

## On the formation mechanisms and properties of MAX phases

### A review

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## Review article

## On the formation mechanisms and properties of MAX phases: A review

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## ABSTRACT

MAX phases are a family of ternary carbide or nitride ceramics possessing a layered crystal structure and, due to their chemical bonds having a mixed covalent-ionic-metallic nature, have unique properties combining those of metals and ceramics. In this review, the formation mechanisms of MAX phases from elemental and compound powders are reviewed in detail, as the formation mechanisms are closely related to the unique properties of well-synthesized MAX phases. The stability of MAX phases in some harsh external environments is significantly influenced by the defect population, allowing the mechanisms of defect formation and migration to strongly influence their self-healing performance and radiation tolerance. The properties of MAX phases can be tailored by creating solid solutions, which have lattice distortions, and texturing which results in the preferential orientation of plate-like grains.

## 1. Introduction

MAX phases are a family of ternary carbide or nitride ceramics all belonging to the hexagonal crystal system and having a layered structure. Their general formula is  $M_{n+1}AX_n$ , where  $n$  usually equals 1–3,  $M$  is a transition metal element,  $A$  is an A group element and  $X$  is C or N. In the last two years, also some MAX phase ceramics with B as the X element have been synthesized [1–3]. Depending on the value of  $n$ , the early generation of MAX phases are classified as 211 phases, 312 phases and 413 phases [4–6]. Their crystal structure can be described as  $M_{n+1}X_n$  layers and A layers alternately stacked along the  $c$ -axis, as shown in Fig. 1 [7]. The  $M_{n+1}X_n$  layers consist of edge-shared  $M_6X$  octahedra with strong M–X bonds, while the  $M_{n+1}X_n$  layers and A layers are combined by the relatively weak M–A bonds. Recently, some other phases with higher “ $n$ ” values have also been discovered in the MAX family, such as 523 phases ( $Ti_5Al_2C_3$ ), 615 phases ( $Ta_6AlC_5$ ), 725 phases ( $Ti_7Si_2C_5$ ), etc. [8]. Unlike bonds in real ceramics, chemical bonds in MAX phases have a mixed covalent-ionic-metallic nature, which results in their unique properties combining those of ceramics and metals, such as being machinable and ductile, light and strong, electrically and thermally conductive, having good oxidation resistance, remarkably high temperature stability and good thermal shock resistance, etc. [9–11],

making them an ideal family of materials suitable for many fields such as thermal shock resistant refractory materials, coatings for electrical contacts, neutron radiation resistant parts for nuclear applications, etc. [12–14].

Due to the relatively weak M–A bonds between the  $M_{n+1}X_n$  layers and A layers, A atoms tend to diffuse outwards and be oxidized more easily when exposed to oxygen at high temperatures. As a result, existing microcracks can be filled by the volume expansion caused by the formation of the A oxides. Therefore, MAX phases are prominent examples of intrinsic self-healing materials [15–17]. The rapid diffusion of A atoms is realized by the formation and migration of point defects; furthermore, the outward diffusion of A atoms will result in the change of compositions, forming substoichiometric  $M_{n+1}A_{1-x}X_n$  phases. Thus, point defects in MAX phases and the stability of defective MAX phases have an important effect on the oxidation resistance and self-healing performance of MAX phases [18,19]. Point defects in MAX phases have also been reported to have a strong relationship with their radiation tolerance, which is important for neutron radiation resistant parts [20].

As MAX phases have a lamellar crystal structure, their properties along different crystal directions are different. If a favorable external condition, such as a uniaxial pressure or a magnetic field, is applied

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during the preparation process of MAX phases, lamellar grains can be preferentially aligned along specific directions, forming textured MAX phases possessing anisotropic properties [21–23]. Texturing of MAX phases can significantly improve their properties along specific directions and extend their application fields.

In this review, an overview of the formation mechanisms of MAX phases from elemental and compound powders is given. In addition, point defects and their influence on the self-healing performance and radiation tolerance, the use of solid solutions to tailor properties, and texture formation and anisotropic properties of MAX phases are discussed.

## 2. Formation mechanisms

As a MAX phase is composed of three different elements, it must be synthesized from mixed powders of several kinds of elemental or binary compound powders containing the three elements. In this section, the formation mechanisms of MAX phases from different starting materials are discussed.

### 2.1. Formation mechanisms from elemental powders

The formation process of MAX phases from elemental powders necessarily contains several steps. As the structure of MAX phases can be divided into the  $M_{n+1}X_n$  layers consisting of edge-shared  $M_6X$  octahedra with the strong  $M-X$  bonds and the A layers combined with the  $M_{n+1}X_n$  layers by the weak  $M-A$  bonds, it is reasonable to speculate that the  $M_xX_y$  compound could be an intermediate phase during the synthesis process of MAX phases, which has been proven to be consistent with many experimental results.

Hashimoto et al. [24] studied the formation mechanism of  $Ti_2AlC$

from  $2Ti:1Al:1C$  powders during self-propagating high-temperature synthesis (SHS). After ignition, the exothermic reaction between Ti and C forming TiC leads to the melting of Al, which forms an Al-Ti liquid phase. Subsequently, these TiC crystals are dissolved into the Al-Ti liquid phase, forming  $Ti_2AlC$ . Such a formation process of  $Ti_2AlC$  has also been proven by Thomas et al. [25] who studied the effect of particle sizes of the carbon sources on the phase compositions of samples produced from  $2Ti:1Al:1C$  powders. When carbon fibers were used as the carbon source, the contact area between Al and Ti increased due to the shape and size of carbon fibers, resulting in a high thermal conductivity of the cold pressed reactant.  $Ti_3Al$  alloy and TiC would be formed very fast, and then there would be a rapid cooling. The holding time at high temperatures would not be long enough for formation of  $Ti_2AlC$  from Ti-Al and TiC, as shown in Fig. 2(a). When graphite or carbon black powders were used as the carbon source, the contact area between Al and Ti decreased because they were surrounded by carbon, resulting in a low thermal conductivity of the cold pressed reactant which led to a much slower propagation of the combustion wave and ensured the completion of the reaction between Ti-Al and TiC to form  $Ti_2AlC$ , as shown in Fig. 2(b).

Similar results have also been obtained for the formation process of other MAX phases during SHS or other synthesis methods. Meng et al. [26] studied the reaction paths of SHS-ed  $Ti_3SiC_2$  by quenching at the bottom of a V-groove filled with mixed  $3Ti:1Si:2C$  powders right after ignition, and analyzed the phase compositions of different layers of the sample, as shown in Fig. 3. With the decrease of heat dissipation from bottom to top of the sample, the content of  $Ti_3SiC_2$  increased while the content of TiC and  $Ti_5Si_3$  decreased, indicating a more completed reaction from bottom to top, and demonstrating that TiC and  $Ti_5Si_3$  are the main intermediate phases during the synthesis process of  $Ti_3SiC_2$  from elemental powders. For  $Cr_2AlC$  prepared from  $2Cr:1.2Al:1C$  powders by

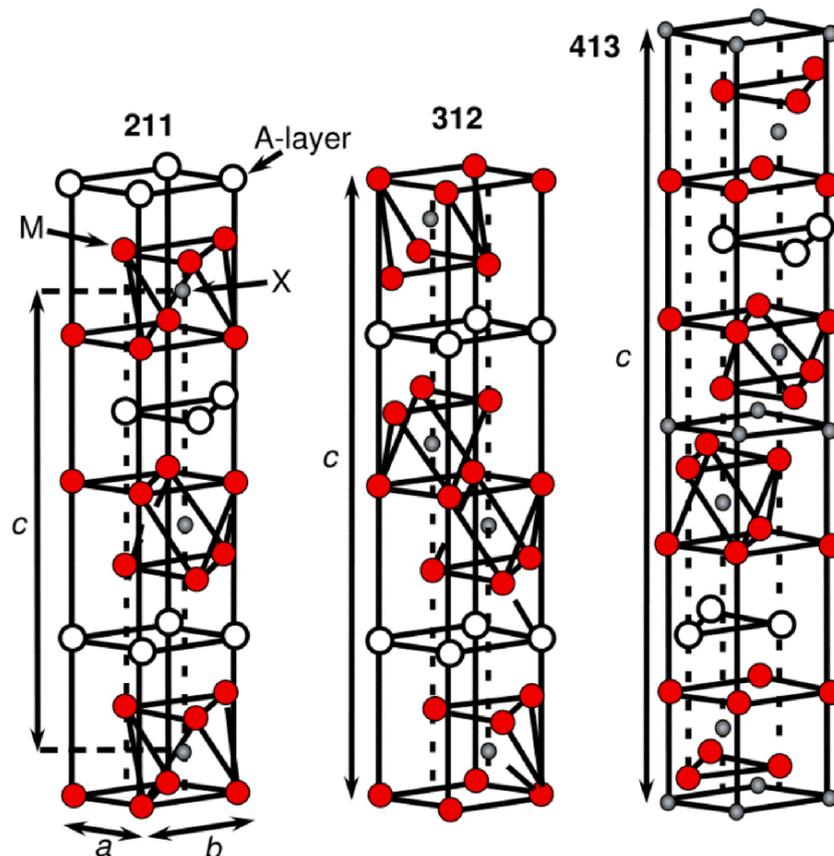


Fig. 1. Schematic diagram of the crystal structures of  $M_{n+1}AX_n$  phases with different  $n$  values. Reproduced with permission from Ref. [7], © 2016 Elsevier B.V.

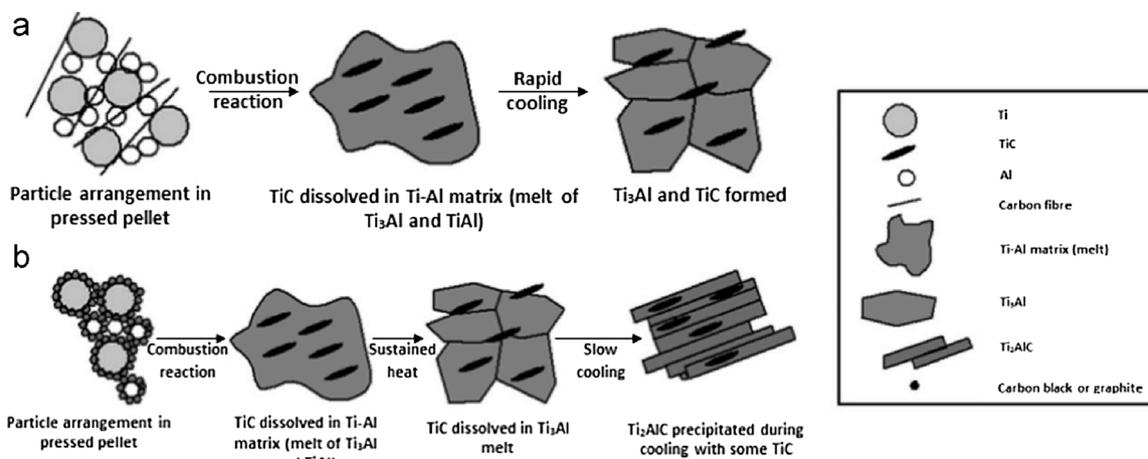


Fig. 2. Schematic diagram of the SHS process of 2Ti:1Al:1C powders with different carbon sources: (a) carbon fibers; (b) carbon black or graphite powders. Reproduced with permission from Ref. [25], © 2015 Elsevier Ltd and Techna Group S.r.l.

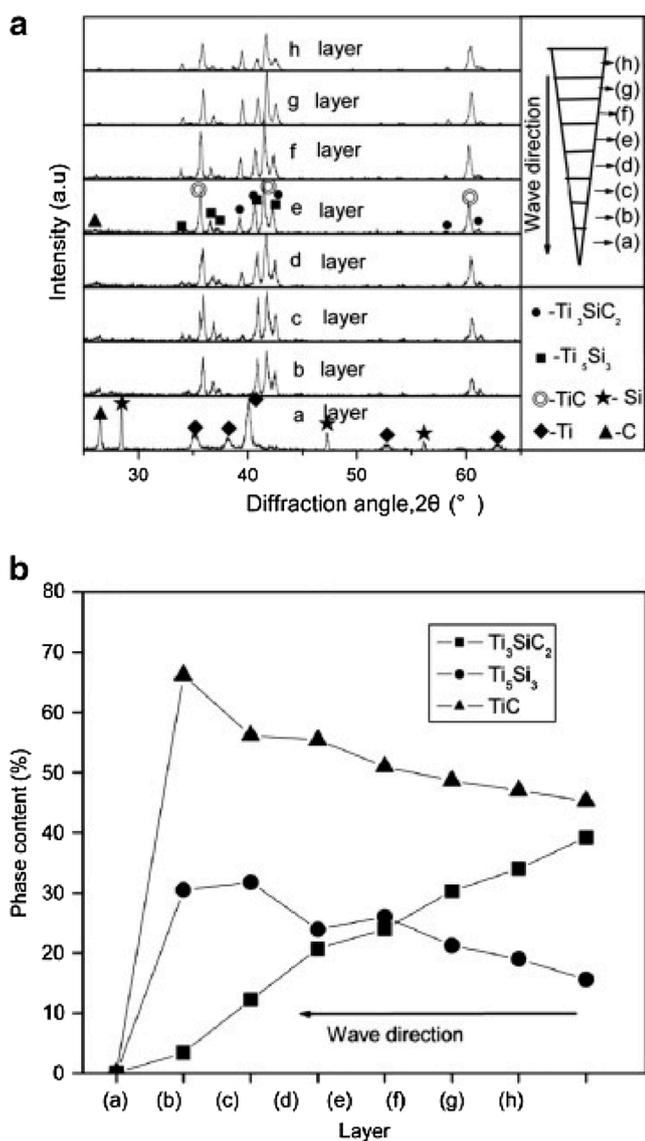


Fig. 3. (a) XRD patterns and (b) phase compositions of different sample layers prepared from mixed 3Ti:1Si:2C powders after combustion front quenching. Reproduced with permission from Ref. [26], © 2013 Elsevier Ltd.

spark plasma sintering (SPS), Cr<sub>7</sub>C<sub>3</sub> and Cr-Al alloys (Al<sub>8</sub>Cr<sub>5</sub>, AlCr<sub>2</sub>) were formed first (at 700~800 °C) and then react to form Cr<sub>2</sub>AlC, as shown in Fig. 4 [27]. TiN and Ti-Al alloys (Ti<sub>3</sub>Al, TiAl) were also observed to be formed first and then react to synthesize Ti<sub>2</sub>AlN for hot pressed samples from Ti-Al-N amorphous powders [28]. For MAX phase borides Zr<sub>2</sub>SB and Hf<sub>2</sub>SB synthesized via solid-state reactions from the stoichiometric mixtures of elemental powders, 15 wt.% ZrB<sub>2</sub> and 1 wt.% HfB<sub>2</sub> were also found to exist in the final samples [29].

The reaction process from M-A-X elemental powders leading to MAX phases can be summarized as elemental powders reacting to form M<sub>x</sub>X<sub>y</sub> phases and M<sub>x</sub>A<sub>y</sub> compounds first, then M<sub>x</sub>X<sub>y</sub> phases are dissolved into M<sub>x</sub>A<sub>y</sub> compounds to form MAX phases. To improve the purity of the synthesized MAX phases, a higher elemental A content in the starting materials than in the targeted MAX product is needed to make up for the vaporization loss of the A element during the high temperature synthesis, otherwise there would be residual M<sub>x</sub>X<sub>y</sub> phases or MAX phases with higher n values in the final product. While too high an elemental A content in the starting materials could result in the residual M<sub>x</sub>A<sub>y</sub> compounds [30–32]. Besides this, a prolonged holding time, or a higher synthesis temperature, could lead to more vaporization of the A element and an impurity residue in the product; while too low a temperature or too short a holding time is not enough for the complete reaction to form MAX phases [33–37]. Therefore, the adjustments of the elemental A

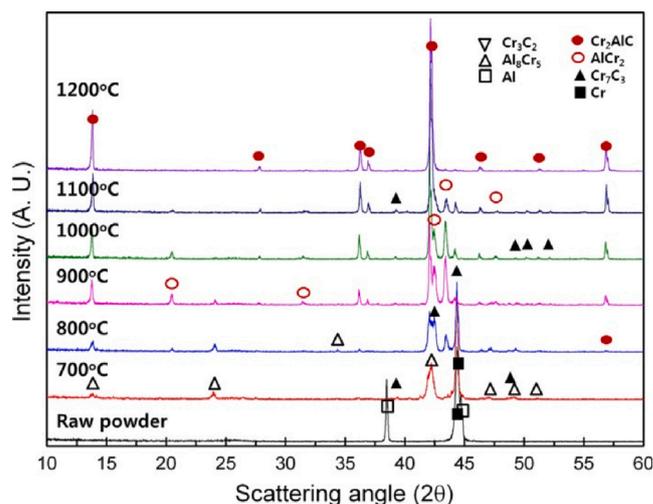


Fig. 4. XRD patterns of raw 2Cr:1.2Al:1C powders and the SPS-ed samples prepared at different temperatures. Reproduced with permission from Ref. [27], © 2013 Elsevier B.V.

content in the starting materials, the synthesis temperature and holding time are important to obtain MAX phases with a high purity.

## 2.2. Formation mechanisms from compound powders

As discussed in Section 2.1,  $M_xX_y$  and  $M_xA_y$  are two types of intermediate compounds during the synthesis of MAX phases from elemental powders. If the intermediate compounds are used as the starting materials, the reaction barrier to form MAX phases can be significantly reduced, thus making it possible to synthesize MAX phases with a higher purity or a decrease in their synthesis temperature.

The M–A bonds between the  $M_{n+1}X_n$  layers and A layers are relatively weaker than the M–X bonds inside the  $M_{n+1}X_n$  layers, which make it possible to prepare MAX phases by the intercalation of the A layers into the  $M_xX_y$  compounds with X vacancies. Riley et al. [38] first demonstrated this preparation idea by preparing SPS-ed  $Ti_3AlC_2$  bulk samples using Al and mechanically alloyed  $TiC_{0.67}$  powders.  $Ti_3AlC_2$  bulk samples were synthesized within 1 h at 1000 °C, which is 400–600 °C lower than the temperature required for SPS using elemental powders. The *in situ* neutron diffraction patterns during SPS are shown in Fig. 5. The absorption of Al by  $TiC_{0.67}$  occurred accompanied by the ordering of carbon vacancies in  $TiC_{0.67}$  (point B), and  $Ti_3AlC_2$  began to be synthesized at point C.

The synthesis temperature of MAX phases by such an intercalation method can be further decreased by long-time annealing. Wang et al. [39] successfully prepared  $Ti_2AlC$  coatings by long-time annealing the as-deposited  $TiC_{0.65}$ -Al alternatingly stacked multilayer coatings at a temperature as low as 550 °C. The  $TiC_{0.65}$ -Al layer boundaries

disappeared after annealing at 550 °C for 100 h, forming  $Ti_2AlC$  (Fig. 6 (a–f)). The content of  $Ti_2AlC$  increases with increasing the annealing temperature or prolonging the annealing time (Fig. 6(g)). It needs to be noted that a prolongation of the annealing time could be more effective than an increase in the annealing temperature, which can be seen from the sample annealed at 580 °C for 100 h, which has a much higher  $Ti_2AlC$  content than one annealed at 600 °C for 20 h. During low-temperature long-time annealing, Al atoms diffuse into  $TiC_{0.65}$  and replace carbon vacancies. With the prolongation of annealing, the structure of  $TiC_{0.65}$ -Al solid solution becomes more ordered where perfect  $Ti_2C$  layers are intercalated by the Al layers, as shown in Fig. 6(h). It has also been proven that using  $TiC_{0.6}$  and Al powders as the starting materials can lower the sintering temperature and shorten the holding time to prepare  $Ti_3AlC_2$  bulk samples with a higher purity and an improved flexural strength [40]. The study of the crystallographic relationship between  $Ti_3SiC_2$  and TiC also provided a theoretical support for the preparation of  $Ti_3SiC_2$  from  $TiC_x$  and Si by such an intercalation method [41].

