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# Thin Film Synthesis and Characterization of New MAX Phase Alloys

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### Abstract

The objective of this Thesis is synthesis and characterization of new MAX phase alloys (M = early transition metal, A = A-group element, and X = C or N) based on incorporation of M and X elements previously not used in any known MAX phases. This is motivated by a search for optimized and unique materials properties, such as different magnetic states.

Two synthesis routes have been used to attain  $Ti_2AlC_{1-x}O_x$ : deposition of  $Ti_2AlC_y$  under high vacuum conditions with residual gas acting as O source, and solid-state reactions following deposition of understoichiometric  $TiC_y$  on  $Al_2O_3$ . Detailed local quantification by analytical transmission electron microscopy (TEM) including electron energy loss spectroscopy (EELS) shows up to 13 at.% O within high quality MAX phase structure. According to previous theoretical work, the range of experimentally obtained O content is enough to observe drastic changes in the materials anisotropic electronic properties. Calculations on effect of substitutional O on shear deformation have also been performed.

In a recent theoretical study by Dahlqvist *et al.*,  $(Cr,Mn)_2AlC$  has been predicted as a new stable magnetic nanoscale laminate. Inspired by this work, thin films of  $(Cr,Mn)_2AlC$ , as well as of a neighboring system  $(Cr,Mn)_2GeC$ , have been synthesized by magnetron sputtering. Incorporation of 8 and 12.5 at.% of Mn, respectively, has been detected by analytical TEM including EELS and energy dispersive X-ray spectroscopy (EDX). The total saturation moment of  $0.36\mu_B$  per Mn atom at 50 K has been measured by vibrating sample magnetometry (VSM) for a  $(Cr,Mn)_2GeC$  sample, providing the first experimental evidence of a magnetic MAX phase.

The experimental results obtained in this Thesis provide a base for expanding the MAX phase definition and materials characteristics into new areas, towards further fundamental understanding and functionalization.

## Preface

This Licenciate Thesis is a part of my Ph.D. studies in the Thin Film Physics Group at the Department of Physics, Chemistry, and Biology (IFM) at Linköping University. The aim of my research is to synthesize and characterize MAX phases with novel properties. The work has been performed in cooperation with RWTH Aachen University (Germany), University of Iceland (Iceland), and Uppsala University. Financial support has been provided by the Swedish Research Council (VR).

### **Included papers**

#### Paper I

Oxygen incorporation in Ti<sub>2</sub>AlC thin films studied by electron energy loss spectroscopy and ab initio calculations **A. Mockute**, M. Dahlqvist, L. Hultman, P.O.Å. Persson, and J. Rosen Manuscript in final preparation

#### Paper II

Nanolaminated (Cr,Mn)<sub>2</sub>AlC alloys by magnetron sputtering and ab initio calculations A. Mockute, M. Dahlqvist, J. Emmerlich, L. Hultman, J.M. Schneider, P.O.Å. Persson, and J. Rosen Manuscript in final preparation

#### Paper III

Magnetic nanoscale laminates from first principles and thin film synthesis A.S. Ingason, **A. Mockute**, M. Dahlqvist, F. Magnus, S. Olafsson, U. Arnalds, B. Alling, I.A. Abrikosov, B. Hjorvarsson, P.O.Å. Persson, and J. Rosen Manuscript in final preparation

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### **1** Introduction

Materials science is an interdisciplinary field involving the study of properties of materials and how those are determined by composition and (micro-)structure. Rapid development of technology as well as urgent necessity to use natural resources more effectively constantly demand materials with better performance. For example, lighter and more heat-resistant material for jet engines would save millions of barrels of fuel per year – and would also have a staggering impact from the economics perspective. Materials science includes design of such new materials as well as modification of the already existing ones, in order to meet various combinations of the requirements.

Materials performance can often be improved by covering it with a suitable coating. The interaction with the environment occurs through the surface, and therefore a proper surface modification can lead to, e.g., reduced friction, less damage, appealing appearance, etc., while allowing easier manufacturing and cheaper price for the bulk material underneath. This makes *thin film* physics an important part of materials science.

The materials in focus of this Thesis belong to a family of  $M_{n+1}AX_n$  (n = 1-4) phases, where M denotes an early transition metal, A – an A-group element, and X – C or N. The first members in the MAX phase family were synthesized already in 1960's [1], but gained the research attention they deserve only in 1990's after the discovery of extremely high thermal shock and mechanical damage tolerance as well as a combination of metallic and ceramic properties of Ti<sub>3</sub>SiC<sub>2</sub> [2].

