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The $M_{n+1}AX_n$ phases: materials science and thin film processing

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ABSTRACT

This article is a critical review of the $M_{n+1}AX_n$ phases (“MAX phases”, where $n = 1, 2$, or 3) from a materials science perspective. MAX phases are a class of hexagonal-structure ternary carbides and nitrides (“X”) of a transition metal (“M”) and an A-group element. The most well known are Ti_2AlC , Ti_3SiC_2 , and Ti_4AlN_3 . There are ~60 MAX phases with at least 9 discovered in the last five years alone. What makes the MAX phases fascinating and potentially useful is their remarkable combination of chemical, physical, electrical, and mechanical properties, which in many ways combine the characteristics of metals and ceramics. For example, MAX phases are typically resistant to oxidation and corrosion, elastically stiff, but at the same time they exhibit high thermal and electrical conductivities and are machinable. These properties stem from an inherently nanolaminated crystal structure, with $M_{n+1}X_n$ slabs intercalated with pure A-element layers. The research on MAX phases has been accelerated by the introduction of thin-film processing methods. Magnetron sputtering and arc deposition have been employed to synthesize single-crystal material by epitaxial growth, which enables studies of fundamental materials properties. However, the surface-initiated decomposition of $M_{n+1}AX_n$ thin films into MX compounds at temperatures of 1000–1100 °C is much lower than the decomposition temperatures typically reported for the corresponding bulk material. We also review the prospects for low-temperature synthesis, which is essential for deposition of MAX phases onto technologically important substrates. While deposition of MAX phases from the archetypical Ti-Si-C and Ti-Al-N systems typically require synthesis temperatures of ~800 °C, recent results have demonstrated that V_2GeC and Cr_2AlC can be deposited at ~450 °C. Also, thermal spray of Ti_2AlC powder has been used to produce thick coatings. We further treat progress in the use of first-principles calculations for predicting hypothetical MAX phases and their properties. Together with advances in processing and materials

analysis, this progress has led to recent discoveries of numerous new MAX phases such as Ti_4SiC_3 , Ta_4AlC_3 , and Ti_3SnC_2 . Finally, important future research directions are discussed. These include charting the unknown regions in phase diagrams to discover new equilibrium and metastable phases, as well as research challenges in understanding their physical properties, such as the effects of anisotropy, impurities, and vacancies on the electrical properties, and unexplored properties such as superconductivity, magnetism, and optics.

1 Introduction

In the 1960s, Hans Nowotny's group in Vienna accomplished a gargantuan feat [1], discovering more than 100 new carbides and nitrides. Among them were the so-called "H phases" and their relatives Ti_3SiC_2 and Ti_3GeC_2 . Despite this impressive accomplishment, these phases remained largely unexplored until the 1990s, when several researchers began to take renewed interest. The breakthrough contribution that triggered a renaissance came in the mid-1990s, when Barsoum and El-Raghy [2] synthesized relatively phase-pure samples of Ti_3SiC_2 and revealed a material with a unique combination of metallic and ceramic properties: like metals, it exhibited high electrical and thermal conductivity, and it was machinable. Still, it was extremely resistant to oxidation and thermal shock, like ceramics. When they later discovered Ti_4AlN_3 , it became clear that these phases shared a basic structure that gave them similar properties. This realization led to the introduction of the nomenclature " $\text{M}_{n+1}\text{AX}_n$ phases" ($n = 1, 2, \text{ or } 3$) or "MAX phases", where M is a transition metal, A is an A-group element, and X is C and/or N [3,4].

Until a dozen years ago, the MAX phases were an uncharted category of solids, which since have turned out to possess unique chemical, physical, electrical, and mechanical properties. Many MAX phases have been reported to have highly unusual properties, including fully reversible dislocation-based deformation, high specific stiffness combined with superb machinability, and excellent thermal and electrical conductivities, among others. They deform by a combination of kink and shear band formation, together with delaminations within grains. Some also exhibit extremely low friction coefficients. These astonishing properties stem from the layered structure of the MAX phases and the mixed metallic-covalent nature of the M-X bonds which are exceptionally strong, together with M-A bonds that are relatively weak. This unique combination of properties

underscores the potential of MAX phases for high temperature structural applications, protective coatings, sensors, low friction surfaces, electrical contacts, tunable damping films for microelectromechanical systems, and many more.

The possibilities to exploit the remarkable combination of metallic and ceramic properties of the MAX phases have led to a rapid global growth in research on the topic as well as commercialization. This article is a critical review of the materials science of the MAX phases from our point of view as thin-film physicists. We begin (section 2) with a review of the fundamentals (basic structure, phase diagrams, and terminology) followed by more complex structural aspects (polymorphism, intergrown structures, vacancies, solid solutions, and the relationship of MAX phases to other nanolaminated structures and phases).

Section 3 reviews thin-film processing methods with emphasis on how they relate specifically to processing of MAX phases; however, many of these processing aspects are of general validity and interest. We further discuss the prospects for low-temperature deposition, where the lowest reported deposition temperature for MAX phases is 450 °C for V_2GeC and Cr_2AlC . Section 4 reviews the relation between thin-film and bulk synthesis; more details on bulk synthesis methods can be found in the focused review on Ti_3SiC_2 by Zhang *et al.* [5]. The recent discoveries of numerous new MAX phases are reviewed as an important contemporary example of an area in materials research where thin-film synthesis, bulk synthesis, and theoretical predictions and explanations have combined to yield a more complete understanding. We also discuss *why* some MAX phases exist and others do not. Section 5 is a review of the nucleation and growth of MAX phases. Electrical, mechanical, tribological, and thermal-stability properties (sections 6-7) are reviewed with an emphasis on features where thin-film processing can contribute to understanding of the complex materials

science problems involved; in particular, we present an extended discussion of the anisotropy in electrical properties. Finally, applications and important future research directions are presented.

2 The $M_{n+1}AX_n$ phases

This section begins with a review of the fundamentals (section 2.1): what is the basic crystal structure of the MAX phases, what are the relevant phase diagrams, and what is the nomenclature? Sections 2.2–2.5 review more complex structural aspects of the MAX phases (polymorphism, intergrown structures, vacancies, and solid solutions). Sections 2.6–2.7 discuss theoretical predictions of new MAX phases and how the MAX phases relate to other nanolaminated structures and phases.

2.1 *Review of fundamentals*

2.1.1 Crystal Structure

As defined by Barsoum [3], the MAX phases have the general formula $M_{n+1}AX_n$ ($n=1, 2$, or 3). The different MAX stoichiometries are often referred to as 211 ($n=1$), 312 ($n=2$), and 413 ($n=3$). The M elements are transition metals from groups 3 (Sc), 4 (Ti, Zr, Hf), 5 (V, Nb, Ta), and 6 (Cr and Mo). No MAX phases with the group-3 elements Y or Lu, or the group-6 element W are known (see section 4.3.2). The A element is from groups 12 (Cd), 13 (Al, Ga, In, Tl), 14 (Si, Ge, Sn, Pb), 15 (P, As), or 16 (S). The label “A” comes from the old American nomenclature for the periodic table (see section 2.1.3.5). The X element is C and/or N (the terms “MAC phases” and “MAN phases” are sometimes used to refer to the MAX-phase carbides ($X = C$) and nitrides ($X = N$), respectively). Table 1 lists all MAX phases known to date.

Figure 1 shows the hexagonal unit cells of the 211, 312, and 413 MAX phases. The unit cells consist of M_6X octahedra, e.g. Ti_6C , interleaved with layers of A elements (e.g., Si or Ge). The difference between the three structures is in the number of M layers separating the A layers: in the

211 phases there are two; in the 312 phases three, and in the 413 phases four. The M_6X edge-sharing octahedral building block in the MAX phases is the same as in the binary carbides and nitrides, MX. In the 312 and 413 MAX structures, there are two different M sites, those adjacent to A, and those not. These sites are referred to as M(1) and M(2), respectively. In the 413 structure, there are also two nonequivalent X sites, X(1) and X(2). In the MAX phases, the MX layers are twinned with respect to each other and separated by the A layer which acts as mirror plane. This is illustrated in Figure 2, which is a high-resolution transmission electron microscopy (TEM) image acquired along the $[11\bar{2}0]$ zone axis of Ti_3SiC_2 . The twinning and the resulting characteristic “zig-zag” stacking of the MAX phases is evident. The MAX structures are anisotropic: the lattice parameters are typically around $a \sim 3 \text{ \AA}$ and $c \sim 13 \text{ \AA}$ (for 211 phases), $c \sim 18 \text{ \AA}$ (for 312 phases), and $c \sim 23\text{--}24 \text{ \AA}$ (for 413 phases). Table 2 lists the structural parameters of the basic MAX structures (see also section 2.2). The space group is $P6_3/mmc$.

2.1.2 Phase diagrams

As a representative example of a phase diagram for an M-A-X materials system, consider the Ti-Si-C system. While a binary phase diagram is usually drawn as a function of composition and temperature, ternary phase diagrams are normally reported as isothermal cross sections. Numerous authors have reported phase diagrams for the Ti-Si-C system, experimentally and/or theoretically determined; examples include those of Viala *et al.* [6], Wakelkamp *et al.* [7], Touanen *et al.* [8], and Sambasivan and Petsukey [9]. Figure 3 shows a simplified 1000 °C isothermal cross section of the Ti-Si-C diagram, adapted from Ref. 6. The silicides Ti_3Si and Ti_5Si_4 (known from the binary phase diagram) are not stable in the presence of carbon, and therefore not shown. Fig. 3 contains one stable ternary phase, the MAX phase Ti_3SiC_2 . Also marked is the MAX phase Ti_4SiC_3 , which is presumed to be metastable (cf. sections 2.6, 4.2.2, and 4.3.1). Further, Ti_5Si_3 can dissolve C, and

should therefore be written $\text{Ti}_5\text{Si}_3\text{C}_x$. Nowotny [1] reported the existence of numerous such phases in the 1960s, e.g., $\text{Zr}_5\text{Si}_3\text{C}_x$ and $\text{V}_5\text{Ge}_3\text{C}_x$. From a structural viewpoint, these “53x” phases are closely related with TiC and the MAX phases, in that they share the fundamental M_6X octahedral building block. However, in the “53x” phases, the M_6X octahedra share faces rather than edges (as in the MAX phases and the binary carbides). The stable binary phases are TiC, SiC, TiSi, and TiSi_2 . Most of these characteristics of the phase diagram of the Ti-Si-C system are typical for the majority of M-A-X systems. There are, however, some important differences: unlike many other M-A-X systems, the Ti-Si-C system does not contain a stable 211 phase (cf. section 4.3.2.3), nor does it contain the inverse perovskite (“311”) phase observed in Ti_3AlC [10,11] and Cr_3GaN [12].

Two reservations are in order. First, phase diagrams represent the situation at thermodynamic equilibrium, while film-growth kinetics are far from equilibrium (cf. sections 3 and 4). Second, many phase diagrams for the M-A-X systems are not sufficiently established (cf. section 4.3.2.3) and it is necessary to interpret phase diagrams with care. An important example is the Ti-Ge-C system, where data are scarce. So scarce, in fact, that the 1995 edition of the *Handbook of ternary alloy phase diagrams* [13] dryly states “no phase diagram is available”. Since the *Handbook* was printed, one report of a Ti-Ge-C phase diagram has been published, and even that phase diagram is relatively schematic [14].

2.1.3 Terminology and notation

In this section, we review the various notations and terminologies used in the MAX-phase literature and discuss the most common errors and sources of confusion.

2.1.3.1 “Thermodynamically stable nanolaminates” and “inherently nanolaminated” materials

Barsoum’s seminal review article [3] from the year 2000 has the title “The $M_{N+1}AX_N$ Phases: A New Class of Solids; Thermodynamically Stable Nanolaminates”. A “nanolaminate” is a material with a laminated – layered – structure in which the thicknesses of the individual layers are in the nanometer range. In principle, a MAX phase does not necessarily (at least not by definition) have to be thermodynamically stable (see for example section 4.3). The term “thermodynamically stable nanolaminates” was used to distinguish them from *artificial* nanolaminates, e.g., superlattice thin films. An equivalent, but more stringent, description to “thermodynamically stable nanolaminates” is to refer to the MAX phases as “inherently nanolaminated” (i.e., they are nanolaminated by nature, not by artificial design). Note, however, that these terms are not restricted to the MAX phases, but include many other phases with a laminated structure (see for example section 2.7).

2.1.3.2 Layered ternary ceramics

The term “layered ternary ceramics” (and its variations) is a collective name for *all* ceramics that contain exactly three elements and have a layered structure. The “MAX phases” are a subgroup of the much larger class of “layered ternary ceramics”. Occasionally, however, “layered ternary ceramics” is incorrectly used as a synonym for “MAX phases”. An example of the *correct* use of the term is the title of the article “TEM investigations on layered ternary ceramics” by Lin *et al.* [15], who investigated a wide range of such ceramics, in addition to MAX phases.

2.1.3.3 H phases or Cr_2AlC -type phases

The term “H phases”, as defined by Nowotny [1], is a synonym for “ M_2AX phases”, which are also referred to as “ Cr_2AlC -type phases” after the archetype Cr_2AlC . There is a common misunderstanding in MAX-phase literature that the terms “H phase” and “Hägg phase” are

synonyms. However, the “H” in “H phases” is *not* an abbreviation for “Hägg”. In Toth’s book *Transition metal carbides and nitrides* [16], the “H Phases or Cr₂AlC Type” phases are clearly listed as *non-Hägg-like* phases. The “H phases” are presumably named following an alphabetic system; for example, Nowotny and his coworkers also studied “D phases” [17,18], “E phases” [19] and “G phases” [20]. The erroneous belief that “H phases” and “Hägg phases” are synonyms does not occur outside the MAX-phase field; in other fields, the latter term is used in its correct sense: “Hägg phases” are carbides, nitrides, borides, and hydrides with close-packed or hexagonal arrays of metal atoms in which C, N, B, or H occupy interstitial octahedral or trigonal sites [16,21]. The “H phases” do *not* fulfill this criterion; the C or N atoms do occupy an interstitial octahedral site, but the metal substructure is not close-packed or nearly close-packed.

2.1.3.4 TMX

The notation originally used by Nowotny was “TMX” [1]. Although largely forgotten, this notation is occasionally used today [22]. However, Nowotny’s “TMX” notation is *not* synonymous with the “MAX phases” (as defined by Barsoum), but refers to the much larger class of materials with the general formula T_xM_yX_z. (T denotes a transition metal, M denotes a group 12-16 element *or* another transition metal, and X denotes C or N). Among the carbides, which were Nowotny’s focus, this group included (according to Nowotny’s definition) T₃MC (inverse perovskite, e.g. Ti₃AlC), T₃M₂C, T₂MC (H phases), T₃MC₂ (i.e., the phases that today are called the 312 MAX phases), T₅M₃C_x (e.g., Ti₅Si₃C_x), and many more. The “MAX phases” are therefore a small (but important) subset of the “TMX phases”.

2.1.3.5 MBX

In Barsoum’s first publications (and some others) from the latter half of the 1990s [23], the notation “MBX phases” instead of “MAX phases” is used. The origin of this notation is the two old

nomenclatural systems for the periodic table, from the Chemical Abstract Service (CAS), a division of the American Chemical Society, and the International Union of Pure and Applied Chemistry (IUPAC). The CAS system was common in America and the IUPAC system used more in Europe. In the IUPAC system, the letters “A” and “B” referred to the left (A) and right (B) parts of the periodic table, while the CAS system used “A” and “B” to designate main group elements and transition elements, respectively. The present IUPAC nomenclature, introduced in the period 1985-1990, uses the labels “groups 1-18”, and does not include “A” or “B” (in practice, the older systems remain in widespread parallel use). In his first work, Barsoum retained the old IUPAC label of the “B” element. After some time, he realized that if he used the old CAS nomenclature instead, he would obtain the much catchier acronym “MAX”. (Note that there is one MAX phase, Ti_2CdC , where the “A” element is from group 12, or group IIB with the old CAS notation; the label “A” in “MAX phases” is therefore not strictly accurate.) Ever since, the “MAX” notation has been ubiquitous, while the “MBX” notation is not in use today, and should be avoided not only because it is obsolete, but also because the “B” can be confused with the element boron. For example, Mo_2BC (where B refers to boron!) is *not* a M_2AX phase [24].

2.1.3.6 MaxPhase and maxfas

The terms *MaxPhase* and *maxfas* are trade names used by Impact Coatings AB. These names, however, do *not* necessarily refer to a MAX phase, but to a Ti-Si-C-based nanocomposite coating [25,26,27]. The trade name *MaxPhase* originates from the first generation of such coatings, which were synthesized by sputtering from Ti_3SiC_2 targets (see section 3.1.1.2), i.e., the *target* – not the coating – was a MAX phase. While it is often used in public relations material, the press, and popular science articles, the trade name *MaxPhase* should not be used in the scientific literature since it will inevitably be confused with the “MAX phases”.

2.2 Polymorphism of MAX phases

Two different types of polymorphism have been demonstrated in MAX phases. One type has been observed for the 312 phases (and possibly also for Ti_4AlN_3) and involves shearing of the A layers. The other type of polymorphism has been observed for Ta_4AlC_3 , but not for the other known 413 phases. Table 2 lists the structural parameters of the MAX-phase polymorphs.

