD employing a point focus mode with Cu Kα radiation. An X-ray poly-capillary lens with crossed slits were used as incident beam optics and a parallel plate collimator with a 0.18 ° acceptance angle and a flat graphite monochromator were used as diffracted beam optics.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique which is based on the photoelectric effect. It all starts with the emission of a photoelectron, which can be ejected from a material when it is exposed to X-rays. By measuring the kinetic energy of the emitted electron, it is possible to determine its binding energy. Each element has a unique set of photoelectrons originating from the atomic orbitals, which makes it possible to identify the different elements present in the sample [77]. The exact binding energy of an
electron depends not only upon the level from which the emission occurred, but also upon the formal oxidation state of an atom and the local chemical and physical environment. This chemical shift makes it possible to draw conclusions about the chemical bonding of the element.

The microstructure of the sputtered thin films can be rather complex and is not easily evaluated with XPS. Rather small shifts between bonding states can make it difficult to unambiguously attribute peaks to a given chemical environment. One example is the B1s spectrum in Fig. 9. It originates from a Mo-Fe-B film containing 23 at.% Fe which was studied in paper III. The spectrum is relatively broad so we can suspect different contributions. From previous studies on the Mo-B films in paper I we already know that the B1s spectra may consist of two contributions: B bonded to B at lower binding energies and B bonded to Mo at higher binding energies. Adding Fe to the system should introduce a third contribution where B is bonded to Fe in-between the B-B and B-Mo binding energies. However, since these films are amorphous with many different bonding states and the chemical shifts between the B-B, B-Fe and B-Mo states are small, it is very difficult to make a scientifically

![B1s spectrum](image)

*Fig. 9 XPS B1s peak of Mo-Fe-B thin film with 23 at.% Fe with fitting lines from different bonding contributions (adapted from paper III).*
relevant peak fitting to quantify the relative contribution of the different bonding states. This is why the contributions in Fig. 9 are depicted using broad hatched lines.

The analysis depth in XPS is determined by the electron mean free path. The latter depends directly on the kinetic energy of the electron, which in turn depends on the X-ray source energy. The XPS spectra in this work were acquired using Al Kα radiation with energy of 1487 eV. This results in a mean free path of less than 50 Å in most materials [77]. The information depth is defined as the depth from which 95% of all photoelectrons are scattered by the time they reach a surface (3 x inelastic mean free path), so we can estimate the analysis depth to be about 100 Å for a material with an electron mean free path of 30 Å. Consequently, XPS is a surface sensitive analysis technique.

Most surfaces are covered by a thin oxide and adsorbed contaminants. If we want to analyse the clean, unoxidised surfaces, sputter etching is required. This is usually done with energetic Ar⁺ ions which remove atoms in a layer-by-layer fashion. However, this procedure adds complications to the XPS analysis, as the high energy ions can change the chemical bonding of the sample atoms. Preferential sputtering can also change the surface chemical composition. Lewin et al. have shown that sputter damages are indeed present for metastable nanocomposite carbide-based films and that the extend of the damage depends on the ion sputter energy [78]. One of the possible solutions to the problem is to use low energy Ar⁺ sputter ions (used in some cases in this work). An alternative approach would be to use X-rays with higher energy. This results in longer mean free path and therefore a larger analysis depth. This method is known as high kinetic energy XPS (HIKE), or hard XPS (HAXPES). Synchrotron facilities are required for the use of these techniques.

XPS is a relatively fast and efficient technique to determine the chemical composition and bonding states in thin films. In order to use it properly a normalisation of the sensitivity factors is needed. The sensitivity factors used in this research were determined with ion beam analysis (ERDA), as described below.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is an electron imaging technique that allows observation of samples with atomic resolution. The most common and simplest is conventional TEM where high energy electrons (200-300 keV) travel through a thin layer of the desired sample and their interaction with the material is displayed on a fluorescent screen, photographic film or CCD camera. Because of the short de Broglie wavelength of the electrons, atomic resolution is possible. The samples can be imaged in two modes: the bright field where the primary beam electrons (or the main transmission from a diffraction point of view) are observed and the dark field where the reflections not coming
from the main beam are observed (certain orientation grains can be then identified). The HR-TEM is TEM at higher magnifications, meaning that the interaction of the electrons with the material is significant and no longer can be treated as simple transmission (electron beam interaction result in CTF). This requires knowledge and quite often simulation of the interaction, to explain the results. Apart from the imaging mode TEM can also be used for diffraction studies. In the diffraction mode TEM is tuned to view diffraction plane and electron wavelength results in a larger Ewald sphere than e.g. X-rays, therefore a lot of diffraction spots are on the Ewalds sphere and it can then be viewed and identified.

A special variant of TEM is scanning transmission electron microscopy (STEM) where the electron beam is focused on a small spot and scanned over the sample surface. If a high angle annular detector (HAADF) is used, we can obtain high resolution images with a strong z-contrast, where the contrast is directly related to the difference between atomic numbers. STEM can also be used in combination with EDX spectroscopy, which makes elemental mapping possible. In EDX, the electron beam and sample interaction yields emission of X-rays, which can be detected and identified for different elements. Therefore, elemental mapping is possible. The latter is usually used for mapping grains, grain boundaries or interfaces as it gives information about the elemental distribution in these structures. The limitations of EDX come from the sample itself, because of its small volume, the X-rays count is often rather small and there is a risk of X-rays coming from the sample holder and column, which is not desired.

Another technique used with TEM is EELS (electron energy loss spectroscopy). The mode is still STEM, and nothing is changed regarding the beam geometry, but we now analyse only electrons that are not scattered, i.e. electrons that lost energy via interaction with the material. Because we know the energy of the incoming electrons and can measure the electron energy after the interaction, the interaction energy can be calculated, this empowers one to separate elements and measure their surroundings – that is their chemical bonding states. Nevertheless, the large energy spread (tails) of different elements result in complicated spectra with a lot of overlap, artefacts as well as a combination of all the factors mentioned above making the analysis rather complex. One example of an EELS spectrum is shown in Fig. 10, where two different bonding states of B are observed. They originate from B in MoB_{2-x} and B in a boron-rich tissue phase, respectively. The spectra were cleaned from the main beam tail, plural scattering and the influence of other elements. TEM is hence a very powerful technique, but it comes at a price. The sample preparation takes a lot of time and energy and the success rate can be rather low. The sample preparation can also give rise to changes in the material, which are not always easily identified. One of the most common problems is contamination of the sample. Another artefact can be beam-induced structural changes such as crystallization of an amorphous film [79].
In this thesis, cross-section and top-view images of the MoB\textsubscript{2-x}, Mo-B-C and Mo-Fe-B films were acquired with TEM. The cross-section samples were prepared from as-grown films using a traditional “sandwich” method. The films were cut into small pieces, mounted into the Ti grid and glued with high temperature glue (Gatan G-1 epoxy). After that they were polished to a thickness of approximately 50 µm. A Gatan precision ion polishing system (PIPS) with Ar\textsuperscript+ ion milling using a 5 keV ion energy at 5° from both sides were used to thin the samples further. The Ar\textsuperscript+ ion energy was gradually reduced to 2 keV during the final step of the milling to minimize the surface damage. The plan-view samples were cut with an ultrasonic cutter and polished to a thickness of 100 µm, fitted into a special plan-view holder, and sputtered with Ar\textsuperscript+ ions only from the substrate side using the same steps as for the cross-section samples. STEM combined with HAADF, STEM EDX and STEM EELS analysis were performed with the double-corrected Linköping FEI Titan 60–300 instrument, operated at 300 keV. EELS analyses were performed using a Gatan GIF Quantum ERS post-column imaging filter with 1 kHz spectral acquisition. High resolution STEM (HRSTEM) imaging was recorded by using an optimized 30 mrad convergence angle, which provided sub-angstrom resolution probes and a 70–140 mrad HAADF detector acceptance angle range. The EDX mapping was performed with a high sensitivity Super-X EDX detector (Fig. 15).

![Fig. 10 EELS B K edge spectra for the MoB\textsubscript{2-x} grain and tissue phase in a plan view Mo-B sample (adapted from paper 1).](image)

The HEA and multicomponent carbides electron transparent cross-section TEM samples were prepared from as-grown films using a FEI Strata DB235 FIB/SEM. The TEM investigations were carried out in the STEM mode on a probe corrected FEI Titan Themis instrument operated at 200 kV acceleration.
voltage and equipped with the SuperX EDS system. The additional technique that we applied only to the multicomponent carbides was µProbe STEM. The electron beam in the TEM was then set up to a nearly parallel beam condition and focused to approximately 5 nm after which a STEM image was recorded. The beam was then positioned at different areas of interest in the µProbe STEM image to acquire electron diffractions patterns with nearly 5 nm lateral resolution. The recorded spot diffraction patterns were evaluated using the software tool CrysTBox [80–82].

Other characterisation methods

Apart from methods mentioned above, I also used other techniques. Scanning electron microscopy (SEM) was applied to investigate the morphology of my films. SEM is a microscopy technique where an electron beam is used as an imaging source. The image consists usually of secondary electrons scattered from the sample. In addition, the electron beam interaction leads to emission of X-rays (as well as Bremsstrahlung background radiation). This makes it possible to identify elements by EDX – energy dispersive X-ray spectroscopy. In this thesis, SEM was used to study samples using a Merlin field emission SEM equipped with EDS: X-Max 80 mm² silicon drift detector with high sensitivity and high count rates.