Even when  $M_xA_y$  compound powders and X elemental powders are used as the starting materials, MAX phases would still be formed via the intermediate phases  $M_xX_y$ , which themselves can be formed by the diffusion of the X element into the  $M_xA_y$  compounds. Xiao et al. [42] studied the formation mechanism of  $Ti_2AlC$  from carbon coated Ti–Al alloy slices during hot pressing (HP). Firstly, carbon atoms diffuse into the Ti–Al alloy and form a  $TiC_x$  layer between the Ti–Al alloy and carbon. Under these conditions, there are many carbon vacancies and residual Al atoms in the  $TiC_x$  region away from carbon and near to the Ti–Al alloy, which make Al atoms easily diffuse into  $TiC_x$  and replace these carbon vacancies, forming  $Ti_2AlC$ . Stacking faults and micro-twins generated in the Ti–Al alloy under the uniaxial pressure provide fast atomic diffusion channels and act as quick nucleation zones for  $TiC_x$ .

The introduction of intermediate phases  $M_xX_y$  in the starting materials is a more favorable route to improve the purity of MAX phases in the final product. Meng et al. [26] compared the phase compositions of the SHS-ed samples prepared using 3Ti:1SiC:1C powders and 1Ti:1Si:2TiC powders, as shown in Fig. 7. Samples prepared using 1Ti:1Si:2TiC powders have a higher  $Ti_3SiC_2$  content and lower intermediate phases (TiC and  $Ti_5Si_3$ ) content than those prepared using 3Ti–SiC–C powders. Using  $Cr_3C_2$  as the carbon source (Fig. 8) is also more favorable for the  $Cr_2AlC$  phase formation as it allows a lower synthesis temperature than using elemental powders (Fig. 4) [27]. The introduction of TiC as the carbon source and the introduction of TiN as the nitrogen source were both proven to be beneficial to the purity improvement of  $Ti_3AlC_2$  and  $Ti_2AlN$  phases, respectively [43,44].

## 3. Point defects in MAX phases

The natural behavior of intrinsic point defects in MAX phases has a significant and positive influence on the neutron radiation tolerance and self-healing performance of MAX phases. In this section, the research on the defective properties of MAX phases including defect formation and defect migration are reviewed. The stability of MAX phases with A vacancies, which is related to their self-healing performance, and the radiation tolerance of MAX phases, which is largely determined by their defective properties (mainly the formation of  $M_A$ - $A_M$  anti-site pairs) are discussed in detail.

### 3.1. Formation and migration of point defects

The intrinsic point defects in MAX phases can be divided into vacancies, interstitial atoms and anti-site defects. For  $M_2AX$  phases, there are 3 types of vacancies ( $V_M$ ,  $V_A$ , and  $V_X$ ) and 6 types of anti-site defects ( $M_A$ ,  $M_X$ ,  $A_M$ ,  $A_X$ ,  $X_M$ , and  $X_A$ ); while for  $M_nAX_{n-1}$  phases ( $n > 2$ ), there are more types of vacancies and anti-site defects due to different chemical environments for the M atoms. For example, there are 2 types of Ti atoms for  $Ti_3AlC_2$  phases,  $Ti_I$  and  $Ti_{II}$  at  $2a(0, 0, 0)$  and  $4f(1/3, 2/3,$

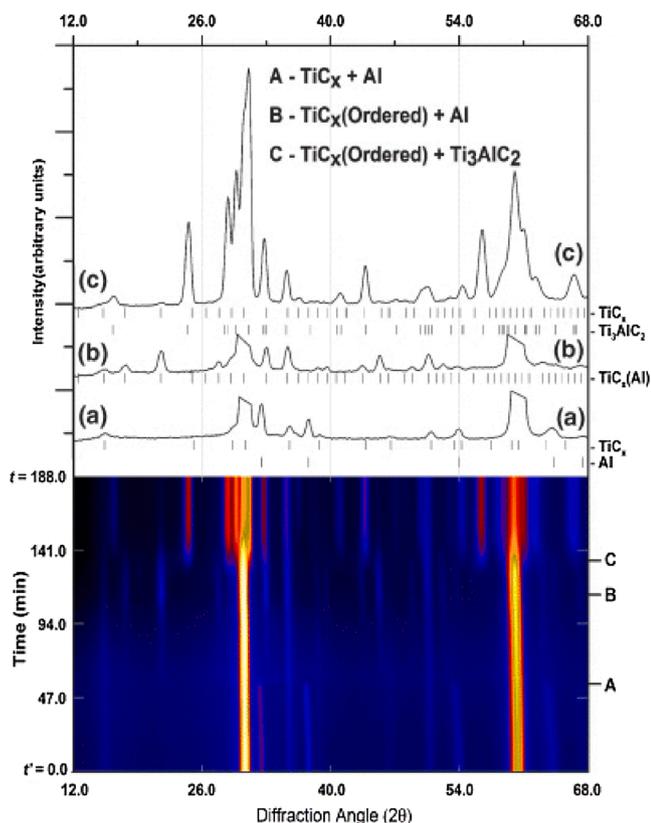
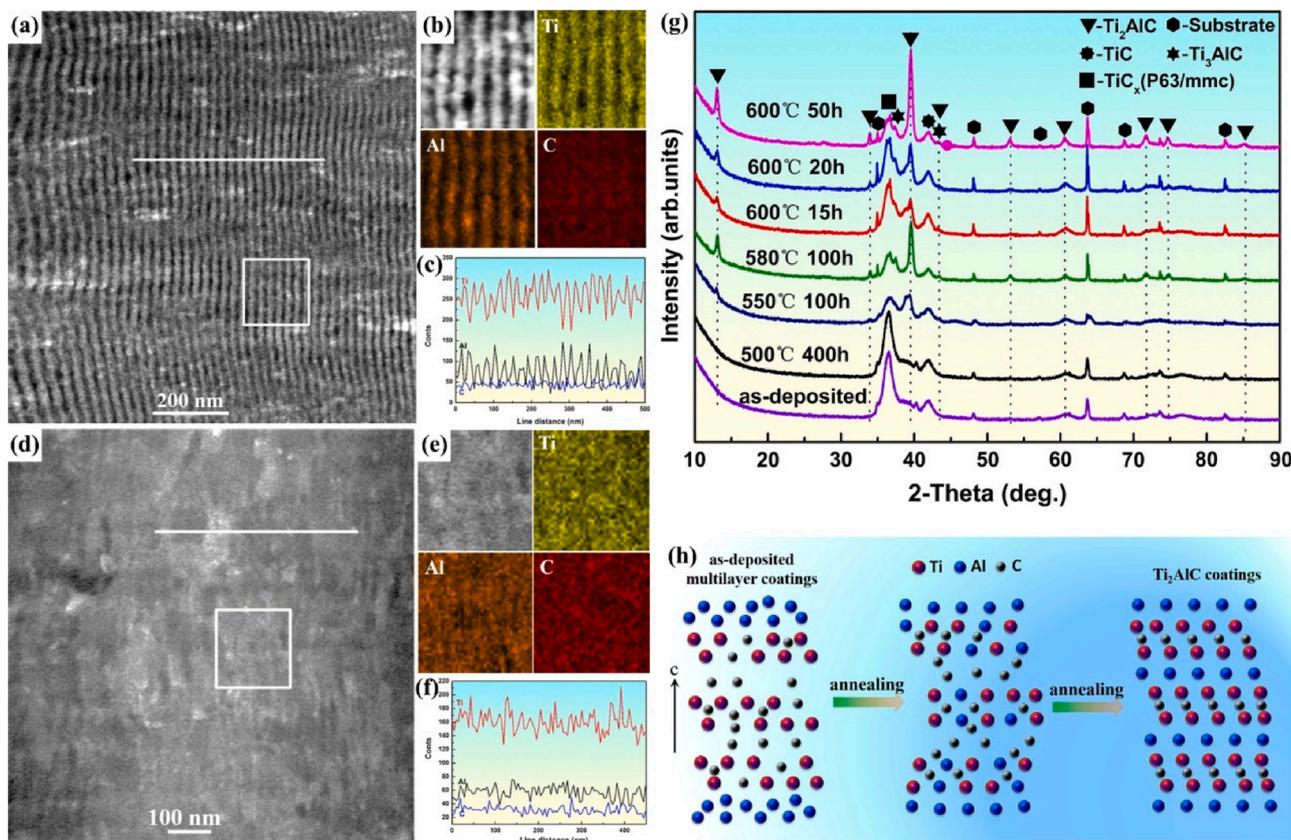


Fig. 5. Neutron diffraction intensity versus diffraction angle and time (Intensity is represented by color; letters mark significant stages during SPS) and the corresponding diffraction patterns at these stages: (a, A) The melting of Al at 660 °C; (b, B) Al absorbed by  $TiC_{0.67}$  accompanied by its spontaneously ordering at 700 °C; (c, C) the beginning of  $Ti_3AlC_2$  formation. Reproduced with permission from Ref. [38], © 2007 The American Ceramic Society.



**Fig. 6.** Preparation of  $\text{Ti}_2\text{AlC}$  coatings by low-temperature long-time annealing: (a–c) STEM analysis of the deposited  $\text{TiC}_{0.65}/\text{Al}$  multilayer coatings: (a) STEM image, (b) energy dispersive X-ray spectroscopy (EDX/EDS) mapping of the square area in (a), and (c) elemental concentrations from EDS line scan along the line in (a); (d–f) STEM analysis of coatings annealed at  $550\text{ }^\circ\text{C}$  for 100 h: (d) STEM image, (e) EDS mapping of the square area in (d), and (f) elemental concentrations from EDS line scan along the line in (d); (g) XRD patterns of coatings annealed at different temperatures for different time; (h) Schematic diagram of the formation process of  $\text{Ti}_2\text{AlC}$  during annealing of the as-deposited  $\text{TiC}_{0.65}/\text{Al}$  multilayer coatings. Reproduced with permission from Ref. [39], © 2019 Elsevier B.V.

z) Wyckoff positions, respectively, as shown in Fig. 9 [45], thus there are 4 types of vacancies and 8 types of anti-site defects. While the positions of interstitial atoms are more complex. Taking  $\text{Ti}_3\text{AC}_2$  phases as an example (Fig. 9), its crystal structure can be divided into 2 blocks, the  $\text{ATi}_{\text{II}}$  and  $\text{Ti}_3\text{C}_2$  blocks. The initial interstitial positions in the  $\text{ATi}_{\text{II}}$  block include the *a*, *b*, *c*, and *d* positions between the A atomic layer and  $\text{Ti}_{\text{II}}$  atomic layer, the *b*, *c*, and *d* positions in the A atomic layer, and the *a*, *c*, and *d* positions in the  $\text{Ti}_{\text{II}}$  atomic layer. The initial interstitial positions in the  $\text{Ti}_3\text{C}_2$  block include the I- $\text{Ti}_{\text{II}}\text{C}$  position between the  $\text{Ti}_{\text{II}}$  atomic layer and C atomic layer, the I- $\text{Ti}_1\text{C}$  position between the  $\text{Ti}_1$  atomic layer and C atomic layer, the I- $\text{Ti}_1$  position in the  $\text{Ti}_1$  atomic layer, and the I-C position in the C atomic layer. Interstitial atoms on different interstitial positions have different defect formation energies. Some positions, which vary depending on the compositions of MAX phases, are dynamically unstable [45,46]. The formation energies of interstitial atoms mentioned in the following text refer to those thermodynamically stable positions with the lowest formation energies. Generally, the formation energy of a point defect is lower when it is located in the  $\text{M}_{n+1}\text{A}$  block than in the  $\text{M}_{n+1}\text{X}_n$  block, which is attributed to the relatively weak M–A bonds between the  $\text{M}_{n+1}\text{X}_n$  layers and A layers [20,45].

Upon the formation of an interstitial atom, an atom leaves its lattice position and then is embedded in an interstitial position, forming a Frenkel pair consisting of a vacancy at the original lattice position of this atom and an interstitial atom at the interstitial position. The formation of Frenkel pairs (FP) in MAX phases is related to their structural stability in some harsh external environments (e.g., neutron radiation). Lower formation energies of FP indicate more persistent defects which can lead to a disordering of the structure [46]. If a vacancy is occupied by an

interstitial atom near to this vacancy, the two point defects will be annihilated, which is called *i-v* recombination [47]. If the interstitial atom during this *i-v* recombination is not the same as the original atom at this vacancy, an anti-site defect will be formed. Using the Kröger-Vink notation [48], the formation of anti-site defects by *i-v* recombination in MAX phases can be described as Eqs. (1–6) [49]:



Furthermore, an interstitial atom could also take the place of a nearby lattice atom, making the original lattice atom become a new interstitial atom. The displacement of lattice atoms by interstitial atoms can be described as Eqs. (7–12) [49]:



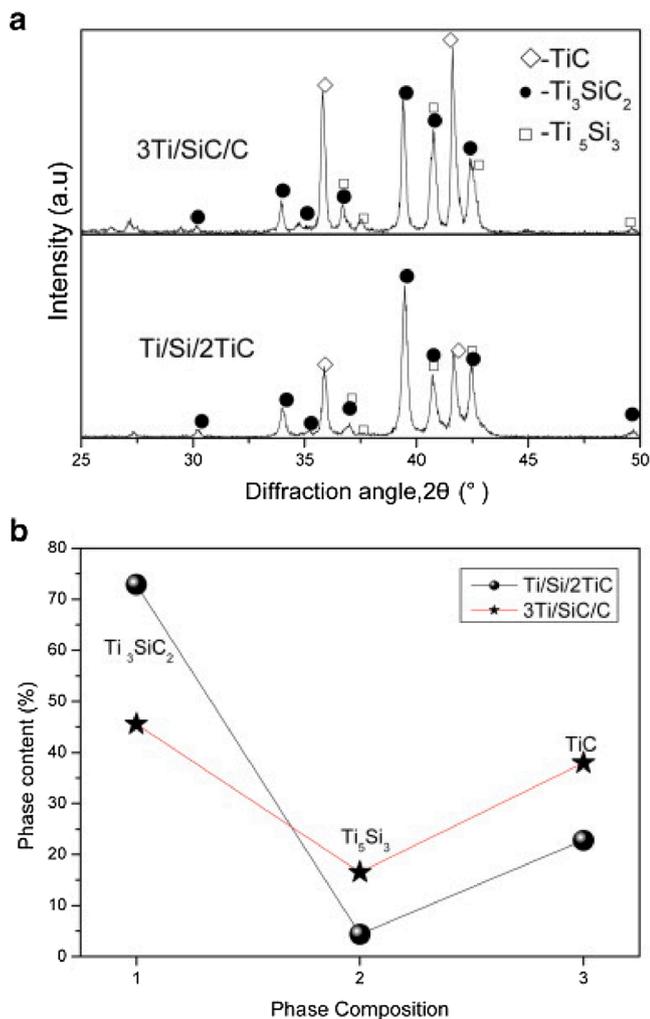


Fig. 7. (a) XRD patterns and (b) phase compositions of the SHS-ed samples prepared using 3Ti:1SiC:1C and 1Ti:1Si:2TiC.

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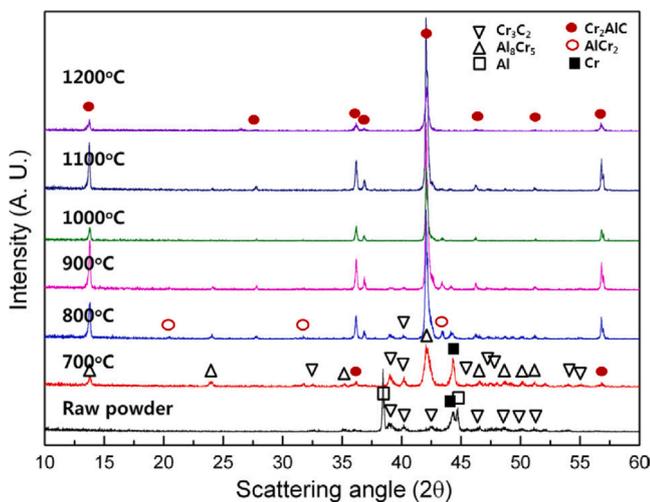


Fig. 8. XRD patterns of raw 1Cr:2.4Al:1Cr<sub>3</sub>C<sub>2</sub> powders and the SPS-ed samples prepared at different temperatures.

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Table 1 gives the calculated defect formation energies of FP and anti-site pairs and corresponding reaction energy barriers in Eqs. (1–12) for some typical MAX phases. It should be noted that the reaction energy barrier of one *i-v* recombination is not the formation energy of its corresponding anti-site defect. The formation energy of an anti-site defect includes the energy barriers of all reactions required starting from the defect-free state. For example, the formation energy of the  $M_X-X_M$  anti-site pair equals the sum of the formation energies of  $M_{FP}$  and  $X_{FP}$  and the reaction energy barriers of Eqs. (1) and (2).

The formation energies of defects vary depending on the compositions of MAX phases. Overall, the formation energies of  $A_{FP}$  and  $X_{FP}$  are lower than that of  $M_{FP}$ . Some MAX phases with low magnetic moments of the M element, e.g., Cr-based MAX phases having a magnetic moment of  $\sim 0.002 \mu_B$  per Cr atom, could have a lower formation energy of  $M_{FP}$  than  $A_{FP}$  compared with other MAX phases [50]. The low formation energy of  $A_{FP}$  results from the relatively weak M–A bonds between the  $M_{n+1}X_n$  layers and A layers, which is also consistent with the fact that the A atomic layers in MAX phases can be etched out from the layered structure, forming MXene [51–54].

The formation energies of the  $M_A-A_M$  anti-site pairs of MAX phases are much lower than those of  $M_X-X_M$  and  $A_X-X_A$  anti-site pairs, which is in correspondence with the fact that the M–A bonds are relatively weaker than the M–X bonds. Besides, the reaction energy barriers of the *i-v* recombination in Eqs. (5, 6) for all MAX phases are negative, indicating that a vacancy at an A atom lattice position and an interstitial M atom near it, or a vacancy at a M atom lattice position and an interstitial A atom near it, can recombine spontaneously at low temperatures. To some extent, the formation energies of the  $M_A-A_M$  anti-site pairs are influenced by the electronegative differences between M and A atoms, as shown in Fig. 10. The formation energy increases with the increase of the electronegative difference, which could provide important guidance on the choice of which type of MAX phase to use in neutron radiation resistant components.