The first indications of polymorphism in the MAX phases came in the late 1990s, when discrepancies were found between the structures of Ti_3SiC_2 , Ti_3AlC_2 , and Ti_4AlN_3 determined by Rietveld refinement of X-ray and neutron diffraction data and the corresponding transmission electron microscopy (TEM) results [3,28,29,30]. At the time, it was argued that this was due to a polymorphic phase transition involving shear of the Si or Al layers, which could conceivably occur during the TEM sample preparation process. The polymorphs were labeled α - and β - Ti_3SiC_2 . As defined by Farber *et al.* [30], the difference between α - and β - Ti_3SiC_2 is that Si atoms occupy the $2b$ Wyckoff position with the fractional coordinates (0, 0, 1/4) in α - Ti_3SiC_2 , while in the β -phase the Si atoms fill the $2d$ Wyckoff position with the fractional coordinates (2/3, 1/3, 1/4) (see Table 2). However, these conclusions were based only on high-resolution TEM imaging, which has the important limitation that one cannot be certain that the results are macroscopically representative – especially since the α - β phase transformation seemed to be induced by the TEM sample preparation procedure. Therefore, it was significant that synchrotron X-ray diffraction showed that the β polymorph of Ti_3GeC_2 can be formed at high pressure (> 26 GPa) together with shear in a diamond anvil cell [31]. On the other hand, a similar study indicated that α - Ti_3SiC_2 was structurally stable up to 61 GPa [32]. It has been suggested that the α - β phase transformation occurs at much higher pressure (~90 GPa) in Ti_3SiC_2 [33], although it was referred to as “a more condensed state”

of Ti_3SiC_2 – the β polymorph was not unambiguously identified. There are also theoretical results that suggest that this type of polymorphism may be possible for the 211 phases [34].

The second type of polymorphism in MAX phases has been experimentally proven for Ta_4AlC_3 . Manoun *et al.* [35] performed a high-pressure study on sintered Ta_4AlC_3 with synchrotron X-ray diffraction (XRD) and assumed the same structure as Ti_4AlN_3 . There were large differences between experimental and calculated intensities in the XRD pattern; Manoun *et al.* tentatively (and most likely incorrectly) explained these discrepancies as a consequence of preferred orientation. Shortly afterwards, however, Lin *et al.* [36,37] presented high-resolution TEM images showing that their hot-pressed Ta_4AlC_3 samples exhibited a different stacking sequence than that of Ti_4AlN_3 , and followed this up with a Rietveld refinement analysis that proved that the proposed structure was consistent with their data on hot-pressed Ta_4AlC_3 , with only small differences between the experimental and calculated patterns. However, our data on Ta_4AlC_3 powder showed that Ta_4AlC_3 has the same structure as Ti_4AlN_3 [38]. Etzkorn *et al.* [39] independently arrived at the same conclusion. We attempted to refine our XRD data to the structure proposed by Lin *et al.*; however, this refinement was not possible since the experimental peak intensities differed strongly from the calculated intensities, in many cases by more than an order of magnitude. The combination of these results proved that Ta_4AlC_3 has two polymorphs, which today are called α (the same structure as Ti_4AlN_3) and β . In retrospect, it seems virtually certain that the samples studied by Manoun *et al.* [35] were β - Ta_4AlC_3 . The polymorphism of Ta_4AlC_3 is different than the one observed in the 312 phases, where the difference is in the A-element layers. The difference between α - and β - Ta_4AlC_3 is in the positions of the Ta(2) and C(2) atoms (See Table 2). According to several recent DFT investigations, the α phase is the more stable of the two polymorphs at room temperature and pressure [40,41,42].

Shortly after the discovery of Ta_4AlC_3 , the 413 phases Nb_4AlC_3 and V_4AlC_3 were reported (see section 4.3). For the two latter phases, polymorphism was *not* observed. Wang *et al.* [40] recently proposed an elegant explanation for this. Figure 4 (reproduced from Ref. 40) shows the calculated (by density functional theory (DFT)) difference in the Gibbs free energy, ΔG , between the α and β polymorphs of Ta_4AlC_3 , Nb_4AlC_3 , V_4AlC_3 , and Ti_4AlN_3 . As shown in Figure 4, phase stability reversal for Ta_4AlC_3 was predicted at 1875 K (i.e., the β polymorph becomes more stable than the α polymorph). For the other 413 phases, the α polymorph is the more stable of the two over the entire temperature range up to 3000 K. The rapid decrease in ΔG for Ta_4AlC_3 is attributed to the unusually large difference in the strength of Ta-C(2) bonds in the two Ta_4AlC_3 polymorphs. This explains why the β - Ta_4AlC_3 polymorph exists, but the corresponding polymorphs do not appear to exist for Nb_4AlC_3 , V_4AlC_3 , and Ti_4AlN_3 . Note, however, that vacancies and impurities could also affect the stability of the polymorphs.

The two types of polymorphism in MAX phases appear to be fundamentally different. As discussed in the previous paragraph, the polymorphism in Ta_4AlC_3 is most likely *thermodynamically* driven. On the other hand, the polymorphic phase transformation observed for the 312 phases (and possibly in high-resolution TEM for Ti_4AlN_3) is driven by *shear strain* – it corresponds to shearing of the A-element layer [43]. This transformation can occur under high-pressure conditions and/or during TEM sample preparation. There are, however, theoretical indications that the α - β phase transformation in Ti_3SiC_2 and Ti_3GeC_2 may also be induced by thermodynamic competition between the α and β polymorphs [44] at high temperature, similar to Ta_4AlC_3 .

2.3 Intergrown Structures – Hybrid “523” and “725” MAX Phases

Palmquist *et al.* [45] first demonstrated the MAX-phase “intergrown structures”. Film-growth experiments showed the existence of two previously unknown types of MAX phases, $\text{Ti}_5\text{Si}_2\text{C}_3$ and $\text{Ti}_7\text{Si}_2\text{C}_5$, or “523” and “725” phases. The same phases were later demonstrated in the Ti-Ge-C system as well [46]. The “523” and “725” phases were observed as minority phases together with, e.g., Ti_3SiC_2 . The c axes of the unit cells were determined to 30.4 Å for $\text{Ti}_5\text{Si}_2\text{C}_3$ and 40.4 Å for $\text{Ti}_7\text{Si}_2\text{C}_5$, respectively [45]. In the literature, the “523” and “725” phases are referred to as both “intergrown structures” and “new types of MAX phases”. The reason for this somewhat confusing terminology is that it was initially unclear whether the “523” and “725” structures should be regarded as *separate* phases or simply a variation of the basic MAX-phase structure.

The structure of 523 can be described as a combination of half-unit cells of 312 and half-unit cells of 211 (cf., Figs 1 and 5); similarly, the structure of 725 corresponds to a combination of 312 and 413 unit cells. This regular structure is then repeated over significant distances and yields clear XRD signatures. However, this description of the c axis cannot fully correctly reproduce the stacking sequence of the 523 and 725 phases. The alternating stacking of even and odd numbers of Ti layers induces a translation of the Si position in the lattice, i.e., the Si atoms are not positioned above each other. This requires three repetitions instead of two. The diffraction pattern from these intergrown structures is instead indexed based on a hexagonal lattice with a c axis 1.5 times the basic hexagonal c axis, i.e., 45.63 Å and 60.62 Å for $\text{Ti}_5\text{Si}_2\text{C}_3$ and $\text{Ti}_7\text{Si}_2\text{C}_5$, respectively. In such a structure, the observed 000 l reflections in the θ -2 θ diffractogram are indexed with $l = 3n$ ($n = 1, 2, 3, \dots$) [45]. Thus, the description of the “523” and “725” phases as a combination of half-unit cells of 312 and half-unit cells of 211 or 413, respectively, is not completely accurate, but a close approximation and sufficient for most purposes.

Zhou *et al.* [47] recently reported a 523 phase, $(V,Cr)_5Al_2C_3$, as a minority phase in bulk samples consisting primarily of $(V,Cr)_2AlC$ and $(V,Cr)_3AlC_2$. Figure 5, reproduced from Ref. 47, shows non-filtered and filtered high-resolution Z-contrast TEM images showing the alternating stacking of two and three transition metal carbide layers in one slab, forming an ordered structure of $(V_{0.5}Cr_{0.5})_5Al_2C_3$. The existence of $(V,Cr)_5Al_2C_3$ is noteworthy and suggests that there may be many more “523” and “725” phases.

Some confusion has been caused by the fact that there is another use of the term “intergrown structure” or “intergrowth” in the MAX-phase literature, which refers to cases of *irregular* stacking within a MAX-phase grain (for example, the irregular stacking of a few unit cells of “ Ta_2AlC ” within a Ta_4AlC_3 grain [38], or “ Ti_2AlC ” within epitaxial Ti_3AlC_2 thin films [48] and Ti_3AlC_2 bulk material [49]). Related observations are the reports of Ta_6AlC_5 and Ti_7SnC_6 stacking sequences of a few unit cells in Ta_4AlC_3 and Ti_2SnC samples, suggesting the possible existence of “higher-order” MAX phases (i.e., $M_{n+1}AX_n$ phases with $n > 3$) [50,51]. Note, however, that these observations *suggest* but do not *prove* that higher-order MAX phases exist. These results show local “615” or “716” stacking sequences that are not repeated over significant distances and thus do not meet the definition of a phase (unlike, for example, the “523” and “725” *phases* described above). The terms “intergrowth” or “intergrown structure” has also been used at times to refer to crystallographically related binary-carbide inclusions in MAX phases.

2.4 Vacancies

As stated above, the MAX phases are described by the general formula $M_{n+1}AX_n$ ($n = 1, 2$, or 3), with the different MAX stoichiometries often referred to as 211 ($n = 1$), 312 ($n = 2$), and 413 ($n = 3$).

However, this notation does not imply that “211”, “312”, and “413” are necessarily the exact stoichiometries. In fact, the MX building blocks in the MAX-phases are monocarbides and mononitrides, which frequently exhibit wide homogeneity ranges. TiC, for example, has a very broad single-phase field ranging from approximately $\text{TiC}_{0.5}$ to $\text{TiC}_{0.98}$. Substoichiometry of the X component in the MAX phases is therefore expected. In the first reports on Ti_4AlN_3 [28], the stoichiometry was stated to be $\text{Ti}_4\text{AlN}_{3-\delta}$ with $\delta \approx 0.1$ (determined from Rietveld refinement of X-ray and neutron diffraction data), i.e., the Ti_4AlN_3 structure was reported to be slightly substoichiometric in N. This is supported by DFT calculations, which indicate that introduction of N vacancies in $\text{Ti}_4\text{AlN}_{3-\delta}$ is energetically favorable compared to stoichiometric Ti_4AlN_3 [52]. On the other hand, a recent calculation for $\alpha\text{-Ta}_4\text{AlC}_3$ by Du *et al.* [53] indicated that the introduction of only a small amount of C vacancies in Ta_4AlC_3 results in reduced stability compared to the stoichiometric structure, and there are no experimental indications that $\alpha\text{-Ta}_4\text{AlC}_3$ is understoichiometric in C [39]. Therefore, it is possible that the X-site vacancy-bearing abilities of the known 413 phases differ. Similarly, the first report on Ti_3AlC_2 stated the stoichiometry as “312” [54], while Tzenov and Barsoum [55] determined the stoichiometry to be $\text{Ti}_3\text{AlC}_{1.8}$. It is likely that for most MAX phases, there is a stoichiometry range for vacancies on the X site. This is important both for the formation and stability of MAX phases [56].

For vacancies on the A site, most studies have focused on MAX phases in the Ti-Al-C system, due to their importance for the oxidation resistance of bulk MAX phases and the formation of a protective Al_2O_3 oxide scale [57,58,59,60]. Theoretical predictions have indicated that Ti_2AlC remains structurally stable to a composition of $\text{Ti}_2\text{Al}_{0.5}\text{C}$, i.e., 50 % vacancies on the A site, before forming a twinned TiC structure [61,62]. Furthermore, a recent calculation by Liao *et al.* [63]

predicts that impurities (O and N) affect the Al vacancy formation energy in Ti_2AlC , indicating the general importance of impurities for vacancy stability in MAX phases.

2.5 Solid solutions

The MAX phases can form a large number of isostructural solid solutions. From a researcher's point of view, this degree of freedom is important for understanding the role of *chemistry* in controlling physical properties.

2.5.1 M and A site solid solutions

Numerous MAX-phase solid solutions have been synthesized as bulk materials. Examples of solid solutions on the M site are $(\text{Ti,V})_2\text{AlC}$, $(\text{Ti,Cr})_2\text{AlC}$, $(\text{Ti,Nb})_2\text{AlC}$, $(\text{Cr,V})_2\text{AlC}$, and $(\text{Ti,V})_2\text{SC}$ [3,64,65,66]. Sun *et al.* [67] and Wang *et al.* [68] predicted that the solid solutions of $(\text{M1,M2})_2\text{AlC}$ (M1 and $\text{M2} = \text{Ti, V, Cr}$) would be more stable than the physical mixtures, and should exhibit enhanced bulk moduli compared to the end members. The prediction of a solid-solution strengthening effect has been corroborated by experiments. For example, Meng *et al.* [69] reported that the Vickers hardness, flexural strength, and shear strength were enhanced by 29%, 36%, and 45%, respectively, for $(\text{Ti}_{0.8}\text{V}_{0.2})\text{AlC}$ compared to Ti_2AlC . Many A-site MAX phase solid solutions also exist, with $\text{Ti}_3(\text{Si,Al,Ge,Sn})\text{C}_2$ being the most studied [70,71,72,73].

2.5.2 X site solid solutions

MAX carbonitrides, i.e., $\text{M}_{n+1}\text{A}(\text{C,N})_n$ phases, are the most important example of MAX-phase solid solutions on the X site. For example, bulk $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$ has been reported [74] to be significantly harder and stiffer than either of its end members Ti_2AlC and Ti_2AlN , and there may be other ratios of C and N with even better properties. A continuous series of solid solutions, $\text{Ti}_2\text{AlC}_{0.8-x}\text{N}_x$, where $x = 0\text{--}0.8$, was reported by Pietzka and Schuster [75]. Preliminary results [76] from thin film

deposition in the $\text{Ti}_2\text{Al}(\text{C},\text{N})$ and $\text{Ti}_3\text{Si}(\text{C},\text{N})_2$ systems indicate an enhanced tendency for $\text{TiC}:\text{N}$ binary phase formation by competitive growth, possibly due to the very narrow process window (with respect to N_2 partial pressure) for deposition of Ti_2AlN (cf. section 3.1.1.3).

Recently, it was reported that a MAX oxycarbide, $\text{Ti}_2\text{Al}(\text{C},\text{O})$, can form, either due to incorporation of oxygen from the residual gas in a vacuum deposition process [77], or due to a reaction between a TiC or Ti_2AlC film with an Al_2O_3 substrate. The latter reaction was first reported (but not fully identified) by Wilhelmsson *et al.* [48] and later explained by Persson *et al.* [78,79]. The expected difference between the MAX carbonitrides and oxycarbides is that the local bonding environment for substitutional impurity atoms (N or O) in Ti_2AlC is different from that for interstitial situations. For the case of N substitution on C sites, the N and C atoms have similar chemical bonding characteristics, resembling those in binary TiC and TiN compounds. As a result, $\text{Ti}_2\text{Al}(\text{C},\text{N})$ forms a wide range of solid solutions. In contrast, Ti-O bonding (such as in TiO_2) is different than that of Ti-N and Ti-C. Therefore, for O substitution on C sites, the valence electrons provided by O atoms may reduce the structural stability of $\text{Ti}_2\text{Al}(\text{C},\text{O})$. This effect was predicted for $\text{Ti}_3\text{Si}(\text{C},\text{O})_2$ by Medvedeva *et al.* [80]. The oxygen saturation content on C sites in $\text{M}_{n+1}\text{A}(\text{C},\text{O})_n$ solid solutions is not known, but there are preliminary indications that it may be strikingly large, in the 25–75 % range [81].

An important future research direction for MAX-phase solid solutions is systematic experimental studies to elucidate the role of chemistry on phase stability and properties. Here, combinatorial thin film materials synthesis will be required to identify solid solutions with attractive, and quite possibly novel, combinations of properties. “Combinatorial” means to employ physical vapor deposition (PVD) processes (with multiple magnetron or cathodic arc sources) to deposit films with

compositional gradients over the area of a large substrate, e.g. a sapphire or silicon wafer. Thereby, large portions of a phase diagram can be mapped out in one film sample with otherwise constant synthesis conditions. One example system for which a combinatorial approach has been employed for MAX-phase synthesis is the (ternary) Cr-Al-C system [82].

2.6 Predictions of new MAX phases

The history of theoretical predictions of new MAX phases begins with the debate on the structure of Ti_4AlN_3 , which in the 1990s was proposed to be either Ti_3AlN_2 or $\text{Ti}_3\text{Al}_2\text{N}_2$ [83,84], but was finally determined to be Ti_4AlN_3 [85,86,87]. This conclusion inspired Holm *et al.* [88] to perform DFT calculations of the stability of the $\text{M}_{n+1}\text{AX}_n$ phases in the Ti-Al-N system. Their results indicated that the hypothetical Ti_3AlN_2 phase was metastable. For comparison, they performed similar calculations for the Ti-Si-C system. The sentences “*With the above arguments in mind, we study the hypothetical solid Ti_4SiC_3 . It also turns out to be meta stable [sic!], and we find the lattice parameters to be $a = 3.03 \text{ \AA}$ and $c = 22.8 \text{ \AA}$.*” are merely a side comment in the paper by Holm *et al.*. This comment turned out to be very important – Ti_3SiC_2 had just been synthesized in thin-film form [89], and it was logical to proceed with an attempt to synthesize Ti_4SiC_3 . It worked [45], and this result was the initial inspiration for many of the research efforts aimed at predicting and discovering new MAX phases (see section 4.3). Not much later, Ti_4GeC_3 was synthesized too [46]. A range of other hypothetical MAX phases have been predicted (e.g., Nb_3SiC_2 , Nb_4SiC_3 , V_2SiC , and V_3SiC_2 to name a few) [90,91,92,93]. Some of these predictions are based on insufficiently known phase diagrams and should be regarded with skepticism (see section 4.3.2.3). Nevertheless, such predictions are important because they give experimentalists indications of what materials systems to investigate in their quest for new MAX phases. An extended discussion of the discoveries of new MAX phases can be found in section 4.3.