~60 MAX phases have been synthesized to date, most of them in polycrystalline bulk form. Research on MAX phase thin films began in 2002 with deposition of  $Ti_3SiC_2$  [3] which has accelerated the expansion of the field even further. Since then, a large part of the work on MAX phase thin films has been concentrated on identifying growth conditions for single crystalline material and subsequent characterization. During the past two decades the MAX phase field has advanced enormously and these exciting materials still have a lot left to offer. Currently, the research efforts are directed towards for example 2D structures, such as graphene-like exfoliated MAX phase sheets (MXenes) [5, 6] and MAX phase nanotubes [7], search for magnetic MAX phases [8-10], and understanding their optical [11] and anisotropic [12, 13] properties.

In this Thesis, the possibility to add novel properties to MAX phases, as well as to tune the already existing ones, has been investigated through alloying known phases with hitherto unexplored M- and X-elements.

## 2 MAX phases

The elements forming MAX phases are marked in the periodic table in Figure 2.1, where M elements are highlighted in red, A in blue, and X in black, corresponding to early transition metals, A-group elements, and carbon/nitrogen, respectively.



Figure 2.1. Periodic table illustrating elements forming all MAX phases known to date.

MAX phases acquire a hexagonal crystal structure (space group P6<sub>3</sub>/mmc), which can be described as  $M_6X$  edge sharing octahedra interleaved by layers of A element. The general composition can be written as  $M_{n+1}AX_n$ , where n is an integer number. Different stoichiometries ( $M_2AX$ ,  $M_3AX_2$ , etc.) are often referred to as 211, 312, etc. The corresponding unit cells together with the resulting nanolaminated structure are shown in Figure 2.2. The lattice becomes more complex with increasing n value, which reduces the thermodynamic stability of the MAX phase with respect to competing phases. This is well reflected by the range of reported MAX phases: more than 40 belong to the 211 subgroup, followed by six 312 and seven 413 phases, while (Ti<sub>0.5</sub>Nb<sub>0.5</sub>)<sub>5</sub>AlC<sub>4</sub> has been synthesized as the first 514 phase only very recently [14].



Figure 2.2. Unit cells of a) 211, b) 312, and c) 413 MAX phases [15] and a TEM image of  $Ti_2Al(C,O)$  illustrating the characteristic nanolaminated MAX phase structure .

The inherently layered crystal structure together with the presence of metallic (*M*-*A*) and covalent (*M*-*X*) bonds results in a unique combination of both metallic and ceramic properties. MAX phases are typically good thermal and electrical conductors (e.g., the electrical conductivity of  $Ti_3SiC_2$  is double that of pure Ti [16]), as well as thermodynamically stable at high temperatures, hard, wear- and oxidation resistant. In addition, MAX phases exhibit extreme thermal shock resistance, damage tolerance, and are easily machinable (e.g., can be cut with a manual hacksaw). The latter properties stem from the characteristic deformation mechanism via formation of kink bands, which effectively lock internal delaminations by dislocation walls (see Figure 2.3 a)), hindering the crack growth and subsequent failure on the macroscopic scale. The exceptional damage tolerance of MAX phases is illustrated in Figure 2.3 b): surface dents are the only effect of hitting a Ti<sub>2</sub>AlC block with a hammer.



Figure 2.3. a) Characteristic deformation of MAX phases. Note that delamination ends are stopped by kink bands which prevents further growth of the crack [17], b) dents on a  $Ti_2AIC$  block left after repeatedly hitting it with a steel hammer (courtesy of 3-ONE-2).

All these characteristics make MAX phases promising candidates for many industrial applications, e.g., as high temperature and/or corrosive environment components, sliding electrical contacts, contacts for 2D electronic circuits, wear protective and lubricant coatings, etc. In fact, the collaboration between scientific and industrial communities has been very close. MAX phase powders were commercialized already in 2001 (only five years after the first publication on remarkable Ti<sub>3</sub>SiC<sub>2</sub> properties) by 3-ONE-2/Kanthal AB under the brand names Maxthal211 (Ti<sub>2</sub>AlC) and Maxthal312 (Ti<sub>3</sub>SiC<sub>2</sub>). As Ti<sub>2</sub>AlC is extremely oxidation resistant, gas burner nozzles manufactured from Maxthal211 showed better performance compared to the steel ones (Figure 2.4 a)), and Maxthal211 heating elements were cycled between RT and 1350°C 10000 times with no resulting damage (Figure 2.4 b)). Close to the market are drills for dry milling in concrete, where Co in the usual diamond-Co drills has been replaced by Maxthal312 (Figure 2.4 c)). Another example is MAX phases tested as formers for fully dense and hollow objects (Figure 2.4 d)).