Besides the formation energies of intrinsic point defects, their migration energies, which have not received widespread attention, also influence the *i-v* recombination. The lower the migration energy, the easier the point defect can be annihilated by *i-v* recombination. The lamellar structure of MAX phases makes the migration of point defects along layers much easier than that through layers. The strong M–X bonds in the  $M_{n+1}X_n$  layers and the weak M–A bonds between the  $M_{n+1}X_n$  layers and A layers also make the  $M_{n+1}A$  block act as a defect sink and provide convenient defect migration along or near to the A layers, which has been proven by Middleburgh et al. [56] for  $Ti_3AlC_2$  and  $Ti_3SiC_2$  (Table 2). For  $Ti_3AlC_2$ , the migration energy barrier of  $V_{Ti}$  along the  $Ti_{II}$  atomic layers is 3.11 eV, which is lower than the 4.27 eV for migration along the  $Ti_I$  atomic layers (the configurations of  $Ti_{II}$  and  $Ti_I$  are shown in Fig. 9), because the  $Ti_{II}$  atomic layers are near to the Al atomic layers while the  $Ti_I$  atomic layers are “sandwiched” by the C atomic layers. The migration energy barriers along the Al atomic layers, are 0.61 eV, 0.40 eV, 1.02 eV and 0.55 eV, respectively. For  $Ti_3SiC_2$ , the migration energy barriers of  $V_C$  along and through layers are 4.13 eV and 4.71 eV, respectively. These defects located in or near to the Si atomic layers, also have lower migration energy barriers than other defects. Similar results have also been obtained by Wang et al. [45] who proved that the  $Ti_A$  anti-site defects can migrate via a neighboring  $V_A$  along the A layers with low energy barriers, which are 0.6 eV and 0.3 eV for  $Ti_3AlC_2$  and  $Ti_3SiC_2$ , respectively. One difference between  $Ti_3AlC_2$  and  $Ti_3SiC_2$  is that one of the most preferential sites for  $C_i$  is located between the Al atomic layer and  $Ti_{II}$  atomic layer in  $Ti_3AlC_2$ , while all the preferential sites for  $C_i$  are located in the Si atomic layer in  $Ti_3SiC_2$ , which makes  $C_i$  more easily to migrate and be recombined with  $V_C$  for  $Ti_3AlC_2$  and attributes to its better radiation tolerance than  $Ti_3SiC_2$ .

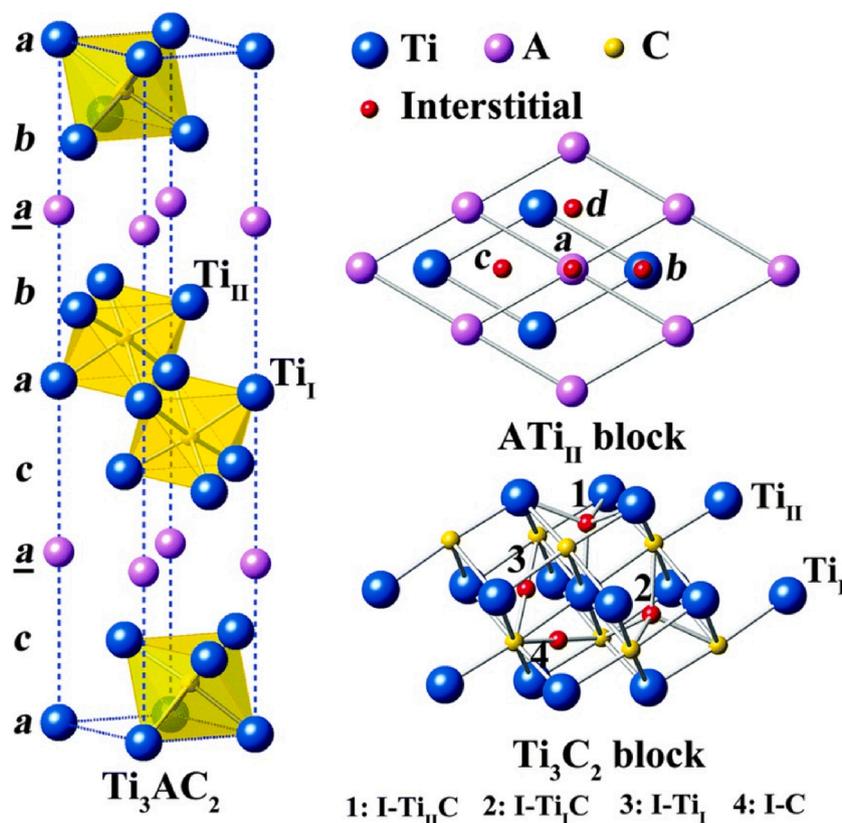


Fig. 9. Schematic diagrams of the crystal structure and initial interstitial positions of  $\text{Ti}_3\text{AC}_2$ . Reproduced with permission from Ref. [45], © the PCCP Owner Societies 2015.

### 3.2. Stability of MAX phases with A vacancies

A-related defects usually have relatively low formation energies (Table 1), and migrate easily along the A layers, especially for  $\text{A}_1$  (Table 2), so the transport of A atoms is relatively fast and this is important for the self-healing behavior of MAX phases when a micro-cracked material is exposed to air or combustion gas residues at high temperatures. Furthermore, the oxidation of A atoms also results in the formation of new A vacancies in MAX phases which travel in the opposite direction as the growth direction of the oxide. The issue of the phase stability in case of a high concentration of A vacancies has not been assessed widely, but plays an important role in setting the self-healing potential of MAX phases.

It has been proven that  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  can retain their layered structure after losing some of their Si or Al atoms. Fig. 11 [57] shows the cross-sectional TEM images of a  $\text{Ti}_3\text{SiC}_2$  film after annealing in vacuum at 1100 °C for 25 h. There is a thin protective layer of  $\text{TiO}_2$  (a thickness of 3–4 nm), which has been typically observed on  $\text{Ti}_3\text{SiC}_2$  films.  $\text{TiC}_{0.67}$ , which was decomposed from  $\text{Ti}_3\text{SiC}_2$ , is between the protective layer and the  $\text{Ti}_3\text{SiC}_2$  matrix. A residual amount of Si still exists in the form of locally remaining Si layers (white arrowheads) in the  $\text{TiC}_{0.67}$  layer, indicating that  $\text{TiC}_{0.67}$  is formed by diffusion and oxidation of Si in the  $\text{Ti}_3\text{SiC}_2$  matrix. The elemental concentrations from EDX line scan (the dash line corresponds to the interface between the  $\text{TiC}_{0.67}$  layer and the  $\text{Ti}_3\text{SiC}_2$  matrix) shows that there is less Si content in the  $\text{Ti}_3\text{SiC}_2$  area near to the  $\text{TiC}_{0.67}$  layer, indicating that  $\text{Ti}_3\text{SiC}_2$  can retain its layered structure after partial loss of Si. Fig. 12 [58] shows the high-resolution TEM (HRTEM) images and EDX spectra of  $\text{Ti}_3\text{AlC}_2$ -Cu composites HP-ed at 950 °C. Al diffused from  $\text{Ti}_3\text{AlC}_2$  into the Cu, forming the Cu (Al) solid solution and TiC. EDX spectra demonstrate the partial loss of Al in the defective  $\text{Ti}_3\text{AlC}_2$  after HP, and the HRTEM images prove the structural stability of the defective  $\text{Ti}_3\text{AlC}_2$ .

Calculations by Wang et al. [59] demonstrated that  $\text{Ti}_2\text{AlC}$  can

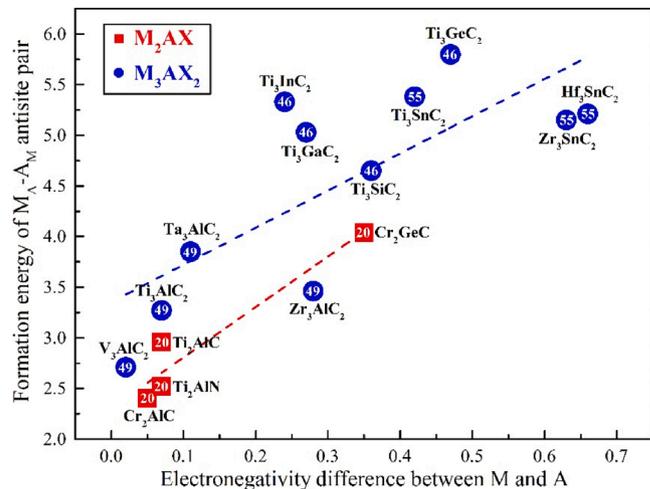
maintain its lamellar structure after losing as many as half of its Al atoms, as shown in Fig. 13. A positive cohesive energy difference  $\Delta E_{\text{coh}}$  between the defective  $\text{Ti}_2\text{Al}_x\text{C}$  and its decomposition products ( $\text{Ti}_2\text{C}$ - $x\text{Al}$ ) means that the defective  $\text{Ti}_2\text{Al}_x\text{C}$  is stable relative to  $\text{Ti}_2\text{C}$  and Al, while a negative  $\Delta E_{\text{coh}}$  means that the defective  $\text{Ti}_2\text{Al}_x\text{C}$  will decompose into  $\text{Ti}_2\text{C}$  and Al (Fig. 13(a)). Therefore, the defective  $\text{Ti}_2\text{Al}_x\text{C}$  with  $x > 0.5$  would not decompose. Fig. 13(b) reflects that the lattice parameters of  $\text{Ti}_2\text{Al}_x\text{C}$  change only marginally for  $0.5 < x < 1.0$ , while the lattice parameter  $c$  decreases dramatically with the decrease of  $x$  from 0.5 to 0, indicating that the Ti–Al bonds between the  $\text{Ti}_2\text{C}$  layers and  $\text{Al}_x$  layers are strong enough to maintain the phase stability of  $\text{Ti}_2\text{Al}_x\text{C}$  with  $x > 0.5$ , while the further loss of Al will result in a rapid structure shrinkage along the  $c$ -axis, that is, the collapse of the layered structure of  $\text{Ti}_2\text{AlC}$ .

### 3.3. Effect of defective properties on radiation tolerance

Due to their unique properties combining those of metals and ceramics, their good high temperature stability and their lower neutron absorption cross-section than refractory metals, MAX phases have been proposed as candidate structural materials for components to be exposed to extreme radiation conditions as in future nuclear reactors [60–63]. Therefore, research on the radiation tolerance of MAX phases is important to screen out ideal MAX phases suitable for this field. Neutron or ion radiation can result in the accumulation of Frenkel defects (vacancies and interstitial atoms) caused by displacement cascades in materials, which would lead to amorphization if materials cannot accommodate these point defects [47,64]. As discussed in Section 3.1, vacancies and interstitial atoms can be annihilated by the  $i$ - $v$  recombination, which would form anti-site defects if the interstitial atom during the  $i$ - $v$  recombination is not the same as the original atom at this vacancy. Therefore, the formation of anti-site defects can accommodate significant concentrations of point defects, among which the  $\text{M}_A\text{-A}_M$  anti-site pairs have the lowest formation energy, as shown in Table 1,

**Table 1**  
Calculated defect formation energies and reaction energy barriers (eV) of some typical MAX phases.

Researcher	Xiao et al. [20]	Christopoulos et al. [46]	Christopoulos et al. [49]
MAX phase	Cr <sub>2</sub> AlC	Ti <sub>3</sub> AlC	Ti <sub>3</sub> AlC <sub>2</sub>
M <sub>FP</sub>	7.05	7.57	7.43
A <sub>FP</sub>	7.26	3.67	6.12
X <sub>FP</sub>	3.14	4.01	1.46
M <sub>X</sub> -X <sub>M</sub>	7.53	11.78	6.31
A <sub>X</sub> -X <sub>A</sub>	8.86	9.41	2.73
M <sub>X</sub> -A <sub>M</sub>	2.40	2.96	10.60
M <sub>i</sub> + V <sub>X</sub> → M <sub>X</sub>		3.45	9.36
X <sub>i</sub> + V <sub>M</sub> → X <sub>M</sub>		-0.41	2.71
A <sub>i</sub> + V <sub>X</sub> → A <sub>X</sub>		-0.06	-0.63
X <sub>i</sub> + V <sub>A</sub> → X <sub>A</sub>		0.06	0.14
A <sub>i</sub> + V <sub>M</sub> → A <sub>M</sub>		-3.15	0.12
M <sub>i</sub> + V <sub>A</sub> → M <sub>A</sub>		-2.69	0.21
M <sub>i</sub> + X <sub>X</sub> → M <sub>X</sub> + X <sub>i</sub>		6.54	-5.38
X <sub>i</sub> + M <sub>M</sub> → X <sub>M</sub> + M <sub>i</sub>		6.89	-5.62
A <sub>i</sub> + X <sub>X</sub> → A <sub>X</sub> + X <sub>i</sub>		3.03	-1.72
X <sub>i</sub> + A <sub>A</sub> → X <sub>A</sub> + A <sub>i</sub>		3.25	2.10
A <sub>i</sub> + M <sub>M</sub> → A <sub>M</sub> + M <sub>i</sub>		4.16	7.70
M <sub>i</sub> + A <sub>A</sub> → M <sub>A</sub> + A <sub>i</sub>		0.50	8.58
			8.78
			6.84
			5.55
			3.71
			6.42
			2.99
			3.12
			0.87
			0.15



**Fig. 10.** The relationship between the formation energies of the M<sub>A</sub>-A<sub>M</sub> anti-site pairs and the electronegativity differences (from the periodic table of electronegativity by Pauling scale) between M and A atoms of some typical MAX phases. (Reference numbers are shown in the circles or squares).

**Table 2**

Calculated migration energy barriers (eV) of intrinsic point defects in Ti<sub>3</sub>AlC<sub>2</sub> and Ti<sub>3</sub>SiC<sub>2</sub>.

	V <sub>Ti</sub>	V <sub>C</sub>	V <sub>A</sub>	A <sub>i</sub>	Ti <sub>i</sub>	C <sub>i</sub>	Ti <sub>A</sub>
Ti <sub>3</sub> AlC <sub>2</sub>	3.11 <sup>a</sup> (Ti <sub>II</sub> )	3.50 <sup>b</sup>	0.61 <sup>a</sup>	0.40 <sup>a</sup>	1.02 <sup>a</sup>	0.55 <sup>a</sup>	0.60 <sup>b</sup>
Ti <sub>3</sub> SiC <sub>2</sub>	3.51 <sup>a</sup> (Ti <sub>II</sub> )	4.13 <sup>a</sup> , 3.60 <sup>b</sup> (//)	0.61 <sup>a</sup>	0.02 <sup>a</sup>	0.99 <sup>a</sup>	0.45 <sup>a</sup>	0.30 <sup>b</sup>
		4.71 <sup>a</sup> (⊥)	0.90 <sup>b</sup>			1.40 <sup>b</sup>	

<sup>a</sup>Ref [56]; <sup>b</sup>Ref [45]; //: migration along layers; ⊥: migration through layers; Energy barriers without notes indicate migration along layers.

making the formation of the M<sub>A</sub>-A<sub>M</sub> anti-site pairs an effective way to annihilate point defects.

As TiC and TiN ceramics both possess a high radiation tolerance, it is reasonable to speculate that Ti<sub>n+1</sub>AC<sub>n</sub> and Ti<sub>n+1</sub>AN<sub>n</sub>, which have similar Ti—C and Ti—N bonds to those in TiC and TiN, could also have a good radiation tolerance [65,66]. Therefore, out of all MAX phases, Ti<sub>n+1</sub>AC<sub>n</sub> and Ti<sub>n+1</sub>AN<sub>n</sub> are the most studied ones for their radiation tolerance. It has been observed that Ti<sub>3</sub>AlC<sub>2</sub> possesses a better structural stability than Ti<sub>3</sub>SiC<sub>2</sub> under radiation, as shown in Fig. 14(a–l) [67]. The lamellar structure of Ti<sub>3</sub>AlC<sub>2</sub> is well maintained upon radiation leading to 10 displacements per atom (dpa) at room temperature, while the nano-lamellar structure of Ti<sub>3</sub>SiC<sub>2</sub> is heavily damaged. As indicated by the white arrows in Fig. 14(e, k), for both Ti<sub>3</sub>AlC<sub>2</sub> and Ti<sub>3</sub>SiC<sub>2</sub>, the (000) (l = 8n) diffraction spots get stronger while the (̄110l) (l = 8n and 8n ± 1) diffraction spots get weaker upon radiation leading to 5 dpa, which is attributed to the increase of symmetry caused by the phase transformation from α-Ti<sub>3</sub>AC<sub>2</sub> to β-Ti<sub>3</sub>AC<sub>2</sub> (A = Al or Si) leading to a change in the stacking sequence of ABABACAC in α-Ti<sub>3</sub>AC<sub>2</sub> to a sequence of ABCBACBC in β-Ti<sub>3</sub>AC<sub>2</sub>. However, the simulated electron diffraction pattern of traditional β-Ti<sub>3</sub>AlC<sub>2</sub> (Fig. 14(m)) is still not in agreement with the observed pattern (Fig. 14(e)) due to the formation of Ti<sub>Al</sub>-Al<sub>Ti</sub> anti-site defects which lead to the mixture of the Ti atomic layers and Al atomic layers and the rearrangement of C atoms. The simulated electron diffraction pattern of modified β-Ti<sub>3</sub>AlC<sub>2</sub> after mixing Ti and Al atoms and rearranging C atoms (Fig. 14(n)) is well consistent with the observed pattern. For Ti<sub>3</sub>SiC<sub>2</sub>, dislocation loops and stacking faults are observed upon radiation leading to 5 dpa (Fig. 14(h)), and a further increase of dpa results in the formation of nanodomains with different stacking

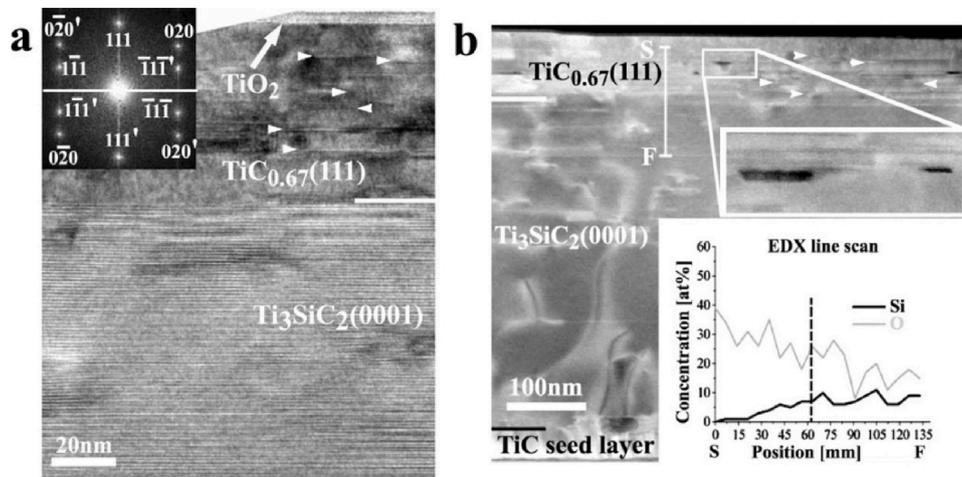


Fig. 11. Cross-sectional TEM images of a  $\text{Ti}_3\text{SiC}_2$  film after annealing in vacuum at  $1100\text{ }^\circ\text{C}$  for 25 h: (a) TEM image with a fast Fourier transformation (FFT) from  $\text{TiC}_{0.67}$ ; (b) Scanning TEM image with the elemental concentrations from EDX line scan along S-F. Reproduced with permission from Ref. [57], © 2006 Acta Materialia Inc. Published by Elsevier Ltd.