The chemical compositions of many films in my thesis were determined with elastic recoil detection analysis (ERDA). This technique requires a source of ions in the high energy range (i.e. mega electron-volt range (MeV)). In ERDA, the masses and energies of atoms knocked-out (recoiled) by the ion beam are detected. It is realised with a time-of-flight (TOF) technique. ERDA is not affected by the bonding states, is sensitive to light elements (H or D) and can reach depths of up to 1 µm and is therefore well-suited for composition analysis of thin films. Since it requires accelerator facilities and is rather expensive, it was only used to determine the chemical composition of a few standard samples in order to calibrate the XPS sensitivity factors. The ERDA measurements in the thesis were carried out at the Tandem laboratory at Uppsala University using $^{127}$I$^{8+}$ ions with an energy of 36 MeV.

Some analyses of wear tracks were carried out with Raman spectroscopy. In this technique a laser with a specific wavelength is used to excite vibrational and rotational states of the materials. The inelastic scattering of the photons (Raman scattering) can be detected and a spectrum can be recorded for the sample. The Raman scattering is surface sensitive for borides and strongly dependent on the structure and chemical bonding in the investigated material. The technique is therefore suitable for analysis of, for example, wear-tracks in tribological studies (see Fig. 11). In this thesis, the Raman spectroscopy experiments were carried out on a Renishaw Invia Raman spectrometer.
equipped with 532 nm green light laser. Raman Stokes vibrations were measured in the range from 20 cm\(^{-1}\) to 2000 cm\(^{-1}\) in order to determine the surface and wear track chemical environments.

**Characterisation of properties**

Measurement of mechanical properties is an important part of thin film characterisation. For thin films nanoindentation is usually used. The measurements are usually carried out with a diamond tip. The tip is pressed into the surface and the penetration depth as a function of pressure is measured during both loading and unloading. The hardness of the film is calculated from the maximum displacement and estimated indent area, while the elastic modulus is calculated from the slope of the curve. To avoid substrate effects, it is important to use an indentation depth, which is less than 10% of the total film thickness.

In this thesis, the mechanical properties (hardness, elastic modulus) were measured using a CSM Instruments Ultra Nano Hardness Tester (UNHT) equipped with diamond Berkovich tip. Load-displacement curves were measured at 20 different spots on the sample with 70 nm displacement and an unloading and loading rate of 1.5 Nm/min. The hardness and elastic modulus were determined by the Oliver-Pharr method and the results were averaged based on at least 15 indentation spots [83]. A similar Berkovich tip was used for ductility tests on MoB\(_{2-x}\) and Mo-Fe-B samples. The CSM UNHT was used

![Figure 11 Raman spectra of a MoB\(_{2-x}\) sample before (black line) and after (red line) a friction test (from paper I).](image_url)
to perform ductility tests on HEAs and multicomponent carbides, where the tip is pushed with 7 mN force into the sample to a depth of ~85 % of the film thickness. A subsequent SEM study give information on the film ductility based on the presence of cracks, pile up or shear band formation.

Optical profilometry was used to study wear tracks and surface curvature in the stress analysis. This technique is based on the interference of the light reflected by the surface. The measurements can be carried out with VSI (vertical scanning interferometry) where the light reflected from a reference mirror combines with the light reflected from a sample to produce interference fringes. This enables measurement on rough surfaces (roughness of up 1 µm). A more precise analysis can be carried out with PSI (phase shifting interferometry) which operates in the same way as VSI, but the white-light beam is filtered to get only red light and the system records the intensity of the resulting interference pattern at many different relative phase shifts. The, intensity to wave front (phase) data are converted by integrating the intensity data. This makes it possible to identify small surface structures, with a size up to 1 Å.

In this thesis, the wear rate was roughly estimated by measuring the wear track with a WYKO NT1100 optical profilometer (VSI). The same equipment was used to measure the surface roughness (PSI) and curvature as well as to estimate the stress in the films using the Stoney’s equation [84].

The tribological properties of the films were studied with a so-called ball-on-disk set-up (see Fig. 12). In this set-up a ball or pin is allowed to wear a surface in a continuous circular track. The friction coefficient, µ, is calculated by dividing the friction force with the applied normal force F_n. Important parameters include the applied load, ball diameter, sliding speed etc. It is important to remember that friction is a system property and that the calculated friction values are dependent on for example the material in the counter surface, surface roughness and humidity.

A ball-on-disc set-up was applied for friction measurements using stainless steel balls (100Cr6) with a 3 mm radius and a load of 1 N. All measurements were carried out in the ambient atmosphere with 55 % relative humidity at a temperature of 22 °C using a sliding speed of 0.1 m/s.

Electrical resistivity is an intrinsic electrical property that indicates how strongly a given material opposes the flow of electric current through it. Thin films exhibit higher electrical resistivity values than corresponding bulk samples, because of the reduced dimensionality. In my thesis the electrical resistivity was measured with a four-point probe AIT CMT-SR2000N Sheet Resistance/Resistivity Measurement System, based on the averaging measurements from five different spots.

To characterised the multicomponent carbides were potentiodynamic polarization measurements were also used to evaluate the corrosion resistance of the coatings. These electrochemical experiments were performed in a 1.0 M HCl aqueous electrolyte using a VersaSTAT4 (Princeton Applied Research) potentiostat/galvanostat. A three-electrode cell containing the sample as the
working electrode, a Pt wire counter electrode and a saturated Ag/AgCl reference electrode was used. The electroactive area of all samples was 0.196 cm² and all potentials are given with reference to the Ag/AgCl reference electrode. In the experiments, the open circuit potential (OCP) was first measured during one hour. The sample was then polarized using a potential of -1.5 V for 300 s to reduce surface oxides. A polarization curve was finally recorded between -0.2 V and +1.5 V at a scan rate of 1 mV/s. The corrosion potential ($E_{corr}$), passivation potential ($E_{pass}$) and the passive current density ($j_{passive}$) were then determined from the polarization curves. Materials used as the reference for corrosion studies were a hyper-duplex stainless steel (SAF 3207 HD, Sandvik AB).

![Fig. 12 Pin-on-disk tribological set-up.](image)
Results and discussion

Synthesis and characterisation of MoB$_{2-x}$ thin films

In paper I, binary Mo-B films were deposited at two temperatures (300 °C and 600 °C) and a XPS analysis of the films deposited from a MoB$_{1.5}$ target shows a strong substoichiometry with a total film composition of MoB$_{1.65}$, corresponding to a boron content of 62 at.%. The oxygen and carbon contents in the films were determined to be less than 2 at.% and 1 at.%, respectively. The above value is much lower than the one in the target, indicating that the target is porous and contain gases and moisture adsorbed from atmosphere.

The X-ray diffractograms in Fig. 13 (for 0 at. % C) show that the deposited films consist of the hexagonal hP3-MoB$_2$ phase with the well-known AlB$_2$ type structure where the planar B-layers are separated by planar metal layers (Fig. 2). This phase is metastable, and should according to the phase diagram only be formed at elevated temperatures. At the deposition temperatures, the thermodynamically stable phase should be the rhombohedral hR18-MoB$_2$, but this phase is not observed in the diffractograms. The formation of the hP3-MoB$_2$ phase in the sputtering process can be explained by the difference in structural complexity. The crystal structure of the hP3-MoB$_2$ phase is rather simple with the hexagonal repeating stacking sequence AHAH, where A and

![Fig. 13 GI-XRD of the Mo-B and Mo-B-C samples with C content up to 37 at.%, including the HT sample with 31 at.% C; Red and blue dashed lines with indices and x are attributed to hexagonal MoB$_2$ phase and Mo adhesion layer, respectively (from paper I).](image-url)
H are close-packed Mo and planar B layers, respectively. In contrast, the thermodynamically stable hR18-MoB2 structure is very complex with a stacking of many layers and a large unit cell (~ 21 Å, Fig. 2b) [39]. Hence, the formation of the hR18-MoB2 phase should require substantial surface diffusion, which is not likely for the experimental conditions used in our study. Therefore, the simple but metastable hP3-MoB2 phase is formed.

A TEM analysis was performed in order to investigate the structure of the produced films (Fig. 14). TEM showed hP3-MoB2 grains (~ 10 nm) surrounded by a tissue phase. The SAED reflections match those of the hP3-MoB2 lattice fringes and are in agreement with the results of the XRD study.

![SAED](image)

*Fig. 14 Cross section HR-TEM results for a binary Mo-B sample grown at 300 °C (adapted from paper I).*

To investigate the tissue phase further, plan view TEM and EELS were performed (Fig. 15). The STEM-HAADF image (Fig. 15c) shows ~10 nm Mo-rich boride grains surrounded by a Mo-poor tissue phase (B-rich). Therefore, the films are made of nanocrystalline MoB2-x grains surrounded by a boron-rich tissue phase. The EELS analysis (see Fig. 10 and Fig. 15b) confirms this. The B-K edge in the EELS spectra is very different for the tissue phase with two distinct peaks compared to the broad peak due to the grains (Fig. 15b). This EELS fine structure is most likely the result of two chemical structures in the tissue phase. One consists of amorphous boron which gives rise to the slowly varying background in this spectrum and the small shoulder slightly above 190 eV energy loss, while the two sharper features at ~195 and ~204 eV energy loss match to the signature from the B-O bonds [85]. How this oxygen is embedded into the tissue phase is still unclear but it can originate from an oxidation of the samples in ambient air prior to the TEM analysis or an introduction into the material during the sample preparation.