More recently, theoretical predictions of a more speculative, but very exciting, nature have appeared. The existence of magnetic MAX phases, with the general formula $\text{Fe}_{n+1}\text{AC}_n$ ($n = 1, 2, 3$, and $\text{A}=\text{Al, Si, or Ge}$), has been proposed based on DFT calculations [94]. For example, the hypothetical phase Fe_3AlC_2 was predicted to be ferromagnetic with an average magnetic moment of $0.73\mu_B$ per Fe atom (μ_B = Bohr magneton). Perhaps the most fascinating prediction is that of Ti_3SiC_2 nanotubes [95]. While highly speculative, this idea is in one sense quite logical, as many layered phases have corresponding nanotubular structures (graphite and carbon nanotubes are the most well known examples, but there are many others). It remains an open question whether any of these phases can be synthesized.

2.7 Related inherently nanolaminated phases

Music and Schneider [96] proposed that nanolaminates can be generally described as interleaved layers of high and low electron density, within a single unit cell. This description applies to the MAX phases, but also to many other phases with an inherently nanolaminated structure (cf. section 2.1.3.1), such as Al_3BC_3 , $\text{Zr}_2\text{Al}_3\text{C}_5$, W_2B_5 -based phases, cubic perovskite borides, and $\text{Y}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ ($n=1, 2, 3, \dots$), as reviewed in Ref. 96. Recent progress in research on inherently nanolaminated ternary carbides in the Zr-Al-C and Hf-Al-C systems, including their relation to the MAX phases, were recently reviewed by Wang and Zhou [97]. It remains to be seen whether Music and Schneider's description is generally valid for *all* inherently nanolaminated phases, and if it can also be used as a design criterion for *artificial* nanolaminates.

3 Thin-film processing of MAX phases

Thin-film synthesis of MAX phases can be categorized into three main approaches: physical vapor deposition (PVD, section 3.1), chemical vapor deposition (CVD, section 3.2), and solid-state reaction synthesis (section 3.3). Section 3.4 is a discussion of MAX-phase synthesis by thermal spraying, which is a method for producing *thick* ($\geq 100\text{ }\mu\text{m}$) coatings.

3.1 Physical Vapor Deposition (PVD) methods

Much work on thin-film synthesis of MAX phases has been performed using physical vapor deposition (PVD), primarily by sputtering techniques (section 3.1.1). A more recent successful approach is cathodic arc deposition (section 3.1.2), while several attempts at pulsed laser deposition (PLD, section 3.1.3) have yielded inconclusive results with respect to MAX-phase formation. Most PVD syntheses of MAX phases have been performed at substrate temperatures in the range 800–1000 °C, limiting the use of temperature-sensitive substrates. An important objective in the PVD field has therefore been to reduce the deposition temperature. Encouraging results have demonstrated that Cr_2AlC [98] and V_2GeC [99] can be synthesized at 450 °C, sufficiently low to permit deposition onto, e.g., certain steels. For a discussion on why some MAX phases can be synthesized at lower temperature than others, see section 4.

3.1.1 Sputtering

Seppänen *et al.* [100] and Palmquist *et al.* [89] first demonstrated the feasibility of Ti_3SiC_2 MAX-phase thin-film synthesis using sputtering, from elemental sources (Ti, Si, and graphite sputtering targets or Ti and Si sputtering targets combined with C_{60} evaporation) and from a Ti_3SiC_2 target (sections 3.1.1.1 and 3.1.1.2, respectively). For the MAX nitrides, reactive sputtering (section

3.1.1.3) is the method of choice. Section 3.1.1.4 discusses the prospects for MAX-phase synthesis by high-power impulse magnetron sputtering (HIPIMS).

3.1.1.1 dc sputtering with 3 sources

For the MAX carbides, sputtering from M, A, and graphite targets is the most common method for laboratory-scale synthesis, and has been employed for deposition of a wide range of MAX phases. As noted in Table 1, $M_{n+1}AX_n$ phases synthesized in this manner are Ti_3SiC_2 [45,89,100,101,102], Ti_4SiC_3 [45,102,103], Ti_2GeC , Ti_3GeC_2 , Ti_4GeC_3 [46,104], Ti_2SnC , Ti_3SnC_2 [105], Ti_2AlC , Ti_3AlC_2 [48,106], Cr_2AlC [82], V_2AlC [107], V_3AlC_2 , V_4AlC_3 [108], V_2GeC [99], and Nb_2AlC [109], plus the intergrown structures (see section 2.3) $Ti_5Si_2C_3$, $Ti_7Si_2C_5$, $Ti_5Ge_2C_3$, and $Ti_7Ge_2C_5$ [45,46,102,104]. The most advantageous aspect of using three elemental targets is the flexibility achieved by the individual control of the elemental fluxes. Figure 6, adapted from Ref. 45, shows a typical result: the use of Ti, Si, and graphite targets permits epitaxial growth of Ti_3SiC_2 , Ti_4SiC_3 , $Ti_5Si_2C_3$ and $Ti_7Si_2C_5$, (marked “312”, “413”, “523” and “725”, respectively; cf., section 2.3). This flexibility is also the main reason for the popularity of elemental targets in fundamental research. In particular, combinatorial synthesis (i.e., in which the composition is varied over a large substrate such as a silicon wafer) from elemental targets permits rapid mapping of compositional variations in a M-A-X system and corresponding property variations as demonstrated for, e.g., Cr-Al-C [82].

3.1.1.2 dc sputtering with compound targets

For industrial PVD processes, compound targets are generally preferred for reasons of simplicity and repeatability. The pioneering work of Seppänen *et al.* [100] and Palmquist *et al.* [45] demonstrated synthesis of Ti_3SiC_2 (0001) thin films on MgO(111) substrates with a TiC_x (111) seed layer using a Ti_3SiC_2 target. More recently, Ti_2AlC [110,111] and Cr_2AlC [98,112] have been deposited by sputtering from compound targets. Compound-target sputtering is, however, plagued

with a general problem, namely that the film composition may deviate strongly from that of the target. This problem is not specific to MAX phases, but commonly observed for compound-target sputtering. For MAX phases, laboratory scale studies have shown that sputtering from a Ti_3SiC_2 target results in films with a C content of 50 at. % or more, much higher than the nominal C content in the target of 33 at. % [25,113]. Addition of Ti to the deposition flux from a Ti_3SiC_2 target has been shown to promote MAX-phase growth by compensating for the excess C [113]. Additionally, a substoichiometric TiC_x buffer layer can be employed as a C sink, i.e., the excess C is accommodated by the buffer layer [113]. Deposition from a Ti_2AlC target has also been shown to result in off-stoichiometric films, and the excess C can be compensated by addition of Ti [110,111]. One difference between Ti_2AlC and Ti_3SiC_2 is the higher tendency for desorption of Al than Si (cf. section 4.2.1), yielding Al-deficient films at high temperature (above 700 °C). However, sputtering from a Cr_2AlC target has been reported to yield a film composition reasonably close to that of the target, with films consisting mainly of Cr_2AlC [98,112], although no results on the homogeneity in the film composition was presented. Recent preliminary results on industrial-scale deposition of Cr_2AlC from Cr_2AlC targets showed strong inhomogeneity in the film composition [114]. Nevertheless, it seems clear that Cr_2AlC differs from the TiC-based MAX phases in this context.

The reasons behind these phenomena are only partially understood. For compound-target sputtering in general, however, the film composition may differ from the nominal target composition due to a wide range of process phenomena. Here, we summarize these phenomena and discuss those which are relevant for MAX phases. More thorough descriptions can be found in textbooks [115,116]. These phenomena can be categorized into processes that occur (1) at or in the target, (2) during the transport through the gas, and (3) at the substrate.

(1) Processes in or at the target. First, for sputtering from compound targets in general, it cannot be ruled out that the outgoing flux from the target is different from the nominal target composition, e.g., due to continuous diffusion mass transfer inside the target without reaching steady state. This effect has been demonstrated for, e.g., YBaCuO targets [117]. However, there are no indications that this effect occurs in MAX-phase (or at least Ti_3SiC_2) targets [113]. Second, the target elements have different angular and energy distributions in the sputtered flux. Simulation of the energy distributions assuming, e.g., the Sigmund-Thompson distribution requires a priori knowledge of the surface binding energy for each element. The angular distribution, on the other hand, can to a reasonable accuracy be described by a $\cos^n$ function, where the exponent n can vary significantly among elements and also depends on the sputtering gas and the energy of the incident sputtering-gas atoms [118,119,120]. For MAX-phase targets, the angular distributions of M, A, and X are neither known nor readily estimated. Nevertheless, it is expected and corroborated by experimental results for Ti_3SiC_2 [113] that the three elements are ejected from the target with different angular distributions. At least for laboratory-scale deposition of Ti_3SiC_2 , the difference in angular distribution strongly affects the film composition. For example, for deposition from a Ti_3SiC_2 target at an Ar pressure of 4 mTorr and a target-to-substrate distance of 9 cm, the C:Ti ratio in the film is ~ 2 for on-axis deposition and ~ 1.2 for 20° off-axis deposition, compared to the nominal target C:Ti ratio of 0.67 [113]. These effects cannot be attributed to gas-scattering alone (cf., pt. (2) below), as discussed in more detail in Ref. 113. The same effects were demonstrated recently by combined experimental and simulation studies by Neidhardt *et al.* [121] for sputtering from Ti-B targets of several compositions. These results also provide a possible reason for the apparent differences between sputtering from Ti_2AlC and Cr_2AlC targets [98,110,111], namely that the emission characteristics of the elements may vary depending on the target. This would not be surprising, since it is known that Ti_2AlC and Cr_2AlC have different bonding character [122,123,124,125,126].

The results from Ti-B [121] and Ti_3SiC_2 targets [113] are highly relevant not only to sputtering from MAX-phase targets, but to sputtering from *any* compound targets, especially those with large mass differences between the target constituents (e.g., most borides, carbides, nitrides, and oxides).

(2) Processes in the gas-transport phase. Gas-phase scattering can be an important cause of differences in composition between film and target. This effect can be modeled by, e.g., Monte Carlo techniques, but can conceptually be illustrated by the relevant example Ti_3SiC_2 [113]. A typical Ar pressure used in this type of sputtering process is ~ 0.5 Pa, where the distance to thermalization of C is similar to or longer than typical target-to-substrate distances, while the corresponding distances for Ti and Si are much shorter. In other words, at 0.5 Pa, transport of C is predominantly in the ballistic regime, i.e. C atoms travel in straight paths from the target to the substrate. On the other hand, Ti (and Si) are to a large extent thermalized, i.e., they have undergone a sufficient number of collisions to lose their initial energy and their motion is random. This has been demonstrated by energy-resolved mass-spectrometry measurements during sputtering from Ti_3SiC_2 and Ti_2AlC targets [111,127]. The gas-phase scattering effect is further evidenced by the pressure dependence of the composition, where higher Ar pressure results in higher relative Ti content and lower C content, as a consequence of increased C scattering.

(3) Processes at the substrate. First, the probability that an atom condenses on the substrate, the *sticking coefficient*, may be lower than unity. Often, the sticking coefficient is assumed to be unity, since it is very difficult to determine and the assumption tends to give correct results for metallic elements. For volatile species, however, this assumption is not valid. A useful qualitative indication of whether variations in sticking coefficient affect the film composition is that such variations result

in a temperature-dependent, but not pressure-dependent, film composition. (This “rule of thumb”, however, is not necessarily always valid [128], and should be used with some skepticism.) For MAX phases, evaporative loss of the A element during thin-film growth has been observed in several MAX-phase systems. Elements with low vapor pressure, e.g., Si and Ge, are typically only affected at deposition temperatures of 850 °C and higher [99,105,113]. Evaporation of Sn and Al, on the other hand, can be a dominant effect already at 700 °C [105,111]. However, deposition of Ti_2AlN has been demonstrated at a temperature as high as 1050 °C, which seems to have been made possible by having exactly the right composition, so that arriving Al atoms bond to Ti_2N slabs [129].

Secondly, *resputtering* may occur. Species condensed on the substrate can be resputtered by sputtering-gas ions or by energetic neutrals backscattered from the target. The former effect is particularly important when high bias voltages are applied to the substrate. Bias is normally applied to increase the ion bombardment and provide additional energy to the growing film (e.g., to improve the film density); however, if the bias is too high, the resputtering effect can be seriously detrimental. For Ti_3SiC_2 , there are preliminary indications that even a moderate bias (as low as 50 V) seems to have a detrimental effect [130]; however, it is not clear whether this effect is due to resputtering. Resputtering by energetic neutrals is especially important if the target contains heavy elements. When sputtering-gas ions (e.g., Ar^+) bombard the target, there is a probability (backscattering yield) that they will be backscattered as neutral atoms. The backscattered Ar neutrals can have a kinetic energies similar to that of the incident Ar ion, whose energy is determined by the target voltage (e.g., for a magnetron, an applied voltage of –500 V yields an incident-ion energy of 500 eV). If a large fraction of the incident Ar ions are backscattered, energetic Ar neutrals will bombard the growing film and affect its composition and microstructure.

A typical example is W-Ti films, where the presence of the heavy element W in the target leads to a large flux of energetic backscattered Ar neutrals. However, Ti is much more prone to resputtering by Ar than W; resulting in Ti-deficient films [131,132]. For MAX phases containing heavy M and/or A elements, resputtering by inert gas neutrals may be relevant and could possibly explain why some initial attempts [108,133] at synthesizing Ta-Al-C MAX-phase thin films were not successful, despite the fact that Ta_2AlC , Ta_3AlC_2 , and Ta_4AlC_3 all exist in bulk form (see section 4.3.1).

For the sake of completeness, it should be mentioned that in general, sputtering-gas ions or energetic backscattered neutrals are not the only possible species that can cause resputtering – any sufficiently energetic species will do. For example, thin-film growth of oxides often yields energetic negative oxygen ions [134,135,136,137,138,139,140,141,142,143].

In summary, there are many possible reasons why the film composition may differ from the nominal target composition when sputtering from compound targets. For MAX-phase targets, at least three important effects have been experimentally demonstrated: gas-phase scattering, A-element evaporation from the growing film at higher temperature, and differences in angular distribution among the target elements. It is very likely that the difference in energy distribution also plays an important role.

3.1.1.3 Reactive sputtering

Reactive sputtering of Ti_2AlN was first demonstrated by Joelsson *et al.* [144,145], who employed sputtering in an Ar/ N_2 mixture from a 2Ti:Al target to synthesize epitaxial single-crystal Ti_2AlN on MgO(111) substrates. Ti_2AlN has also been synthesized using reactive sputtering in N_2 from Ti and Al elemental targets [129,146,147,148]. These publications contain the explanation for why

relatively little work has been devoted to reactive sputter deposition of MAX phases, and why sputter-deposition of MAX nitrides is much less explored than the carbides: the process window (with respect to N_2 partial pressure) for deposition of single-phase Ti_2AlN is extremely narrow [129,145]. Nitrogen-deficient conditions typically yield phase-mixed films comprised of the inverse perovskite Ti_3AlN and the intermetallic phases $TiAl$ and Ti_3Al , while nitrogen-rich conditions yield the binary nitride TiN and/or the solid solution $(Ti,Al)N$.

Other attempts at reactive sputtering of MAX nitrides have been made in the Nb-Al-N [149] and Sc-Al-N systems [150]. The results are inconclusive with respect to MAX-phase formation, but a key result is the discovery of the new inverse perovskite Sc_3AlN [150,151,152].

In general, reactive sputtering of carbides is relatively common, typically with acetylene (sometimes methane) as the reactive gas. However, in light of the difficulty in synthesizing the MAX-nitrides by reactive sputtering, as well as the relative ease with which the MAX carbides can be grown by other sputtering techniques, there has been very little interest in employing reactive sputtering for synthesis of MAX carbides. Only a few unpublished attempts [108] have been made.

3.1.1.4 High-power impulse magnetron sputtering (HIPIMS)

A recent innovative PVD approach is to apply high-power pulses rather than dc or rf to the target [153]. This technique, introduced by Kouznetsov *et al.* [154] and possibly inspired by earlier work of Mozgrin *et al.* [155], is known as high-power impulse magnetron sputtering (HIPIMS) or high-power pulsed magnetron sputtering (HPPMS). A simple way of viewing HIPIMS is as a sputtering technique that emulates cathodic arc deposition, and (ideally!) has the advantages of both sputtering and cathodic arc deposition, but without their respective disadvantages. The high-power pulses applied to the target yield a highly ionized deposition flux similar to that obtained in cathodic arc

deposition [156,157,158,159,160,161]. Thus, HIPIMS allows control of the deposition flux and the ion-energy distribution through applied electric and magnetic fields [162], like cathodic arc deposition. Unlike the latter technique, however, HIPIMS does not suffer from macroparticles ejected from the cathode.

HIPIMS has been employed on the laboratory scale to deposit Ti-Si-C thin films from a Ti_3SiC_2 target [163]. It was demonstrated that the Nowotny phase $\text{Ti}_5\text{Si}_3\text{C}_x$ can be grown; however, Ti_3SiC_2 synthesis by HIPIMS remains to be shown. For HIPIMS deposition from a compound target, the degree of ionization is a particularly important parameter as it differs between elements (e.g., a few percent for C and up to 90 % for Ti). This means that the film structure and composition can be controlled to some extent by an appropriate choice of process parameters such as pressure, substrate inclination angle, and bias. Furthermore, compositional variations for films deposited on inclined substrates at different pressures show that the C content is strongly affected by gas-phase scattering, in parallel to results for dc sputtering. Given the fact that the ionization probabilities of Ti and Si are much higher than that of C, Ti and Si are attracted to the biased substrate to a much larger extent than C.

Very recently, initial attempts at HIPIMS deposition from Ti_3SiC_2 targets using industrial equipment [164,165,166] have been made.

3.1.2 Cathodic arc deposition

Compared to sputtering, cathodic arc deposition is a relative newcomer to MAX-phase synthesis. Rosén *et al.* [167] have reported synthesis of epitaxial Ti_2AlC using a pulsed cathodic-arc setup from elemental Ti, Al, and C cathodes at a substrate temperature of 900 °C. Preliminary work by Flink *et al.* [168] has investigated Ti_2AlN synthesis by reactive cathodic arc deposition from cathodes with a 2Ti:Al composition. Notably, the latter study allowed deposition of Ti_2AlN at a

substrate temperature of 500 °C, ~200° lower than has been reported for sputtering of Ti₂AlN. This indicates that the high degree of ionization (almost 100% for all species) of the deposition flux in cathodic arc deposition may provide the control of ion energy necessary to substantially decrease the deposition temperature (compared to sputtering) for MAX phases. Cathodic arc deposition of Ti₂AlC from a Ti₂AlC cathode has also been attempted; however, the initial results are inconclusive [169].