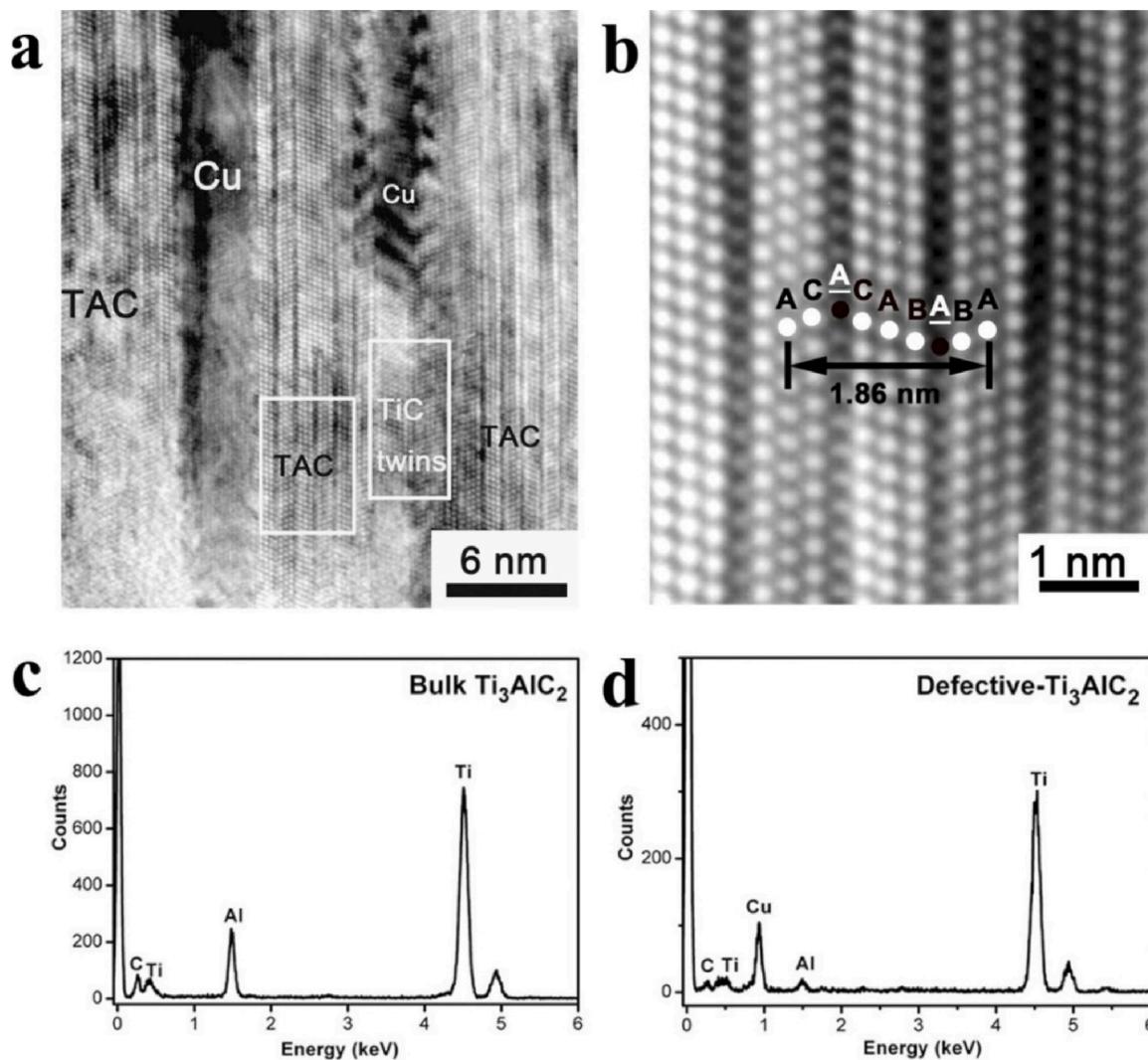


Fig. 12. HRTEM images and EDX spectra of HP-ed  $\text{Ti}_3\text{AlC}_2\text{-Cu}$  composites: (a) HRTEM image contains  $\text{Ti}_3\text{AlC}_2$ , Cu and TiC; (b) HRTEM image of the defective  $\text{Ti}_3\text{AlC}_2$  after losing partial Al; (c) EDX spectrum of the bulk  $\text{Ti}_3\text{AlC}_2$ ; (d) EDX spectrum of the defective  $\text{Ti}_3\text{AlC}_2$ . Reproduced with permission from Ref. [58], © 2007 Acta Materialia Inc. Published by Elsevier Ltd.

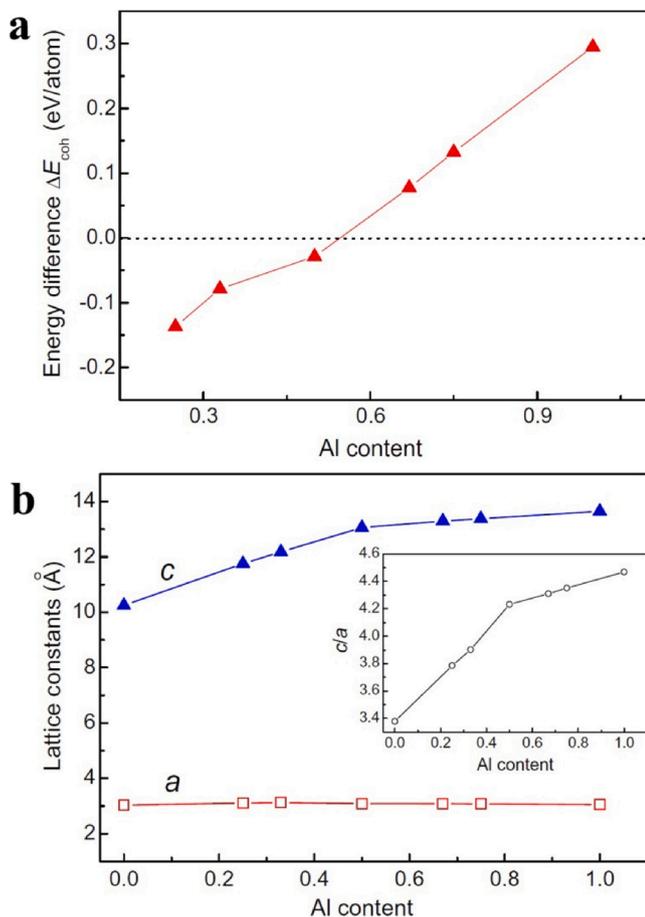


Fig. 13. Dependence of (a) cohesive energy difference  $\Delta E_{\text{coh}}$  between the defective  $\text{Ti}_2\text{Al}_x\text{C}$  and  $\text{Ti}_2\text{C-xAl}$ , and (b) lattice constants  $c$ ,  $a$  and  $c/a$  on Al content.

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sequences (Fig. 14(i)). The arc-shaped diffraction spots also indicate the presence of polygonization (Fig. 14(l)). Fig. 14(o) shows a possible formation process of nanograins with different stacking sequences during radiation, where a symmetry plane B is removed by displacement collision, followed by the lamellar collapse along the  $c$ -axis and the movement of one of the two face-to-face C planes, forming two fcc-structured stacking sequences (ABCABC and CBACBA) having a twinning relationship. Such fcc-structured stacking sequences with a twinning relationship has also been found in  $\text{Ti}_3\text{AlC}_2$  where they expanded to form nanotwins [68,69]. Fig. 14(p) shows the simulated electron diffraction pattern of a  $\{111\}$  twinned fcc structure, which is inconsistent with Fig. 14(l), indicating that nanotwins with the fcc structure in  $\text{Ti}_3\text{SiC}_2$  can be formed upon radiation leading to 10 dpa. The growth of twinned stacking sequences with the fcc structure can form nanotwins with either regular, coherent twin boundaries (CTB) or irregular, incoherent twin boundaries (ITB), in which the CTB can be either a cation layer (Ti and Al/Si) or an anion layer (C), as shown in Fig. 14(q–s). The nanotwins with the fcc structure can also be formed in irradiated  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_2\text{AlN}$  [70,71]. Unlike the formation process of nanotwins in  $\text{M}_3\text{AX}_2$ , nanotwins in  $\text{M}_2\text{AX}$  are formed by inserting an extra B plane into the  $\gamma$ - $\text{M}_2\text{AX}$  with a stacking sequence of ABCACB.

The nanotwins in  $\text{Ti}_3\text{AlC}_2$  can maintain crystalline order upon radiation by Au ions leading to 150 dpa, showing an excellent radiation tolerance [69]. For  $\text{Ti}_3\text{SiC}_2$ , radiation by Xe ions leading to 25–30 dpa could lead to amorphization [72]. The difference between the structural stability of  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{SiC}_2$  probably results from the difference in their A–X interaction. There is a remarkable overlap between C 2p and Si

3p states in  $\text{Ti}_3\text{SiC}_2$ , while such a strong overlap is not observed in  $\text{Ti}_3\text{AlC}_2$ . The weak Al–C interaction in  $\text{Ti}_3\text{AlC}_2$  benefits the  $i$ - $v$  recombination, giving it a high structural stability under radiation. In contrast, the strong overlap between Si–C states in  $\text{Ti}_3\text{SiC}_2$  increases the possibility of forming amorphous SiC on a nanoscale, as the calculated Si–C bond length with the introduction of point defects in  $\text{Ti}_3\text{SiC}_2$  is 0.188 nm, which is consistent with the Si–C bond length in amorphous SiC [20, 73]. Besides, the lower formation energy of the  $\text{Ti}_{\text{Al}}\text{Al}_{\text{Ti}}$  anti-site defect than the  $\text{Ti}_{\text{Si}}\text{Al}_{\text{Si}}$  anti-site defect (Table 1) also gives  $\text{Ti}_3\text{AlC}_2$  a better Frenkel defect annihilation ability by  $i$ - $v$  recombination.

Although the crystalline structure of  $\text{Ti}_3\text{AlC}_2$  is more stable than  $\text{Ti}_3\text{SiC}_2$  under radiation, under low temperature radiation cracks form more easily in  $\text{Ti}_3\text{AlC}_2$  bulk materials, which is probably due to its more significantly anisotropic lattice swelling caused by an accumulation of point defects and a higher  $\beta$ -phase content. The lattice swelling of  $\text{Ti}_3\text{SiC}_2$  under low temperature radiation is not that significant, which always leads to good anti-cracking under low or high temperature radiation (Fig. 15(a, b)). For  $\text{Ti}_3\text{AlC}_2$ , high temperatures can accelerate the  $i$ - $v$  recombination process, preventing the lattice swelling and crack initiation (Fig. 15(c, d)) [67]. The crack initiation due to anisotropic lattice swelling at low radiation temperatures has also been observed in  $\text{Ti}_2\text{AlC}$  [62].

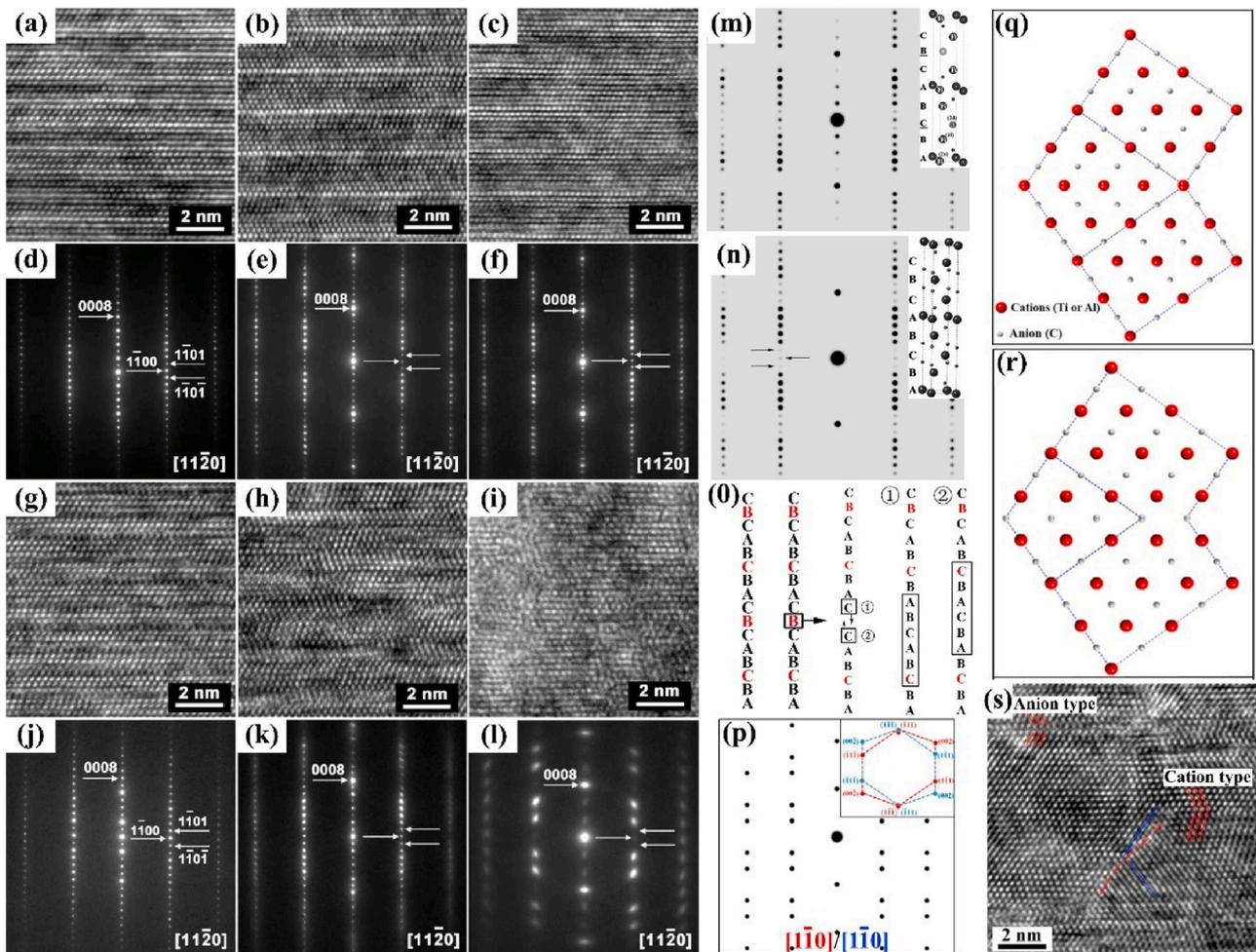
The lattice swelling caused by point defects under radiation at different temperatures is also reflected in the change of hardness values. Hardening after low temperature (400 °C) radiation by Ni ions leading to 10 dpa has been observed in  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_3\text{SiC}_2$ , among which the hardening effect in  $\text{Ti}_3\text{AlC}_2$  is the most significant (1.9 times of that before radiation). Due to the spontaneous annihilation of point defects, the radiation hardening caused by high temperature (700 °C) radiation leading to the same dpa is much weaker [62]. The hardening can also be undone by high temperature annealing after low temperature radiation [74]. The hardening after low temperature radiation has also been observed in some MAX phase solid solutions such as  $\text{Ti}_3\text{Si}_{0.9}\text{Al}_{0.1}\text{C}_2$ ,  $\text{Ti}_3\text{Si}_{0.95}\text{Al}_{0.05}\text{C}_2$  and  $(\text{Ti}_{0.95}\text{Zr}_{0.05})_3\text{Si}_{0.9}\text{Al}_{0.1}\text{C}_2$  [75].

In conclusion, the defect population in MAX phases determines their phase stability in some harsh external environments, among which the formation processes of intrinsic point defects have been widely studied and confirmed to have an important effect on their self-healing performance and radiation tolerance. Defect migration and phase stability of defective MAX phases need to be further studied. Generally, defects are more easily formed in the  $\text{M}_{n+1}\text{A}$  block and migrate along the A layers, making the  $\text{M}_{n+1}\text{A}$  block perform as a defect sink where defect formation, migration and recombination occur, and inducing disorder accommodation and defect recovery.

#### 4. Solid solutions

Different MAX phases, having the same structure but a difference in one of the three components can possess significantly different properties. For example, the electrical conductivities of hot isostatic pressed  $\text{Hf}_2\text{SnC}$  and  $\text{Hf}_2\text{PbC}$  bulk samples are  $2.2 \times 10^6$  ( $\Omega \text{ m}^{-1}$ ) and  $13.4 \times 10^6$  ( $\Omega \text{ m}^{-1}$ ), respectively [76]; the thermal conductivities at room temperature of HP-ed  $\text{Ta}_4\text{AlC}_3$  and  $\text{Nb}_4\text{AlC}_3$  are 38.4 W/(m K) and 13.5 W/(m K), respectively, and their Vickers hardnesses are 5.1 GPa and 2.6 GPa, respectively [77,78]. Adjusting the compositions of MAX phases to create solid solutions could be a possible method to tailor their properties to meet specific requirements.

Interestingly, for some MAX phase solid solutions, solid solutions with a quite high solid solubility can be obtained, while it is impossible to synthesize their pure parent phases. For example,  $(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{AlC}_2$  was successfully synthesized by reactive HP from elemental powders, while  $\text{Cr}_3\text{AlC}_2$  has never been experimentally reported [79]. Similarly, Mn has been used as an alloying element for the M-site atoms in  $\text{Cr}_2\text{AlC}$ , forming  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$  to tailor its magnetic properties, although  $\text{Mn}_2\text{AlC}$  does not exist [80,81]. In this section, the ordered or disordered structures of M alloyed  $\text{M}_{n+1}\text{AX}_n$  phases are presented, and the



**Fig. 14.** Characterization of radiated  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{SiC}_2$ : (a~c) HRTEM images of  $\text{Ti}_3\text{AlC}_2$  radiated by Xe ions at room temperature leading to dpa values of (a) 0, (b) 5, and (c) 10, respectively; (d~f) corresponding selected-area electron diffraction (SAED) patterns of (a~c); (g~i) HRTEM images of  $\text{Ti}_3\text{SiC}_2$  radiated at room temperature leading to dpa values of (g) 0, (h) 5, and (i) 10, respectively; (j~l) corresponding SAED patterns of (g~i); (m) and (n) simulated electron diffraction patterns of traditional and modified  $\beta\text{-Ti}_3\text{AlC}_2$ , respectively; (o) schematic diagram of a possible formation process of nanograins with two different stacking sequences with a twinning relationship; (p) simulated electron diffraction pattern of  $\{111\}$  twinned fcc structure; (q) and (r) two types of CTB in twinned fcc-structured  $(\text{TiAl}_{0.33})\text{C}_{0.66}$  with a cation layer and an anion layer as twin boundaries, respectively; (s) HRTEM image shows an irregular ITB (red dash line) and two types of CTB in radiated  $\text{Ti}_3\text{AlC}_2$ .

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properties of MAX phase solid solutions are discussed.