The nanocomposite structure was confirmed in the XPS analyses. The XPS B1s peaks (a) can be fitted with only two contributions: one originating from
Mo-B bonds and the other from B-B bonds. The Mo-B peak can be attributed to boron in the boride grains and the B-B peak to boron atoms in the B-rich tissue phase as can be seen in the plan-view TEM images in Fig. 15a,c.

![Fig. 15 Mo-B plan-view TEM data: a) STEM image, b) EELS B K edge spectra for the grain and tissue phases, c) HR-STEM image (scale bar also valid for EDX maps) and EDX maps of boron (d) and molybdenum (e) (from paper I).](image)

The composition of the films was estimated to be MoB\(_{1.65}\), but since we observe a Mo-poor tissue phase, we can conclude that the boride grains must be highly substoichiometric with a B/Mo ratio < 1.65. However, to estimate the composition of the metal boride phase is difficult. The formation of a highly substoichiometric hP3-MoB\(_{2-x}\) phase can be explained based on a recent study on the effect of vacancies on the stability of diborides [42]. The hP3 structure is not thermodynamically stable versus the hR18 phase. However, by removing B and creating vacancies, the stability of the hP3 phase can be increased. Furthermore, it should be noted that a small amount of Mo can be present in the tissue phase as well. This has been demonstrated in Cr-B-C films, where Cr is present in the tissue phase between the CrB\(_{2-x}\) grains [86]. In conclusion, the binary Mo-B films can be described as nanocomposites with nanocrystalline substoichiometric hP3-MoB\(_{2-x}\) grains, surrounded by an amorphous boron-rich tissue phase. This type of microstructure has been observed before. It has been reported for magnetron sputtered TiB\(_2\) [56], NbB\(_{2-x}\) [17] and CrB\(_{2-x}\) [20] films and may therefore be an archetypical microstructure for sputtered diboride films deposited from compound targets. Furthermore, the tissue phase can influence film properties such as hardness and friction. Composition and chemical bonding variations in the tissue phase are also important and
small amount of impurities (0.5-1 at.%) of e.g. O and C can have a strong impact on the film properties.

The hardness and elastic modulus of the binary Mo-B films were determined to be 29 GPa and 526 GPa, respectively. The reported literature value for the above is 16.4 GPa [87] for the hP3-MoB₂ AlB₂ type structure, which is significantly lower than our value. Film hardening due to stress can be excluded as the stresses in all films are very low (< 1 GPa). We attribute the higher hardness to the presence of a tissue phase hindering dislocation movements. The H/E ratio is dependent on the ductility of the sample and a material is considered ductile for ratios exceeding 0.1. The binary Mo-B films have an H/E ratio of 0.055 indicating a brittle behaviour of the sample.

The resistivity measurements revealed an electrical resistivity of 175 ± 40 µΩcm for the binary sample which clearly is higher than for bulk MoB₂ (45 µΩcm) [88], but this is not surprising since the value is similar to those previously found for other binary transition metal boride films [17,20].

One of the goals of this study was to investigate the tribological properties of hexagonal hP3-MoB₂ thin films. The metastability of this phase should make it easy to decompose and the formation of molybdenum oxides and boric acid should be favourable in humid air. Easy decomposition and potential low-friction behaviour of these materials could make Mo-B films possible candidates for low-friction materials. The binary Mo-B film dry friction coefficient against steel counter surface was rather high with a value of 1.1 making coating applications rather limited when a sliding motion is required. The Raman spectrum from the tribo track in Fig. 11 shows very strong peaks from mainly MoO₃ and Fe₂O₃ (from the counter surface). So, the oxide formation was indeed favourable under the tested circumstances. This oxide formation in tribocontact was not observed e.g. for CrB₂-x and NbB₂-x films deposited and tested under similar conditions [17,20]. Furthermore, the XPS spectra (see paper I) did not reveal any traces of boric acid or other boron-containing phases on the surface of the tribofilm. The formation of a thick MoO₃ tribolayer is the likely cause for this finding. Clearly, the formation of MoO₃ has no beneficial effect influence on the friction behaviour. However, since molybdenum oxide is known to have a strong lubricating effect mainly at higher temperatures (> 400°C [67]), lower friction coefficients may be observed under other conditions where the temperature of the tribocontact is higher.

The brittleness of the MoB₂-x films is demonstrated in Fig. 16. Here an indentation test was carried out by pressing a Berkovich diamond tip with 50mN force into films deposited on the 316L steel substrates. SEM images acquired after the deformation tests showed a ring-like cracking around the indentation, indicating a brittle nature of this material.
The ternary Mo-B-C system

With the addition of C the idea was initially to deposit the Mo$_2$BC ternary phase (Fig. 17) using elemental Mo, B$_4$C and C targets. The depositions were started at room temperature and resulted in completely amorphous films (Fig. 8, RT). In order to form the wanted phase (Mo$_2$BC) the depositions were performed at elevated temperatures (Fig. 8, 550 °C), but only the cubic MoC phase was formed. Emmerlich et al. [5] were able to deposit this phase at ~ 900 °C but our growth chamber heater could not generate temperatures higher than 600 °C.

Due to the difficulties associated with the deposition of Mo$_2$BC films, it was decided to study the Mo-B-C system using a MoB$_{1.65}$ compound target.

![Fig. 16 SEM image of the Berkovich indent on a MoB$_{2-x}$ sample. The ring-like cracks indicate a brittle behaviour.](image)

![Fig. 17 Ternary phase diagram of Mo-B-C with the sample compositions shown as solid dots (the line is a guide to the eye). The hollow symbol represents the high temperature (HT) sample.](image)
and a separate C target. The main objective with this study was to improve the tribological properties of the binary Mo-B films as described above. The ternary phase diagram (Fig. 17) shows the compositions of the deposited films with the relative ratio of B/Mo constant. One extra sample was prepared at a higher deposition temperature (600 °C) with a moderate content of C to investigate the growth temperature effect. The chemical composition of the Mo-B-C films were analysed with ERDA.

Upon addition of carbon (Fig. 13), the crystallinity of the films is reduced. The grain size of the MoB$_{2-x}$ grains decreases rapidly and is only 2 nm at 23 at.% C. Above 23 at.% C, the films become X-ray amorphous. The Mo-B-C diffraction peaks also shifts to lower 2θ values, indicating a limited carbon incorporation into the boride structure. The high temperature sample (HT) exhibits more pronounced hP3-MoB$_2$ reflections with 3 nm size grains as determined by the Scherrer equation. The grain refining effect of carbon is not unexpected. The solubility of carbon into the diboride is very limited and the added carbon hence segregates to the surface of the growing diboride grains. This favours a renucleation of new grains. The surface segregation effect will increase with an increased carbon content giving rise to a smaller grains and finally a more or less amorphous structure.

Fig. 18 Cross-section TEM results of Mo-B-C samples grown at 300 °C (top) and 600 °C (bottom). Some of the few crystalline grains in the Mo-B-C films are outlined (adapted from Paper II).
Fig. 18 shows the cross-section HRTEM images of Mo-B-C thin films with 31 at. % C, grown at 300 °C (top) and 600 °C (bottom) with some grains outlined. SAED, DF and HRTEM revealed that the binary film contained many nanocrystalline particles, with a size of ~ 10 nm (Fig. 14). In the Mo-B-C film the grain size was reduced to ~ 3 nm and a few grains were observed to be embedded in an amorphous tissue phase in the 31 at.% films, which consequently resulted in broad rings in the electron diffraction patterns. Slightly larger and more pronounced grains (~ 5 nm, also embedded in amorphous tissue phase) were observed for the high temperature film.

XPS B1s spectra for the Mo-B-C films are shown in Fig. 19. As can be seen, the addition of carbon gives rise to a shoulder at higher binding energies, corresponding to the boron bonded to carbon (B-C). The B-C contribution increases with higher C content. In summary, the XPS results suggest that a significant amount of carbon is bonded in a BCx-phase surrounding the Mo-rich phase. It is possible that the amorphous BCx-phase also contains Mo but this cannot be verified based on the available data.

![High resolution XPS B1s spectra for the Mo-B and Mo-B-C samples up to 37 at. % C, including the HT sample. Dashed lines are a guide for an eye used to indicate the fitted peak positions (adapted from paper II).](image)

Fig. 19 High resolution XPS B1s spectra for the Mo-B and Mo-B-C samples up to 37 at. % C, including the HT sample. Dashed lines are a guide for an eye used to indicate the fitted peak positions (adapted from paper II).

The Mo-B-C sample deposited at a higher temperature (600 °C instead of 300 °C) shows two main differences compared to its low temperature equivalent: more crystalline diboride phase, also seen in the diffractogram (Fig. 13),
and a larger amount of the a-BCₙ tissue phase. Furthermore, the crystalline cell volume decreases to a level comparable with that for the 8 at.% C sample. All three observations can be explained by the increased adatom mobility at higher temperatures, yielding higher diffusion lengths and a stronger phase separation where C is not trapped in an amorphous Mo-rich phase and instead contributes to an increased amount of the a-BCₙ tissue phase and more extensive crystallization of MoB₂₋ₓ. The addition of carbon lowers the hardness and elastic modulus to 22 GPa and 326 GPa (Fig. 20a), respectively. The hardness decrease correlates well with the increase in the relative amount of a-BCₙ tissue phase (see Fig. 20b), which thus is the likely cause of the softening [89,90]. Since the sample deposited at the higher temperature fall into the same linear trend (see Fig. 20b) it is likely that the amount of tissue phase is what primarily is determining the material hardness for these samples.