3.1.3 Pulsed laser deposition

The idea of using PLD for MAX-phase synthesis is appealing. Since the method produces species with significantly higher energy than sputtering and has the ability to maintain even very complex target stoichiometries, PLD has the potential to lower the process temperature for MAX-phase synthesis and to permit synthesis using a single MAX-phase target.

An indication of the possibility to synthesize MAX phases using PLD came from Phani *et al.* [170], who deposited Ti-Si-C films over the temperature range 25–600 °C. These films predominantly consisted of TiC and amorphous phases; however, an unidentified XRD peak at 44.5° 2 θ (Cu K α radiation) was observed for films deposited on steel substrates at 25, 200, and 400 °C. Phani *et al.* speculated that this peak could be due to Ti₃SiC₂ formation caused by diffusion of carbon into the steel substrate, thus achieving the correct stoichiometry for Ti₃SiC₂. However, Phani *et al.* also pointed out the inconsistencies with this speculation; primarily that the peak is *not* present at 600 °C, where more diffusion is expected. Further, the peak position did not fit to any Ti₃SiC₂ peak. Consequently, it is unlikely that the peak was due to Ti₃SiC₂. Nevertheless, the idea is the same as the “C sink” discussed in section 3.1.1.2, and is interesting because a substrate that can

accommodate excess C could potentially be a means of compensating for the off-stoichiometry often observed in sputter-deposition from C-containing compound targets.

Hu *et al.* [171] synthesized Ti-Si-C films using PLD from a Ti_3SiC_2 target at substrate temperatures of 100–300 °C. The films exhibited promising mechanical properties with a friction coefficient of ~ 0.2 . A controversy surrounding this paper [172,173] was the phase identification, where Hu *et al.* attributed two X-ray diffraction features to the $10\bar{1}2$ and 0008 peaks of Ti_3SiC_2 . These peaks, however, also fit the TiC 111 and 200 peaks, and the TEM images presented did not show the characteristic structure of Ti_3SiC_2 [172]. Most likely, Hu *et al.* did not synthesize Ti_3SiC_2 , but a nanocomposite TiC-based material similar to that reported by many other authors at low substrate temperature [25,26,170,174,175,176,177,178,179,180,181]. More recently, Lange *et al.* [182] employed PLD to synthesize Ti-Si-C thin films from a Ti_3SiC_2 target, and obtained mainly X-ray amorphous films (however, a small TiC peak was detected) despite the relatively high deposition temperature of 700 °C.

To conclude the discussion on PLD synthesis of Ti-Si-C materials, the method has some unique attributes that, in principle, provide the possibility to synthesize Ti_3SiC_2 at low temperatures. This has been attempted by some authors, but no unambiguous evidence of Ti_3SiC_2 formation in PLD films has been presented. Nevertheless, the method has potential and should be investigated further.

3.2 Chemical Vapor Deposition (CVD)

In 1972, Nickl *et al.* [183] published the first paper on CVD of a MAX-phase. They deposited Ti_3SiC_2 from a gas mixture of TiCl_4 , SiCl_4 , CCl_4 and H_2 . Later, CVD growth of Ti_3SiC_2 was also reported by Goto and Hirai [184], Pickering *et al.* [185], and Racault *et al.* [186]; the latter group

used CH₄ rather than CCl₄ as a carbon source. It is interesting to note that these authors discussed very early the exceptional thermal and mechanical properties of Ti₃SiC₂ and its potential as a soft ceramic coating. A general observation in these conventional CVD studies is that rather high temperatures (typically 1000-1300 °C) are required for the formation of Ti₃SiC₂. This is much higher than for magnetron sputtering (see section 3.1). Furthermore, it seems to be more difficult to obtain single-phase Ti₃SiC₂ films by CVD compared to PVD. In most CVD films, Ti₃SiC₂ coexists with other phases such as TiC, TiSi₂, SiC, and Ti₅Si₃C_x. This is possibly because of the higher deposition temperatures, but may also be an inherent problem in the CVD process. At present, it is unclear why such high temperatures are required for CVD of MAX phases. Possibly, the CVD process is affected by the presence of strongly adsorbed surface species that reduce the surface diffusion which is required to form the complex nanolaminated structure of MAX phases. Indications of such behavior for binary carbides have been observed in CVD of MoC [187].

An interesting observation in CVD of Ti₃SiC₂ is that Ti₃SiC₂ may be formed not only by the simultaneous deposition of all elements, but by a reaction between the gas and a solid phase such as TiC [183,185]. This concept, termed reactive CVD (RCVD), has been used by Jacques *et al.* [188] and Faikh *et al.* [189,190]. In this process, Ti₃SiC₂/SiC multilayer coatings were deposited by a sequential process at approximately 1100 °C. Initially, a thin SiC film is deposited, followed by a TiCl₄/H₂ pulse, and Ti₃SiC₂ is formed by a reaction between the gas and the SiC. The process can be repeated, leading to a Ti₃SiC₂/SiC multilayer coating. This type of reactive CVD has not yet been able to reduce the deposition temperature or to produce single-phase films, but the results are interesting and merit more attention. Another important future research direction is to synthesize MAX phases other than Ti₃SiC₂ by CVD.

3.3 Solid-state reactions

Solid-state reactions as a thin-film synthesis method can be broadly categorized into two groups: one based on film/substrate reactions and the other based on film/film reactions. For MAX phases, the most well-known example of the first category of reactions is Ti_3SiC_2 which is often found at the interface when Ti and SiC are in contact at higher temperatures, e.g., when Ti is used as braze material to bond SiC to SiC or in Ti-reinforced SiC metal matrix composites [3]. The most relevant example as a *thin-film* synthesis method is Ti_3SiC_2 synthesized by annealing of Ti-based contacts used as electrodes in SiC-based semiconductor devices [191,192,193,194]. Another example relevant to the semiconductor industry is Ti_2GaN which can form at the interface between Ti-based films on GaN substrates [195].

The second solid-state reaction category involves deposition of a film containing the three elements M, A, and X in the appropriate composition; the film should be in a metastable state, e.g., amorphous or an (artificial) multilayer. The deposition is then followed by annealing above the deposition temperature, to initiate transformation to the MAX phase. Examples include Ti/AlN multilayers [196], where the transformation to a phase-pure Ti_2AlN film was reported to occur as low as 500 °C, the transformation of TiN/TiAl(N) multilayers into (Ti,Al)N/ Ti_2AlN [197], and other TiN/Al-based multilayers [198]. There are also indications that a nominally amorphous Ti-Al-C film deposited below 200 °C can transform to Ti_2AlC when annealed at high temperature [199].

3.4 Thermal spraying

Thermal spraying techniques have only seen limited use for the MAX phases, although there is a patent on thermal spraying of 211 and 312 phases [200]. The main interest is to employ thermally sprayed MAX-phase coatings in corrosion-, oxidation-, and wear-resistant coatings. Recently, high-

velocity oxyfuel (HVOF) spraying has been demonstrated [201] for spraying of dense Ti_2AlC coatings from Ti_2AlC powder. The coatings contained mainly Ti_2AlC , with minority phases of Ti_3AlC_2 , TiC , and TiAl_x . Plasma spraying of powder mixtures of Ti, SiC and graphite has been reported to yield Ti-Si-C coatings with 15-19 vol. % Ti_3SiC_2 and a large fraction of, e.g., TiC_x and Ti_5Si_3 [202]. These techniques are potential processing approaches to fabricate Ti_2AlC and Ti_3SiC_2 as coatings on large engineering components. However, a remaining issue with thermal spraying of MAX phases is the ability to obtain sufficiently phase-pure coatings and to achieve the desired resistance to corrosion and oxidation.

4 Comparison of thin-film and bulk synthesis of MAX phases

This section addresses the relation between thin-film and bulk synthesis of MAX phases, and relevant theoretical work. We discuss aspects of bulk synthesis and investigations of structure and properties on bulk MAX phases; the emphasis is on correlating these studies to thin-film work. Section 4.1 briefly covers bulk synthesis methods for MAX phases. Section 4.2 discusses the relation between thin-film and bulk synthesis. Section 4.3 reviews the recent discoveries of new 312 and 413 phases, both in bulk and thin-film form, as well as the reasons why some hypothetical MAX phases do *not* appear to exist.

4.1 Bulk synthesis methods

A full review of bulk synthesis of MAX phases is beyond the scope of the present work. The early progress was partially covered in Barsoum's review from 2000 [3]; however, the focus was on property-structure correlations rather than synthesis methods. The progress in bulk synthesis of Ti_3SiC_2 during the last decade was recently reviewed by Zhang *et al.* [5]. Here, we will mention the most important methods and point the reader to relevant references. The seminal 1996 paper by Barsoum and El-Raghy [2] demonstrated hot isostatic pressing (HIP) as a method to obtain >95 % phase pure bulk Ti_3SiC_2 . While hot-pressing has remained an important method for bulk synthesis [203,204,205,206,207,208] for research purposes, pressureless sintering [209,210,211,212,213, 214,215] may be more commercially viable. Other methods for processing of bulk MAX phases are variations of self-propagating high-temperature synthesis [216,217,218,219,220], spark plasma sintering [221,222,223,224,225] or pulse discharge sintering [226,227,228,229,230,231], and solid-liquid reaction synthesis [232,233,234]. Recent innovative approaches to bulk synthesis include three-dimensional printing [235], the use of Al or Sn, respectively, as catalysts for growth of

Ti₃SiC₂ and Ti₃AlC₂ [210,236,237], and design of crystalline precursors for solid phase reaction synthesis [238].

4.2 Differences and similarities between bulk and thin-film MAX-phase synthesis

The fundamental difference between most bulk synthesis methods and the PVD methods used for MAX phases is that the former operate (or are assumed to operate) relatively close to thermodynamic equilibrium, while the latter proceed far from thermodynamic equilibrium. In this sense, the CVD and solid-state reaction approaches to thin-film synthesis (see sections 3.2 and 3.3, respectively) are more similar to bulk methods than to PVD.

For thin-film synthesis in general, the above-mentioned fundamental difference is important, because energy can be provided to the growing film by means other than temperature, e.g., by an energetic growth flux or ion bombardment. For MAX-phase thin film synthesis in particular, there are several potential advantages of this degree of freedom. One, it offers the opportunity to reduce the synthesis temperature of MAX phases substantially. Section 4.2.1 discusses the temperature ranges for MAX-phase thin film synthesis. Two, it offers the possibility of growing metastable phases, discussed in section 4.2.2. However, ion bombardment may have competing detrimental effects; this is reviewed in section 4.2.3.

4.2.1 Temperature ranges for MAX-phase synthesis

Here, we discuss the crucial issue of whether thin-film MAX phases can be deposited at low substrate temperature. The work on sputter-deposition of MAX phases has demonstrated that Cr₂AlC and V₂GeC can be synthesized at a relatively low temperature (450 °C), that Ti₂AlC and

Ti₂GeC can be grown at intermediate temperature (~700 °C), and that Ti₃SiC₂, Ti₃GeC₂, Ti₃AlC₂, and to an even larger extent, the 413 phases require synthesis temperatures in the range 800–1000 °C. All these temperatures are lower than the typical ranges used for bulk MAX-phase synthesis, and clearly indicate that the energetic atomic flux incident on the substrate does enable significant reduction of the formation temperature for MAX phases compared to bulk synthesis.

These results also indicate that the order of the MAX phase (211, 312, or 413) is important in determining the growth temperature. Larger unit cells require higher formation temperature, due to the longer diffusion length compared to smaller unit cells, and the corresponding need for thermal activation. As a general estimate, it can therefore be argued (with everything else equal) that 211 phases can be synthesized at lower temperature than 312 and 413 phases. A parallel to this general argument can be found in bulk synthesis, where for example Ti₃AlC₂ [239], Ta₄AlC₃ [240], and Nb₄AlC₃ [241] can be synthesized in relatively phase-pure form by annealing of Ti₂AlC, Ta₂AlC, and Nb₂AlC, respectively, at temperatures of 1400–1700 °C, which leads to an inter-conversion to higher-order MAX phases.

Furthermore, diffusion is related to bonding energies. Typically, the activation energy for surface diffusion on metals is 5-20% of the bonding energy [242], and we expect that the surface diffusion rates (or activation energies for diffusion) of species on the MAX-phase film are proportional to bonding energies. The M-C bonding energy decreases going from group 4 to 6 (e.g., from Ti to Cr). It should be pointed out, though, that the M-A bond strength may show a different behavior [243]. From this perspective, kinetics should favor M and C diffusion in MAX phases with group 5 and 6 transition metals (e.g., V and Cr). Therefore, the diffusion arguments and the experimental results combine to yield the conclusion that *211 phases based on group 5 or 6 transition metal carbides*

should require the lowest synthesis temperatures among the MAX carbides. For the nitrides, the question is more open, since MAX nitrides outside the TiN-based systems have not been sufficiently investigated.

In this context, it should be mentioned that some unsubstantiated claims of MAX-phase thin-film synthesis at low temperature (100-300 °C) have been made. The PLD work of Hu *et al.* [171], who incorrectly claimed to have synthesized Ti_3SiC_2 at 100 °C [172], was discussed in section 3.1.3. Very recently, Shtansky *et al.* [244] claimed to have synthesized Cr_2AlC by magnetron sputtering at 300 °C; this was based on an ambiguous electron-diffraction pattern which was directly contradicted by XRD. Some other groups have presented similar unsupported claims at conferences. The lowest reliable reported deposition temperature for MAX phases remains 450 °C for V_2GeC and Cr_2AlC [98,99].

The second aspect of temperature ranges for thin-film MAX-phase synthesis is whether there is an *upper* limit. Here, the main limitation seems to be the A element. Segregation and evaporation of the A element during thin-film growth has been observed or inferred in the Ti-A-C (A = Si, Ge, Sn, Al) MAX-phase systems, and in the V-Ge-C system. This effect is largely determined by the vapor pressure of the A element. This is supported by studies on decomposition of MAX-phases (cf., section 7). For example, during post-annealing, Si starts to evaporate from Ti_3SiC_2 thin films in vacuum at 1000–1160 °C [245,246], which is consistent with studies on bulk Ti_3SiC_2 in vacuum [247]. On the other hand, if the A element has a high vapor pressure, decomposition to MX can occur at much lower temperature, as demonstrated for Ti_2InC [248] and Ti_2AlN [147]. Note, however, that the effect of oxygen and the presence of a protective oxide, as well the difference in the actual length scales between bulk and thin film, are also important in decomposition studies. For

example, the decomposition temperature of bulk MAX phases is typically much higher than the 1000–1200 °C range, due to the formation of protective oxides.

There are indications that the limitation of A-element evaporation can be overcome by providing for sufficiently stoichiometric deposition conditions with respect to MAX phases. Persson *et al.* [129] demonstrated growth of Ti_2AlN at a substrate temperature of 1050 °C. Off-stoichiometric deposition conditions resulted in highly Al-deficient films; however, in a narrow process window, Ti_2AlN could be grown, suggesting that Al bonds to Ti_2N slabs in the MAX phases, thus overcoming the Al-desorption problem.

4.2.2 Metastable phases

Metastable materials are common in thin films. A standard example from the coating industry would be the solid solution $(\text{Ti,Al})\text{N}$ with the TiN NaCl-structure. $(\text{Ti,Al})\text{N}$ forms a metastable solid solution deep into the miscibility gap; the synthesis of this metastable phase is enabled by the fact that the PVD methods employed operate far from thermodynamic equilibrium. For the MAX phases, interest in growing metastable MAX phases was triggered by the theoretical prediction of the existence of Ti_4SiC_3 (discussed in section 2.6) which was suggested to be metastable, and the synthesis of Ti_4SiC_3 and Ti_4GeC_3 in the form of epitaxial thin films using magnetron sputtering. However, later theoretical work [45] suggested that Ti_4SiC_3 was actually stable rather than metastable. It would thus be worthwhile to attempt to synthesize Ti_4SiC_3 and Ti_4GeC_3 in bulk form.

4.2.3 Ion bombardment effects

As discussed above, the energetic growth flux in PVD has enabled MAX-phase synthesis at reduced temperature compared to bulk. Another established manner in thin-film processing to provide energy and momentum to the adatoms on the surface of the growing film is by ion bombardment,

most commonly by application of a substrate bias voltage. This parameter has been less thoroughly investigated than substrate temperature for MAX phases, but there are indications that a relatively low bias may have detrimental effect [130]. At bias above 40 V, a detrimental effect on Ti_3SiC_2 growth has been suggested [130]. This may be due to ion-induced reduction in A-element supersaturation by, e.g., stimulated desorption. At higher bias (~ 100 V), preferential resputtering or ion-bombardment-induced defects are expected [249] and would prevent the complex MAX-phase structure from forming.

4.3 Thin-film and bulk synthesis of new MAX phases

4.3.1 Recent discoveries of new MAX phases

Perhaps the most important example of an area in MAX-phase research where bulk synthesis, thin-film synthesis, and theoretical predictions have progressed together is the recent work leading to the discoveries of numerous new 312 and 413 phases. The majority of the MAX phases are 211 and it was long believed that the only 413 phase was Ti_4AlN_3 . Even in some recent papers, one can find erroneous statements of the type “there are only three 312 phases (Ti_3SiC_2 , Ti_3GeC_2 , and Ti_3AlC_2) and one 413 phase (Ti_4AlN_3)”. However, the theoretical prediction of the existence of Ti_4SiC_3 (discussed in section 2.6) triggered interest in experimental research aimed at discovering new MAX phases. Relatively soon, Ti_4SiC_3 and Ti_4GeC_3 could be synthesized in the form of epitaxial thin films using magnetron sputtering [45,46]. Still, at that time, it was generally believed that new MAX phases in general were metastable and could only be synthesized under nonequilibrium conditions such as magnetron sputtering with epitaxial stabilization. The breakthrough came from investigations on bulk synthesis in the Ta-Al-C system, where Ta_2AlC was previously the only known MAX phase. Around 2006, Ta_4AlC_3 was discovered independently by several groups [36,37,38,39,240,250], and Ta_3AlC_2 was first reported by Etzkorn *et al.* [39]. Initially, there was

some debate regarding the exact structure of Ta_4AlC_3 ; this debate was resolved by the finding [38] that Ta_4AlC_3 has two polymorphs (α and β , see section 2.2).