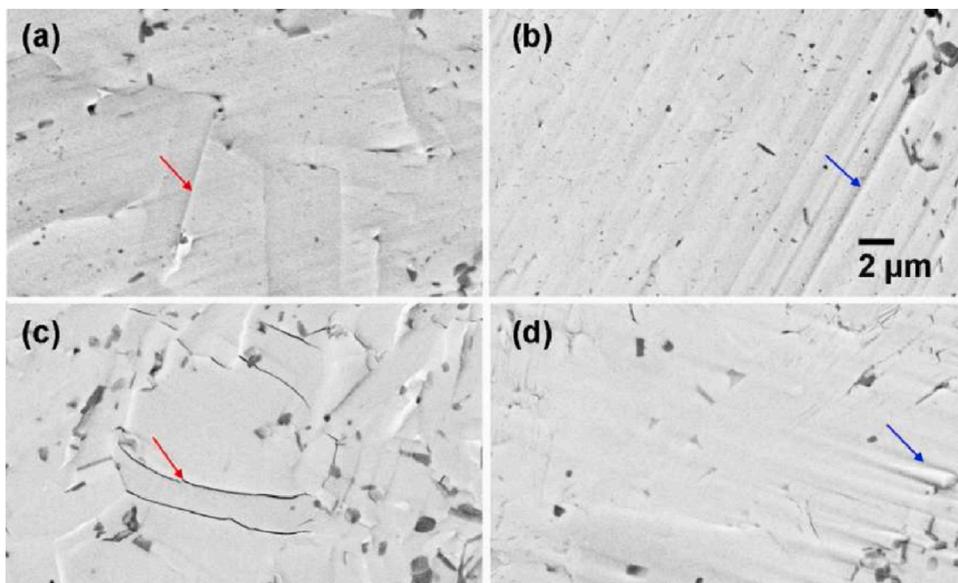
#### 4.1. Occupied positions of alloying M atoms

M alloyed  $\text{M}_{n+1}\text{AX}_n$  phases being the most widely studied MAX phase solid solutions system, possess more than one type of Wyckoff positions of M atoms when  $n > 1$ . For  $\text{M}_3\text{AX}_2$ , the Wyckoff positions of M atoms in one  $\text{M}_3\text{X}_2$  block include one inner  $2a$  (0, 0, 0) positions and two outer  $4f$  ( $1/3, 2/3, z$ ) position. For  $\text{M}_3\text{AX}_2$ , the Wyckoff positions of M atoms in one  $\text{M}_4\text{X}_3$  block include two inner  $4f$  ( $1/3, 2/3, z$ ) positions and two outer  $4e$  (0, 0,  $z$ ) positions. Thus, the alloying M atoms could orderly occupy some Wyckoff positions.

In 2014, Liu et al. [82] reported two new MAX phase solid solutions,  $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$  and  $(\text{Cr}_{5/8}\text{Ti}_{3/8})_4\text{AlC}_3$  prepared by hot pressing elemental powders, and speculated that it could be possible to synthesize  $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$  where Cr and Ti atoms occupy  $4f$  and  $2a$  Wyckoff positions, respectively. Soon after, Liu et al. [83] synthesized the first M-ordered MAX phase solid solution,  $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$  by heating mixed  $1\text{TiC}:1\text{Cr}_2\text{AlC}$  powders at  $1500^\circ\text{C}$  for 30 min under flowing Ar. They proved that Ti atoms occupy  $2a$  Wyckoff positions, which are

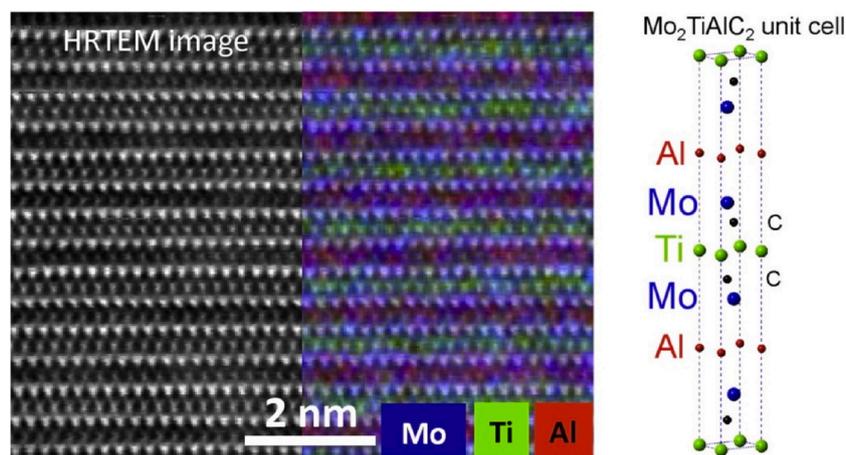
sandwiched by  $4f$  Wyckoff positions occupied by Cr atoms as deduced via combined ND and XRD Rietveld refinement methods. They speculated that such an ordered structure could be formed by the insertion of a single TiC layer into the  $\text{Cr}_2\text{AlC}$  unit cell. Caspi et al. [84] synthesized M-ordered  $(\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n$  by heating mixed  $0.5(n+1)\text{Cr}:0.5(n+1)\text{V}:1.1\text{Al}:n\text{C}$  elemental powders. This is the first reported M-ordered MAX phase solid solution synthesized from mixed elemental powders. By ND Rietveld refinement, it was proved that for  $n = 1$ , Cr and V atoms are completely disordered; for  $n = 2$ ,  $2a$  positions are fully occupied by V atoms and  $4f$  positions are occupied by Cr atoms and remaining V atoms; for  $n = 3$ , V and Cr atoms occupy 84 % and 16 % of  $4f$  positions, respectively, and remaining V and Cr atoms occupy 32 % and 68 % of  $4e$  positions, respectively (not fully ordered but somehow mixed).

Anasori et al. [85] firstly observed such M-ordered structure in  $\text{Mo}_2\text{TiAlC}_2$  prepared by heating mixed  $2\text{Mo}:1\text{Ti}:1.1\text{Al}:2\text{C}$  elemental powders at  $1600^\circ\text{C}$  for 4 h under flowing Ar, as shown in Fig. 16, where Ti and Mo atoms occupy  $2a$  and  $4f$  Wyckoff positions, respectively. Then they synthesized M-ordered  $\text{Mo}_2\text{Ti}_2\text{AlC}_3$  using mixed  $2\text{Mo}:2\text{Ti}:1.1\text{Al}:2.7\text{C}$  elemental powders [86]. The formation enthalpies of M-ordered  $\text{Mo}_2\text{TiAlC}_2$  and  $\text{Mo}_2\text{Ti}_2\text{AlC}_3$  at 0 K were calculated to be



**Fig. 15.** Surface morphologies of  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  bulk samples radiated by Xe ions leading to 5 dpa at different temperatures: (a)  $\text{Ti}_3\text{SiC}_2$  radiated at room temperature; (b)  $\text{Ti}_3\text{SiC}_2$  radiated at 600 °C; (c)  $\text{Ti}_3\text{AlC}_2$  radiated at room temperature; (d)  $\text{Ti}_3\text{AlC}_2$  radiated at 600 °C. (Red arrows indicate cracks; blue arrows indicate polishing scratches) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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**Fig. 16.** HRTEM image, high-resolution EDX map and schematic diagram of the crystal structure of  $\text{Mo}_2\text{TiAlC}_2$ .

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–18 meV/atom and –17 meV/atom, respectively, while those of  $\text{Mo}_3\text{AlC}_2$  and  $\text{Mo}_4\text{AlC}_3$  are both positive. Compared with  $\text{Mo}_2\text{TiAlC}_2$  in which 2a Wyckoff positions are fully occupied by Ti atoms, the order degree of  $\text{Mo}_2\text{Ti}_2\text{AlC}_3$  in which 14 % of 4f Wyckoff positions are occupied by Mo atoms is a little lower. This phenomenon is similar to the research of Caspi et al. [84], and indicates that the higher configurational entropy of  $\text{M}_{n+1}\text{AX}_n$  phases with higher  $n$  values stabilizes their disordered structures to some extent.

Meshkian et al. [87] synthesized M-ordered  $\text{Mo}_2\text{ScAlC}_2$  in which the Sc atomic layers are sandwiched by the Mo atomic layers and calculated its formation enthalpy to be –24 meV/atom, although its parent phases  $\text{Mo}_3\text{AlC}_2$  and  $\text{Sc}_3\text{AlC}_2$  are both dynamically unstable. They also prepared the first Sc-containing MXene with a sandwiched structure by selective etching of Al.

Dahlqvist et al. [88] calculated the formation enthalpies of ordered and disordered  $(\text{M}, \text{Ti})_{n+1}\text{AlC}_n$ , where  $\text{M} = \text{Zr}, \text{Hf}$  (group IV);  $\text{V}, \text{Ta}, \text{Nb}$  (group V);  $\text{Cr}, \text{Mo}, \text{W}$  (group VI). For  $\text{TiM}_2\text{AlC}_2$ , the M-ordered structure where the Ti atomic layers are sandwiched by the M atomic layers is thermodynamically stable for all M atoms from group IV and V. For  $\text{Ti}_2\text{M}_2\text{AlC}_3$ , the sandwiched structure is thermodynamically stable for  $\text{M} = \text{Nb}, \text{Mo}, \text{W}$ . At higher temperatures, an order-disorder transformation temperature  $T_{\text{disorder}}$  was predicted taking configurational entropy into

account. For  $\text{M}_2\text{TiAlC}_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) and  $\text{M}_2\text{Ti}_2\text{AlC}_3$  ( $\text{M} = \text{Mo}, \text{W}$ ),  $T_{\text{disorder}} > 1773$  K, which is higher than the usual temperature for the synthesis of bulk MAX phases, thus they can be prepared with ordered structures where M atoms preferentially occupy the outer 4f (for  $\text{M}_2\text{TiAlC}_2$ ) or 4e (for  $\text{M}_2\text{Ti}_2\text{AlC}_3$ ) Wyckoff positions which are near to the Al layers. The stability of these ordered structures was attributed to the presence of the Ti atomic layers which break the energetically unfavorable stacking of M and C and a larger electronegativity of M than Al. More recently, Dahlqvist et al. [89] did a theoretical screening of the phase stability for M-ordered or disordered  $\text{M}_3\text{AlC}_2$  and  $\text{M}_4\text{AlC}_3$  phase solid solutions, where M comes from groups III to VI (Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W). They found that the M atomic layer near to the Al layer that does not form a rock-salt MC structure, a small size difference between the two M elements and a large electronegativity difference between Al and the M element near to Al are favorable for the formation of M-ordered MAX phase solid solutions. Based on these criteria, they predicted 7 M-ordered and 38 disordered MAX phase solid solutions.

As these M-ordered  $\text{M}_{n+1}\text{AX}_n$  ( $n > 2$ ) phase solid solutions mentioned above all have an out-of-plane ordered structure where different M atoms orderly occupy different Wyckoff positions located at different layers, they are also called o-MAX phases [90]. For  $\text{M}_2\text{AX}$ , there is only one type of Wyckoff positions, 4f (2/3, 1/3, 1/12), of M atoms, thus it is

much more difficult to synthesize  $M_2AX$  phases with the out-of-plane ordered structure. Dahlqvist et al. [88] calculated the formation enthalpies and  $T_{\text{disorder}}$  for ordered and disordered  $TiMAiC$  ( $M = Zr, Hf, V, Nb, Ta, Cr, Mo$  and  $W$ ), and found that only  $TiVAiC$ ,  $TiNbAlC$  and  $TiTaAlC$  have a thermodynamically stable ordered structure with  $Ti$  and  $M$  atomic layers alternatively appearing along the  $c$ -axis at 0 K. However, for all of them,  $T_{\text{disorder}} < 650$  K, which means that these materials cannot be prepared under the usual synthesis temperature of bulk MAX phases. Ingason et al. [91] predicted from theory that the out-of-plane ordered  $(Cr_{0.75}Mn_{0.25})_2GeC$  with one  $Mn_2GeC$  unit existing after every three  $Cr_2GeC$  units can only be prepared at a temperature lower than 600 K, and they prepared a  $(Cr_{0.75}Mn_{0.25})_2GeC$  film with a disordered occupation by UHV magnetron sputtering at a deposition temperature of 600 °C. HRTEM observations (Fig. 17) show that  $Cr$  and  $Mn$  atoms are completely mixed in the  $M_{n+1}X_n$  layers and  $Ge$  atoms occupy the  $A$  layers. Dahlqvist et al. [92] calculated the formation enthalpy of  $(Cr_{1-x}Mn_x)_2AlC$  by *ab initio* calculations and found that the out-of-plane

ordered  $(Cr_{1-x}Mn_x)_2AlC$  with the  $Mn_2AlC$  and  $Cr_2AlC$  units alternatively stacked is thermodynamically stable at 0 K. However, it has been proven by Mockute et al. [93] via *ab initio* calculations that  $(Cr_{1-x}Mn_x)_2AlC$  with a disordered occupation is thermodynamically stable after synthesized at a temperature higher than 600 K when taking the configurational entropy into account. They also successfully prepared a  $(Cr_{0.84}Mn_{0.16})_2AlC$  film with  $Cr$  and  $Mn$  completely intermixed by magnetron sputtering at 600 °C.

Although no experimentally produced out-of-plane ordered  $M_2AX$  phase solid solutions has been reported,  $M_2AX$  phase solid solutions with in-plane order, which are called "*i*-MAX phases", have attracted much attention since Tao et al. [94] synthesized the first *i*-MAX phase  $(Mo_{2/3}Sc_{1/3})_2AlC$  by heating stoichiometric mixed elemental powders at 1500 °C for 20 h under flowing Ar and prepared  $Mo_{1.33}C$  MXene with *d* *i*-v acancy ordering by selectively etching Al and Sc atoms in 2017. The  $(Mo_{2/3}Sc_{1/3})_2AlC$  crystallized in the monoclinic  $C2/c$  structure, which is the first synthesized MAX phase not belonging to the hexagonal

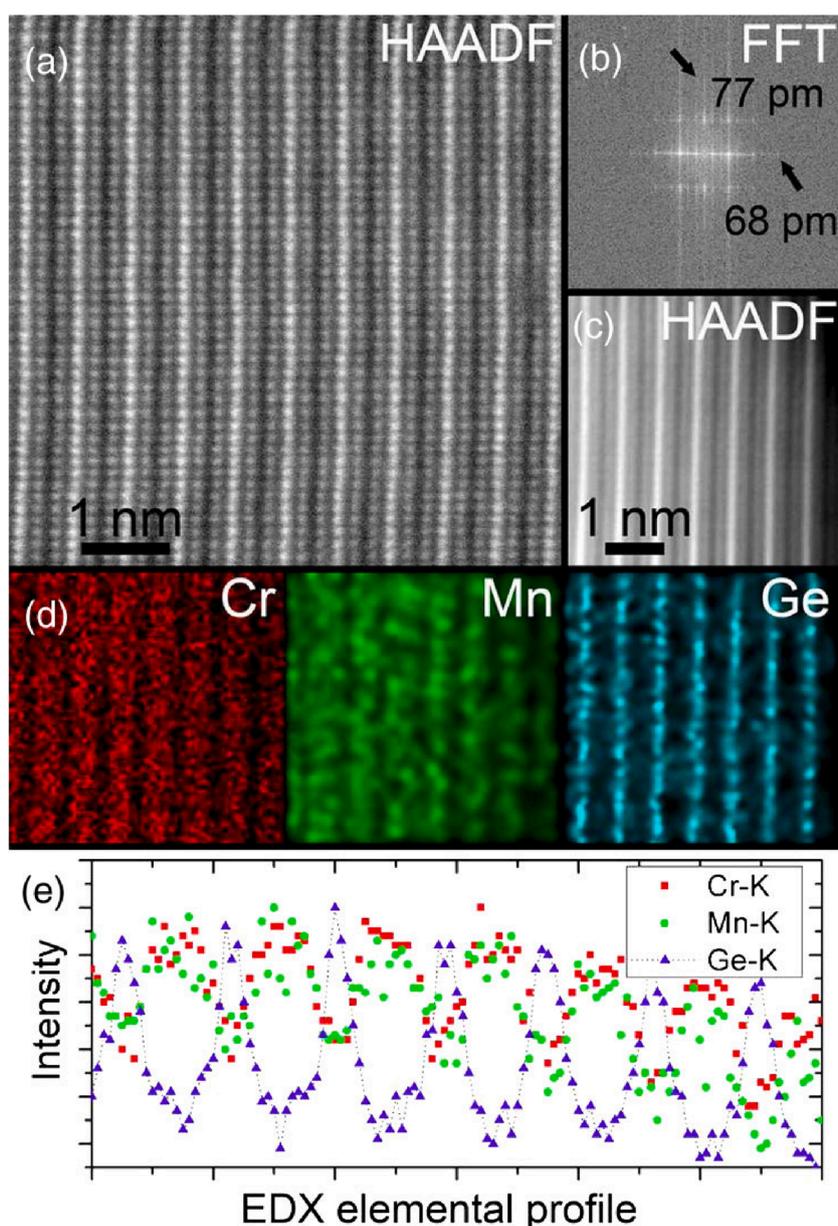
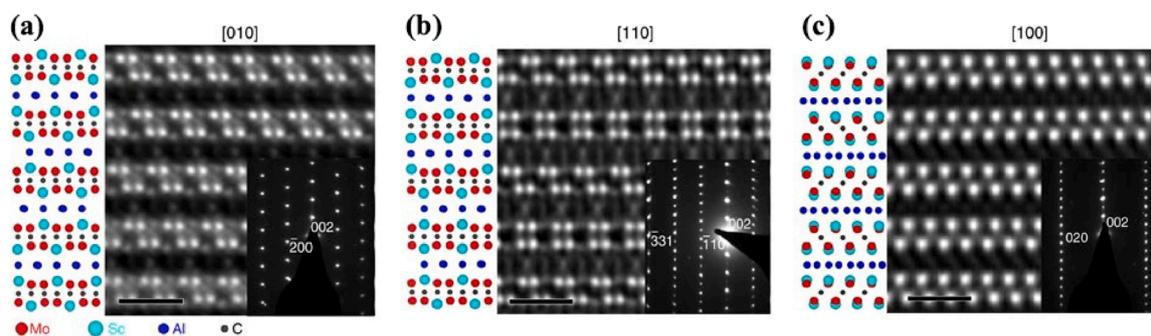


Fig. 17. TEM analysis of  $(Cr_{0.75}Mn_{0.25})_2GeC$ : (a) high-resolution scanning TEM image; (b) FFT from (a); (c) an area from (a); (d) high resolution EDX maps corresponding to (c); (e) elemental concentrations from EDX line scan across layers in (c).

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**Fig. 18.** STEM images, SAED patterns and schematic diagram of the crystal structure of  $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$  along different directions: (a) [010]; (b) [110]; (c) [100]. Reproduced with permission from Ref. [94], © 2017 The Author(s).

$P6_3/mmc$  structure. Fig. 18 shows the STEM images, SAED patterns and schematic diagram of the crystal structure of  $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$  along different directions. In the M atomic layers, the Sc atoms are located at the centers of the Mo atomic hexagons and extend out of the M atomic layers to Al layers to some extent. It has been proven that the Al atoms are arranged on a Kagomé-like lattice, which deviates slightly from the ideal Kagomé lattice, in many synthesized *i*-MAX phases such as  $(\text{V}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ ,  $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlC}$  and  $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$  in the  $C2/c$  structure, and  $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$  and  $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{GaC}$  in the  $Cmcm$  structure [95,96].

Tao et al. [97] discovered a class of rare-earth containing *i*-MAX phases,  $(\text{Mo}_{2/3}\text{RE}_{1/3})_2\text{AlC}$  (RE = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu). Most of  $(\text{Mo}_{2/3}\text{RE}_{1/3})_2\text{AlC}$  (RE = Tb, Nd, Gd, Dy, Ho, Er, and Tm) crystallized in the monoclinic  $C2/c$  structure;  $(\text{Mo}_{2/3}\text{Ce}_{1/3})_2\text{AlC}$  and  $(\text{Mo}_{2/3}\text{Pr}_{1/3})_2\text{AlC}$  crystallized in the monoclinic  $C2/m$  structure;  $(\text{Mo}_{2/3}\text{Sm}_{1/3})_2\text{AlC}$  crystallized in both the monoclinic  $C2/m$  and  $C2/c$  structures;  $(\text{Mo}_{2/3}\text{Gd}_{1/3})_2\text{AlC}$  crystallized in both the orthorhombic  $Cmcm$  and the monoclinic  $C2/c$  structures, as shown in Fig. 19.