![Graphs](image)

**Fig. 20 a)** Hardness, elastic modulus and H/E ratio for the Mo-B-C films **b)** Hardness and resistivity plotted as a function of the relative B-C contribution in the B1s XPS spectra (see a). The solid markers denote the values for the samples deposited at 300 °C while the open symbols denote the sample deposited at 600 °C. The lines are a guides to the eye (adapter from paper II).

The H/E ratio increases upon addition of carbon, which indicates the attainment of a slightly more ductile behaviour. This is an interesting observation, considering that both Nb-B-C and Cr-B-C in the work of Nedfors et al. show the opposite trend [20,21]. There is presently no obvious explanation for this difference.

One of the goals with this study was to investigate the tribological properties of Mo-B-C thin films. However, the observed coefficient of friction (COF) of 0.85 with C present was just slightly lower than that for the binary Mo-B film (~1.1). The tribotests with the steel counter surface confirmed a significant formation of molybdenum and boron oxide formation in all the samples (Raman and XPS studies not shown). This type of oxide formation is not observed for e.g. CrB₂₋ₓ and NbB₂₋ₓ films deposited and tested under similar conditions [17,20]. This correlates well with a lower friction coefficient and shows that under the tested conditions (room temperature) the oxides are in fact not lubricating, but rather the opposite. The XPS spectra (not shown) suggest that no boric acid is present on the surface of the tribofilms after the
experiments. Raman studies of the wear tracks also reveal stronger carbon D and G bands on Mo-B-C thin films, which correlate with the lower friction coefficient. An interesting observation is the presence of non-carbidic carbon in all wear-track (see XPS spectra in paper II). The carbon is bonded as C-C and C-O.

To test the electrical properties, the electrical resistivity of the Mo-B-C films was measured. The resistivity spans from $175 \pm 40 \, \mu\Omega\text{cm}$ for the binary sample up to $395 \pm 33 \, \mu\Omega\text{cm}$ for ternary Mo-B-C samples and the values are similar to those previously found for Nb-B-C thin films [21]. The observed increase in resistivity for the samples deposited at 300 °C correlates well with the B-C contribution to the XPS B1s spectra, and could therefore be explained by an increasing amount of covalent bonds in the material. However, as the sample deposited at 600 °C does not follow this trend, other factors are of importance.

The ternary Mo-Fe-B system

The ternary Mo-Fe-B films were deposited using MoB$_{1.5}$ and Fe targets in paper III (Fig. 21). The relative ratio of B/Mo was kept constant in order to investigate the Fe content influence on film structure and properties. One extra sample was prepared at a higher deposition temperature (600 °C) with moderate content of Fe (23 at.%) to investigate growth temperature effect. The chemical composition of the Mo-Fe-B films were analysed with ERDA.

![Fig. 21 Ternary phase diagram of Mo-Fe-B with the sample compositions shown as solid dots (the line is a guide to the eye). The hollow symbols represent high temperature (HT) samples.](image)
The addition of Fe to Mo-B binary system has a strong impact on the phase composition and crystallinity of the films (Fig. 22). As described above, the diffractogram for the binary Mo-B film shows peaks from the hP3-MoB2 phase. At 7 at.% Fe, the peaks from this phase are weaker and broader. If the Fe content is increased to 14 at.%, the films become X-ray amorphous. GI-XRD scans of the HT film deposited at 600 °C shows no observable improvement of film crystallinity. The peaks at 2θ = 38 - 41° originates from the metal adhesion layers (Mo for pure MoB2 and Nb for Mo-Fe-B samples).

TEM of films with 23 at.% Fe deposited at 300 °C and 600 °C are shown in Fig. 23. For the films deposited at 300 °C, the TEM and SEAD images show a completely amorphous structure without any spots in SAED indicating crystalline structure. The HT (600 °C) growth temperature results only in slightly stronger SAED rings indicating a higher close order, but no hP3-MoB2 crystallite formation (Fig. 23 SAED). A closer look at the TEM results indicates that the structure consists of two separate phases: a metal-rich phase (with higher Mo and Fe content) separated by an amorphous boron-based tissue phase (which may contain a small amount of metals). An amorphous structure is not unexpected since, it is know from literature that Mo-Fe-B forms amorphous structures for 10-30 at.% B [62]. Thus, it can be expected that B has a limited solid solubility and therefore the metal rich and amorphous boron areas are formed as a consequence of this. The exact composition of the two phases are not determined yet, but XPS suggests that the metal rich areas contain both Mo and Fe, and that the relative contribution of Fe increases with increasing Fe content in the film.

Fig. 22 GI-XRD of the Mo-B and Mo-Fe-B samples with a Fe content of up to 37 at.% including the HT sample at 23 at.%. The red and blue dashed lines with indices and x are denoted to the hexagonal MoB2 phase and Mo and Nb adhesion layer, respectively (adapted from paper III).
TEM shows that the HT samples have the same two amorphous phase structure, but also that small crystallites form at this temperature, which can be confirmed by SAED and FFT (Fig. 23 c,d) stronger rings, which can be attributed to hexagonal diboride AlB$_2$ type structure. The formation of crystallites is expected, due to the higher diffusion rates at higher growth temperatures (600 °C compared to 300 °C). With the present set-up we were unable to reach higher growth temperatures, therefore higher crystallinity and other phases (like MoFe$_2$B$_4$ and Mo$_2$FeB$_2$) are expected at higher growth temperatures.

The EELS study showed that significant amounts of oxygen (10-30 at.%) are present in TEM prepared samples, although both ERDA and XPS showed < 1 at.% O. The high oxygen content in the EELS analysis can be explained by oxidation in air during the sample transfer prior to the TEM analysis.

Fig. 23 Cross-section TEM results of Mo-Fe-B samples grown at 300 °C and 600 °C, respectively. Here SAED – selective area electron diffraction and big picture is HR-TEM. Scale bar valid for all images (adapted from paper III).
The XPS analysis shows that the addition of Fe (Fig. 24) shifts the B1s peak to lower binding energies. From paper I we know that binary Mo-B XPS B1s peak can be fitted using two contributions: boron bonded to molybdenum (B-Mo) and boron bonded to boron (B-B) (see the detailed description in the binary MoB\textsubscript{2-x} paragraph). The introduction of Fe yields B-Fe bonds and a shift in the peak position. This is the case as can be seen in Fig. 24, where addition of Fe leads to a peak shift to lower binding energies compared to for the MoB\textsubscript{x} films. The B1s peak fitting is best done using a binding energy of 187.9 eV, which is close to the literature values for B-Fe bonds [91]. Depending on the Fe content, the relative intensities of the sub-peaks (B-Mo, B-Fe, B-B) change, but due to the strong overlap of the contributions an exact fit is very difficult. As can be seen, the B-Mo contribution decreases, while the B-Fe contribution increases with increasing Fe content. The XPS Fe 2p and Mo

![Fig. 24 High resolution XPS B1s spectra from Mo-B and Mo-Fe-B samples up to 37 at. % Fe. The dashed lines are guides to the eye to indicate the fitted peak positions (paper III).](image-url)
3d peaks exhibit no observable change with Fe content increase and are therefore not presented here. The XPS B1s peak for the HT sample exhibits an increase in the B-Mo contribution and a decrease of B-Fe contribution, which is in agreement with the TEM results for small crystallite formation at HT.

In summary, we can conclude that the films consist of a nanocomposite comprising two amorphous phase material with metal-rich and amorphous boron-based tissue phases. The results above clearly show that no ternary phases such as Mo$_2$FeB$_2$ are formed. As can be seen from Fig. 21, at equilibrium the composition is in the three-phase regions for several ternary phases. The problems to deposit ternary films can be attributed to the complex crystal structures, as the ternary phases would have large unit cells and hence would require significant surface diffusion in order to form.

Addition of Fe to the binary Mo-B films results in a hardness decrease to 18.7 GPa for the highest iron content (Fig. 25). The elastic moduli feature a similar decrease from 526 GPa to 353 GPa. This behaviour can be explained by the amorphous structure of the material, which leads to softer films [92]. The hardness and elastic modulus are not significantly different in the film deposited at 600 °C (Fig. 25 open markers). Fig. 25 also shows the variation of the H/E ratio as a function of Fe-content. A material is considered ductile if the H/E ratio exceeds 0.1 [60,93–95]. As can be seen, the Mo-Fe-B series exhibits low H/E values (varying from 0.052 to 0.055, Fig. 25 blue curve), indicating that the films are less ductile.

![Fig. 25 hardness, elastic modulus and the H/E ratio of Mo-Fe-B samples up to 37 at. % of C. The solid markers are used for samples deposited at 300 °C, while open markers are employed for the sample deposited at 600 °C. The lines are a guide for the eye (adapted from paper III).](image)

The brittleness of the amorphous Mo-Fe-B films is demonstrated in Fig. 26. Here an indentation test has been carried out by pressing a Berkovich diamond tip with 50mN force into films deposited on the 316L steel substrates. The
SEM images acquired after the deformation tests showed strong cracking of the films, indicating a brittle nature. As all samples exhibit cracks, but Fig. 26 only shows two examples for films with 23 and 37 at.% of Fe. Although those films are amorphous, no shear bands can be observed.

![Fig. 26 SEM images of Berkovich indent of amorphous Mo-Fe-B films with 23at% (a) and 37 at. % Fe (b). The cracks are typical for a brittle material.](image)

Investigation of the tribological properties of Mo-Fe-B thin films were one of the objectives of this study. The coefficient of friction (COF) was around ~0.85 after the introduction of Fe. The Raman, XPS and SEM analysis of the wear track reveal significant wear, molybdenum oxide formation and transfer of counter surface as in the Mo-B-C case, which is not surprising, since the COF is similar to that found for the Mo-B-C system.