Figure 2.4. Potential applications of MAX phases: a) a gas burner nozzle manufactured from  $Ti_2AIC$  demonstrated longer lifetime compared to the usual steel ones, b)  $Ti_2AIC$  heater at 1723 K, c) diamond- $Ti_3SiC_2$  concrete dry drill experienced much less wear than the diamond-Co one, d) a glove former. (Courtesy of 3-ONE-2)

### 2.1 MAX phase alloys

MAX phases, constituting a family of materials composed of neighboring elements in the periodic table and with the same crystal structure, provide ideal possibilities for alloying on either site. Alloying on *M* and *A* sites has been extensively studied and a large number of MAX phases synthesized, e.g.,  $(Ti,V,Nb,Cr)_2AlC$  [18, 19] and  $Ti_3(Si,Al,Ge,Sn)C_2$  [20, 21]. Solid solutions on *X* site have also been investigated, e.g.,  $Ti_2Al(C,N)$  [22] and  $Ti_3Al(C,N)_2$  [20], but alloying possibilities are limited due to only two elements available.

The partial replacement of one element by another enables fine tuning of the properties, e.g., hardness or electrical resistance, by properly adjusting the percentage of the substituted atoms. For instance, Vickers hardness of Ti<sub>2</sub>AlC linearly increases from 3.5 to

4.5 GPa as 20% of Ti is substituted by V [23]. In some cases solid solutions may exhibit superior characteristics compared to the pure constituents, e.g., bulk Ti<sub>2</sub>AlC<sub>0.5</sub>N<sub>0.5</sub> has been observed to be much harder and stiffer than Ti<sub>2</sub>AlC or Ti<sub>2</sub>AlN [22]. Another interesting example is  $(V_{0.5}Cr_{0.5})_3AlC_2$  – neither V<sub>3</sub>AlC<sub>2</sub> nor Cr<sub>3</sub>AlC<sub>2</sub> exist separately [24]. This all demonstrate that solid solutions of MAX phases are well worth investigating. However, the substituting elements are generally chosen from those used in previously synthesized MAX phases. *M*, *A*, and *X* elements outside conventional compositions are likely to provide more pronounced changes in the properties, or even new characteristics. Promising candidates are those neighboring the already tested elements, due to similar atom size and electronic structure.

One such example is incorporation of O into the well known  $Ti_2AlC$ . An initial study showed experimental indications of O substituting C while still retaining the MAX phase structure [25], suggesting O as a potential X element besides C and N. Subsequent calculations indicated that O prefers the C site under oxygen-lean conditions and high temperature [26] and that up to at least 75% of C may be replaced by O [27]. Supporting experimental evidence on O taking the C positions in the lattice was provided by electron energy loss spectroscopy (EELS) combined with theoretical simulations [28]. Potential properties of this alloy are discussed below.

#### 2.2 Anisotropy

Large c/a lattice constant ratio (see unit cell axis in Figure 2.2) combined with different nature of bonds within and between atomic layers result in highly anisotropic MAX phase properties. Due to strong covalent *M-X* bonds, MAX phases are hard and stiff primarily along the c-axis [29-31], while metallic *M-A* bonds provide good electric and thermal conductivity in plane [12, 13, 29]. Most of the publications to date regarding anisotropic properties of MAX phases are based on theoretical calculations. To assess experimental data, materials properties obtained from bulk samples should be measured on single grains, which is experimentally challenging. For thin films, depending on the

property, one of the unit axis directions is generally difficult to access, e.g., hardness measurements along a-axis and conductivity measurements along c-axis.

The MAX phase oxycarbide  $Ti_2AlC_{1-x}O_x$  has been investigated in this Thesis. A previous theoretical study of the electronic structure of  $Ti_2AlC$  shows anisotropy, with indications of metallic behavior in plane and insulating behavior out of plane (in c-direction) [12]. However, the conductivity along the c-direction has been suggested to change as C is substituted by O, from insulating, via n-type, to p-type, for an O concentration up to 12.5 at.% [12]. Mechanical characteristics are affected as well, e.g., bulk modulus B increase from 140 to 161 GPa is calculated as O gradually replaces all C atoms [27]. Thus, the anisotropic properties of  $Ti_2AlC$  may be tuned by adjusting the amount of substitutional O. Therefore, the attainable O concentration range in  $Ti_2AlC_{1-x}O_x$  has been explored in Paper I.