After the discovery of Ta_4AlC_3 , the related phases V_4AlC_3 (discovered in parallel by Etzkorn *et al.* and Hu *et al.* [251,252]), Nb_4AlC_3 (discovered by Hu *et al.* [241]), the solid solution $(\text{V,Cr})_4\text{AlC}_3$ (discovered by Zhou *et al.* [47]) , and very recently Ti_4GaC_3 (discovered by Etzkorn *et al.* [253]) have been synthesized in bulk, a fact that has led to the realization that the 413 group is much larger than initially believed. Several new 312 phases have also been reported. Other than Ta_3AlC_2 [39] mentioned above, Högberg *et al.* discovered the new phase Ti_3SnC_2 in 2006 [105], and Ti_3SnC_2 was later synthesized in bulk [254]. Very recently, V_3AlC_2 [108] and the solid solution $(\text{V,Cr})_3\text{AlC}_2$ [47] have been reported.

One important question remains, however: can the discoveries of all these new MAX phases help us improve the understanding of *why* they exist?

4.3.2 Why do some MAX phases exist and others not?

4.3.2.1 Intrinsic stability

The first aspect of whether a MAX phase – or any phase – can exist is its *absolute* or *intrinsic* stability. “Intrinsic stability” means that the Gibbs free energy of the structure is at a local minimum with respect to small deformations (lattice vibrations). Preliminary results from a very recent comprehensive computational study [255] for 240 M_2AX phases, including all hypothetical compositions and including W as the M element (normally, W is not listed among the M elements for MAX phases, since no W-containing MAX phases are known), indicated that ~20 M_2AX phases are intrinsically *unstable*. Among these phases, the ones containing W and Mo as the M element

dominated, which explains why there are no known W-containing MAX phases and only one with $M = \text{Mo}$. (These calculations did predict that Mo_2GaC , which does exist, is stable, and the calculated lattice parameters were relatively close to those determined experimentally by Nowotny in the 1960s.) However, these unstable Mo- and W- containing M_2AX phases seem to be the exception rather than the rule; the vast majority of M_2AX phases *are* intrinsically stable.

Further, there is the concept of (intrinsic) mechanical stability, which means that a crystal structure fulfils the Born stability criterion that the elastic energy density is a positive definite quadratic function of strain; this criterion can be formulated mathematically in terms of the elastic constants c_{ij} . The intrinsic mechanical stability has rarely been discussed for the MAX phases, but a good example is a recent calculation for Nb_4AlC_3 [256].

4.3.2.2 Composition gap among the Ti_2AC phases

There is a “composition gap” for M_2AC phases with group 15 A-elements. For example, the Ti_2AC phases with A elements in group 13 (Al, Ga, In, and Tl) or 14 (Ge, Sn, and Pb) exist (the exception Ti_2SiC is discussed in section 4.3.2.3) and so does Ti_2SC , i.e., with a group-16 A element. However, no Ti_2AC phase with group-15 A elements (P, As, Sb, Bi) appears to exist. Hug [22] explained this based upon DFT calculations which showed that the three hypothetical phases Ti_2SiC , Ti_2PC , and Ti_2AsC are intrinsically stable and probably thermodynamically metastable (see section 4.2.2). This result is consistent with calculations by Palmquist *et al.* [45] that also indicated that Ti_2SiC should be stable or near the limit of stability.

Hug showed that the composition gap originates from electronic structure of the Ti_2AC phases ($A = \text{Al, Si, P, S, Sn, Ga, In, Ge, As, Pb, and Tl}$). Among these A elements, all but Si, P, and As give rise to stable compounds whose bonding is driven by the hybridization of Ti d -A p and Ti d -C p . The

Ti d -A p hybridized states are located just below the Fermi level, while the Ti d -C p hybridized states are at lower energies. The Ti d -A p bands are driven to lower energy as a function of the p -state filling of the A element (i.e., going to the right in the periodic table). A transition occurs for the group-15 elements, P and As, whose p levels match those of C. This transition provides an explanation for why the phases Ti_2PC and Ti_2AsC are not observed. P and As would link more favorably with C than with Ti, rendering the MAX-phase structure much less stable. Finally, for Ti_2SC , the Ti d -S p bonds are at lower energy and are stiffer than the Ti d -C p bonds, a fact that makes this compound stable, but also gives it rather different properties compared to the other Ti_2AC phases (see section 6).

4.3.2.3 Can Ti_2SiC exist?

Returning to the archetypic M-A-X system of Ti-Si-C, we now discuss the hypothetical phase Ti_2SiC . Since Ti_3SiC_2 and Ti_4SiC_3 exist, it would be compelling to expect that Ti_2SiC can be synthesized as well. The first point is that the 211 stacking sequence does exist in the Ti-Si-C system, in the “523” structure (see section 2.3). However, while intrinsically stable, the Ti_2SiC phase has not been reported. The reason for this is presumably because the possibility of formation of a compound depends on competition with other phases in the phase diagram (see section 2.1.2).

In the Ti-Si-C case, Ti_4SiC_3 is on the tie line between Ti_3SiC_2 and TiC , a simply balanced system. In contrast, Ti_2SiC lies in a three-phase region, and competes with Ti_3SiC_2 , TiSi_2 , and Ti_5Si_3 . Calculations of the phase stability of Ti_2SiC [45,22] have indicated that its formation should actually be favored by the thermodynamic competition with the other three competing phases, although the energy difference ΔE is small (8 meV/atom [45]). This result is in contradiction to the fact that Ti_2SiC has not been synthesized; there are at least two reasons for this contradiction. One, the calculated energy difference between the competing phases is based on Ti_5Si_3 without C

incorporation. It is likely that ΔE would change sign if the calculations had been performed for $\text{Ti}_5\text{Si}_3\text{C}_x$ since incorporation of C is known stabilize the Ti_5Si_3 phase. Similar arguments apply for several predicted hypothetical MAX phases, e.g., Nb_3SiC_2 , V_2SiC , and V_3SiC_2 [90,91,93], that have been predicted to be stable or nearly stable, and one might therefore expect them to be possible to synthesize at least by nonequilibrium methods such as magnetron sputtering. These predictions have not been corroborated by experimentalists, who have been unable to synthesize the V-Si-C or Nb-Si-C MAX phases [104].

Seemingly, the issue here is that the assumptions behind these predictions do not accurately portray reality: the competing silicides are stabilized by incorporation of C (which is not included in the calculations). Another issue is that many phase diagrams are not sufficiently well known. At least in the (Ti,V)-Si-C systems, unknown phases have showed up during attempts at thin-film synthesis of Ti_2SiC [257] and V_2SiC [258]. The unknown phase that appeared in the Ti-Si-C system was tentatively suggested, based on electron diffraction, to be a tetragonal Ti_2Si phase, with $a = b = 2.596 \text{ \AA}$ and $c = 13.56 \text{ \AA}$; however, this structure could not be confirmed by XRD. The problem with these insufficiently charted phase diagrams is that they are the assumptions behind phase-stability calculations, which consequently do not realistically simulate the actual thermodynamic competition situation.

In conclusion, the hypothetical MAX phase Ti_2SiC is intrinsically stable, but it has not yet been synthesized, due to thermodynamic competition with other phases in the complex Ti-Si-C phase diagram. The same argument applies to other $\text{M}_{n+1}\text{SiC}_n$ phases that have been predicted, but not synthesized (e.g., Nb_3SiC_2 , V_2SiC , and V_3SiC_2).

4.3.2.4 Outlook: 312 and 413 phases

So far, the discussion has focused on the 211 phases, simply because there are many more 211 phases than 312 or 413 phases. Today, however, we begin to realize that the 312 and 413 groups are much larger than previously thought. At least six 312 phases and seven 413 phases exist, and more can be expected to be found. A key contribution to future research on MAX phases would therefore be to perform similar systematic theoretical studies for hypothetical 312 and 413 phases as were done for 211 phases. This would enable experimentalists to narrow the search pattern for new 312 and 413 MAX phases.

5 Nucleation and growth of MAX phases

5.1 Growth mode as a function of temperature

As a representative example of MAX-phase nucleation and growth, let us look at the growth of Ti-Si-C films onto single-crystal substrates. Figure 7, adapted from Emmerlich *et al.* [101], shows X-ray diffractograms in the 2θ range between 34° and 42° for 200-nm-thick Ti_3SiC_2 films deposited by sputtering from elemental targets (see section 3.1.1.1) at different substrate temperatures, T_s , onto $\text{Al}_2\text{O}_3(0001)$ single-crystal substrates. Epitaxial growth was obtained for $T_s \geq 750^\circ\text{C}$ with the best crystal quality achieved for $T_s = 900^\circ\text{C}$. Films deposited at $T_s = 700^\circ\text{C}$ contained mainly TiC_x , with a significant amount of (0001)-oriented (observed in TEM, not shown here) Ti_3SiC_2 inclusions [101]. Below $T_s = 650^\circ\text{C}$, the XRD peaks from Ti_3SiC_2 are not present. Instead, the intensity of the TiC_x 111 peak is stronger at $T_s = 650$ and 700°C than at $T_s \geq 750^\circ\text{C}$. The peak at $34.7^\circ 2\theta$ comes from $\text{Ti}_5\text{Si}_3\text{C}_x$; this phase is typically present also in the range $350\text{--}650^\circ\text{C}$. Deposition of Ti-Si-C films in the temperature range below 300°C yields a nanocomposite or nanocrystalline structure with the crystalline TiC_x phase and, depending on film composition, usually amorphous (or at least X-ray amorphous) phases such as SiC. Such nanocomposite thin films represent an important research area in its own right, and have seen widespread use in mainstream applications as electrical contacts (see section 2.1.3.6 and section 8), but are not reviewed here. See, e.g., Refs. 25, 26, and 179.

The main trends in these results for the Ti-Si-C system are typical for MAX-phase thin films grown on single-crystal substrates. At high temperature, epitaxial growth of a nearly phase-pure MAX phase is typically obtained, provided that the substrate is suitable. A reduction in temperature yields polycrystalline MAX-phase growth, often (depending on composition) with competing phases such

as $\text{Ti}_5(\text{Si}, \text{Ge})_3\text{C}_x$ in the Ti-(Si,Ge)-C system [46,101] or the inverse perovskite Ti_3AlC in the Ti-Al-C system [48]. Further reduction in temperature yields the binary carbide as the main crystalline phase, either in a nanocomposite structure together with amorphous phases [25] or in solid solution [48]. Low-temperature films differ among M-A-X systems. For example, Al tends to dissolve in TiC forming a metastable solid solution (Ti,Al)C [48], while the solubility of Si in TiC is much lower; thus, the latter system tends to yield nanocrystalline TiC together with amorphous phases (e.g., SiC) [25,101].

Growth of MAX-phases on polycrystalline substrates is similar to that on single-crystal substrates with the obvious exception that global epitaxial growth is not obtained. Instead, the temperature range in which polycrystalline growth of relatively phase-pure MAX phases can be obtained is increased. Examples include deposition of Ti_3SiC_2 on bulk Ti_3SiC_2 (which gives *local* homoepitaxial growth [102]) and Cr_2AlC onto steel [98]. One important aspect that has not been investigated for MAX phases is whether local epitaxial growth can also be obtained for important technological substrates such as steel (from a technological point of view, local epitaxy would be important for adhesion).

5.2 Nucleation

5.2.1 Nucleation layers

Some of the initial work [45,89,100,101] on epitaxial growth of MAX phase thin films suggested the importance of using a seed layer to promote nucleation of the MAX phase. Typically, a $\text{TiC}_x(111)$ seed layer was employed for the TiC-based MAX phases. The idea behind using a TiC seed layer is that the $\text{Ti}_3\text{SiC}_2\{0001\}$ and $\text{TiC}\{111\}$ planes can form epitaxial and coherent interfaces [259]. This follows from the isomorphism of the $\text{TiC}(111)$ and the $\text{Ti}_3\text{SiC}_2(0001)$

surfaces and the corresponding strong tendency for basal-plane-oriented growth of Ti_3SiC_2 on $\text{TiC}\{111\}$ planes. $\text{TiC}(111)$ provides a crystallographic template upon which Ti_3SiC_2 can grow.

Figure 8, adapted from Emmerlich *et al.* [101], shows an example of the use of seed layers for MAX phases. For the case of an intentionally deposited TiC_x seed layer [see Fig. 8(a)], the nucleation of Ti_3SiC_2 was delayed by 10–20 nm as the TiC_x phase continued to grow (the horizontal line across the image represents the onset of the Si codeposition). Thus, the 312 phase is *not* nucleated instantly or simultaneously across the surface of the seed layer. Fig. 8(b) shows a Ti_3SiC_2 film deposited *without* a TiC_x seed layer. TiC_x grows for ~ 10 nm before the onset of Ti_3SiC_2 formation. Similar to what can be seen in Fig. 8(a), nucleation is not simultaneous across the sample. Thus, Ti_3SiC_2 growth tends to yield a TiC_x “incubation layer” even when no intentional seed layer is deposited. However, there are numerous examples where no incubation layer is found, e.g., Ti-Al-C [48] and V-Ge-C [99]. These observations indicate that while a seed layer can promote MAX-phase nucleation, it is not necessary as long as two conditions are fulfilled: one, that the substrate is epitaxially related to the MAX phase and two, that the A-element supersaturation is sufficient. TiC seed layers or “buffer” layers, may however have other benefits for promoting MAX-phase formation: a substoichiometric $\text{TiC}_x(111)$ buffer layer has the ability to accommodate the excess C in the Ti-Si-C deposition flux from Ti_3SiC_2 targets (cf. section 3.1.1.2).

5.2.2 Homogeneous or heterogeneous nucleation?

In classical nucleation theory, *homogeneous nucleation* means that the probability for nucleation is the same at any point in a given volume. When the term is used in thin-film growth, the concept normally refers to homogeneous *surface* nucleation, i.e., that the probability for nucleation is the same at any point on a given *surface*. In principle, the nucleation of a MAX phase may be either homogeneous or heterogeneous; for example, buildup of a Si reservoir on the growth surface

[101,113] increases the driving force (Si supersaturation) for homogeneous nucleation. However, in practice, in epitaxial growth of MAX phases, nucleation occurs heterogeneously over a surface, i.e., the probability for a nucleation event is higher at preferential nucleation sites such as steps, edges, kinks, and ledges. The latter are typically due to the presence of screw dislocations. Surface defects act as suitable heterogeneous nucleation sites.

5.3 Growth mode

During epitaxial growth of MAX phases, the growth mode is approximately step-flow, in which the growth rate along the c axis much lower than the in-plane growth rate. Figure 9, adapted from Emmerlich *et al.* [101], shows AFM images of the surface of a typical Ti_3SiC_2 film deposited at 900 °C. In overview [Fig. 9(a)], growth mounds around screw dislocations are seen. The hexagonal crystal shape is evident from the exposed low-energy faces (0001) and $(10\bar{1}0)$. Flat terraces and surface steps are seen at higher resolution in Fig. 9(b). The observed step heights can be divided into two categories with heights of approximately one unit cell and half-unit cells, respectively, i.e., the growth mode is lateral (step-flow) by the propagation of half- or full-unit cells. Two half-unit-cell layers growing on top of each other eventually merge to form a full-unit cell.

These observations are also relevant to the growth of bulk MAX phases. The hexagonal crystal shape can be observed in as-grown bulk MAX phases. An example is shown in Fig. 10, adapted from Luo *et al.* [234], who synthesized Ti_3SiC_2 by solid-liquid reaction. These “freely grown” Ti_3SiC_2 grains [234] are on the micrometer scale corresponding to the early stages of growth of bulk single crystals. In general, the growth morphology of a crystal is determined by the relative growth rates of all possible faces, i.e., the faces with the lowest growth rate will determine the morphology. These experimental results are consistent with the simulated [260] crystalline shape from nucleation

and growth theory. Further, lower growth rates along c than along a axes is general for the MAX phases, and the reason why bulk synthesis of MAX phases often yields grains with a platelike appearance [261,262,263].

A related observation is that of tilted growth in MAX-phase epitaxy. As shown in Fig. 11, reproduced from Emmerlich *et al.* [101], growth of Ti_3SiC_2 on $\text{MgO}(100)$ substrates results in a preferred $\langle 10\bar{1}5 \rangle$ out-of-plane orientation. Pole figures of the Ti_3SiC_2 0008 and TiC_x 111 peaks (Figs. 11 (a) and (b)) show that Ti_3SiC_2 basal planes grow parallel to $\text{TiC}(111)$ planes. The atomic force microscopy (AFM) image in Fig. 11(c) shows two sets of orthogonal parallel basal-plane stacks. The cross-sectional TEM image in Fig. 11(d) shows that grains nucleate in four different directions on the fourfold-symmetric $\text{TiC}_x(100)$ seed layer. Voids form at the substrate or when tilted basal planes grow into each other. Similar observations were made for local homoepitaxial growth of Ti_3SiC_2 onto bulk Ti_3SiC_2 [102]. The reason for the observations of tilted growth is that Ti_3SiC_2 grown on TiC (or any NaCl-structured substrates lattice-matched to $\text{TiC}(111)$) will be oriented in such a way that the epitaxial relations between TiC and Ti_3SiC_2 (i.e., out-of-plane: $\text{Ti}_3\text{SiC}_2(0001)//\text{TiC}(111)$ and in-plane $\text{Ti}_3\text{SiC}_2(2\bar{1}10)//\text{TiC}(10\bar{1})$) are maintained. These crystallographic orientation relationships are common for other MAX phases with respect to their MX counterparts [102,106,147].