One of the motivations for this study was the potential use of this material in sliding electrical contacts. The observed resistivity in combination with the lowering of the hardness could give rise to a low contact resistance. However, the high coefficient of friction makes the Mo-X-B (X= C, Fe) thin films unsuitable for sliding electrical contacts.

### The CrNbTaTiW-C system

In papers IV and V, the magnetron sputtering of CrNbTaTiW HEA films was studied with and without the addition of carbon. To investigate the influence of the metal composition, films were deposited with different metal content. In paper IV, near equimolar films (NE) and Ta/W-rich (TaW) films deposited at 300 °C with the addition of about 8 at% C were investigated. In paper V, we investigated the influence of both composition and temperature on the properties of carbide films (~ 40 at.% C) including also a Nb-rich film. The films in these two studies are summarized in Table 1. It should be noted that
the carbidic films in paper V deposited at 300 °C were used as reference samples in paper IV.

Table 1. Sample name (letter represents the dominant elements and number represents growing temperature), growth temperature, composition, phase, observed cell parameters, hardness, Elastic modulus and H/E ratio (From papers IV and V).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth T (°C)</th>
<th>Composition (at. %)</th>
<th>Phase</th>
<th>a (±0.02 Å)</th>
<th>H (±2.2 GPa)</th>
<th>E, E₀ (±34 GPa)</th>
<th>H/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE</td>
<td>300</td>
<td>Ti 21 Cr 29 Nb 16 Ta 16 W 18 C 18 O 0</td>
<td>bcc</td>
<td>3.15</td>
<td>13.3</td>
<td>-</td>
<td>185</td>
</tr>
<tr>
<td>NE(C)</td>
<td>300</td>
<td>Ti 15 Cr 27 Nb 16 Ta 15 W 19 C 8 0</td>
<td>Amorph.</td>
<td>-</td>
<td>14.9</td>
<td>-</td>
<td>210</td>
</tr>
<tr>
<td>NEC600</td>
<td>600</td>
<td>Ti 12 Cr 14 Nb 14 Ta 13 W 13 C 36 &lt; 2</td>
<td>NaCl</td>
<td>4.34</td>
<td>26.5</td>
<td>445, 330</td>
<td>0.060</td>
</tr>
<tr>
<td>NEC450</td>
<td>450</td>
<td>Ti 13 Cr 15 Nb 9 Ta 13 W 13 C 35 &lt; 2</td>
<td>NaCl</td>
<td>4.34</td>
<td>21.4</td>
<td>444, 329</td>
<td>0.048</td>
</tr>
<tr>
<td>NEC300</td>
<td>300</td>
<td>Ti 13 Cr 13 Nb 8 Ta 13 W 13 C 40 &lt; 1</td>
<td>NaCl</td>
<td>4.34</td>
<td>15.7</td>
<td>367, 287</td>
<td>0.043</td>
</tr>
<tr>
<td>NECRT</td>
<td>~20</td>
<td>Ti 12 Cr 14 Nb 9 Ta 14 W 13 C 33 &lt; 2</td>
<td>NaCl</td>
<td>4.32</td>
<td>16.9</td>
<td>371, 288</td>
<td>0.046</td>
</tr>
<tr>
<td>TaW</td>
<td>300</td>
<td>Ta 3 Cr 3 Nb 14 Ta 13 W 25 C 36 &lt; 1</td>
<td>bcc</td>
<td>3.24</td>
<td>14.7</td>
<td>-</td>
<td>321</td>
</tr>
<tr>
<td>TaW(C)</td>
<td>300</td>
<td>Ta 3 Cr 3 Nb 11 Ta 13 W 38 C 38 &lt; 8</td>
<td>bcc</td>
<td>3.28</td>
<td>19.1</td>
<td>-</td>
<td>322</td>
</tr>
<tr>
<td>TaWC600</td>
<td>600</td>
<td>Ta 4 Cr 4 Nb 5 Ta 25 W 25 C 35 &lt; 2</td>
<td>BCT</td>
<td>4.35</td>
<td>35.5</td>
<td>487, 350</td>
<td>0.073</td>
</tr>
<tr>
<td>TaWC450</td>
<td>450</td>
<td>Ta 4 Cr 4 Nb 5 Ta 25 W 25 C 35 &lt; 2</td>
<td>BCT</td>
<td>4.36</td>
<td>35.3</td>
<td>418, 315</td>
<td>0.084</td>
</tr>
<tr>
<td>TaWC300</td>
<td>300</td>
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<td>NaCl</td>
<td>4.36</td>
<td>26.8</td>
<td>568, 390</td>
<td>0.047</td>
</tr>
<tr>
<td>TaWCRT</td>
<td>~20</td>
<td>Ta 4 Cr 4 Nb 6 Ta 24 W 24 C 36 &lt; 2</td>
<td>NaCl</td>
<td>4.33</td>
<td>20.2</td>
<td>387, 298</td>
<td>0.052</td>
</tr>
<tr>
<td>Nb300</td>
<td>300</td>
<td>Nb 3 Cr 4 Ta 51 Nb 2 Ta 4 W 36 &lt; 0</td>
<td>NaCl</td>
<td>4.42</td>
<td>11.7</td>
<td>550, 376</td>
<td>0.021</td>
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</table>

The diffractograms for the equimolar series (NE, NE(C), NEC) and Ta/W rich (TaW, TaW(C), TAWC) series grown at 300°C are shown in Fig. 27. The metallic NE films with 0% C exhibits peaks at ~40.5° and ~88°, which can be attributed to simple bcc crystalline structure. The film has a <110> preferred orientation without indications of additional phases in the diffraction pattern, which was also confirmed by GI-XRD (not shown here). The unit cell can be determined to a = 3.15 Å. The NE(C) film with 8 at% carbon is completely X-

Fig. 27 θ-2θ XRD scans (normalised with respect to the highest intensity) of a) near-equimolar and b) TaW-rich films deposited at 300 °C. NEC and TaWC corresponds to NEC300 and TaWC300 in Table 1. The sapphire (006) reflection was removed prior to the normalisation (adapted from paper IV).
ray amorphous films (broad low intensity peaks). The sharp peaks in this diffractogram originates from the L\textsubscript{a1} and K\textsubscript{\beta} lines due to the α-Al\textsubscript{2}O\textsubscript{3} (006) and (0012) substrate reflections. Finally, the addition of 40 at\% C (NEC300 in Table 1) gives films with a cubic Fm-\textit{3}m (NaCl) structure with a preferred <111> orientation typical for metal carbides.

Fig. 27b depicts the diffractograms from the Ta/W-rich series. The carbon-free TaW rich film crystallizes in a simple bcc structure as well, exhibiting peaks at ~39° and ~84.5° corresponding to a unit cell \(a = 3.24\) Å. An addition of 8 at.\% carbon leads to a shift of the (110) peak to lower 2θ angles and an expansion of the unit cell to \(a = 3.28\) Å while retaining the bcc structure without the formation of additional phases. Finally, an increase in the carbon content to 38 at.\% results in a structural change from bcc to fcc (Fm-\textit{3}m NaCl) and the formation of a multicomponent carbide film with a preferred <111> orientation. A detailed description of the structural properties of these multi-component carbides will be discussed below.

Fig. 28 STEM HAADF cross section overview of the a) TaW b) TaW(C) c) NE(C) and HR-STEM HAADF of the d) TaW e) TaW(C) f) NE(C). The column boundaries are marked with black lines (adapted from paper IV).

Fig. 27b depicts the diffractograms from the Ta/W-rich series. The carbon-free TaW rich film crystallizes in a simple bcc structure as well, exhibiting peaks at ~39° and ~84.5° corresponding to a unit cell \(a = 3.24\) Å. An addition of 8 at.\% carbon leads to a shift of the (110) peak to lower 2θ angles and an expansion of the unit cell to \(a = 3.28\) Å while retaining the bcc structure without the formation of additional phases. Finally, an increase in the carbon content to 38 at.\% results in a structural change from bcc to fcc (Fm-\textit{3}m NaCl) and the formation of a multicomponent carbide film with a preferred <111> orientation. A detailed description of the structural properties of these multi-component carbides will be discussed below.

STEM HAADF cross section micrographs of the TaW, TaW(C) and NE(C) films are presented in Fig. 28. Both the TaW and TaW(C) films exhibit a columnar and dense structure, while the amorphous NE(C) film exhibit a feature-free smooth structure. The columns extend all the way from the substrate to the film surface in the TaW and TaW(C) films. The width of the columns in the metallic TaW film can be estimated to around 25 nm (Fig. 28d). The addition of carbon to the TaW(C) film on the other hand leads to a column re-
finement yielding an average value of about 5 nm (Fig. 28e). The grain boundaries of both films exhibit a coherent relationship. The HR-STEM image of the amorphous NE(C) cross-section shows no crystalline phases as well.