#### 2.3 Magnetism

The magnetic state of a material is very sensitive to the local atomic environment, which in thin film systems may be possible to change in a controlled way. This results in phenomena not observed in the materials' bulk counterparts, such as interfacial stress induced magnetic anisotropy, stabilization of new phases, interlayer exchange coupling, tunnel magnetoresistance, and giant magnetoresistance. These discoveries have revolutionized applications of data storage and magnetic recording as well as created the new field of spintronics.

Magnetic MAX phases would be excellent candidates for layered magnetic materials with strain- and dislocation-free interfaces, as they all exhibit similar in-plane lattice constants. In search of magnetic MAX phases most attention has been directed towards the hypothetical *M*-element Fe, due to its well known ferromagnetic properties and the many ferromagnetic compounds that it forms. Luo *et al.* predicted Fe<sub>3</sub>AlC<sub>2</sub> to be stable and ferromagnetic with magnetic moment of  $0.73\mu_B$  per Fe atom ( $\mu_B$  – Bohr

magneton) [10]. However, a recent theoretical study by Dahlqvist *et al.* identifies a different set of most competing phases in the Fe-Al-C system, which results in positive formation enthalpy of Fe<sub>3</sub>AlC<sub>2</sub> ( $\Delta$ H = 0.25 eV/atom), and thus thermodynamic instability [9]. The same study suggests (Cr,Mn)<sub>2</sub>AlC as a stable and potentially magnetic MAX phase, with magnetic moment gradually increasing with Mn content. The material is expected to posses either ferromagnetic or antiferromagnetic properties, depending on the Cr and Mn atomic configuration on the *M* sublattice. The Curie temperature is roughly estimated to being close to or above room temperature [9]. Furthermore, (Cr,Mn)<sub>2</sub>GeC, being a similar system to (Cr,Mn)<sub>2</sub>AlC, has also been predicted stable, and with potentially similar magnetic properties [8].

In the work of this Thesis, both  $(Cr,Mn)_2AlC$  (Paper II) and  $(Cr,Mn)_2GeC$  (Paper III) thin films have been synthesized. Magnetic measurements have been performed on  $(Cr,Mn)_2GeC$  samples, showing evidence of the first magnetic MAX phase.

The possibility of tuning the magnetic state by simply increasing/decreasing the Mn content would enable growth of thin films with a gradient in magnetic moment, or growth of magnetic/non-magnetic multilayers. An advantage originating from the inherent nanolaminated MAX phase structure is the possibility to form atomic-thin magnetic layers, which would be extremely challenging to obtain artificially.

### 3 Thin film synthesis

Most vacuum based thin film synthesis techniques can be divided into two groups: chemical vapor deposition (CVD) and physical vapor deposition (PVD). PVD involves purely physical processes such as atoms/ions being released from a target with subsequent condensation on a substrate. CVD growth occurs through chemical reactions between volatile precursors on a surface, which often require high temperature and therefore limit the choice of substrate material.

Two PVD techniques have been used in this Thesis: pulsed cathodic arc and magnetron sputtering.

### 3.1 Cathodic arc

The principle behind cathodic arc is a discharge between a cathode (target) and an anode. A microexplosion creates a molten pool, called an arc spot, on the cathode surface, from which cathode material and electrons are emitted. The resulting plasma has a high degree of ionization (close to 100%), including presence of multiply charged ions with inherent high ion energies. A high ionization degree is advantageous through the availability of manipulating the plasma by electric or magnetic fields. This is beneficial in terms of process control, and allows deposition of stable as well as metastable phases.

In order to ignite and sustain a stable arc discharge, the cathode material must be conductive. There have been attempts to overcome the difficulties posed by poorly conducting cathodes, e.g., Si and B, by heavy doping [32] and cathode pre-heating before ignition [33], however, their use still remain challenging and limited.

An arc discharge is a violent process (can be imagined as thousands of volcano eruptions on the micro-scale), in which not only atoms/ions/electrons are emitted, but also cathode material in the form of microdroplets. These adhere to the growing film, resulting in lower crystal quality, non-uniform composition, and a rough surface. To suppress droplet formation and hinder their arrival to the growth zone, reduction (steered arc, pulsed arc) or removal (shaded arc, filtered arc) techniques are used, respectively. A combination of these techniques is also common.

Cathodic arc may be used in two different modes: continuous direct current (DC) and pulsed arc. DC arc is widely employed for industrial applications due to the high growth rates and the possibility to build large-scale deposition systems. Pulsed arc is more beneficial for scientific purposes including high control of composition, as less than a monolayer of the cathode material can be released in each pulse (e.g., growth rate of Al is ~0.3 Å/pulse). This allows fine adjustment of the plasma composition, and, in turn, precise control of the growing film stoichiometry.