Dahlqvist et al. [96] calculated the formation enthalpies and  $T_{\text{disorder}}$  of 12 *i*-MAX phases,  $(\text{Mo}_{2/3}\text{M}^2_{1/3})_2\text{AC}$  ( $\text{M}^2 = \text{Sc}, \text{Y}$  and  $\text{A} = \text{Al}, \text{Ga}, \text{In}, \text{Si}, \text{Ge}, \text{In}$ ) in the  $C2/c$  and  $Cmcm$  structures, among which 7 phases ( $\text{M}^2 = \text{Sc}, \text{A} = \text{Al}, \text{Ga}$  and  $\text{M}^2 = \text{Y}, \text{A} = \text{Al}, \text{Ga}, \text{In}$ ) were predicted to be thermodynamically stable at 0 K and 5 phases ( $\text{M}^2 = \text{Sc}, \text{A} = \text{Al}, \text{Ga}, \text{In}, \text{Sn}$  and  $\text{M}^2 = \text{Y}, \text{A} = \text{Al}, \text{Ga}, \text{In}$ ) could retain the in-plane ordered structure up to 1773 K. They synthesized  $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$  and  $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{GaC}$  in the  $Cmcm$  structure by solid-state reaction from elemental powders. Based on their theoretical analysis results, it was predicted that a bigger size difference between the two M metals, a smaller size of the A element and fewer electrons populating antibonding orbitals are favorable for the formation of *i*-MAX phases.

During the past three years, the family of *i*-MAX phases has expanded

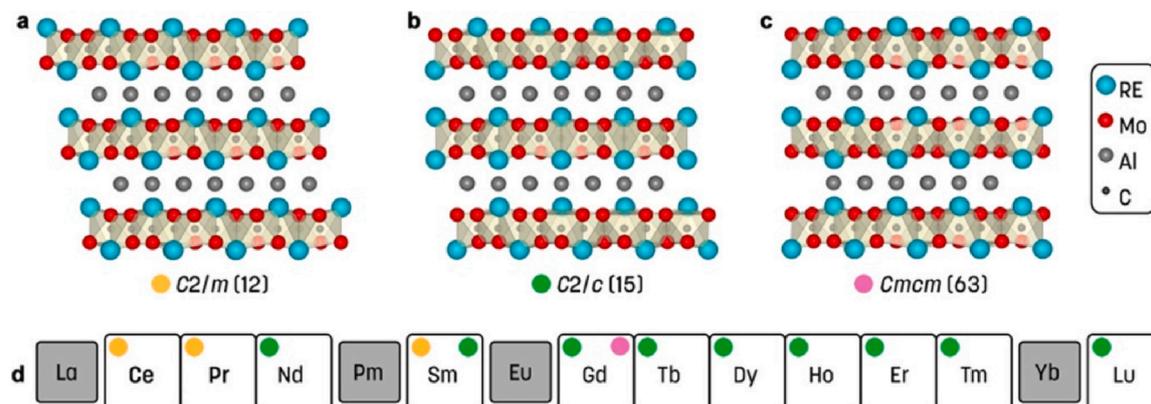
rapidly. Other experimentally reported *i*-MAX phases include  $(\text{Cr}_{2/3}\text{Zr}_{1/3})_2\text{AlC}$  [98],  $(\text{W}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$  and  $(\text{W}_{2/3}\text{Y}_{1/3})_2\text{AlC}$  [99],  $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$  and  $(\text{Cr}_{2/3}\text{Y}_{1/3})_2\text{AlC}$  [100],  $(\text{Cr}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$  and  $(\text{Mn}_{2/3}\text{Sc}_{1/3})_2\text{GaC}$  [101],  $(\text{Mo}_{2/3}\text{RE}_{1/3})_2\text{GaC}$  (RE = Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) [102],  $(\text{V}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$  [103], etc. The discovery of such a huge family of *i*-MAX phases provides a method to tailor the structure and properties of MXenes [104,105].

#### 4.2. Properties of MAX phase solid solutions

MAX phase solid solutions have been widely studied to improve their mechanical properties by solid solution strengthening and hardening. Physical properties such as the thermal expansion, electrical conductivity, and magnetic properties of MAX phases can also be tailored by creating solid solutions. Table 3 lists the lattice parameters and mechanical and physical properties of some typical Ti-based MAX phase solid solutions.

##### (1) Mechanical properties

Compressive strength, flexural strength and Vickers hardness can be improved by solid solution strengthening and hardening. The strengthening effect seems to be more significant for MAX phases with larger grain sizes, which has been proven by Gao et al. [109] who studied the mechanical properties of reactive sintered  $\text{Ti}_3\text{Al}_{1-x}\text{Si}_x\text{C}_2$  bulk samples with and without heat-treatment. The grain size of the as-sintered  $\text{Ti}_3\text{Al}_{1-x}\text{Si}_x\text{C}_2$  samples is around 7  $\mu\text{m}$  (12.5  $\mu\text{m}$  for  $x = 0.2$ ), while that of the heat-treated samples is around 25  $\mu\text{m}$ , as shown in Table 3. Compared with the highest values of  $\text{Ti}_3\text{AlC}_2$  and  $\text{Ti}_3\text{SiC}_2$ , the compressive strengths of the  $\text{Ti}_3\text{Al}_{1-x}\text{Si}_x\text{C}_2$  solid solutions increase 7.4 % ( $x = 0.4$ ) and 30.2 % ( $x = 0.6$ ) for the as-sintered and heat-treated



**Fig. 19.** Schematic diagrams of the crystal structure of *i*-MAX phases  $(\text{Mo}_{2/3}\text{RE}_{1/3})_2\text{AlC}$  crystallizing in different structures: (a) monoclinic  $C2/m$ ; (b) monoclinic  $C2/c$ ; (c) orthorhombic  $Cmcm$ .

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**Table 3**  
Lattice parameters and properties of some typical Ti-based MAX phase solid solutions.

Material		Lattice parameters (nm)		Compressive strength (or flexural strength) (MPa)	Vickers hardness <sub>10N</sub> (GPa)	CTE (10 <sup>-6</sup> K <sup>-1</sup> )	Electrical conductivity <sub>25°C</sub> (10 <sup>6</sup> ·Ω <sup>-1</sup> ·m <sup>-1</sup> )
		a	c				
(Ti <sub>1-x</sub> V <sub>x</sub> ) <sub>2</sub> AlC [106]	x = 0	0.3051	1.362	261 <sub>flc</sub>	3.5		
	x = 0.05	0.3049	1.361	325 <sub>flc</sub>	3.9		
	x = 0.10	0.3039	1.358	345 <sub>flc</sub>	4.0 (40 μm)		
	x = 0.15	0.3031	1.355	350 <sub>flc</sub>	4.2		
	x = 0.20	0.3022	1.353	356 <sub>flc</sub>	4.5		
(Ti <sub>1-x</sub> V <sub>x</sub> ) <sub>2</sub> AlC [107]	x = 1	0.2914	1.313	263 <sub>flc</sub>	3.4 (49 μm)		
	x = 0	0.3072	1.854	671 <sub>com</sub> , 360 <sub>flc</sub>	3.1		2.83
Ti <sub>3</sub> Al <sub>1-x</sub> Si <sub>x</sub> C <sub>2</sub> [108]	x = 0.05	0.3073	1.850	783 <sub>com</sub> , 362 <sub>flc</sub>	3.2		2.75
	x = 0.10	0.3073	1.846	816 <sub>com</sub> , 369 <sub>flc</sub>	3.3 (20 μm)		2.73
	x = 0.15	0.3073	1.842	809 <sub>com</sub> , 405 <sub>flc</sub>	3.7 (20 μm)		2.72
	x = 0.20	0.3070	1.837	895 <sub>com</sub> , 408 <sub>flc</sub>	3.8		2.70
	x = 0.25	0.3069	1.832	911 <sub>com</sub> , 409 <sub>flc</sub>	3.9		2.69
	x = 0	0.3072	1.854	1309 <sub>com</sub> (7 μm) 835 <sub>com</sub> (25 μm)	4.1 (7 μm) 4.1 (25 μm)	7.66 (25 °C)	
	x = 0.2	0.3071	1.829	1012 <sub>com</sub> (12.5 μm)	4.8 (12.5 μm)		
Ti <sub>3</sub> Al <sub>1-x</sub> Si <sub>x</sub> C <sub>2</sub> [109]	x = 0.4	0.3070	1.808	1406 <sub>com</sub> (7 μm) 1052 <sub>com</sub> (25 μm)	5.0 (7 μm) 5.2 (25 μm)	7.54 (25 °C)	
	x = 0.6	0.3070	1.788	1312 <sub>com</sub> (7 μm) 1087 <sub>com</sub> (25 μm)	5.6 (7 μm) 5.1 (25 μm)		
	x = 0.8	0.3067	1.773	1285 <sub>com</sub> (7 μm) 1292 <sub>com</sub> (7 μm)	4.9 (7 μm) 4.2 (7 μm)		
	x = 1	0.3065	1.767	740 <sub>com</sub> (25 μm)	4.1 (25 μm)	7.88 (25 °C)	
	x = 0	0.3051	1.364	540 <sub>com</sub> (25 μm)	4.5 (25 μm)	8.2	2.7
Ti <sub>2</sub> AlC <sub>1-x</sub> N <sub>x</sub> [110]	x = 0.5	0.3021	1.361	810 <sub>com</sub> (25 μm)	5.5 (25 μm)	10.5 (25~1300 °C)	3.1
	x = 1	0.2989	1.361	381 <sub>com</sub> (100 μm)	4.0 (100 μm)	8.8	4.0

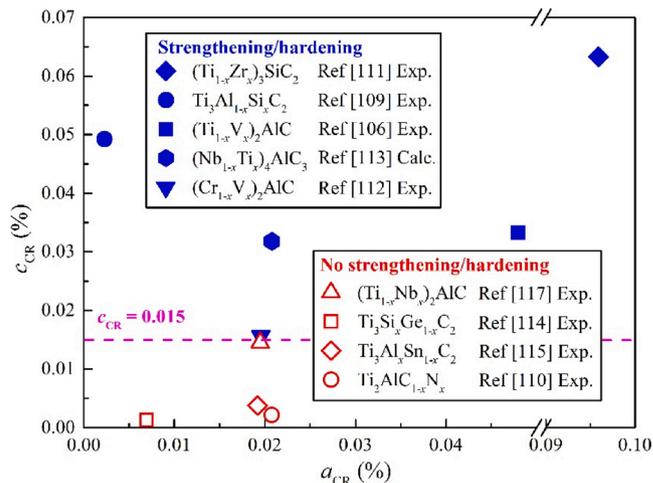
All the listed Vickers hardnesses were measured under a load of 10 N; flexural strength: <sub>flc</sub>; compressive strength: <sub>com</sub>; the grain size is shown in the bracket next to the strength or hardness; the testing temperature of the coefficient of thermal expansion (CTE) is shown in the bracket next to the CTE.

samples, respectively. The actual hardening effect has only a weak relationship with the grain size, as both the as-sintered and heat-treated samples show an ideal hardening effect around  $x = 0.5$ . Such solid solution strengthening/hardening phenomena were also observed by experiments or proven by calculation for other MAX phase solid solutions such as (Ti<sub>1-x</sub>V<sub>x</sub>)<sub>2</sub>AlC [106], (Ti<sub>1-x</sub>Zr<sub>x</sub>)<sub>3</sub>SiC<sub>2</sub> [111], (Cr<sub>1-x</sub>V<sub>x</sub>)<sub>2</sub>AlC [112], (Nb<sub>1-x</sub>Ti<sub>x</sub>)<sub>4</sub>AlC<sub>3</sub> [113], etc. There are also some MAX phase solid solutions, such as Ti<sub>3</sub>Si<sub>x</sub>Ge<sub>1-x</sub>C<sub>2</sub> [114], Ti<sub>3</sub>Al<sub>x</sub>Sn<sub>1-x</sub>C<sub>2</sub> [115,116], (Ti<sub>1-x</sub>Nb<sub>x</sub>)<sub>2</sub>AlC [117], whose mechanical properties are between their end members yet show no solid solution strengthening or hardening effect. Although Ti<sub>2</sub>AlC<sub>0.5</sub>N<sub>0.5</sub> in Table 3 has higher mechanical properties than both Ti<sub>2</sub>AlC and Ti<sub>2</sub>AlN, the grain size of Ti<sub>2</sub>AlN was much larger than those of Ti<sub>2</sub>AlC and Ti<sub>2</sub>AlC<sub>0.5</sub>N<sub>0.5</sub> [110]. It has been reported that the Vickers hardness of the HP-ed Ti<sub>2</sub>AlN bulk samples using SHS-ed Ti<sub>2</sub>AlN powders with a size of 17 μm reaches 5.8 GPa [118]. The SPS-ed Ti<sub>2</sub>AlN bulk samples with a grain size of 5~10 μm has a Vickers hardness higher than 6 GPa [119]. Therefore, the higher mechanical properties of Ti<sub>2</sub>AlC<sub>0.5</sub>N<sub>0.5</sub> than its end members in the work of Barsoum et al. [110] should be attributed to more valence electrons in a N atom than in a C atom and the larger grain size of the Ti<sub>2</sub>AlN sample, but not the solid solution strengthening/hardening effect.

As solid solution strengthening/hardening is attributed to the lattice distortion caused by alloying atoms, it is reasonable to speculate that whether solid solution strengthening/hardening works or not depends on the degree of lattice distortion caused by alloying atoms. Therefore, we define the change rates of lattice parameters  $a$  and  $c$  ( $a_{CR}$  and  $c_{CR}$ ) with the change of the content of alloying atoms in MAX phase solid solutions, which are calculated according to Eq. (13):

$$l_{CR} = \left| \frac{l_{x_2} - l_{x_1}}{\min(l_{x_2}, l_{x_1}) \times (x_2 - x_1)} \right| \quad (13)$$

where  $l$  is the lattice parameter  $a$  or  $c$ ;  $x_1$  and  $x_2$  are two different content values with the changing of the content of the alloying atoms in the solid solutions;  $l_x$  is the lattice parameter corresponding to a specific content  $x$  of the alloying atoms.



**Fig. 20.**  $a_{CR}$  and  $c_{CR}$  in MAX phase solid solutions with or without solid solution strengthening/hardening. (Exp. means data comes from experiments, Calc. means data comes from theoretical calculations).

Fig. 20 shows  $a_{CR}$  and  $c_{CR}$  values either obtained from the lattice parameters of synthesized MAX phase solid solutions or theoretical calculations. These solid solutions are either proven by experiments or speculated by calculation to be with or without solid solution strengthening/hardening. These  $a_{CR}$  and  $c_{CR}$  values in Fig. 20 were obtained from two solid solutions with the largest difference in the content of the alloying atoms in corresponding references. Obviously, solid solutions with higher  $c_{CR}$  values ( $c_{CR} > 0.015$ ) are more likely to show solid solution strengthening/hardening. As MAX phases have a layered structure, and the attractive force between layers is relatively weak, a higher  $c_{CR}$ , which means a more significant lattice distortion through layers, would probably result in a higher deformation resistance along layers. Although this speculation needs further experimental

verification, the hypothesis might guide the readers to select suitable alloying elements to improve mechanical properties of MAX phases by solid solution strengthening/hardening.

The high temperature strength of MAX phases can also be improved by alloying. By replacing 5% of Ti atoms with Zr atoms, the flexural strength at 1200 °C of  $(\text{Ti}_{0.95}\text{Zr}_{0.05})_3\text{Si}_{0.95}\text{Al}_{0.05}\text{C}_2$  can be kept up to 331 MPa, which is 74 % of its strength at room temperature (447 MPa). While the flexural strength at 1100 °C of  $\text{Ti}_3\text{Si}_{0.95}\text{Al}_{0.05}\text{C}_2$  already decreases to 245 MPa, although its strength at room temperature (475 MPa) is a little higher than  $(\text{Ti}_{0.95}\text{Zr}_{0.05})_3\text{Si}_{0.95}\text{Al}_{0.05}\text{C}_2$  [120].

### (2) Thermal expansion

Just as for the mechanical properties, no simple linear relationship exists for the coefficients of thermal expansion (CTEs) of MAX phase solid solutions and their end members. CTEs reflect the average bonding strength in materials. The CTE of  $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$  in the temperature range between 25~1300 °C is higher than both  $\text{Ti}_2\text{AlC}$  and  $\text{Ti}_2\text{AlN}$ , as shown in Table 3, indicating that  $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$  has weaker bonds than its two end members [110]. Similar results have been obtained for  $\text{Ti}_3\text{Si}_{1-x}\text{Ge}_x\text{C}_2$  and  $(\text{Ti}_{1-x}\text{Nb}_x)_2\text{AlC}$ . The CTE between 50~1200 °C of  $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$  ( $9.3 \times 10^{-6} \text{ K}^{-1}$ ) is slightly higher than those of  $\text{Ti}_3\text{SiC}_2$  ( $8.9 \times 10^{-6} \text{ K}^{-1}$ ) and  $\text{Ti}_3\text{GeC}_2$  ( $7.8 \times 10^{-6} \text{ K}^{-1}$ ) [121]. The CTE between 25~1200 °C of  $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$  is  $8.9 \times 10^{-6} \text{ K}^{-1}$ , while those of  $\text{Ti}_2\text{AlC}$  and  $\text{Nb}_2\text{AlC}$  are both  $8.7 \times 10^{-6} \text{ K}^{-1}$  [122].

The CTE of  $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$  at room temperature was measured to be  $7.54 \times 10^{-6} \text{ K}^{-1}$ , which is lower than those of  $\text{Ti}_3\text{AlC}_2$  ( $7.66 \times 10^{-6} \text{ K}^{-1}$ ) and  $\text{Ti}_3\text{SiC}_2$  ( $7.88 \times 10^{-6} \text{ K}^{-1}$ ), indicating a higher bonding strength in  $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$  solid solutions than those in the two end members [109], as reported in Table 3. Similar results have been obtained by Chen et al. [123], who attributed the lower CTE of  $\text{Ti}_3\text{Al}_{1-x}\text{Si}_x\text{C}_2$  to the occupation of Ti *d*-Si *p* and Ti *d*-Al *p* covalent bonding states by the additional valence electron of Si, which results in the strengthening of the attractive force between layers.

It should be noted that none of above known MAX phase solid solutions with higher CTEs than their end members,  $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$ ,  $\text{Ti}_3\text{Si}_{0.5}\text{Ge}_{0.5}\text{C}_2$  and  $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$ , show solid solution strengthening/hardening, as shown in Fig. 20. On the other hand,  $\text{Ti}_3\text{Al}_{0.6}\text{Si}_{0.4}\text{C}_2$ , which shows solid solution strengthening/hardening, possesses a CTE lower than its two end members. This is reasonable as both the CTE and mechanical properties are related to the average bonding strength.

There is also some research about the thermal expansion along different crystal directions of MAX phase solid solutions. For  $\text{Cr}_2\text{Al}_x\text{Ge}_{1-x}\text{C}$ , it was observed by *in situ* XRD that with increasing the Al content from 0 to 1, the CTE along the *a* and *b*-axes (along layers) changed only a little and remained in the range from  $13.3 \times 10^{-6} \text{ K}^{-1}$  to  $14.8 \times 10^{-6} \text{ K}^{-1}$ , while the CTE along the *c*-axis (through layers) decreases from  $17.2 \times 10^{-6} \text{ K}^{-1}$  to  $11.7 \times 10^{-6} \text{ K}^{-1}$  and is equal to the CTE along the *a* and *b*-axes around  $x = 0.75$  [124], which means that  $\text{Cr}_2\text{Al}_x\text{Ge}_{1-x}\text{C}$  solid solutions show different thermal expansion anisotropy with different Al contents. Therefore, the CTEs of  $\text{Cr}_2\text{Al}_x\text{Ge}_{1-x}\text{C}$  bulk materials should be between the two end members, unless there is preferential orientation of grains. For  $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$ , it was calculated that with increasing *x* from 0.167 to 0.667, the CTE along the *a* and *b*-axes increases from  $12.6 \times 10^{-6} \text{ K}^{-1}$  to  $14.7 \times 10^{-6} \text{ K}^{-1}$ , while that along the *c*-axis decreases from  $9.6 \times 10^{-6} \text{ K}^{-1}$  to  $8.7 \times 10^{-6} \text{ K}^{-1}$  [125]. These results provide groundlevel guidelines for tailoring the thermal expansion properties of MAX phase solid solutions by adjusting the contents of alloying atoms.