In summary, the results above clearly demonstrate that CrNbTaTiW HEAs with a bcc structure can be deposited by magnetron sputtering in a wide compositional range. This is not unexpected since Cr, Nb, Ta and W all crystallize in the bcc structure (W-type Im-3m). However, Cr can form Laves phases MCr$_2$ (M= Nb, Ta and Ti). No such phases were observed by XRD and we therefore propose that the alloy can be described as a HEA stabilized by a high entropy of mixing. The addition of 8 at.% C to the NE film results in an amorphous structure. One of the possible causes of amorphisation can be a large atomic size difference between the atoms since it is well known that alloys of three or more elements with a large variation in atomic radii (>12%) easily form metallic glasses [96]. In contrast, the TaW(C) film crystallizes in a bcc structure and an addition of 8 at% C leads to an increase in unit cell from 3.24 Å to 3.28 Å. This indicates that some C atoms are placed on interstitial sites or that atoms with a smaller radii are selectively pushed out of the multicomponent alloy grains. No segregation is observed by EDS (see details in paper IV), which suggest that the C is to a large extent dissolved in interstitial sites within the structure. Usually, the maximum solubility of C in bcc metals is low but the high C contents in the bcc TaW(C) film can be due to an increased solubility in a distorted lattice in the multicomponent alloy.

In paper V, we studied the carbide formation in more detail and the influence of the growth temperature on the film structure. The results from this paper are summarized in Table 1. The carbon content in the films were only 33-40 at.%, which is lower than in stoichiometric monocarbides (MC). The substoichiometric composition was selected to minimize the amount of non-carbidic carbon (free carbon), frequently formed in magnetron-sputtered thin films. As can be seen in Table 1, a series of multicomponent films were deposited from room temperature (RT) to 600 °C, close to equimolar concentrations with respect to the metals (NEC series), Ta/W rich-films (TaWC series) and a Nb-rich film (Nb300). The lattice distortion, δ, for the metal sublattice in the NEC-series was estimated to be about 5% using a 12-coordination radii in eq. (1) above, 3.3 % for the TaWC series and 3 % for the Nb300 film. It should be noted that these values are calculated based on the assumption that the distortion is only affected by the variation in the metal atom radii neglecting the effect of the carbon atoms in the octahedral sites.

HR-XPS analysis showed that all samples exhibit metal core levels that are shifted to higher binding energies compared to the metallic references, thus indicating the formation of a metal carbide. Also, the samples show broad C1s peaks at 282.6-283 eV, which mainly are composed of Me-C contribution and a small amount (4-9 %) of C-C contributions originating from free carbon presumably present in the grain boundaries between carbide grains.
Fig. 29 shows diffractograms from films in the NEC and TaWC series deposited at different temperatures with red triangles indicating a cubic phase with a B1 (NaCl) structures with cell parameters \(a = 4.34\ \text{Å}\). The near equimolar temperature series (Fig. 29a) exhibit strong peaks at \(\sim 36^\circ\) and \(\sim 77^\circ\) together with a \(\text{Al}_2\text{O}_3\) (006) peak from the substrate at 41.62°. The TaWC series (Fig. 29b) show an additional diffraction peak arising at \(\sim 41.5^\circ\) at higher growth temperature (450°C and 600°C). The samples deposited at room temperature (NECRT and TaWCRT, bottom in Fig. 29) show a distinctly broader and lower intensity diffraction peaks, indicating smaller grains and less crystalline material. Without any detailed investigation the XRD pattern could be attributed to a single solid solution carbide phase with a cubic NaCl or B1 \((Fm-3m)\) structure which is normally observed for transition metal carbides.

A more detailed study of the diffraction peaks showed that not all film XRD peaks can be assigned to a cubic \(Fm-3m\) (NaCl-type) structure. This is most clearly seen in the TaWC450 and TaWC600 diffractograms, where the (200) peak is asymmetrical and shifted to lower 2θ angles. Therefore, alternative fittings were tested with FullProf [97] using the Rietveld method [98]. The refinements showed that the NEC series crystallized in the cubic NaCl-structure type (space group \(Fm-3m\), \(a = 4.320(2)\ \text{Å}\)), while the Ta/W rich films deposited at higher temperatures (450°C and 600°C) exhibited a more complex crystal structure. The best fit suggested a tetragonal distortion of the NaCl structure, with \(c = 3.029(1)\ \text{Å}\) and \(a = 4.392(1)\ \text{Å}\), and the space group \(I4/mmm\). This distortion is similar to the initial stage of Bain distortion observed during martensite formation in austenite (Fe-C system). This distortion is illustrated in Fig. S4 in the supplementary information of paper V. A similar distortion has also recently been observed during hydrogen absorption in HfNbTiVZr [99].
In the following, the tetragonal distortion is neglected and it is assumed that all films have a cubic NaCl (B1) structure. Table 1 shows that cell parameters of the films vary from 4.32-4.42 Å depending on their composition. The cell parameters can be directly related to the average atomic radii of the metal atoms in the carbide structure (see Fig. SI 3 in supplementary information of paper V) in a linear fashion.

The diffraction peaks in Fig. 29 from the NEC series show a strong (111) texture, while the Ta/W rich series exhibits a shift from (111) to (200) texture at 450 °C. Furthermore, the peaks in the TaWC450 and TaWC600 diffractograms are broad suggesting either smaller grain sizes or stress. The texture was further investigated by pole figure measurements (for detailed description of results see paper V), which likewise give the in-plane orientation of the films towards the substrate. These results confirmed the XRD results and indicated that the degree of in-plane orientation is highest for the NEC600 film. The in-plane relationship between the substrate and the carbide was found to be MC (111)[-12-1] // Al2O3 (001)[110]. The lattice mismatch between the sapphire substrate and the films is about 11% along the Al2O3[110] direction, which is significant, but other studies also report similar values for carbide films deposited on sapphire substrates [100].

SEM top view images of films grown at 300°C and 600°C are presented in Fig. 30. The NEC300 and Nb300 films exhibited a less dense and triangular surface morphology with grains ranging from 50-100 nm in size. The Ta/W rich films, in contrast, exhibit a closely packed dense structure with just some triangular features (with a size of around 100nm). An increase of deposition temperature results in a more dense surface structure with just some triangular shapes visible on the near equimolar sample (NEC600) and a very smooth surface morphology (feature free) for the Ta/W rich sample (TAWC600).

Fig. 31 shows the STEM bright field cross section FIB lamella micrographs of films deposited at 300 °C and 600 °C. The top regions of the FIB lamellas are thinner as a result of imperfect FIB sample preparation resulting in a contrast variation and should be hence regarded as preparation artefacts. The films deposited at 300°C exhibited not fully dense but columnar structures extending from the substrate to the film surface. Both NEC300 and TaWC300 samples exhibit a narrow columns at the substrate (~ 5 to 10 nm) but expands to about 30 - 50 nm at around 100 nm distance from the substrate and stays roughly the same to the top. The inset SAED patterns show both the film and the substrate reflections in Fig. 31 and indicates a defined diffraction pattern, confirming the epitaxial crystal relation towards the substrate. The reflections of the substrate are sharp whereas the reflections from the film are less defined and broader, indicating that the columns turn and twist as they grow. The microstructures of the films deposited at 600° C and at 300° C differ significantly. The NEC600 films are denser with a columnar structure in the first 230 nm (with a column width of ~ 20 nm), while the TaWC600 films exhibit
only intergrown polycrystalline-like columns. After 230 nm of NEC600 film, the microstructure shifts to polycrystalline like columns. At a first glance, the depicted SAED patterns for the NEC600 and TaWC600 films indicate a polycrystalline structure, but a closer look shows defined diffraction patterns following the substrate orientation from substrate to the film surface.

**Fig. 30 SEM top view images of near equimolar, Ta/W rich and Nb rich samples grown at 300°C and 600°C (adapted from paper V).**

STEM EDX maps of the NEC300 film and the corresponding line scan are presented in Fig. 32. If we examine the Cr map we observe that Cr has segregated to the grain boundaries of the columnar grains. The Cr content at the column grain boundary is ~ 20 at. %, while a content of ~ 10 at.% is observed within the grains. The elemental distribution of the other metals (Ta, Nb, Ti and W) show a decrease of 1 - 2 at. % of the metal content (as can be also observed in the line scan in Fig. 32). The C seems to be evenly distributed and no significant segregation can be observed although it should be pointed out that the quantification of light elements like C is known to be less accurate.
with EDX. Cr enrichment was also observed at the grain boundaries of the NEC600 film (not shown), but to a lower degree while a TaWC series exhibited too low content of Cr for the similar segregation result to be visible. The segregation of Cr to the column boundaries can be explained by several factors: Cr tends to form carbides with low amounts of C (e.g. Cr$_{23}$C$_6$) and it could be energetically beneficial for the forming crystal to push Cr into grain boundaries (thus lowering the total energy).

The CrNbTaTiW films without carbon as well as the carbon containing films in paper IV and V were also characterized with respect to their mechanical properties and their corrosion resistance were likewise evaluated using electrochemical studies in a 1.0 M HCl.

Fig. 31 STEM bright field cross section overview of near equimolar and Ta/W rich samples grown at 300°C and 600°C (adapted from paper V).
Table 1 summarises the mechanical properties like hardness and reduced elastic modulus of the films. The hardness and elastic modulus were measured with a nanoindentation set-up. The film thickness was ~ 600 nm and to minimise the influence from the substrate or surface additional sinus mode hardness measurements on the selected samples were performed. A comparison of the samples deposited at 300 °C shows that the NE film has a hardness of 13.3 ± 0.3 GPa and a reduced elastic modulus of 185 ± 3 GPa. An addition of carbon content to 8 at.% results in an increase of hardness to 14.9 ± 0.4 GPa and a reduced elastic modulus of 210 ± 5 GPa. There was no significant increase

Fig. 32 STEM-ADF and EDX maps of the same area for the near equimolar sample grown at 300°C. The sample growth direction is upward in the images. Line-scan presented top right is the result of an integration of the presented EDX maps (adapted from paper V).
in the hardness or reduced modulus observed for the multicomponent carbide (NEC300). The hardness and the reduced elastic modulus of the TaW films are 14.7 ± 0.3 GPa and 321 ± 5 GPa, respectively. The TaW(C) sample exhibits a hardness of 19.1 ± 0.3 GPa and a reduced elastic modulus of 322 ± 3 GPa. A further increase of hardness to 26.8 ± 2.2 GPa and reduced elastic modulus to 390 ± 34 GPa is obtained for the TaWC300 film.