A triple cathode high current pulsed cathodic arc has been used to grow the  $Ti_2Al(C,O)$  thin films investigated in this Thesis. A schematic of the system as well as an image of the cathodic arc deposition chamber at Linköping University is presented in Figure 3.1.



Figure 3.1. a) Schematics of a pulsed arc system used in this work, b) a pulsed cathodic arc deposition system at Linköping University.

Center triggering was used to ignite the arc [34], and the pulse length adjusted for each cathode individually to ensure effective use of the cathode as the arc spots moved from the center all the way to the edges. Figure 3.2 shows a new and a used Ni cathode.



Figure 3.2. Ni cathodes: a) new and b) used. Note severe surface erosion caused by preferred arc spot tracks.

A curved magnetic filter was employed to remove microdroplets from the plasma plume. The magnetic field guides the electrons towards the substrate, and the ions follow the electrons due to Coulomb attraction and the constraint of a quasineutral plasma. Neutral microdroplets, on the other hand, continue their straight path towards the chamber walls.

#### 3.2 Magnetron sputtering

Magnetron sputtering, compared to pulsed arc, is a gentle deposition technique. In pulsed arc, material from the cathode is released through a violent process leaving the cathode surface highly eroded, while in magnetron sputtering the atoms are relatively gently ejected from the target material under the bombardment of inert gas ions, most often Ar.

A schematic of a typical magnetron sputtering deposition system is presented in Figure 3.3. Ar gas is let into the chamber and Ar atoms are ionized under collisions with other Ar atoms or secondary electrons. A negative bias is applied to the target to accelerate  $Ar^+$  ions towards it, and as Ar ions hit the target, atoms are knocked out

(sputtered). Atoms ejected from the target are transported in the vacuum chamber and condense on the substrate to form a film.

To initiate and sustain a sputtering process, a relatively high Ar partial pressure is needed. This is unfavorable, as target atoms are scattered under their way torwards the growth zone and thus the deposition rate is reduced. Furthermore, processes at the substrate surface, e.g., adatom mobility, may change, resulting in lower crystal quality of the film. The Ar pressure can be reduced by increasing the Ar ion concentration in the vicinity of the target surface, realized by placing magnets underneath the target: Secondary electrons are then trapped by the magnetic field lines and the ionization probability of Ar atoms close to the target is thus increased. A higher concentration of Ar ions at the target area leads to higher sputtering rate, which in turn leads to an increased growth rate of the film.



Figure 3.3. Schematics of a magnetron sputtering system.

In this Thesis three magnetron sputtering systems have been used:

- 4 target magnetron sputtering system in the Materials Chemistry Group at RWTH Aachen University (Germany), for deposition of (Cr,Mn)<sub>2</sub>AlC films (Figure 3.4).
- 3 target magnetron sputtering system in the Thin Film Physics Group at Linköping University and 5 target magnetron sputtering system in the Thin Film

and Nanophysics Group at University of Iceland (Iceland), for deposition of (Cr,Mn)<sub>2</sub>GeC films.



Figure 3.4. Example of magnetron sputtering system used to deposit  $(Cr,Mn)_2AIC$  (courtesy of T. Takahashi). Short (10 cm) sample-target distance allows combinatorial investigations.

### 3.3 Plasma-surface interaction

As plasma reaches the substrate, atoms adsorb on the surface forming two or three dimentional islands, which grow and eventually coalesce to form a continuous film. Depending on the interaction between film/film and film/substrate atoms, the growth can be classified into three characteristic modes, see Figure 3.5: layer-by-layer (also called Frank van der Merve) growth, island (or Volmer-Weber) growth, and Stranski-Krastanov (layer-by-layer followed by island) growth.



Figure 3.5. Thin film growth modes: a) layer-by-layer (or Frank van der Merve), b) island (or Volmer-Weber), and c) Stranski-Krastanov.

Incoming species tend to minimize the total interfacial energy by arranging themselves in a crystallographic relation with the substrate. Such extended growth on a crystalline substrate is called epitaxial growth. Epitaxial growth is often intentionally supported by a proper choice of substrate, e.g.,  $Al_2O_3(0001)$  and MgO(111) are the most common substrates for the growth of (0001)-oriented MAX phase thin films. The epitaxial relation may be further improved by depositing a so called seed layer directly onto the substrate, prior to growing a film.