With respect to the tilted growth phenomenon, it would be interesting to investigate whether it is possible to grow MAX-phase thin films with the c axis oriented in-plane. This has been done for many other materials, such as perovskite oxides, Al_2O_3 and $\text{Ca}_3\text{Co}_4\text{O}_9$, which, however, have much

shorter c axes than the MAX phases. Growth of MAX phases with the c axis in-plane would require the proper choice of substrate to obtain the necessary lattice match to the long c axis.

5.4 Random stacking

Palmquist *et al.* observed via TEM that a Ti_3SiC_2 film can include areas with apparently random stacking sequences of the MX building blocks [45]. Fig 12, adapted from Palmquist *et al.* [45], shows a TEM image in which the MX blocks with three metal layers are replaced by a random sequence of MX blocks with 4, 5, and 10 metal layers. It is possible that the random stacking has been caused by small fluctuations in the flux of incoming atoms during the film growth process. Possibly, such random stacking sequence areas may be common, depending on the growth situation. This is supported by DFT calculations of the cohesive energies of different MAX-phases in the Ti-Si-C system [45]. The calculations show that the extra energy required to insert a Si layer in TiC is more or less independent of the amount of Si layers. This means that the cohesive energy for a 312 phase is about the same as the energy of a 50:50 mixture of 413 and 211. Consequently, the extra energy required to form small regions of a deviated stacking sequence is very low. This may explain both the formation of random stacking areas shown in Fig. 12, as well as the intergrown structures described in section 2.3. However, the calculated cohesive energies of the different MAX phases in the Ti-Al-C system [48] are strongly dependent on the number of inserted A layers; i.e., the average energy required to insert an Al layer is smaller for lower values of n in $\text{Ti}_{n+1}\text{AlC}_n$ (Ti_2AlC is more stable than Ti_3AlC_2). This prediction is consistent with the experimental observation that random stacking sequences and “523” structures are only rarely observed as local deviations in stacking sequence in Ti-Al-C MAX phases thin films [48], since it is energetically less favorable to form random stacking sequences in the Ti-Al-C system than in, e.g., the Ti-Si-C system.

5.5 Artificial MAX structures

The results in the previous sections suggest that it should be possible to control the stacking sequence and design new MAX phases with an artificial stacking. In a wider sense, it has been demonstrated that such artificial structures can be obtained. Emmerlich *et al.* [101] have shown that if the Si flux is interrupted during thin film growth of Ti_3SiC_2 , pure TiC starts to grow epitaxially on top of Ti_3SiC_2 . When Si is added again, Ti_3SiC_2 continues to grow yielding a coherent region of TiC inside the MAX-phase. Wilhelmsson *et al.* [264] used this principle to form artificial nanolaminates (cf. section 2.1.3.1) of $\text{Ti}_3\text{SiC}_2/\text{TiC}_{0.67}$ with periods of 4 – 30 nm. The periodicity depends on how rapidly the A-atom fluxes can be shut off and turned on; in principle, nanolaminates with periodicities of less than ~ 1 nm should be possible to obtain. Therefore, an important future research task would be to attempt to synthesize artificial MAX-phase structures with stacking sequences not observed in normal growth processes. One example of such a structure would be the elusive phase Ti_2SiC (cf. section 4.3.2.3); another would be “higher-order” MAX phases, i.e., $\text{M}_{n+1}\text{AX}_n$ phases with $n > 3$.

6 Properties of MAX phases

This section reviews the electrical (6.1), mechanical (6.2) and tribological (6.3) properties of the MAX phases. The two latter sub-sections provide only a short summary of the main features, together with a discussion of the relationship between properties in bulk and thin-film form, since the mechanical properties of bulk MAX phases were previously reviewed comprehensively by Barsoum [3,265,266] and Zhang *et al.* [5]. Our emphasis is on electrical properties, especially conductivity. We discuss the relationship between electrical properties in thin-film and bulk form (in particular property anisotropies) and correlate these to theoretical studies. The emphasis is to summarize the present understanding of the dependence of macroscopic properties of MAX phases on *intrinsic* (e.g., electronic band structure) and *extrinsic* (microstructure, defects, and impurities) structural features.

We begin with a simple intuitive picture, followed by a discussion based on the free electron model and theoretical calculations of the electronic band structure. As we review in more detail below, both of these approaches are useful and essential to understand the electronic structure and electrical properties of MAX phases. Nevertheless, they fail to give an accurate picture; most importantly, the common statement (which originates from the free electron model) that MAX phases with higher density of states (*DOS*) at the Fermi level (E_f) should be more conductive is oversimplified and *not* consistent with experiments. We end by discussing a more refined picture of conduction in MAX phases and the need for improved understanding.

6.1 *Electrical properties*

6.1.1 Compensated conduction

Many MAX phases are compensated conductors, i.e., both electrons and holes contribute in approximately equal number to electrical conductivity. This is evidenced by measurements of the Hall and Seebeck coefficients, where the measured results tend to fluctuate around zero and give either slightly positive or slightly negative values. Such fluctuations can only occur for compensated conductors. There are exceptions; for example, Ti_3AlC_2 and Ti_4AlN_3 are primarily hole conductors [3], and Ti_2SC [267] is mainly an electron conductor.

6.1.2 Electrical conductivity

For the simplest qualitative picture of electrical conduction in MAX phases, let us look at the example of the Ti-A-C systems. The binary carbide TiC, as well as the other transition-metal carbides, is a typical ceramic with predominantly covalent bonding. The electronic-transport mechanism, however, is that of a metal, i.e., electric charge is transported via conduction electrons. The concentration of conduction electrons is low, and the resistivity of TiC is relatively high, about $200 \mu\Omega\text{cm}$, depending on composition. If A layers are inserted to form the MAX structure, the electrical resistivity is reduced by an order of magnitude. The difference in conductivity can be attributed to the presence of Si or Ge, which weakens the Ti(1)-C bonds and thus enhances the relative strength of the metallic Ti(1)-Ti(1) bonds within the basal planes. Consequently, a material with a stronger metallic character, and hence higher conductivity than TiC, is obtained. According to this reasoning, the more A layers that are inserted into the MAX structure, the higher the conductivity. This argument is corroborated by data from the Ti-(Si,Ge)-C systems; Ti_2GeC is a better conductor than Ti_3SiC_2 and Ti_3GeC_2 , which in turn are better conductors than Ti_4SiC_3 . This intuitive picture of electrical conduction in MAX phases is useful. However, in many aspects it is

too simplistic, as it is in apparent contradiction to the nitrides: in contrast to TiC, the binary nitride TiN is a better conductor than any MAX phase. Ti₂AlN is a reasonably good conductor, and Ti₄AlN₃ is a semimetal. The intuitive reasoning is also contradicted by the fact that, e.g., Ti₃AlC₂ and Ti₂AlC have nearly equal conductivities.

A first step towards insight into the electrical properties of MAX phases is therefore to study their band structure. An indication of the conductivity of a material is given by the density of states at the Fermi level, since in the free electron model, the electron concentration is proportional to $DOS(E_f)$. In turn, the conductivity is proportional to the electron concentration multiplied by the electron mobility. Thus, a material with high $DOS(E_f)$ should be a good conductor. In comparison, for an insulator, $DOS(E_f)$ is zero, since the Fermi level is inside a bandgap. To return to the example of TiC, $DOS(E_f)$ is ~ 0.08 states/(eVcell). In comparison, DFT calculations yield reported $DOS(E_f)$ values of 4.38 states/(eVcell) for Ti₃SiC₂, 4.65 states/(eVcell) for Ti₃GeC₂ [268], and 4.07 states/(eVcell) for Ti₃SnC₂ [269]. These data are consistent with measured conductivities and with the oversimplified picture given above. For the reasons discussed below, however, the argument that MAX phases with higher $DOS(E_f)$ should be better conductors is *not* correct.

Nevertheless, this type of calculation is very useful because it provides information not only on absolute values of density of states, but also *what* states contribute to $DOS(E_f)$ and to electrical conduction. In most MAX phases, conduction is primarily, or almost exclusively, via the M *d* states. This is best understood from the examples of the Ti₃(Si,Ge,Sn,Al)C₂ systems. Figure 13 shows the calculated total and partial density of states for Ti₃AlC₂ and Ti₃SiC₂, adapted from Ref. 268. The densities of states for these two phases are very similar to each other. The dominant contribution to $DOS(E_f)$ comes from the Ti *3d* electrons. However, one key difference is observed:

for Ti_3AlC_2 , $DOS(E_f)$ is 3.72 states/(eVcell) and corresponds to a local *minimum* in the density of states, while for Ti_3SiC_2 , $DOS(E_f)$ is 4.38 states/(eVcell) and corresponds to a local *maximum* in the density of states. A local maximum in the density of states at the Fermi level is to a first approximation often correlated to a degree of structural instability [22], since a dip corresponds to a separation between bonding and antibonding states. This approximation seems to be too simplistic to be fully valid for the MAX phases, since it is not consistent with fact that Ti_3SiC_2 is stable.

The local maximum at the Fermi level observed for Ti_3SiC_2 and Ti_3GeC_2 corresponds specifically to a local maximum in the density of the Ti(2) $3d$ states (where Ti(2) refers to the Ti atoms at $4f$ Wyckoff positions that bond to both A and C, while Ti(1) denotes Ti atoms at $2a$ Wyckoff positions that bond exclusively to C; cf., Table 2). Such a maximum is not observed for Ti_3AlC_2 . The density of states for Ti_3GeC_2 is almost identical to that of Ti_3SiC_2 , although with a slightly higher value of $DOS(E_f)$, 4.65 states/(eVcell) [268]. These predictions are consistent with experimental data from soft X-ray emission spectroscopy studies of Ti_3AlC_2 , Ti_3SiC_2 , and Ti_3GeC_2 films [270]. The theoretical results indicate that, although the Ti d states give the dominant contribution to $DOS(E_f)$, the A element does affect $DOS(E_f)$ through mixing between Ti $3d$ and A p states. Furthermore, the difference in valence electron configuration between A elements in groups 13 (Al) and 14 (Si, Ge) respectively, is important, while the difference is limited for A elements within the same group.

After this discussion of the Ti_3AC_2 systems, let us now continue with the Ti_2AC phases. Table 3, adapted from Ref. 22, shows calculated values of $DOS(E_f)$ for the Ti_2AC phases. $DOS(E_f)$ is a function of the valence electron concentration of the A element: for the group 13 A elements (with s^2p valence electron configuration), $DOS(E_f)$ is in the range 2.35–2.67 states/(eVcell), while for the Ti_2AC phases with A-element s^2p^2 valence electron configuration (i.e., the group 14 elements Ge,

Sn, and Pb), $DOS(E_f)$ is ~ 3.8 states/(eVcell) for A = Ge, Sn and reaches as high as ~ 4.7 states/(eVcell) for Ti_2PbC . For all these phases, the Fermi energy is found in a local minimum between a Ti $d - A p$ hybrid and an unfilled Ti d band; the increase in $DOS(E_f)$ is due to the filling of the p band increases with increasing valence electron concentration (i.e., moving to the right in the periodic table).

The hypothetical phases Ti_2PC and Ti_2AsC were predicted to have even higher $DOS(E_f)$, but are much less stable, as discussed in section 4.3.2.2. However, for the group 16 A element, S, which has an s^2p^4 valence electron configuration, $DOS(E_f)$ is dramatically lower, about 1.5 states/(eVcell), the same result as obtained by Du *et al.* [271]. This reduction in $DOS(E_f)$ is most likely due to an inversion of the energy hierarchy, i.e., the Ti $d - S p$ hybrid is lower than the Ti $d - C p$ hybrid bonds. All these $DOS(E_f)$ data are qualitatively consistent with measured resistivity values for the Ti_2AC phases, which show the same trend, i.e., Ti_2GeC (15-20 $\mu\Omega cm$ [272]) has the lowest resistivity and Ti_2SC ($>50 \mu\Omega cm$ [267]) has the highest, with Ti_2AlC (38 $\mu\Omega cm$ [3]) in between (data for Ti_2PbC are not available in the literature due to the difficulty in synthesis). Therefore, the reasoning that the conductivity increases with $DOS(E_f)$ would appear to be valid thus far.

However, since the M d states are responsible for conduction in the MAX phases, one would expect that the more d electrons in the M element, the better the conduction. This is not what is observed. Moving right in the periodic table from Ti_2AlC (group 4 M element), the p states become partially filled in V_2AlC (group 5 M element), which does not significantly affect the conductivity [273]. However, in Cr_2AlC (group 6 M element), the hybridized M $d - A p$ states become primarily filled [274], leading to a much *lower* conductivity despite the higher $DOS(E_f)$ [273,275]. This is where the argument that the conductivity should increase with $DOS(E_f)$ fails. The reason is that the

conductivity is not proportional to the density of states, but to the carrier concentration multiplied by the carrier mobility.

For compensated conductors, the conductivity σ is thus given by $\sigma = (n\mu_e + p\mu_p)e$, where n and p are the electron and hole concentrations, μ_n and μ_p are the electron and hole mobilities, respectively, and e is the charge of the electron. The mobility of charge carriers is related to the electron-electron and electron-phonon collision terms. For many transition metals (according to Mott theory), the mobility is actually *inversely* proportional to $DOS(E_f)$. Since the main contribution to the conduction in MAX phases comes from the M atoms, it would be reasonable to expect a similar behavior for the MAX phases (note, however, that this argument assumes isotropic mobility, and is therefore only applicable to randomly oriented bulk samples). Although this assumption is somewhat simplified, it is supported by experimental determination of carrier mobilities in MAX phases [275, 276]. Thus, even if one were to accept the assumption that the carrier concentration is proportional to $DOS(E_f)$, as expected for compensated conductors, the conductivity would be *independent* of $DOS(E_f)$. Even that assumption, however, is not supported by experimental data for MAX phases [277], and should be used with care.

Another important issue is: how do we know that that calculated densities of states are valid? While the calculations are reliable for the most-studied MAX phases, the Ti-based 211 and 312 carbides, there are a number of problems with theoretical studies of other MAX phases. Several examples exist, such as α -Ta₄AlC₃ [41,53,278], for which calculated values of $DOS(E_f)$ can differ by as much as much as 50% for the same MAX phase between different calculations. There is also the question of correlating calculated $DOS(E_f)$ values with experiments. Measurements of the heat capacity can be used to experimentally determine the $DOS(E_f)$, since the coefficient, γ , for the electronic heat

capacity is proportional to $DOS(E_f)$. For some MAX phases, such measurements performed on bulk samples match the theoretical predictions [3]; however, there are some major contradictions in the literature, e.g., V_2AlC , Cr_2AlC , and Cr_2GeC [276,279]. For V_2AlC , the measured $DOS(E_f)$ is 7-8 states/(eVcell) compared to the predicted values of 4-5 states/(eVcell). For Cr_2AlC and Cr_2GeC , measured $DOS(E_f)$ values are in the range 15-22 states/(eVcell) [279], 2-3 times higher than the predicted values.

An even more critical problem is that no part of the discussion above accounts for anisotropy. The calculated band structures of all MAX phases, however, are highly anisotropic, which is hardly surprising given their highly anisotropic crystal structure. According to calculations, many MAX phases do not have bands that cross the Fermi level in the c direction [280,281] (some do, e.g. Ti_2AlN [281]). Therefore, one might expect large, even order-of-magnitude differences in conductivity along the c and a axes. However, a few very recent experimental studies have suggested that the anisotropy in the conductivity is rather limited. A comparison of data for Ti_2GeC thin films and bulk samples and an estimate employing an effective medium model yielded a conductivity ratio of 1.6 between the c and a axes [282]. A local-probe electron energy-loss spectroscopy (EELS) determination of the dielectric function followed by semiclassical Drude-Lorentz modeling to obtain the conductivity [283] indicated that the anisotropy in conductivity is a factor of 2–2.5 for Ti_2AlC and Ti_2AlN .

An approach to directly probe the anisotropy in the electronic structure is polarization-dependent soft x-ray emission spectroscopy. A recent measurement for V_2GeC [284] showed strong anisotropy for the Ge states far below the Fermi level, but limited anisotropy for the V $3d$ states that provide the main contribution to electrical conductivity.

Although few, these experimental results suggest that the anisotropy in electrical conductivity is rather limited in the MAX phases, perhaps within at most a factor of approximately two. These observations seem contradictory to the strong anisotropy predicted by theory for many MAX phases, and this is yet another indication that any connection between the band structure and the conductivity must be made with great care. Furthermore, some experimental studies actually suggest that the *c*-axis conductivity for Ti_2GeC [282], Nb_2AlC [109], and Ti_2AlN [283] might be *higher* than the in-plane conductivity. This suggestion could very well be correct (cf., section 6.1.3), but is nevertheless counterintuitive and in apparent contradiction to the theoretical band structure.

These key contradictions in the literature show that electrical properties, and especially anisotropy, of the MAX phases are not satisfactorily understood. The issue is twofold. One side is theoretical: we emphasize again that the common statement that MAX phases with higher $\text{DOS}(E_f)$ should be more conductive is *not* correct. The conductivity is related to the carrier concentration and mobility; the latter depends on electron-electron and electron-phonon collision terms, which are direction dependent and challenging to calculate from theory. The other side is the reliability of the experimental data. The results of measurements of electrical properties depend strongly on not only the presence, but also the distribution, of impurity phases. A clever example of a controlled measurement of this effect for a MAX phase is an investigation [272] of the effect of a deliberately inserted TiC layer in the bulk of a Ti_3SiC_2 epitaxial film; this greatly increases measured resistivity values compared to a pure Ti_3SiC_2 film. Yet, many experimental publications on electrical properties of MAX phases contain limited, if any, information on impurities and minority phases, a problem that often makes it difficult to assess the validity of the results. Another issue is the role of defects, such as vacancies, substitutional atoms, and dislocations, which are well known to affect

the electrical properties, but are difficult to quantify. An indirect macroscopic measure of defects is the residual resistivity ratio (RRR, i.e., the room-temperature resistivity divided by the resistivity measured at low temperature; typically 2–4 K). The RRR can be used to estimate of the effect of defects on the conductivity, and it has been suggested [266,273,277] that the electron mobility of MAX phases at 4 K is proportional to $(RRR-1)/DOS(E_f)$. (Again, this proposition originates from Mott’s theory for transition metals.) The qualitative correlation between mobility and RRR [277] is expected, but the *quantification* needs to be interpreted with care because of the relatively large scatter in available mobility data, and because the proposition is based on data from relatively few MAX phases.