### (3) Electrical conductivity

The alloying atoms in MAX phase solid solutions usually cause solid solution scattering during electron transport, leading to the decrease of the electrical conductivity. It has been reported that the electrical conductivity at room temperature of  $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$  is  $1.28 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$

$\text{m}^{-1}$ , which is much lower than those of  $\text{Ti}_2\text{AlC}$  ( $2.78 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ ) and  $\text{Nb}_2\text{AlC}$  ( $3.57 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ ) [122]. However, the electrical conductivity of  $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$  ( $3.1 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ ) is between those of  $\text{Ti}_2\text{AlC}$  ( $2.7 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ ) and  $\text{Ti}_2\text{AlN}$  ( $4.0 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ ) [110]. The same is true for  $\text{Ti}_3\text{Si}_{1-x}\text{Ge}_x\text{C}_2$ , whose electrical conductivities at  $x = 0, 0.25, 0.5$  and  $1$  are  $3.94 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ ,  $3.75 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ ,  $3.67 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$  and  $3.60 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ , respectively [121]. The change of the electrical conductivity of  $\text{Ti}_3\text{Al}_{1-x}\text{Si}_x\text{C}_2$  with the change of *x* is also not much, which decreases from  $2.83 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$  to  $2.69 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$  with increasing *x* from 0 to 0.25 [108].

It was reported that the electrical conductivities of polycrystalline  $\text{Nb}_2\text{SC}$ ,  $\text{Nb}_2\text{SC}_{0.4}\text{B}_{0.6}$  and  $\text{Nb}_2\text{SB}$  samples at room temperature are  $0.27 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ ,  $0.22 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$  and  $0.77 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ , respectively [126]. Although  $\text{Nb}_2\text{SC}$  has a relatively lower electrical conductivity than most MAX phases, it is one of the nine MAX phases showing superconductivity below critical temperatures [127], and  $\text{Nb}_2\text{SC}_{1-x}\text{B}_x$  ( $0 \leq x \leq 0.6$ ) could maintain the superconductivity while the critical temperature decreased from 4.8 K ( $x = 0$ ) to 2.6 K ( $x = 0.6$ ).

It seems that alloying atoms on the M-site (e.g.,  $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$ ) have a more significant solid solution scattering effect, while alloying atoms on the A-site (e.g.,  $\text{Ti}_3\text{Si}_{1-x}\text{Ge}_x\text{C}_2$ ,  $\text{Ti}_3\text{Al}_{1-x}\text{Si}_x\text{C}_2$ ) or X-site ( $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$ ) only lead to weak additional scattering. This is probably related to the fact that the density of states (DOS) at the Fermi level ( $E_F$ ) of MAX phases is dominated by the *d*-*d* orbitals of M atoms [128]. It has been proven by Magnuson et al. [7] that for several  $\text{M}_2\text{AX}$  phases ( $\text{Ti}_2\text{AlN}$ ,  $\text{Ti}_2\text{AlN}$ ,  $\text{V}_2\text{GeC}$  and  $\text{Cr}_2\text{GeC}$ ),  $\text{M}_3\text{AX}_2$  ( $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{GeC}_2$ ) and their parent binary phases (TiC, TiN and VC), a high DOS at  $E_F$  could lead to a high electrical conductivity. Therefore, it seems reasonable to speculate that alloying atoms on the M-site can result in much more carrier scattering than alloying atoms on other sites. As the *d*-*d* orbitals of M atoms contribute most to the DOS at  $E_F$  which could largely affect the electrical conductivity, the change of M atoms could result in a significant change of their electrical conductivity. For example, the electrical conductivity of  $\text{M}_3\text{SnC}_2$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) increases as the location of the M-element in the periodic table moves down [55]. As a result, the electrical conductivity at room temperature of  $\text{Cr}_2\text{AlC}$  is lower than  $1.4 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$ , while that of  $\text{V}_2\text{AlC}$  reaches  $4.0 \times 10^6 \cdot \Omega^{-1} \text{ m}^{-1}$  [128].

### (4) Magnetic properties

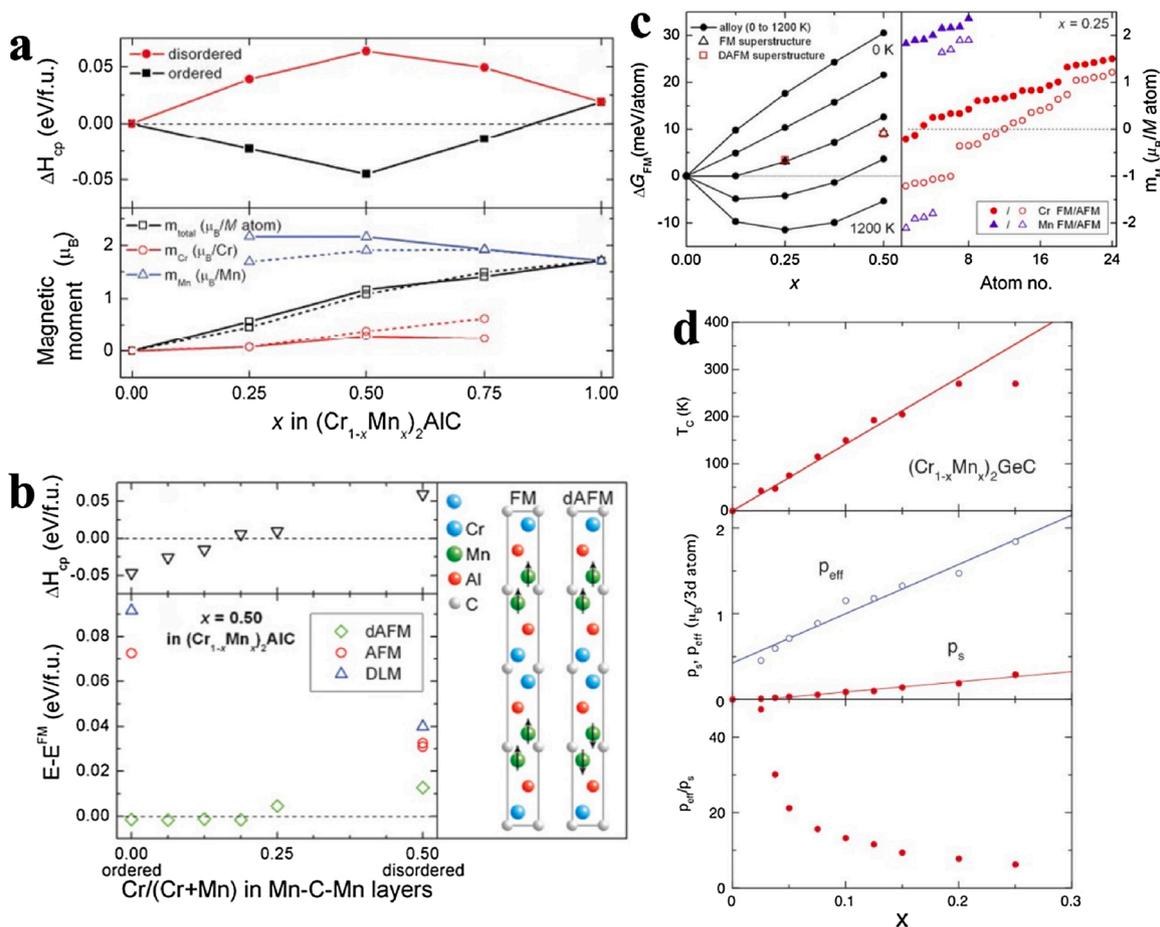
Most existing ternary MAX phases do not show magnetic properties, yet there have been some calculations on possible magnetic MAX phases, especially those with Mn as the M element.  $\text{Mn}_2\text{AlC}$  and  $\text{Mn}_2\text{GeC}$  were both calculated to be magnetic in their ground states with magnetic moments of 1.86  $\mu\text{B}$  and 1.80  $\mu\text{B}$  per Mn atom, respectively [81]. In 2013, Ingason et al. [129] was the first to report the ferromagnetic properties of  $\text{Mn}_2\text{GaC}$  obtained from both calculations and experiments. The formation enthalpy of  $\text{Mn}_2\text{GaC}$  was calculated to be  $-30 \text{ meV/atom}$ , which is the only thermodynamically stable phase among  $\text{Mn}_{n+1}\text{GaC}_n$  phases and predicted to display magnetic ordering with two dynamically stable configurations, the ferromagnetic configuration where all Mn atoms have the same spin direction and the antiferromagnetic  $[0001]_2^A$  configuration where the Mn atoms in two adjacent  $\text{Mn}_2\text{C}$  blocks have different spin directions. The  $\text{Mn}_2\text{GaC}$  film was prepared by magnetron sputter epitaxy and was measured to show ferromagnetic up to 230 K with a saturation magnetic moment of 0.29  $\mu\text{B}$  per Mn atom, which is much lower than the theoretically calculated local Mn moment of 1.6  $\mu\text{B}$  per atom, indicating that the configuration of the synthesized  $\text{Mn}_2\text{GaC}$  is more complex than that of the ideal ferromagnetic configuration. Therefore, they speculated the magnetic ground state of  $\text{Mn}_2\text{GaC}$  to be practically degenerated between the ferromagnetic and antiferromagnetic  $[0001]_2^A$  configurations. Novoselova et al. [130] observed a first order magnetic phase transition at 214 K from AFM at higher temperatures to a non-collinear AFM spin structure at

lower temperatures, with the magnetostriction changing sign at this magnetic phase transition in a  $\text{Mn}_2\text{GaC}$  film prepared by magnetron sputtering. It has been theoretically proven by Dahlqvist et al. [131,132] that the magnetic states and structural parameters of  $\text{Mn}_2\text{GaC}$  can be manipulated through controlling the temperature, the magnetic field or the applied pressure. The temperature and magnetic field dependence of magnetic properties has also been studied for some solid solutions such as  $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$ ,  $(\text{Mo}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$ ,  $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{AlC}$ , etc [133,134], suggesting new pathways for tuning magnetism of MAX phases.

Some magnetic solid solutions based on these ternary MAX phases predicted to be magnetic have also been proven to be synthesizable. Dahlqvist et al. [92] calculated the formation enthalpies and magnetic moments of both ordered and disordered  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$  at 0 K by *ab initio* calculation, as shown in Fig. 21(a). The ordered  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$  with a stacking sequence of Mn-C-Mn-Al-Cr-C-Cr-Al is thermodynamically stable, and the magnetic moment per M-site atom increases with increasing the Mn content. However, the magnetic state of  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$  is influenced by the atomic configuration, as shown in Fig. 21(b). Although the formation enthalpy of  $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{AlC}$  in its most thermodynamically stable magnetic state increases with the increase of the disorder degree characterized by the ratio of the number of Cr atoms to the number of Cr plus Mn atoms in the Mn-C-Mn layers, the energy differences between the antiferromagnetic (AFM), double-layer antiferromagnetic (dAFM), disorder local moment (DLM) states and

the ferromagnetic (FM) state also increase with the increase of the disorder degree, indicating that the FM state becomes more stable relative to other magnetic states with the intermixture between Cr and Mn atoms. The influence of atomic configurations on the magnetic states was also calculated for  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$ , as shown in Fig. 21(c). The disordered  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$  (alloy) becomes more stable relative to FM  $\text{Cr}_2\text{GeC}$  with increasing the temperature. For  $(\text{Cr}_{0.75}\text{Mn}_{0.25})_2\text{GeC}$ , the magnetic moment of Cr atoms is significantly influenced by their atomic configurations, ranging from 0 to  $\pm 1.5 \mu_B$ , while that of Mn atoms keeps around  $\pm 2 \mu_B$  with little change. Therefore, it is possible to tailor the magnetic states through controlling the atomic configurations for both  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$  and  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$ .

It has been experimentally proven that alloying Mn atoms at the M-site could introduce magnetic properties into many MAX phase solid solutions such as  $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$  [135],  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$  ( $x \leq 0.25$ ) [80],  $(\text{Cr}_{0.8}\text{Mn}_{0.2})_2\text{AlC}$  [136],  $(\text{Mo}_{0.5}\text{Mn}_{0.5})_2\text{GaC}$  [133],  $(\text{V}_{0.96}\text{Mn}_{0.04})_2\text{AlC}$  [137]. Liu et al. [80] prepared ferromagnetic  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$  ( $x \leq 0.25$ ) polycrystalline samples via reaction synthesis. Alloying Mn in  $\text{Cr}_2\text{GeC}$  successfully induced ferromagnetic band polarization into the originally spin-unpolarized structure. The Curie temperature  $T_C$  and the spontaneous magnetic moment  $p_s$  per M-site atom both increase with increasing the Mn content, as shown in Fig. 21(d). The ratio of  $p_{\text{eff}}$  (the effective moment in the paramagnetic state) to  $p_s$  decreases to a low value with increasing the Mn content, indicating



**Fig. 21.** Magnetic properties of  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$  and  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$ : (a) Formation enthalpies of ordered and disordered FM  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$ , and the magnetic moments of M-site atoms in ordered (solid lines) and disordered (dash lines)  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}$ ; (b) Formation enthalpies and energy differences between other states and the ferromagnetic (FM) state of  $(\text{Cr}_{0.5}\text{Mn}_{0.5})_2\text{AlC}$  with the change of the disorder degree; (c) Formation energies of  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$  relative to FM  $\text{Cr}_2\text{GeC}$ , and the magnetic moments of M-site atoms in FM and AFM  $(\text{Cr}_{0.75}\text{Mn}_{0.25})_2\text{GeC}$  for different configurations; (d)  $T_C$ ,  $p_s$ ,  $p_{\text{eff}}$  and  $p_{\text{eff}}/p_s$  of  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$ . (a, b): Reproduced with permission from Ref. [92], <https://doi.org/10.1103/PhysRevB.84.220403>, © 2011 American Physical Society; (c): Reproduced with permission from Ref. [91] <https://doi.org/10.1103/PhysRevLett.110.195502>, © 2013 American Physical Society; (d): Reproduced with permission from Ref. [80], <https://doi.org/10.1103/PhysRevB.89.054435>, © 2013 American Physical Society.

that the ferromagnetism of  $(\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}$  is a typical itinerant-electron ferromagnetism. Mockute et al. [136] detected the magnetic response in the  $(\text{Cr}_{0.8}\text{Mn}_{0.2})_2\text{AlC}$  film synthesized by cathodic arc deposition up to at least room temperature, verifying the prediction of the antiferromagnetic or ferromagnetic ground state in  $(\text{Cr}_{0.8}\text{Mn}_{0.2})_2\text{AlC}$ . Although  $\text{Fe}_3\text{AlC}_2$ , which was predicted to show ferromagnetic properties with a magnetic moment of  $0.73 \mu\text{B}$  per Fe atom [138], has been calculated to be thermodynamically unstable [92],  $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{AlC}$  ( $x \leq 0.017$ ) has been synthesized by Hamm et al. [139] which shows increasing paramagnetic magnetization with increasing the Fe content.

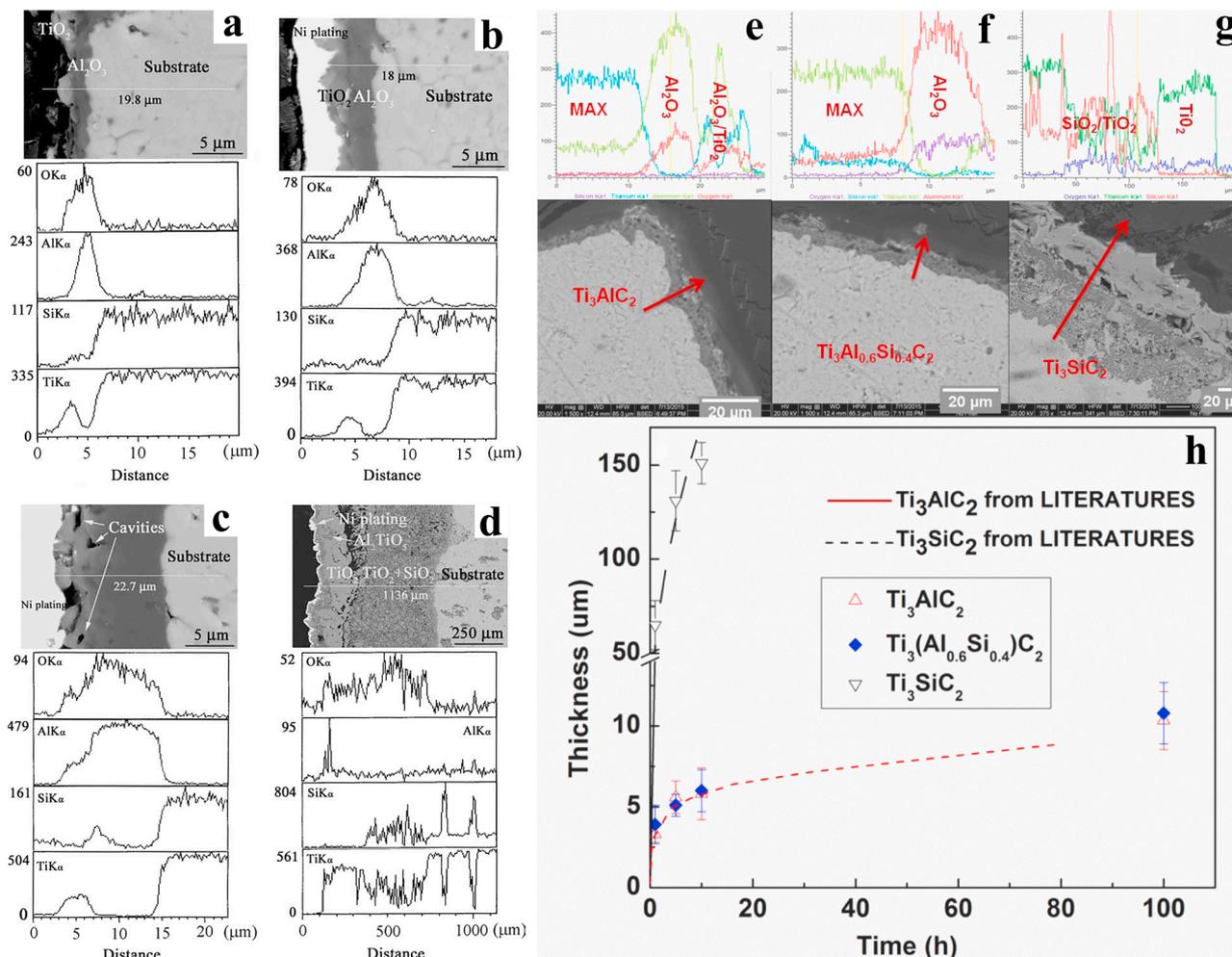
Recently, Li et al. [140] reported 15 inherently nano-laminated A alloying  $\text{V}_2(\text{A}_x\text{Sn}_{1-x})\text{C}$  phases ( $\text{A} = \text{Fe}, \text{Co}, \text{Ni}, \text{Mn}$ , and combinations thereof, with  $x \sim 1/3$ ) prepared by an alloy-guided reaction method, which could tailor the magnetic properties by atomic-level control in the processing. The magnetic properties were found to be greatly enhanced for  $\text{V}_2(\text{Fe}_x\text{Co}_y\text{Ni}_z\text{Sn}_{1-x-y-z})\text{C}$  with A layers containing multi-elements.