It should be noted, that the composition of the plasma and the composition of the resulting film is often non-equivalent. Different species have different sticking coefficients, which also may vary depending on the choice of substrate, growth temperature, etc. Light atoms can be resputtered from the film surface by the heavier ones. It has been noted, e.g., that the number of Al pulses in arc growth of Ti<sub>2</sub>AlC must be set somewhat higher than the calibration-based value [35], which is most likely the result of a lower Al sticking coefficient at higher temperatures combined with resputtering caused by Ti. Furthermore, if a compound target is used, the composition of the film is not necessary the same as that of the target, due to different energy and angular distributions of the sputtered elements. For example, magnetron sputtering from a single Ti<sub>3</sub>SiC<sub>2</sub> target resulted in highly off-stoichiometric films with  $\geq 50$  at.% C [4].

Besides the plasma composition, sticking coefficient and effects from resputtering, the surface atom mobility strongly influences what phases nucleate on the substrate. Sufficient diffusion lengths allow atoms to acquire positions of lowest energies and to form large grains of the most energetically favorable phases. The surface mobility is most

often enhanced by heating the substrate. Relatively high temperatures (450-1000°C) are required for growth of MAX phase thin films. At lower temperatures the diffusion length is shorter which results in numerous small grains and a nanocrystalline film structure, as well as considerable amount of competing phases. Amorphous films form closer to room temperature, as the atoms tend to stick to the surface in the positions where they arrive. However, if the samples are subsequently annealed, atoms may gain enough energy to rearrange into more complex structures, and amorphous/nanocrystalline films may transform into single crystal films.

It is clear, that thin film synthesis is a complex process, depending on a large number of factors. These must be finely controlled and adjusted to yield thin films of high crystal quality.

### 4 MAX phase synthesis

Bulk synthesis techniques, such as hot isostatic pressing, have been the primary methods for synthesizing MAX phase materials. However, the bulk samples are polycrystalline and often contain lots of defects, such as inclusions of other phases, unreacted starting components, impurity atoms, grain boundaries, etc. These all affect any measured values of materials' properties. For example, hardness reported for bulk and thin film samples differ drastically, e.g., 5 GPa [36] and 24 GPa [37], respectively, for  $Ti_3SiC_2$ . Therefore, material's *intrinsic* properties can only be determined by investigating thin films, which are much closer to the idealized defect-free crystal than corresponding bulk samples.

The first MAX phase thin films were grown by CVD [30], however, using the PVD approach has demonstrated superficial results in terms of process control and resulting crystal quality. Magnetron sputtering has so far been the most widely used technique for MAX phase depositions, employing both elemental [3, 37, 38] and compound targets [3, 39], also including reactive growth [40]. There have also been attempts to use pulsed laser deposition [41] and high power impulse magnetron sputtering (HiPIMS) [42]. Although the applicability of these techniques for MAX phase growth remains to be shown, both methods demonstrate promising characteristics such as production of highly energetic species, which could be beneficial for lower deposition temperatures. Hence, these methods should be investigated further.

A relatively new, compared to magnetron sputtering, method to synthesize MAX phase thin films is cathodic arc. Successful growth of high quality  $Ti_2AIC$  films has been demonstrated by pulsed arc [43, 44] and  $Ti_2AIN$  films by DC arc [45].

Solid-state reactions either at film/substrate or film/film interfaces can be employed for thin film synthesis. The latter method resulted in the lowest reported formation temperature of  $Ti_2AIN$  of 450°C, as Ti/AIN multilayers transformed to pure  $Ti_2AIN$  films [46]. The most well-known example of film/substrate reaction is  $Ti_3SiC_2$  formation at

Ti/SiC interface by annealing Ti-based electrodes in SiC-based semiconductor devices [47]. Furthermore, understoichiometric  $TiC_x$  deposited onto  $Al_2O_3$  substrates at 900°C has been reported to transform into  $Ti_2Al(C,O)$  throughout a 150 nm thick films as a result of substrate decomposition followed by Al and O diffusion into  $TiC_x$  [48].

### 5 Thin film characterization

In order to find optimal experimental conditions for a specific purpose, feedback on the sample elemental composition, phases present, crystal orientation, crystal quality, physical properties, etc. is needed. In this work, the following thin film characterization techniques have been used.

#### 5.1 X-ray diffraction

X-ray diffraction (XRD) is a simple and non-destructive analysis technique which provides means to identify different phases and their distribution in the sample, texture, evaluate average grain size, internal stress, etc.