For all these reasons, understanding the electrical properties of the MAX phases is one of the most important – and difficult – research challenges in the field. From the experimental side, a reliable determination of the anisotropy in conductivity is needed. In general, a direct measurement of the conductivity along different crystal orientations requires sufficiently large bulk single crystals. Until such MAX-phase crystals are available, indirect approaches are required, for example local EELS measurements on individual grains oriented in different crystallographic orientations. The initial approach to draw conclusions about the anisotropy in electrical properties by comparing transport data for single-crystal epitaxial films with the corresponding bulk MAX-phases [109,282] is insufficient without detailed information on minority phases, defects, and impurities (as in Ref. 282). Therefore, improved experimental control over defects (vacancies and substitutional atoms) is needed. One example is the recent work of Scabarozzi *et al.* [285], who compared Ti_2AlN samples with slight variations in N content. Another important contribution would be the synthesis of epitaxial thin films with other out-of-plane orientations than [0001] (cf., section 5.3). This would potentially allow a direct measurement of the anisotropy in the conductivity. From the theoretical

side, calculations to elucidate the roles of impurities and vacancies on the density of states are important [53,62,63].

6.1.3 Thermopower

The thermopower or Seebeck coefficient, S , of a material is defined as $\Delta V/\Delta T$, the voltage ΔV that develops across a material in a temperature gradient of ΔT . The efficiency of a thermoelectric material is given by its figure of merit $S^2\sigma/\kappa$, where σ and κ are the electrical and thermal conductivities, respectively. A good thermoelectric material should therefore have a high value of S , although the situation is complicated since S , σ , and κ are mutually dependent. Ti_3SiC_2 is astonishing in this regard: bulk samples of Ti_3SiC_2 exhibit negligible S over a very wide temperature range, from 300 K to 850 K [286]. Chaput *et al.* [287,288] proposed an explanation for this amazing phenomenon. Based on DFT calculations, they predicted that two types of bands are the main contributors to thermopower; a hole-like band in the ab -plane and an electron-like band along the c axis. For Ti_3SiC_2 , the predicted thermopower in the c direction was twice that in the a direction, but with opposite sign. Therefore, the contributions in the a , b , and c directions would macroscopically sum up to zero in a randomly oriented sample. It must be emphasized that this result was obtained under the assumption that relaxation can be approximated by a term proportional to the inverse of $\text{DOS}(E_f)$, which means that it is isotropic (cf., section 6.1.2). Therefore, the main term contributing to the anisotropy of S would be the carrier velocity at the Fermi surface. These predictions are consistent with, and provide an elegant explanation for, the observed near-zero thermopower in Ti_3SiC_2 . However, there is as yet no direct experimental confirmation, although preliminary measurements on Ti_3SiC_2 epitaxial thin films [289] indicate that these films exhibit higher S than polycrystalline Ti_3SiC_2 over the 4–300 K temperature range. Furthermore, the phenomenon of orientation-dependent conduction sign reversal is not unheard of

and is exhibited by, e.g., $\text{ReSi}_{1.75}$ and CsBi_4Te_6 [290], a fact that lends support to the proposed explanation for the near-zero thermopower of Ti_3SiC_2 .

6.1.4 Superconductivity

The superconducting properties of some MAX phases are not well understood. Interest has focused on 211 phases. Already in the 1960s, it was reported that Mo_2GaC was a superconductor with a critical temperature of ~ 3.9 K [291], while eleven other H phases did not exhibit superconductivity above 1.1 K [292]. Today, superconductivity has been reported for the bulk MAX phases Mo_2GaC [291], Nb_2SnC [293], Nb_2SC [294], Nb_2AsC [295], Nb_2InC [296] and Ti_2InC [297], although other data indicate that Nb_2SnC is not a superconductor [275]. Very recently, Scabarozi *et al.* [109] reported that epitaxial Nb_2AlC thin films exhibit a superconducting transition at 440 mK. Further, theoretical studies have suggested that superconducting MAX phases should primarily be found among those whose corresponding MX phases are superconductors [298]. It is therefore remarkable that superconductivity has been reported for Ti_2InC , despite the fact that it has never been reported for TiC , and it would be worthwhile to investigate whether any other TiC-based MAX phases are superconductors. Another intriguing observation is that while superconductivity is well known for TiN [16], it has not been observed for Ti_2AlN [285].

6.2 Mechanical properties

The mechanical properties of bulk MAX phases were previously reviewed by Barsoum [3,265] and by Zhang *et al.* [5]. In summary, the reported mechanical properties of the MAX phases are remarkable: fully reversible dislocation-based deformation and high specific stiffness together with high machinability. The MAX phases deform by a combination of kink and shear band formation, together with delaminations within grains. Bulk Ti_3SiC_2 is an unusually tough ceramic even at room temperature, because microcracking, delamination, crack deflection, grain push-out, grain pull-out

and buckling of individual grains act as energy absorbing mechanisms during deformation [299,300]. This behavior is due to an anisotropic structure which renders basal plane dislocations mobile at room temperature, providing the ability to form kink bands under applied load [301].

Deformation-induced kink formation was observed in compression studies of bulk Ti_3SiC_2 [301]. It is not surprising that Ti_3SiC_2 is susceptible to kink-band formation; kinking is predicted in hexagonal crystals having a c/a ratio greater than 1.732 [265]. According to Barsoum *et al.*, the deformation modes observed in Ti_3SiC_2 , namely shearing, kinking, buckling, and delamination can be explained by the generation and glide of dislocations along the basal planes, without the activation of additional non-basal slip systems. Based on indirect evidence (hysteresis curves observed in nanoindentation), Barsoum *et al.* also suggested the reversible formation and annihilation of incipient kink bands (IKBs) [302] at room temperature. However, direct evidence is lacking and Barsoum's IKB model needs to be tested, for example by *in-situ* nanoindentation in a TEM. It is worth noting that Joulain *et al.* [303] recently suggested the existence of a *non-basal* dislocation segment in Ti_4AlN_3 , and an in-plane shear component of stacking faults.

For the mechanical properties of MAX-phase thin films, we will use Ti_3SiC_2 epitaxial thin films as a representative example, mainly based on the work of Molina-Aldareguia *et al.* [304] and Emmerlich *et al.* [101]. Figure 14(a), reproduced from Ref. 101, shows an indentation loading–unloading curve for epitaxial Ti_3SiC_2 thin films. Pop-in events (sudden penetrations of the indenter as indicated by arrows) are repeatedly observed in the loading curves. There are large pile-ups of material around the residual imprint, as shown in the AFM image in Fig. 14(b). Such pile-ups are typical for ductile materials and characteristic of Ti_3SiC_2 [300,305]. Figure 15, reproduced from Molina-Aldareguia *et al.* [304], shows bright-field XTEM images of indents made at maximum

loads of 20, 30 and 40 mN. Most of the material transport in the film occurs from below the indented zone to the sides of the indent, via shearing and delamination along the layers and buckling of the layers at the free surface by the formation of kink bands. This mechanism explains the observed pile-up behavior (Fig. 14). Figure 16, from Molina-Aldareguia *et al.* [304], is an illustration of this mechanism: if only basal plane dislocations are mobile at room temperature and assuming no dislocation climb, material flow can only occur along the basal planes from the center of the indented area to the sides, but cannot give rise to pile-up around the indentations. However, kink-band formation provides a mechanism to transport the material pushed by the indenter towards the free surface.

Figure 17, reproduced from Emmerlich *et al.* [101], is a plot of the hardness, H , and Young's modulus, E , versus the normalized contact depth in $\text{Ti}_3\text{SiC}_2(0001)$ thin films on $\text{Al}_2\text{O}_3(0001)$ substrates (denoted with squares) and on $\text{MgO}(111)$ substrates (denoted with stars) obtained by nanoindentation with (a) a cube corner and (b) a Berkovich indenter. The film on MgO was phase-mixed with Ti_4SiC_3 and had a hardness of almost 30 GPa as measured by both indenters. With increasing indentation depth, however, hardness decreased to approximately 18 GPa for the measurements with a Berkovich indenter [Fig. 17(a)] and to a continuously decreasing value below 15 GPa, in the case of the cube-corner indentations [Fig. 17(b)]. Young's moduli for shallow-indented films on MgO and Al_2O_3 were determined to be 370 and 343 GPa, respectively, using a Berkovich tip and 312 and 318 GPa for a cube-corner indenter, respectively. An approximately constant value between 250 and 280 GPa was obtained for larger indents.

The above hardness values are much higher than those stated for bulk MAX phases, which are typically 2-4 GPa [3]. In part, this may be due to hardness anisotropy [43]. However, the *initial*

peak hardness measured (at low load, less than a few millinewton, in a measurement on bulk Ti_3SiC_2) can typically reach 25–30 GPa [306], which is expected for low loads. The fact that the hardness decreases with increased indentation depth can be attributed to the established kink formation and accompanying delamination, because the size of the residual imprint is disproportionally enlarged. For bulk Ti_3SiC_2 , the hardness reaches plateau values of 4–5 GPa [3,306], but the maximum force can be as high as 500 mN. This value is more than an order of magnitude higher than one would use in measurements on thin films, since the influence of the substrate properties becomes pronounced with deeper indents. Therefore, the bulk hardness value for MAX phases is not observed in thin-film measurements.

6.3 Tribological properties

The tribological properties of MAX phases attracted much attention following the results of low-micrometer-scale friction measurements (typical normal forces $F_N \sim 4\text{--}5\text{ }\mu\text{N}$) on Ti_3SiC_2 bulk samples using lateral force microscopy that revealed an ultra-low friction coefficient (μ) of 0.005 [307,308]. In that experiment, the torsion (due to frictional forces) of a calibrated cantilever was measured while sliding it over a cleaved basal plane of an individual Ti_3SiC_2 grain. Normal loads in the mN–N range, however, generally result in much higher μ , typically in the range from 0.15 to 0.45 [309] due to debris accumulated between disc and pin. The calculated wear rate is faster for fine-grained samples due to grain pull-out. Self-lubricating properties of Ti_3SiC_2 were found against an oscillating diamond pin ($\mu = 0.05\text{--}0.1$), but not against Ti_3SiC_2 itself. This means that self-lubrication is not an intrinsic property of Ti_3SiC_2 [310]. Furthermore, Souchet et al. [311] performed scratch tests on fine- and coarse-grained polycrystalline Ti_3SiC_2 samples with steel and Si_3N_4 balls. They observed a tribological duality of two different friction regimes with a low μ -value of 0.15 and an increased μ of 0.3–0.5 in the second regime. The reason for the duality may be

the formation of an initial tribofilm of TiC_xO_y , which adheres to the Ti_3SiC_2 sample and thus, subsequently, seizure occurs between the adhering Ti_3SiC_2 on the tribofilm and the sample surface.

Emmerlich *et al.* [312] provided an explanation for the large scatter of μ values in the published data by studying the wear mechanism and friction coefficient of epitaxial $\text{Ti}_3\text{SiC}_2(0001)$ films at the microscale ($F_N = 100 \mu\text{N}$ to 1 mN) using diamond as the counterpart and at the macroscale ($F_N = 0.24\text{--}1 \text{ N}$) against an alumina ball. With high loads ($F_N = 500 \mu\text{N}$ to 0.24 N), μ was in the range $0.4\text{--}0.8$ due to third-body abrasion, with strong wear and delamination failure (see Fig. 18, reproduced from Ref. 312). However, small F_N ($100\text{--}200 \mu\text{N}$) resulted in a μ of ~ 0.1 without observable wear or deformation. The reason for this remarkably low friction coefficient may possibly be the formation of low-friction surface layers of TiO_2 and graphitic carbon plus adsorbed water molecules. These results show that the friction coefficients of Ti_3SiC_2 can indeed be very low; however, the normal force that can be applied is limited due to easy delamination and kinking resulting in third-body abrasion and heavy wear.

7 Thermal stability and decomposition

The thermal stability of bulk MAX phases has previously been reviewed by Barsoum [3] and in a focused review on Ti_3SiC_2 by Zhang *et al.* [5]. This section briefly discusses the general aspects of the thermal stability and decomposition of the MAX phases, followed by a review of the decomposition of MAX-phase thin films and the observed apparent differences between decomposition of thin-film and bulk MAX phases.

7.1 Thermal stability – general aspects

The MAX phases do not melt congruently, but decompose according to the following reaction:

The decomposition of MAX phases can be exemplified by Ti_3SiC_2 . In Ti_3SiC_2 , the $\text{TiC}(111)$ layers alternate between Si sheets. The Ti_3C_2 layers are twinned to each other separated by the Si layer acting as a mirror plane (cf., Fig. 2). Removal of the Si plane yields a twinned $\text{TiC}_{0.67}$ structure. Detwinning to regular TiC is obtained by rotation of the Ti_3C_2 layer. Thus, the decomposition of MAX phases is initiated by loss of the A element. Reported decomposition temperatures vary over a wide range: from 850 °C for bulk Cr_2GaN [313] to 1800 °C [314,315], possibly even above 2300 °C [316], for Ti_3SiC_2 . A complicating factor is that the decomposition temperature depends strongly on the environment and on impurities. For example, the claim that bulk Ti_3SiC_2 is thermally stable above 1800 °C is valid for Ti_3SiC_2 of sufficient purity in ambient air. The decomposition temperature is lower than stated above if a driving force is provided for increasing the Si segregation. This has been shown to occur through carburization [317] or immersion in molten cryolite [318] or molten Al [319]. Furthermore, Zhou *et al.* [320] reported that Ti_3SiC_2 decomposes

in the presence of Cu at temperatures above 900 °C. Depending on the temperature and the amount of Cu, the formed products are Cu(Si) (solid solution of Si in Cu), TiC, Cu₅Si, and Cu₁₅Si₄. Tzenov *et al.* [321] reported that only 1 at. % of Fe and V impurities in hot isostatic pressed Ti₃SiC₂ lead to a highly porous structure, which reduces the decomposition temperature below 1600 °C. Racault *et al.* [186] found that polycrystalline Ti₃SiC₂ bulk material decomposes at 1300 °C in vacuum triggered by the chemical reaction between Si and the surrounding C crucible. An alumina crucible in an Ar atmosphere of 100 kPa increases the decomposition temperature to 1450 °C [186].

The main conclusion that can be drawn from these results is that the decomposition temperature is environment-dependent. For example, the high thermal stability and oxidation resistance reported for bulk Ti₂AlC and Ti₃AlC₂ is contingent upon the formation of a dense, protective Al₂O₃ oxide scale [57,58,59,60].

7.2 Decomposition mechanism of MAX phase thin films

Several reports [245,246] have indicated that there is an apparent difference between epitaxial thin-film samples and bulk samples with respect to the decomposition of MAX phases. This is partly a consequence of the fact that the diffusion length scales and the sensitivity of the analysis methods are different. More important, however, is again the fact that the decomposition temperature depends strongly on the environment and on impurities. Annealing of epitaxial Ti₃SiC₂ thin films in vacuum [245,246] showed the onset of Ti₃SiC₂ decomposition in the range 1000–1100 °C rather than 1800 °C as reported for bulk [314,315]. With the presence of an interface to ambient, the chemical potentials for the elements are reduced, while in the presence of oxygen, surface oxides form diffusion barriers against further decomposition. Initial annealing experiments by Emmerlich [245] with two Ti₃SiC₂(0001) films mechanically placed face-to-face showed that the Ti₃SiC₂ films

were stable to at least 1400 °C. The observed increase in decomposition temperature compared with the vacuum-annealed samples can be attributed to the absence of an interface to vacuum, and to the entrapment of Si by the surface oxide. These results indicate that the thermal stability of Ti_3SiC_2 can be increased by preventing Si removal from the surface.

Emmerlich *et al.* [245] developed a model for the decomposition of Ti_3SiC_2 epitaxial thin films in vacuum; this model is relevant to any MAX-phase vacuum annealing experiment. Figure 19 is a schematic illustration of the mechanism of Ti_3SiC_2 decomposition [245]. In short, the decomposition process has four stages. Stage I (Fig. 19(a)) involves the out-diffusion and evaporation of Si over the temperature range 1000 – 1100 °C. For 25 h annealing at 1100 °C, the MAX phase decomposed to a depth of ~60 nm [245]. Si enrichment on the free surface at 1000 °C was also observed via in-situ photoemission studies [246] of $\text{Ti}_3\text{SiC}_2(0001)$ thin films annealed in ultra-high vacuum. Si evaporation at the free film surface takes place since the Si vapor pressure is of the same order of magnitude as the pressure range used during annealing. Stage II (Fig. 19(b)) involves O uptake and evaporation of SiO. In the presence of an oxygen ambient (residual gas in the evacuated furnace), the Si-depleted highly defective structure formed under Stage I is prone to O in-diffusion. Furthermore, O may be incorporated in the material, e.g., by saturating the dangling bonds created by the Si-deficiency and thus creating O mirror planes between Ti_3C_2 slabs ($\text{Ti}_3\text{C}_2/\text{O}/\text{Ti}_3\text{C}_2$). Stage III (Fig 19(c)) involves Ti_3C_2 relaxation, detwinning, and $\text{TiC}_{0.67}$ formation by C-redistribution with void formation. This stage is activated at $T_a \geq 1100$ °C. Here, the twinned Ti_3C_2 slabs ($\text{Ti}_3\text{C}_2/\text{Ti}_3\text{C}_2$) formed in Stages I and II relax toward each other. This stage is accompanied by a large reduction of volume as the Si-depleted hexagonal unit cell shrinks. The relaxation process also includes C redistribution from within the Ti_3C_2 slabs to the Si-depleted mirror planes. In stage IV (Fig 19(d)), above 1300 °C, the transformed $\text{TiC}_{0.67}$ layer undergoes both

growth and recrystallization within the film as the final stage of the Ti_3SiC_2 decomposition process, accompanied by an increased pore size. Residual mirror planes containing Si as well as C and/or O may be present even up to an annealing temperature of 1300 °C, as indicated by a large number of planar faults [245]. Recrystallization is most likely assisted by the enthalpy released in the above described reactions as well as by the relatively high planar-fault density and lattice point defects.