The influence of temperature on the mechanical properties was only investigated for the multicomponent carbide films in paper V. The highest hardness of 36GPa was observed for the TaWC600 sample. The hardness decreases with deposition temperature for both the NEC and the TaWC series. In the NEC series, the hardness decreases from 26.5 GPa for NEC600 to 17 GPa for the NEC300 film. The TaWCRT film exhibited a hardness of 20.2 GPa. The elastic moduli of the film follow the same trend as the hardness with the Nb300 films as an exception. As can be seen in Table 1 the H/E ratios vary from 0.02 to 0.08, thus indicating that the multicomponent carbides exhibit limited ductility [60,93].

An interesting question yet not discussed is how the mechanical properties of a HEA alloy or a multicomponent carbide is affected by the large number of elements in these materials. Very hard films of binary bcc alloys as well as hard and ductile bcc metals with <10 at% C have been described in the literature. For example, a hardness of 14.3 GPa was reported by Wang et al. for TaW thin films and explained based on nanocrystalline microstructure [101]. We can also not see a clear correlation between the lattice distortion and the hardness in our studies. This suggest that the mechanical properties of the films in papers IV and V are strongly affected by also other factors such as the microstructure (film density, grain size, texture, precipitates) and stresses. The high hardness of the TaW and NE films is most likely a result of the highly dense packed nanosized columns where the movement of dislocations are hindered by the column boundaries. The increased hardness seen in the TaW(C) film is most likely a result of grain refinement, that is a higher grain boundary density probably combined with an interstitial carbon solid solution hardening in the bcc structure. The hardness of the XRD amorphous film (NE(C)) is around 1 GPa higher than for the NE film, indicating that high hardness can stem not only from the grain size, but also from the chemical bonding in a non-crystalline structure. Although the NE(C) film is amorphous according to XRD and TEM, minor nano crystalline precipitates may have formed causing a hardening effect. Future studies, e.g. involving SAXS and APT are needed to completely rule out the formation of such precipitates.
The toughness of the films was investigated with nanoindentation experiments, where a Berkovich tip is pressed into the sample to a depth of ~85 % of the film thickness. The NEC (Fig. 33e) and the TaWC (Fig. 33f) films exhibit severe cracking at the corners of the indent. This is expected since they are ceramic carbides with limited ductility. The metallic NE and TaW films exhibited no cracks but a significant pile-up around the indents (Fig. 33a-b). Such pile-ups are typical for plastic deformation in rather ductile metals and alloys [102]. The amorphous NE(C) films also exhibited pile-ups with a clear shear band deformation typically observed in metallic glasses [103]. In comparison with the amorphous Mo-Fe-B films in Fig. 26, the NE(C) film exhibited a more ductile behaviour. The most interesting result can be seen for the TaW(C) film in Fig. 33d. Here, no cracks or pile-ups can be observed. The film is highly ductile and yet exhibit a relative high hardness (20 GPa). Previous results showed similar results when alloying group 6 metals with p-block elements and this was explained based on the non-columnar microstructure yielding a toughening effect [104,105]. However, we observe toughness in highly columnar coatings as well.

![Fig. 33 SEM images of the indents on a) NE b) TaW c) NE(C) d) TaW(C) e) NEC f) TaWC.](image)

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It is well-known that HEAs have promising corrosion properties [26]. Since transition metal carbides also are known to exhibit excellent corrosion resistance [8–11], it is reasonable to assume that carbon-containing HEAs and multicomponent carbides also may exhibit excellent corrosion resistance. In papers IV and V, the corrosion resistance of our films were investigated in a 1M HCl solution and compared with a very corrosion-resistant steel reference sample (SAF 3207 HD). The corrosion potential ($E_{\text{corr}}$) was seen to vary greatly depending on the chemical composition of the films. The metallic NE and TaW films showed corrosion potentials of 0 V and 0.72 V, while the NE(C) and TaW(C) films displayed more similar corrosion potentials (between 0.45 and 0.59 V, respectively). A more detailed description of the corrosion resistance related properties of these films can be found in paper IV.

Potentiodynamic polarization curves obtained for the multicomponent carbide films and a stainless steel reference material (i.e. SAF 3207 HD) are shown in Fig. 34. The corrosion potentials for the Nb rich, equimolar and the Ta/W rich samples were 0.69 V, 0.83 V and 0.96 V, respectively, whereas the corresponding corrosion potential for the reference hyper-duplex stainless was

![Fig. 34 Corrosion behaviour of carbide films in 1 M HCl. a) Potentiodynamic polarisation curves for near equimolar, Ta/W rich and Nb rich films as well as a hyper-duplex stainless steel (SAF 3207 HD). The surface morphology of the TaWC300 film b) before and c) after the corrosion measurements shows that the film surface is more or less unaffected (adapted from paper V).](image)
0.34 V. The corrosion potentials of the carbide thin film samples were thus significantly more positive than that for the hyper-duplex reference sample. Furthermore, the current densities for our films were at least 10 times lower than that for the stainless steel reference sample. Investigations of the surface morphologies of the samples after the corrosion measurements with SEM revealed no pitting behaviour for any of the carbide films. A thin surface oxide layer was observed on the Nb rich and near equimolar samples (not shown). The morphology of the W/Ta-rich film was, however, completely unaffected by the corrosion experiment as can be seen in Fig. 34. In short all films show a very similar transpassive behaviour (higher than ~1 V). This indicates that the same dissolution behaviour occur in all multicomponent films as well as in the steel reference samples. Cr is the only metal present in all samples including the reference and XPS analysis of the surface oxides (see paper IV) also confirm a loss of Cr from the corroded samples. This suggest that a further improvement of the corrosion properties can be obtained by removing Cr from the films possibly exchanging to a metal with a more inert surface oxide.

![Fig. 35 EDX maps of the NEC, NE(C) and NE sample surfaces after corrosion.](image)

Consequently, the results in papers IV and V show that our multicomponent films have an excellent corrosion resistance limited by the presence of Cr but still superior to highly corrosion resistant steels. The general trend in corrosion resistance is illustrated with the SEM EDS maps in Fig. 35. After the tough corrosion test (1.5V in 1 M HCl) the NE film shows a signs of a significant pitting (the black areas shows the exposed Al₂O₃ substrate). The pitting is strongly reduced with only 8 at% C in the NE(C) film. In contrast, no pitting is observed for the NEC film.
Mo-B coatings with a B/Mo ratio of ~1.6 have been deposited with magnetron sputtering using a MoB$_{1.5}$ compound target for the first time. The films have a dense, columnar structure and mainly consist of ~10 nm large hP3-MoB$_{2x}$ (x>0.4) grains. XPS, TEM and EELS show that the metal boride grains are surrounded by a boron-rich tissue phase. The Mo-B films have relatively high hardness of 29 ± 2 GPa, an elastic modulus of 526 ± 26 GPa and exhibit low tensile stress of (0.09 ± 0.01) GPa. The hardness is higher compared to bulk crystals and suggests a hardening effect caused by the nanocomposite coating structure. In a tribocontact, a thin tribolayer with surface-enriched MoO$_3$ is formed. The friction coefficient of the Mo-B films at room temperature was high ~1.1.

Upon addition of carbon, the crystallite size decreases and the films are mainly amorphous for a carbon content exceeding 23 at.%. The added carbon forms an a-BC$_x$ tissue phase surrounding the boride phase. The compositions of the a-B and a-BC$_x$ tissue phases could not be quantified and they may both contain Mo. The XRD results suggest that some carbon is dissolved in the boride structure. The formation of an amorphous boride phase at high carbon contents is also observed in the Cr-B-C system and may be typical for group 6 transition metals.

The hardness and elastic modulus decrease with increased carbon content correlating with the amount of a-BC$_x$ tissue phase in the films. This suggests that the mechanical properties are strongly affected by the amount of tissue phase. The H/E ratio increases upon addition of carbon, and, thus, indicates a slightly more ductile behaviour. Addition of carbon resulted in lower friction coefficient of ~0.8 for carbon contents above about 23 at.%. Raman studies of the wear tracks revealed that this was correlated to the presence of stronger carbon D and G bands typical of amorphous carbon based phases. Resistivity measurement revealed moderate resistivity spanning from 175 ± 40 μΩcm for binary films to 499 ± 16 μΩcm for HT Mo-B-C films with 31 at.%. The increase in resistivity could also be directly correlated to the amount of BC$_x$ tissue phase.

Introduction of Fe into the MoB$_2$ binary system results in a crystallinity decrease and amorphisation of the structure. With an increase of the growth temperature from 300 °C to 600 °C the observable amorphous structure becomes more defined, indicating less distribution of local order areas. The hardness decreases monotonically with increasing carbon content to 18.7 ± 2 GPa.
for Mo-Fe-B with 37 at. % of Fe. The Young’s modulus exhibits an analogous decrease to 353 ±24 GPa for the Mo-Fe-B film with 37 at. % of Fe. The stresses are relatively low (less than 0.2 GPa) in the films and are compressive. Addition of iron lowers the friction coefficient to 0.85 ± 0.2. Consequently, Fe is not inducing a significant friction reduction. After the tribology test, the wear track is all cracked and full of Mo- and Fe- oxides, which is confirmed by EDS and Raman measurements. XPS shows that there is no or very little amount of boron left, suggesting that the tribocontact is formed from boron and iron oxides.