X-rays are electromagnetic waves with wavelength (0.5-50 Å) comparable to atomic separation distances. When propagating through a crystal, the X-rays interact with the lattice and are diffracted according to the Bragg's law

 $2d\sin\theta = n\lambda$ 

where d is the atomic spacing,  $\theta$  is the scattering angle, n is an integer number, and  $\lambda$  is the wavelength.



Figure 5.1. Schematic illustration of an XRD  $\theta/2\theta$  measurement.

As the combination of constituent atoms, crystal structure, and lattice constants is different for different materials/phases, XRD results in a unique set of diffraction angles and diffracted beam intensities, which make phase identification possible. Measurements in  $\theta/2\theta$  configuration (detection angle twice as large as incidence angle, see Figure 5.1) are most common. Only lattice planes oriented parallel to the surface are probed; in case of epitaxial MAX phase films, these correspond to the so called basal planes, i.e., atomic layers of M-X-M-A (for 211 phases). An XRD scan of (Cr,Mn)<sub>2</sub>AlC MAX phase with marked peaks originating from the basal planes, is presented in Figure 5.2.



Figure 5.2. XRD scan of  $(Cr,Mn)_2AIC$  MAX phase deposited on  $Al_2O_3(0001)$  substrate. Peaks originating from the basal planes of 211 MAX phase are marked with filled circles.

### 5.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is an invaluable analysis technique for materials investigation on the nanoscale.

The working principle of TEM is very similar to a conventional optical microscope, with electrons used instead of visible light. The wavelength of highly energetic electrons (e.g., an acceleration voltage of 200 kV results in  $\lambda = 2.5$  pm) is considerably shorter than the wavelength of visible light (400-750 nm). This leads to a much higher point resolution (down to 2 Å), enabling investigation of sample features on the atomic level.

Conditions for direct lattice observation are called high-resolution (HR) TEM imaging. Figure 5.3 represents a HR image of a (Cr,Mn)<sub>2</sub>AlC MAX phase.



Figure 5.3. HR-TEM image of a (Cr,Mn)<sub>2</sub>AlC MAX phase.

A pattern of diffracted electrons can also be analyzed. An electron diffraction (ED) image provides crystallographic information, such as crystal structure, presence of preferred orientations, and defects.

Electron beam interaction with a sample in a TEM is far from trivial. Besides transmission, electrons experience absorption, diffraction, and scattering. Furthermore, Auger and secondary electrons are emitted, and X-rays are generated. Analysis of these signals can be used to extract information about the sample's composition, impurities

present, the nature of bonding, and is often combined with a scanning mode to obtain maps of a selected area.

Although TEM is a non-destructive technique, the conventional thin film sample preparation for TEM analysis requires sample cutting, grinding, and ion beam milling in order to create electron transparent (thickness < 100 nm) regions. Alternatively, a TEM-sample can be prepared by focused ion beam (FIB), which is more expensive and time consuming, but causes less damage for the sample and allows the possibility to select a specific area of interest.

#### 5.2.1 Electron energy loss spectroscopy

In electron energy loss spectroscopy (EELS), the change in the electron kinetic energy after inelastic interaction with the specimen is measured. Depending on the scattering atom, incident electrons experience different energy loss. In which amount, is dependent on the atomic element, making mapping of local film composition possible. Furthermore, the local surrounding of the atom results in fine adjustments of the characteristic energy loss, which gives information about the bonding state of the atom.

#### 5.2.2 Energy dispersive X-ray spectroscopy

In energy dispersive X-ray spectroscopy (EDX), the incident electron beam excites electrons in the sample atoms to higher levels. De-exitation to the ground state occurs by either emission of an Auger electron (primarily for lighter elements) or an X-ray photon (primarily for heavier elements). Each element has a unique set of energies of the emitted X-rays, which makes elemental identification and composition mapping of a selected sample area possible.

### 5.3 Vibrating sample magnetometry

Vibrating sample magnetometry (VSM) is a technique to measure a materials magnetic moment. A uniform magnetic field is applied on a sample, aligning its magnetic spins along the field lines. The sample is then vibrated, which induces a current in the pickup coils surrounding the sample, proportional to the magnetic moment. Measurements are typically made at cryostatic temperatures to increase signal-to-noise ratio. Temperature dependent measurements are performed to obtain transition temperatures between different magnetic states. The schematics of a VSM system is given in Figure 5.4.



Figure 5.4. Schematics of a VSM system.