All these results further underline the main point that the decomposition temperature depends strongly on the environment and on impurities. The latter are, e.g., C vacancies and O interstitials, which eventually migrate to form the voids, but also any residual substitutional Si species. The vacuum annealing experiments demonstrate that the chemical potential of Si in the various environments will determine the effective Ti_3SiC_2 stability. This reasoning is generally applicable to all MAX phases.

8 Applications

Because of their combination of properties, many applications have been proposed for MAX phases. The list here is not intended to be exhaustive, but rather to indicate the wide range of potential uses for MAX phases. In bulk form, the MAX phases are attractive for high-temperature structural applications, rotating electrical contacts and bearings, heating elements, nozzles, heat exchangers, tools for die pressing, and as impact-resistant material [3]. More recent suggestions include the possible use of Ti_3SiC_2 as radiation-resistant cladding material in the nuclear industry [322,323] and the demonstration of Ti_3SiC_2 as a material for electromagnetic interference shielding [324,325]. Potential thin-film applications for the MAX phases include low friction surfaces, electrical contacts, sensors, tunable damping films for microelectromechanical systems, and many more.

Sputter-deposited Cr_2AlC has been tested as coatings on turbine blades [114]. MAX phases synthesized by solid state reactions or sputter deposition can potentially be used as electrodes in SiC-, AlN-, or GaN-based semiconductor devices or sensor applications [195,198,326]. “Ti-based” contacts to SiC are in use and typically contain Ti_3SiC_2 formed by solid state reactions [191,192,326]. A more exotic suggestion is the claim (based on theoretical calculations of the dielectric function and infrared emittance [327,328]) that Ti_4AlN_3 and V_4AlC_3 have the potential to be used as a coating on spacecrafts to avoid solar heating and also increase the radiative cooling in future space missions to Mercury. The most widespread application resulting from the research on thin-film MAX phases is, however, not a MAX-phase thin film, but a Ti-Si-C-based nanocomposite coating marketed under the trade name *MaxPhase* (originally synthesized by sputtering from Ti_3SiC_2 targets, hence the trade name, see sections 2.1.3.6 and 5.1). This type of nanocomposite

coating is today commercialized in mainstream electrical-contact applications in the telecommunications industry, and has further potential applications in, e.g., high-power devices and electrodes in batteries and fuel cells.

9 Outlook

In his seminal review from 2000 [3], Barsoum stated that “despite the relatively short time these compounds have been identified as having unusual properties, we have come a long way in understanding their physical, mechanical and chemical properties.” Indeed, it was an impressive achievement, especially considering that the research field had only “existed” for four years! Still, despite the remarkable progress in the MAX-phase research field since 1996, some important research questions remain and several new ones have appeared.

On the synthesis side, research directions that should be pursued further include low-temperature deposition of MAX phases, where novel approaches to reduce the deposition temperature below the present 450 °C [98,99] would be important for widespread applications. Note, however, that there have been several unsubstantiated claims of MAX-phase thin-film synthesis at temperatures of 100-300 °C (see section 4.2.1). The importance of not making such claims without unambiguous evidence cannot be overemphasized.

Further, the possibility to synthesize artificial MAX-phase structures with stacking sequences not observed in normal growth processes is intriguing. One example of such a structure would be the elusive phase Ti_2SiC (cf. section 4.3.2.3); another would be a systematic attempt to synthesize “higher-order” MAX phases (i.e., $\text{M}_{n+1}\text{AX}_n$ phases with $n > 3$). A specific thin-film synthesis contribution would be to design an experiment in which it is possible to grow MAX-phase thin films with the c axis oriented in the plane; this would require a specific choice of substrate to obtain the necessary lattice match to the long c axis.

Additionally, the recent discoveries of numerous new 312 and 413 phases should be pursued, and here it is important that bulk synthesis, thin-film synthesis, and theory progress together. Today, we appreciate that the 312 and 413 groups are much larger than previously thought. At least six 312 phases and seven 413 phases exist, and more can be expected to be found. An important future contribution will be to perform systematic theoretical studies for potential 312 and 413 phases, to predict which ones may exist and enable experimentalists to narrow the search pattern for new 312 and 413 MAX phases.

There is also room for exploring completely new directions in synthesis, such as to follow up on the highly speculative, but exciting, predictions of Luo *et al.* [94] and Enyashin *et al.* [95] and attempt to synthesize magnetic MAX phases (with $M = \text{Fe}$) and Ti_3SiC_2 nanotubes, respectively.

The second set of research challenges involves understanding of the physical properties of MAX phases. Here, one of the most important challenges is the development of detailed understanding of the electrical properties of MAX phases. Especially, there is a strong need to probe anisotropy effects on conductivity, dielectric function, etc, as well as the roles of impurities and vacancies in determining electrical properties. Other unexplored properties include superconductivity and magnetism. For mechanical properties, Barsoum's "incipient kink band" model [302] requires testing by, for example, *in-situ* nanoindentation in a TEM.

Finally, we pose the question: to what extent can the properties of the MAX phases be tuned? Here, an important future research direction would be systematic experimental studies of MAX-phase solid solutions to elucidate the role of chemistry on phase stability and properties. One could conceivably engineer the band structure of MAX phases by appropriate dopants, so as to achieve

desired properties. For example, we envision shifting the Fermi level to tune the material from metal to semiconductor in a controlled manner. These aspects should preferably be addressed by a combined theoretical/experimental approach in an iterative process with theoretical predictions of effects of specific dopants and solid solutions on the band structure and corresponding properties and experimental work aimed at introducing dopants and forming solid solutions in a controlled manner. Here, combinatorial thin film materials synthesis will be useful to identify MAX-phase solid solutions with attractive, and quite possibly novel, properties.

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FIGURES

Figure 1. Crystal structure of the 211, 312, and 413 MAX phases. From Högberg *et al.* [104], adapted from Barsoum [4].

Figure 2. High-angle annular dark field TEM image, acquired along the $[11\bar{2}0]$ zone axis of Ti_3SiC_2 , showing twinning and the resulting characteristic “zig-zag” stacking of MAX phases. Image courtesy of P. O. Å. Persson.

Figure 3. Simplified isothermal cross section of the Ti-Si-C phase diagram, adapted from Viala *et al.* [6]. The MAX phase Ti_4SiC_3 , which has been presumed to be metastable (cf. sections 2.6, 4.2.2, and 4.3.1), is indicated.

Figure 4. Temperature dependences of free energy differences (relative phase stability) of Ti_4AlN_3 and M_4AlC_3 ($\text{M} = \text{V}, \text{Nb}, \text{and Ta}$) α and β polymorphs. From Wang *et al.* [61].

Figure 5. Nonfiltered and filtered high-resolution Z-contrast TEM images showing the alternating stacking of two and three transition-metal carbide layers in one slab, forming an ordered $(V_{0.5}Cr_{0.5})_5Al_2C_3$ “523” structure. From Zhou *et al.* [47].

Figure 6. X-ray diffractograms from (top) a single-phase epitaxial $Ti_3SiC_2(0001)$ film deposited at 900 °C on an $MgO(111)$ substrate (middle, upper) phase-mixed Ti_3SiC_2/Ti_4SiC_3 film containing $Ti_7Si_2C_5$, (middle, lower) phase-mixed $Ti_3SiC_2/Ti_5Si_2C_3$ film, and (bottom) Ti_4SiC_3 deposited at 1000 °C on $Al_2O_3(0001)$. TiC seed layers were used (cf. section 5.2.1). Adapted from Palmquist *et al.* [45].

Figure 7. X-ray diffractograms over the 2θ range 34° to 42° , from 200-nm-thick Ti_3SiC_2 films deposited by magnetron sputtering from elemental targets. Adapted from Emmerlich *et al.* [101].

Figure 8. Example of the use of seed layers for MAX phases. Ti_3SiC_2 film deposited onto (a) an intentionally deposited TiC_x seed layer on $\text{MgO}(111)$ and (b) without an intentionally deposited TiC_x seed layer; but with a TiC_x incubation layer. From Emmerlich *et al.* [101].

Figure 9. (a) Overview and (b) higher-resolution atomic force microscopy (AFM) images of the surface of a typical epitaxial Ti_3SiC_2 film deposited at 900 °C. Adapted from Emmerlich *et al.* [101].

Figure 10. Hexagonally-shaped Ti_3SiC_2 grains grown by solid-liquid reaction. Adapted from Luo *et al.* [234].

Figure 11. Ti_3SiC_2 grown on $\text{MgO}(100)$ at 900°C yielding Ti_3SiC_2 with a preferred $\langle 10\bar{1}5 \rangle$ out-of-plane orientation. (a) Ti_3SiC_2 0008 pole figure plot, (b) TiC_x 111 pole figure plot, (c) atomic force microscopy image of the surface, and (d) cross-section TEM image. The (0001) basal plane traces are indicated. From Emmerlich *et al.* [101].

Figure 12. TEM image of a Ti-Si-C MAX-phase film where the stacking sequence has been disturbed and each successive set of Si layers is separated by a random number of TiC layers. Modified from Palmquist *et al.* [45].

Figure 13. Calculated total density of states (DOS) and partial density of states (PDOS) associated with Ti(1), Ti(2), Al or Si, and C atoms in (a) Ti_3AlC_2 and (b) Ti_3SiC_2 . From Zhou *et al.* [268].

Figure 14. (a) Indentation loading/unloading curves for epitaxial Ti_3SiC_2 (0001) thin films. (b) AFM image of the resulting indent. From Emmerlich *et al.* [101].

Figure 15. Bright-field cross-sectional TEM images of indents made at maximum loads of (a) 20 mN, (b) 30 mN, and (c) 40 mN for epitaxial Ti_3SiC_2 (0001) thin films. From Molina-Aldareguia *et al.* [304].

Figure 16. Sequence of events for the formation of kink bands in Ti_3SiC_2 during indentation, as proposed by Molina-Aldareguia *et al.* [304]. (a) Surface radial compression forces the layers to buckle away at the free surface to a tilted position. This is possible due to delamination and shear between the layers. (b) As the indenter penetrates further, more layers buckle-out and the delamination crack moves deeper below the film surface. From Molina-Aldareguia *et al.* [304].

Figure 17. Hardness H and Young's modulus E versus the normalized contact depth in $\text{Ti}_3\text{SiC}_2(0001)$ thin films on $\text{Al}_2\text{O}_3(0001)$ substrates (denoted with squares) and on $\text{MgO}(111)$ substrates (denoted with stars) obtained by nanoindentation with (a) cube-corner and (b) Berkovich indenters. From Emmerlich *et al.* [101].

Figure 18. SEM micrograph of the side of the wear track on an epitaxial $\text{Ti}_3\text{SiC}_2(0001)$ film after 150 cycles of sliding against an alumina ball counterpart showing (a) delamination at different film thicknesses and (b) kink formation. From Emmerlich *et al.* [312].

Figure 19. Schematic illustration describing the different stages of phase transformations occurring during the decomposition of $\text{Ti}_3\text{SiC}_2(0001)$, as proposed by Emmerlich *et al* [245].

TABLE CAPTIONS

Table 1. The known $M_{n+1}AX_n$ phases, sorted by stoichiometry (“211”, “312”, and “413”) and valence electron configuration for the M and A elements. Phases marked with an asterisk (*) have been reported in thin-film form by physical and/or chemical vapor deposition (PVD/CVD) and in bulk form. Phases marked with a dagger (†) have only been reported in thin-film form (PVD).

Table 2 Structural parameters of the MAX phases, including the α and β polymorphs of the 312 and 413 structures. The space group is $P6_3/mmc$. The listed z atomic positions are for the archetypical phases Ti_2AlC , Ti_3SiC_2 and Ta_4AlC_3 [30,36,37,38,329,330].

Table 3. Calculated density of states at the Fermi level, $DOS(E_F)$, for the Ti_2AC phases including the hypothetical Ti_2SiC , Ti_2PC , and Ti_2AsC . Adapted from Hug [22].

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TABLE 1. The known $M_{n+1}AX_n$ phases, sorted by stoichiometry (“211”, “312”, and “413”) and valence electron configuration for the M and A elements. Phases marked with an asterisk (*) have been reported in thin-film form by physical and/or chemical vapor deposition (PVD/CVD) and in bulk form. Phases marked with a dagger (†) have only been reported in thin-film form (PVD).

A-element: s^2 (group 12) s^2p^1 (group 13) s^2p^2 (group 14) s^2p^3 (group 15) s^2p^4 (group 16)

211 phases:

<i>M 3d</i>	Ti ₂ CdC	Sc ₂ InC *Ti ₂ AlC Ti ₂ GaC Ti ₂ InC Ti ₂ TiC *V ₂ AlC V ₂ GaC *Cr ₂ AlC Cr ₂ GaC *Ti ₂ AlN Ti ₂ GaN Ti ₂ InN V ₂ GaN Cr ₂ GaN	*Ti ₂ GeC *Ti ₂ SnC Ti ₂ PbC *V ₂ GeC Cr ₂ GeC	V ₂ PC V ₂ AsC	Ti ₂ SC
<i>M 4d</i>		Zr ₂ InC Zr ₂ TiC *Nb ₂ AlC Nb ₂ GaC Nb ₂ InC Mo ₂ GaC Zr ₂ InN Zr ₂ TiN	Zr ₂ SnC Zr ₂ PbC Nb ₂ SnC	Nb ₂ PC Nb ₂ AsC	Zr ₂ SC Nb ₂ SC
<i>M 5d</i>		Hf ₂ InC Hf ₂ TiC Ta ₂ AlC Ta ₂ GaC	Hf ₂ SnC Hf ₂ PbC Hf ₂ SnN		Hf ₂ SC

312 phases:

<i>M 3d</i>	*Ti ₃ AlC ₂ *V ₃ AlC ₂ (or (V,Cr) ₃ AlC ₂)	*Ti ₃ SiC ₂ *Ti ₃ GeC ₂ *Ti ₃ SnC ₂
<i>M 5d</i>	Ta ₃ AlC ₂	

413 phases:

<i>M 3d</i>	Ti ₄ AlN ₃ V ₄ AlC ₃ Ti ₄ GaC ₃	†Ti ₄ SiC ₃ †Ti ₄ GeC ₃
<i>M 4d</i>	Nb ₄ AlC ₃	
<i>M 5d</i>	Ta ₄ AlC ₃	

TABLE 2. Structural parameters of the MAX phases, including the α and β polymorphs of the 312 and 413 structures. The space group is $P6_3/mmc$. The stated z atomic positions are for the archetypical phases Ti_2AlC , Ti_3SiC_2 and Ta_4AlC_3 [30,36,37,38,329,330].

Ti_2AlC

Name	x	y	z	Wyckoff notation
Ti	1/3	2/3	0.084	$4f$
Al	1/3	2/3	3/4	$2d$
C	0	0	0	$2a$

α - Ti_3SiC_2

Name	x	y	z	Wyckoff notation
Ti(1)	0	0	0	$2a$
Ti(2)	2/3	1/3	0.1355	$4f$
Si	0	0	1/4	$2b$
C	1/3	2/3	0.0722	$4f$

β - Ti_3SiC_2

Name	x	y	z	Wyckoff notation
Ti(1)	0	0	0	$2a$
Ti(2)	2/3	1/3	0.1355	$4f$

Si	2/3	1/3	1/4	2 <i>d</i>
C	1/3	2/3	0.0722	4 <i>f</i>

α -Ta₄AlC₃

Name	x	y	z	Wyckoff notation
Ta(1)	1/3	2/3	0.05453	4 <i>f</i>
Ta(2)	0	0	0.15808	4 <i>e</i>
Al	1/3	2/3	1/4	2 <i>c</i>
C(1)	0	0	0	2 <i>a</i>
C(2)	2/3	1/3	0.1032	4 <i>f</i>

β -Ta₄AlC₃

Name	x	y	z	Wyckoff notation
Ta(1)	1/3	2/3	0.05524	4 <i>f</i>
Ta(2)	1/3	2/3	0.65808	4 <i>f</i>
Al	1/3	2/3	1/4	2 <i>c</i>
C(1)	0	0	0	2 <i>a</i>
C(2)	0	0	0.10324	4 <i>e</i>

TABLE 3. Calculated density of states at the Fermi level, $DOS(E_F)$, for the Ti_2AC phases including the hypothetical Ti_2SiC , Ti_2PC , and Ti_2AsC . Adapted from Hug [22].

Ti_2AC phase	$DOS(E_F)$ [states/(eV·cell)]
Ti_2AlC	2.67
Ti_2GaC	2.55
Ti_2InC	2.39
Ti_2TlC	2.35
Ti_2GeC	3.83
Ti_2SnC	3.71
Ti_2PbC	4.73
Ti_2SC	1.55
Ti_2SiC	3.17
Ti_2PC	5.99
Ti_2AsC	5.25

Per Eklund received his PhD in materials science, in particular thin film physics, from Linköping University, Sweden, in 2007. His thesis topic was multifunctional nanocomposite and MAX-phase carbide thin films in the Ti-Si-C and related materials systems. After a postdoctoral position in 2007-2008 at the Interdisciplinary Nanoscience Center (iNano) at the University of Aarhus, Denmark, he held a 3-month Visiting Senior Researcher position at the Centre National de la Recherche Scientifique (CNRS) in Châtillon (Paris), France. In 2009, he joined the faculty at the Thin Film Physics Division at Linköping University, where he is Assistant Professor in nanostructured functional ceramics. Apart from the MAX phases and nanocomposite carbides, his research interests include complex thin-film oxide materials for energy applications (e.g., fuel cells) and hard coatings.

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