A general observation in papers I-III was the difficulties to deposit phases with a complex crystal structure. In the Mo-B system, the metastable hP3 phase was formed instead of the thermodynamically but more complex hR18 phase. Furthermore, it was not possible to deposit any ternary phases in the Mo-B-C or Mo-Fe-B systems. This was due to temperature restrictions on the heater stage in the sputter chamber during the growth. For future work, an improved heater, designed for higher temperatures (>900 °C) is probably required to solve this problem.

In summary, the results show that is very difficult to deposit ternary Mo-B and Mo-B-X phases with interesting predicted properties such as high hardness combined with high ductility. All films exhibited high friction coefficients, which can be attributed to the formation of non-lubricating molybdenum oxides and the absence of boric acid formation. Thus, the Mo-B, Mo-B-C and Mo-Fe-B films deposited in this study are not suitable for application in e.g. sliding electrical contacts.

In papers IV and V, HEAs and multicomponent transition metal carbides with Cr, Nb, Ta, Ti, W were successfully deposited by magnetron sputtering. XRD shows that a cubic and in some cases distorted cubic structure is formed in a wide composition range. EDX analysis of the multicomponent carbides shows a significant Cr segregation from the bulk of the grains to the column boundaries. The XRD and TEM results suggest an epitaxial or highly textured (110) for the HEAs and (111) for the multicomponent carbides growth on the Al2O3 (001) surface. At 300 °C, the films exhibited a typical columnar microstructure, where each column consists of a single grain extending from the substrate to the film surface. At 600 °C, however, the films are denser with an extensive twinning. The NE(C) sample was X-ray amorphous, which was explained by the large difference of the atomic radii in a multicomponent system.

The hardness values of the HEAs are very high, but is increased even further upon the addition of small amounts of C. The hardness of multicomponent carbides varies from about 12 GPa to 35 GPa. No correlation was observed between the hardness and lattice distortion. The results suggest that variations in the microstructure was the most important factor controlling the film hardness. The results also showed that Ta/W-rich films with 8 at% combined very high hardness with a high ductility.
Finally, the corrosion behaviour of the HEAs and multicomponent carbides were analysed in 1.0 M HCl and compared with that of a hyper-duplex stainless steel reference material. In comparison with the reference material, all films showed higher corrosion potentials and lower oxidation current densities. The highest corrosion potential (i.e. 0.96 V) was observed for the Ta/W rich film, which also exhibited the lowest oxidation current density. The excellent corrosion properties can probably be improved further by removing Cr from the film. The results suggest that carbon-containing HEAs and multicomponent carbide films may have a potential use as corrosion resistant coatings. A very promising continuation of these thesis studies should therefore be to design a multifunctional coating based on a carbon-containing HEA (or carbide) combining extremely high hardness, high wear rate and toughness and a superior corrosion resistance.

I detta doktorsarbete har tunna filmer framställda med s.k. magnetronsputtering studerats i fyra system. De tre första (Mo-B, Mo-B-C, Mo-Fe-B) baseras på Mo som övergångsmetall. Ett mål i dessa studier har varit att syntetisera och karakterisera filmer med olika sammansättningar men också att försöka deponera ternära föreningar som med materialmodellering har förutspått uppvisa unika kombinationer av hårdhet och duktilitet. Det fjärde systemet baseras på en s.k. högentropilegering (TiCrNbTaW) där inverkan av tillsatt kol har studerats i detalj. Högentropimaterial utgör en ny grupp av föreningar som stabiliseras av en hög blandningsentropi. De har många intressanta egenskaper och har bara i liten utsträckning studerats som tunnfilmsmaterial. I alla studier har icke-reaktiv DC magnetron sputtering med olika katoder använts.

De binära Mo-B filmerna uppvisade en nanokompositstruktur med ~16 nm stora MoB₂₋ₓ (x> 0.4) korn omgivna av en bor-rik bindefas. Bildningen av en metastabil och understökiometrisk hP3-MoB₂ struktur (AlB₂-typ) förklaras med de kinetiska begränsningar som finns för att bilda den termodynamiskt stabila hR18-MoB₂ fasen som har en mycket komplex kristallstruktur. Detta beror på att bildning av en fas med så stor enhetsscell kräver en högre diffusionshastighet för ytatomerna än den som finns tillgänglig vid 300-600 °C. När kol tillsätts förändras fasinnehållet och mikrostrukturen. Filmer med mindre än 23 at.% kol består fortfarande av nanokristallina MoB₂₋ₓ korn, nu omgivna av en amorf vävnads fas av a-BCₓ. Med ökande kolhalt (över 23 at%) och minskade kornstorlek från 16 till 5 nm var filmerna helt röntgenamorfa. Transmissionselektronmikroskopi (TEM) och röntgenspektroskopi visade att fil-

De binära Mo-B filmerna visade en relativt hög hårdhet av (29 ± 2) GPa, vilket är högre än för bulkprover. Den höga hårdheten kan förklaras av en härdande effekt som uppstår när den omgivande bindefasen förhindrar dislokationsrörelser i boridkristallerna. I Mo-B-C filmerna minskade hårdheten och elasticitetsmodulen med kolhalten från ~29 till ~22 GPa och ~526 till ~326 GPa. Dessa värden ger ett H/E-tal på 0,06 till 0,07, vilket tyder på en relativt spröt material. För Mo-Fe-B filmerna minskade hårdheten och elasticitetsmodulen med ökande Fe-innehåll från ~ 29 till ~ 19 GPa och ~ 526 till ~ 353 GPa.

En tribologisk studie av binära prover bekräftade en signifikant bildning av en tribofilm bestående av molybdenoxid och boroxid utan några smörjande effekter vid rumstemperatur. Mo-B och Mo-B-C filmer med låg kolhalt upvisade en friktionskoefficient på 1.1 mot stål, vilket minskade till 0.8 vid höga kolhalter. Analys av tribofilmen visade även för Mo-B-C filmerna en avsevärd bildning av molybdenoxid och amorft kol i nötningsspåren, dock utan signifikant smörjande effekt vid rumstemperatur. Närvaron av Fe i filmerna reducerade friktionskoefficienten mot en stältyta till 0,85. Även i detta fall berodde de höga friktionsvärdena på bildningen av Mo och Fe-oxider i nötningsspåren.

Sammanfattningsvis visar resultaten att varken Mo-B-C eller Mo-Fe-B filmar är lämpliga för tillämpningar där låg friktion krävs. Dock kan den relativt höga hårdheten göra dessa material intressanta för andra tillämpningar speciellt om de ternära föreningarna kan syntetiseras vid en högre deponeringstemperatur.

Högentropilegeringar och multikomponentkarbider med olika metallinnehåll (nära ekvimolära, Ta / W-rika och Nb-rika) deponerades i temperaturintervallet rumstemperatur till 600 °C. Högentropilegeringarna kristalliserade i enkel kubisk bcc struktur utan några ytterligare faser. Tillsats av 8 at.% kol resulterade i antingen amorfa filmer eller i kristallina filmer med bcc struktur. De flesta multikomponentkarbidfilmer kristalliserade i den kubiska B1-strukturen som vanligtvis observeras. Röntgendiffraktion (XRD) visade på en stark preferentiell oriertering i <110> riktningen för alla högentropilegeringar förutom den legeringen med 8 at% kol, som var röntgenamorf. XRD visar att de karbider som var nästan ekvimolära hade en stark <111> oriertering. Däremot uppges Ta/W-serien ett skift från <111> textur till <100> textur vid 450 °C.
Den epitaxiella relationen bestämdes till MC (111) [- 12-1] // Al2O3 (001) [110] med en mismatch på ca 11% längs Al2O3 [110] riktningen. Filmerna deponerade vid 300 °C upprysade en inte fullständigt tät kolumnär struktur som sträcker sig från substratet till filmytan, medan filmer deponerade vid 600 °C upprysar tvillingbildad polykristallin kolumnär struktur. En segregering av Cr som ledde till en anrikning i korngränserna hittades i alla karbidfilmer, det är dock oklart om det också förekommer i högentropilegeringarna.

Mikrostrukturen och bindningarna mellan kol och metall visade sig vara de viktigaste faktorerna för hög hårdhet hos tunna filmer av högentropilegeringar och multikomponentkarbider. De mindre täta Nb-rika och nära ekvimolära filmerna deponerade vid låg temperatur uppvisande den lägsta hårdheten (12 GPa), medan de mycket täta och tvillingbildade Ta/W-rika högtemperaturfilmerna visade sig vara hårdaste (36 GPa). Ingen korrelation hittades mellan gitterförvrängning och hårdhet.

Korrosionsstudier avslöjade att multikomponentfilmerna uppvisade utmärkt korrosionsbeständighet i en mycket sur miljö som överträffar det för ett referens hyperduplex rostfritt stål. Duktilitetstester utfördes på Mo-B, Mo-Fe-B, högentropilegeringar och multikomponentkarbider. Duktilitetstesterna visade att Mo-B och Mo-Fe-B var spröda och att högentropilegeringar av TiCrNbTaW med låga mängder kol (~ 8 at%) visade de bästa duktilitetsresultaten.
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References


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)

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