### 6 Summary of the papers

### 6.1 Paper I T<sub>2</sub>AI(C,O) MAX phase

The substitutional O content in  $Ti_2AlC$  thin film samples has previously been measured by elastic recoil detection analysis (ERDA) (20 at.%) [48] and roughly estimated by EELS (5-10 at.%, depending on the choice of the model) [28]. ERDA results must be interpreted with care, as they may also include O contribution from grain boundaries and other structural imperfections acting as O getters. In this Thesis unambiguous measurements on the content of the substitutional O locally in  $Ti_2AlC$  MAX phase have been performed employing a reference-based EELS.

The range of O concentration attained in MAX phase oxycarbide  $Ti_2AlC_{1-x}O_x$  was explored using two thin film synthesis routes; deposition of  $Ti_2AlC_y$  by pulsed cathodic arc under high vacuum conditions, and solid-state reactions following deposition of understoichiometric  $TiC_y$  on  $Al_2O_3$ . An O concentration of 10-13 at.% was measured. Furthermore, calculations were performed to investigate the effect of substitutional O on the shearing behavior. A linear increase in the ideal strength for [-1010](0001) and [1-210](0001) shear paths was found for an increased O content.

The obtained O concentration range is wide enough to allow experimental observations of the previously suggested (from theory) change in anisotropic conductivity with increasing O content [12], as well as to measure any accompanying change in the bulk modulus. Altogether, the results show an O concentration range allowing tuning of the material's electronic and mechanical properties.

## 6.2 Paper II (Cr,Mn)<sub>2</sub>AIC – the first MAX phase containing Mn

In this paper, theoretical predictions and experimental observations of the first Mn containing MAX phase are reported.

Temperature dependent stability of  $(Cr_{1-x}Mn_x)_2AlC$  with  $0.0 \le x \le 0.5$  has been theoretically investigated assuming a random Cr-Mn intermixing on the *M*-site. The results indicate 211 MAX phase stability over the considered composition range for temperatures  $\ge 600$  K.

The  $(Cr_{1-x}Mn_x)_2AIC$  thin films were deposited on  $Al_2O_3(0001)$  substrates by magnetron sputtering from four elemental targets. XRD phase analysis shows that the films predominantly consist of epitaxially oriented 211 MAX phase. Calculations of the change in lattice parameters upon addition of Mn have been performed, indicating a linear decrease in the c-axis and no significant change of the a-axis. However, the predicted XRD peak shift with respect to pure Cr<sub>2</sub>AlC is too small to allow quantification of the Mn concentration.

Analytical TEM including EELS and EDX has been used in scanning mode for elemental mapping in MAX phase areas of high structural quality. A Cr/Mn based MAX phase alloy was revealed, including a Mn concentration of 8 at.%.

## 6.3 Paper III (Cr,Mn)<sub>2</sub>GeC – evidence of a magnetic MAX phase

In this paper, a new family of inherently nanolayered magnetic materials is uncovered. Phase stability and magnetic properties of  $M_{n+1}\text{GeC}_n$  (M = Ti, V, Cr, and Mn) have been investigated from first principles and  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$  was identified as a stable magnetic MAX phase alloy. Several configurations of Cr and Mn atoms on the *M* sublattice were considered in different magnetic states for x=0.25 and x=0.50.

 $(Cr_{1-x}Mn_x)_2GeC$  thin films have been deposited on MgO(111) substrates by magnetron sputtering. XRD  $\theta/2\theta$  analysis shows high quality epitaxial MAX phase structure. Elemental mapping from (S)TEM equipped with EDX reveals Mn concentration of 12.5at.%.

Magnetic response in the temperature range of 50-300 K has been measured by VSM. The thin film is magnetic at room temperature, though with a total saturation moment per Mn atom experimentally determined to be a factor of 6 smaller than predicted theoretically. Calculated moments are generally lower than those obtained experimentally, but the discrepancy may be explained by the concentration of Mn allowing varying Cr-Mn interaction, with a resulting combination of antiferromganetic and ferromagnetic coupling.

### 7 Future research

The focus of this Thesis is synthesis and characterization of MAX phases with novel properties. The results obtained are promising and encourage continued investigations.

A stage for *in situ* conductivity measurements is being designed to allow experimental evaluation of potentially tunable anisotropic conductivity of Ti<sub>2</sub>Al(C,O).

The growth conditions of  $(Cr,Mn)_2AlC$  will be further optimized in order to exclude secondary phases and allow unambiguous magnetic characterization. As magnetic response is determined by Mn, attempts to increase Mn content in both  $(Cr,Mn)_2AlC$  and  $(Cr,Mn)_2GeC$  will be performed through synthesis at lower temperatures followed by annealing. In addition, experiments on bulk synthesis of  $(Cr,Mn)_2AlC$  have been initiated.

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