Related research to date is still focused on the prediction, discovery and determination of the fundamental magnetic properties of MAX phases and their solid solutions. However, the observed tunability of the magnetic properties by controlling the atomic configuration of alloying atoms on the M-site in simulations, by introducing multiple alloying elements on the A-site in experiments, and by controlling the

temperature, the magnetic field or the applied pressure in both simulations and experiments, will guide the development of magnetic MAX phases and their solid solutions with promising properties for electronics, spintronics, refrigeration, etc [6,91,92,130–134,140].

#### (5) Oxidation resistance and self-healing

Due to the high diffusion rate of Al along the A layers at high temperatures and the good oxidation resistance of the well-bonded  $\text{Al}_2\text{O}_3$  scale which forms upon oxidation, the oxidation resistance of some MAX phases can be significantly improved by partially replacing the A atoms with Al [17,109,141]. Fig. 22 shows the SEM analysis results of the oxidation resistance of  $\text{Ti}_3\text{Si}_{1-x}\text{Al}_x\text{C}_2$  solid solutions. For  $\text{Ti}_3\text{Si}_{0.9}\text{Al}_{0.1}\text{C}_2$ , the oxide scale contains an inner continuous and dense  $\text{Al}_2\text{O}_3$  layer and an external discontinuous  $\text{TiO}_2$  layer after oxidation below  $1200^\circ\text{C}$  for 20 h (Fig. 22(a, b)). Such a structure of the oxide scale indicates that the oxidation of Ti is realized by the out-diffusion of Ti, while the oxidation of Al is realized by the in-diffusion of oxygen to the interface between the oxide layer and the MAX phase matrix and the out-diffusion of Al atoms from the MAX phase matrix to the interface, which has also been proven by Wang et al. [142]. A higher oxidation temperature ( $1300^\circ\text{C}$ ) triggers the reaction between  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ , forming an outside  $\text{Al}_2\text{TiO}_5$  layer on the dense  $\text{Al}_2\text{O}_3$  layer (Fig. 22(c)). A further increase of



**Fig. 22.** SEM analysis results of the oxidation resistance of  $\text{Ti}_3\text{Si}_{1-x}\text{Al}_x\text{C}_2$  solid solutions: (a~d) back-scattered electron SEM images with the elemental concentrations from EDX line scan along the white lines of cross-section for  $\text{Ti}_3\text{Si}_{0.9}\text{Al}_{0.1}\text{C}_2$  oxidized at  $1100^\circ\text{C}$ ,  $1200^\circ\text{C}$ ,  $1300^\circ\text{C}$  and  $1350^\circ\text{C}$  for 20 h, respectively; (e~g) back-scattered electron SEM images with the elemental concentrations from EDX line scan along the red arrows of cross-section for  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{Si}_{0.4}\text{Al}_{0.6}\text{C}_2$ , and  $\text{Ti}_3\text{SiC}_2$  oxidized at  $1200^\circ\text{C}$  for 10 h, respectively; (h) Oxide layer thickness vs. oxidation time at  $1200^\circ\text{C}$  of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{Si}_{0.4}\text{Al}_{0.6}\text{C}_2$ , and  $\text{Ti}_3\text{SiC}_2$ . (a~d): Reproduced with permission from Ref. [141], © 2004 Acta Materialia Inc. Published by Elsevier Ltd.; (e~h): Reproduced with permission from Ref. [109], © 2016 Elsevier B.V (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

the oxidization temperature (1350 °C) leads to a depletion of the Al<sub>2</sub>O<sub>3</sub> formed from only 10 at.% Al in the Ti<sub>3</sub>Si<sub>0.9</sub>Al<sub>0.1</sub>C<sub>2</sub> matrix, leading to the quick in-diffusion of oxygen and oxidization of Si, forming a loose oxide layer which cannot resist further oxidation (Fig. 22(d)). By comparing the oxide compositions and thicknesses of Ti<sub>3</sub>AlC<sub>2</sub>, Ti<sub>3</sub>Si<sub>0.4</sub>Al<sub>0.6</sub>C<sub>2</sub>, and Ti<sub>3</sub>SiC<sub>2</sub> (Fig. 22(e–h)), it is concluded that the dense Al<sub>2</sub>O<sub>3</sub> layer, which does not exist in the Ti<sub>3</sub>SiC<sub>2</sub> sample, effectively prevents the further oxidization of the MAX phase matrix and gives Ti<sub>3</sub>Si<sub>0.4</sub>Al<sub>0.6</sub>C<sub>2</sub> an oxidation resistance comparable to Ti<sub>3</sub>AlC<sub>2</sub>. Besides, the outside oxide layer of Ti<sub>3</sub>AlC<sub>2</sub> is composed of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, while that of Ti<sub>3</sub>SiC<sub>2</sub> is only composed of TiO<sub>2</sub>, indicating that the atomic mobility for the Si sublattice is relatively low, which has also been proven by Barsoum et al. [143].

MAX phases with a good self-healing performance should have a high diffusion rate and preferential oxidation of the A element, a good bonding strength and oxidation resistance of the A oxide formed and an E-modulus and CTE of the oxide formed in the microcracks matching that of the MAX phase matrix [17]. The application of these 6 criteria identified several promising self-healing MAX phases containing Al as the A element. Given the reaction kinetics of Al<sub>2</sub>O<sub>3</sub> the healing of such MAX phases has to take place at relatively high temperatures. For example, Cui et al. [144] proved by conventional Differential ThermoGravimetry (DTG) analysis that the formation temperature of Al<sub>2</sub>O<sub>3</sub> is above 1000 °C for bulk Ti<sub>2</sub>AlC materials. For the non-Al containing Ti<sub>3</sub>SiC<sub>2</sub>, although Si<sub>i</sub> has a lower migration energy barrier than Ti<sub>Si</sub> along the Si layers, the self-diffusion rate of Si is much lower than that of Ti [17]. Therefore, Ti is easier to diffuse out and be oxidized than the relatively immobile Si, thus the oxide layer on Ti<sub>3</sub>SiC<sub>2</sub> is composed of an outside TiO<sub>2</sub> layer formed by the out-diffusion of Ti and an inside porous TiO<sub>2</sub> + SiO<sub>2</sub> mixed layer formed by the in-diffusion of oxygen (Fig. 22(g)). Such a porous oxide scale cannot prevent further oxidation of the MAX phase matrix, thus Ti<sub>3</sub>SiC<sub>2</sub> is not an ideal self-healing material. Its self-healing performance can be improved somewhat by partially replacing Si with Al due to the faster diffusion and oxidation of Al and a good oxidation resistance of Al<sub>2</sub>O<sub>3</sub>. The oxidation temperature of Al in Ti<sub>2</sub>AlC could be lowered to 900 °C by partially replacing Al with Sn, as reported by Bei et al. [145]. SnO<sub>2</sub> itself can be formed at temperatures below 600 °C in Ti<sub>2</sub>Al<sub>1-x</sub>Sn<sub>x</sub>C, which could give Ti<sub>2</sub>Al<sub>1-x</sub>Sn<sub>x</sub>C an attractive crack filling potential at lower temperatures. However, due to the poor bond strength and the poor mechanical strength of the SnO<sub>2</sub> the recovery of the mechanical strength would only be modest.

## 5. Texture and anisotropy

MAX phases belong to the hexagonal crystal system and possess a lamellar crystal structure. Therefore, like other materials belonging to the hexagonal crystal system [146–150], it is possible to fabricate textured bulk MAX phases composed of plate-like grains with preferential orientation under a favorable external condition (e.g., a uniaxial pressure or a magnetic field). Textured bulk MAX phases have anisotropic properties due to the lamellar crystal structure, which can improve their properties along specific directions and make them applicable to more harsh service environments. In this section, texture formation techniques and anisotropic properties of textured bulk MAX phases are discussed.

### 5.1. Texture formation techniques

The most widely used technique to prepare textured bulk MAX phases is pressure-assisted sintering, e.g., HP and SPS. For unknown reasons, direct hot pressing or spark plasma sintering of MAX phases does not result in highly textured microstructures, which is different from other materials belonging to the hexagonal crystal system [21, 151, 152]. Two methods have been developed to improve the degree of texture of pressure-assisted sintered bulk MAX phases: the first one is performing ball milling treatment to the as-synthesized MAX samples

with relatively coarse grains to obtain fine plate-like grains, and then using these ball milled plate-like grains to prepare textured bulk MAX phases by HP or SPS, as shown in Fig. 23(a) [23]; the other is called edge-free SPS (EFSPS), i.e., there is no constraint to the lateral surfaces of the sintered sample, which can provide enough space for plate-like grains to deform and rotate under the applied uniaxial pressure, thus resulting in preferential orientation, as shown in Fig. 23(b) [153]. Fig. 23(c) and (d) shows the morphologies of the side surface parallel to the applied compression direction of textured Ti<sub>2</sub>AlC composites prepared by HP using reactive ball milled powders, where plate-like Ti<sub>2</sub>AlC grains are oriented with their *c*-axis parallel to the applied compression direction. The reactive ball milling process introduced some oxygen, which reacted with Al in the Ti<sub>2</sub>AlC matrix, forming Al<sub>2</sub>O<sub>3</sub> (dark particles in Fig. 23(c)).

Most MAX phases are magnetically anisotropic, i.e., their magnetic susceptibilities along different crystallographic directions are different. Therefore, the preparation of so-called ‘green bodies’ (i.e. objects composed of raw powders stuck together and to be used for subsequent sintering) by slip casting or gel-casting in a magnetic field before sintering could be an effective technique to orient MAX phase grains. For MAX phases belonging to the hexagonal crystal system, the anisotropy of the magnetic susceptibilities  $\Delta\chi$  is expressed as Eq. (14) [154]:

$$\Delta\chi = \chi_c - \chi_{a,b} \quad (14)$$

where  $\chi_c$  and  $\chi_{a,b}$  are the magnetic susceptibilities along the *c*-axis and *a* and *b*-axes, respectively.

When a MAX phase particle is placed in a magnetic field, this particle tends to rotate, making the crystallographic axis with a higher  $\chi$  value align parallel to the magnetic field direction. If the driving energy of rotation  $\Delta E$  is higher than the thermal motion energy  $U$ , the particle can be rotated by the magnetic field.  $\Delta E$  and  $U$  are given by Eqs. (15) and (16), respectively [154,155]:

$$\Delta E = |\Delta\chi|VB^2/2\mu_0 \quad (15)$$

$$U = 3nN_0k_B T \quad (16)$$

where  $V$  is the volume of the particle;  $B$  is the magnetic flux density;  $\mu_0$  is the permeability in vacuum;  $n$  is the mole content of the MAX phase in the particle;  $N_0$  is the Avogadro constant;  $k_B$  is the Boltzmann constant;  $T$  is the temperature. Ball milling of the synthesized bulk MAX phases before MA is an effective method to further improve the degree of texturing, as the rotation of fine particles in a magnetic field is more easy to achieve than that of coarse particles [156].

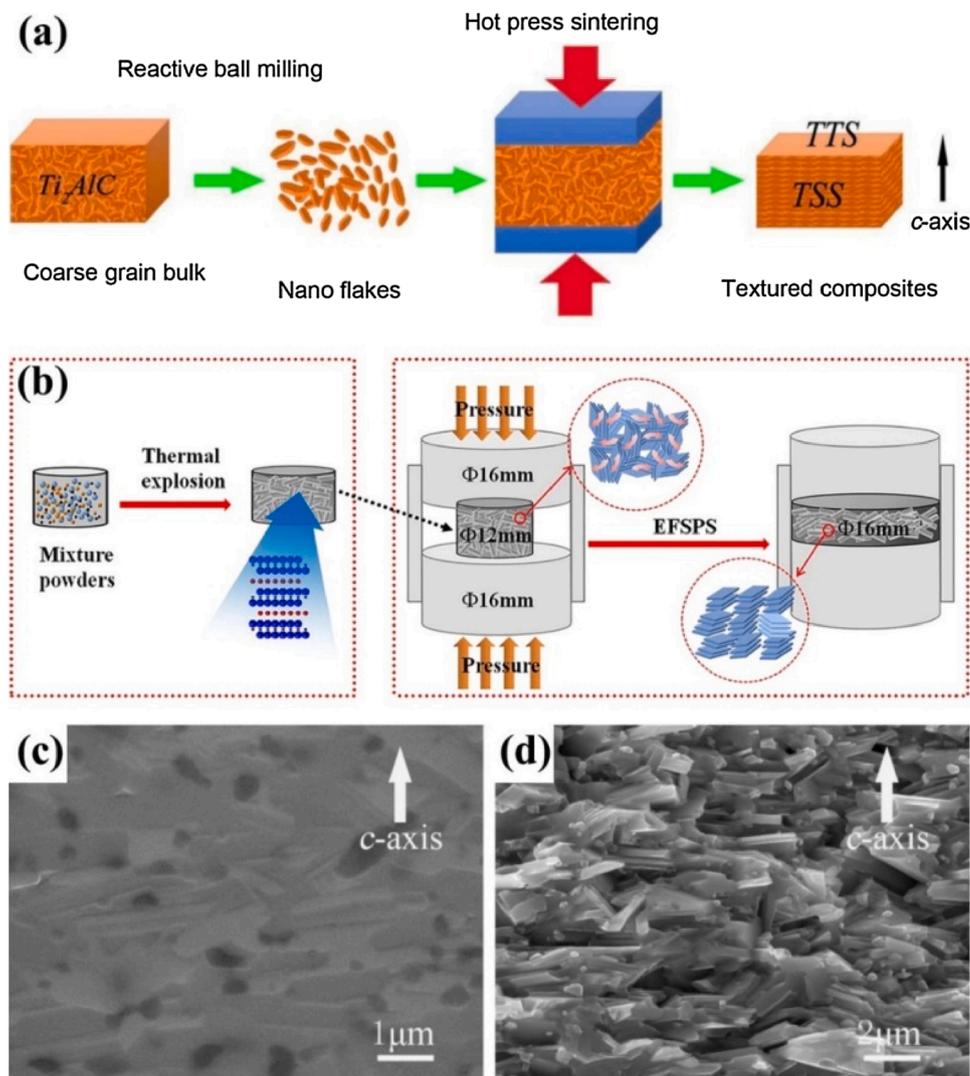
Due to the lamellar structure of MAX phases, their degree of texturing can be quantitatively characterized by the Lotgering orientation factor  $f_{00l}$ , which is calculated according to Eqs. (17) and (18) [157]:

$$f_{00l} = \frac{P - P_0}{1 - P_0} \quad (17)$$

$$P \text{ and } P_0 = \frac{\sum I_{00l}}{\sum I_{hkl}} \quad (18)$$

where  $\sum I_{00l}$  and  $\sum I_{hkl}$  are the sums of the diffraction peak intensities of all (00*l*) and (*hkl*) crystal planes, respectively.  $P$  is calculated from the measured XRD data of the textured sample surfaces, and  $P_0$  is calculated from standard JCPDS cards. For one textured MAX phase bulk sample, a higher  $f_{00l}$  for its sample surface perpendicular to the preferential orientation of the *c*-axis (e.g., the surface perpendicular to the pressure direction during SPS) indicates more (00*l*) planes on this surface, i.e., a higher degree of texture.

The magnetic anisotropy is different for different MAX phases. Some MAX phases possess a higher magnetic susceptibility along the *c*-axis (e.g., Nb<sub>4</sub>AlC<sub>3</sub> [158]), which will be aligned with the *c*-axis parallel to the magnetic field direction; while some MAX phases (e.g., Ti<sub>3</sub>SiC<sub>2</sub> [159])



**Fig. 23.** Preparation processes and morphologies of textured bulk MAX phases: (a) HP using ball milled powders from the as-synthesized sample; (b) EESPS using as-synthesized sample; (c) and (d) polished morphology and fracture morphology of the side surface parallel to the applied compression direction of textured  $\text{Ti}_2\text{AlC}$  composites by the process in (a). (a, c, d): Reproduced with permission from Ref. [23], © 2020, Elsevier; (b): Reproduced with permission from Ref. [153], © 2017 Acta Materialia Inc. Published by Elsevier Ltd.

possess a higher magnetic susceptibility along the  $a$  and  $b$ -axes, resulting in the  $c$ -axis becoming perpendicular to the magnetic field direction. For these MAX phases with a higher  $\chi_c$ , all plate-like grains can be oriented well, forming a highly textured microstructure. However, for these MAX phases with a higher  $\chi_{a,b}$ , the  $c$ -axis of plate-like grains will be randomly oriented in the plane perpendicular to the magnetic field direction. Applying a rotation to the suspension mold in the magnetic field parallel to the horizon is an effective technique to improve the grain orientation (*i.e.*, orient the  $c$ -axis of anisometric grains to one direction) for MAX phases and other hexagonal materials with a higher  $\chi_{a,b}$  [22,159–161].

MAX phase particles can be magnetically rotated as long as the magnetic field is strong enough. However, as the magnetic susceptibilities of most MAX phases are very low (*e.g.*, the magnetic susceptibility of  $\text{Ti}_3\text{SiC}_2$  was measured to be  $4.1 \times 10^{-6}$  [162]), a strong magnetic field (usually higher than 10 T) is needed to orient them, greatly restricting the widespread use of this technique.

For HP or SPS, the rotation under the uniaxial pressure can take place when the starting particles have anisometric shapes, yet even then the rotation process during sintering is hindered by the “house of cards” structure composed of plate-like particles. Therefore, MA by slip casting or gel-casting in a magnetic field and then sintering the textured green body can result in a higher degree of texture. Lapauw et al. [163] prepared textured  $\text{Ti}_3\text{SiC}_2$  bulk samples with a Lotgering factor  $f_{001}$  of 0.52 on the sample surface perpendicular to the applied compression direction by SPS at 1350 °C/30 MPa for 5 min and then edge-free deformed at

1350 °C/70 MPa, while the  $\text{Ti}_3\text{SiC}_2$  sample prepared by Sato et al. [22] by slip casting in a magnetic field of 12 T and then pressureless sintering (PLS) at 1400 °C for 2 h possesses a higher  $f_{001}$  of 0.97.

The two texturing methods, pressure-assisted sintering (*i.e.*, HP and SPS) and MA, can also be combined to realize the highest degree of texture. For example, Hu et al. [164] prepared textured  $\text{Nb}_4\text{AlC}_3$  bulk samples with a high Lotgering orientation factor  $f_{001}$  close to 1 by slip casting in a magnetic field of 12 T and subsequent SPS at 1450 °C/30 MPa for 10 min.

## 5.2. Anisotropic properties

Texturing of MAX phases can improve their properties along specific directions. Different deformation mechanisms and fracture modes along different directions give them anisotropic mechanical properties. The lamellar structure gives them anisotropic thermal conductivity and electrical conductivity. Table 4 lists the anisotropic properties of some typical bulk MAX phases.

### (1) Mechanical properties

Grain orientation of MAX phases has a significant influence on their deformation mechanisms. Kink band formation under an external pressure is much easier for plate-like grains parallel to the sample surface [168]. Kink bands are formed by the sideward deflection of the

**Table 4**  
Anisotropic properties of some typical textured bulk MAX phases.

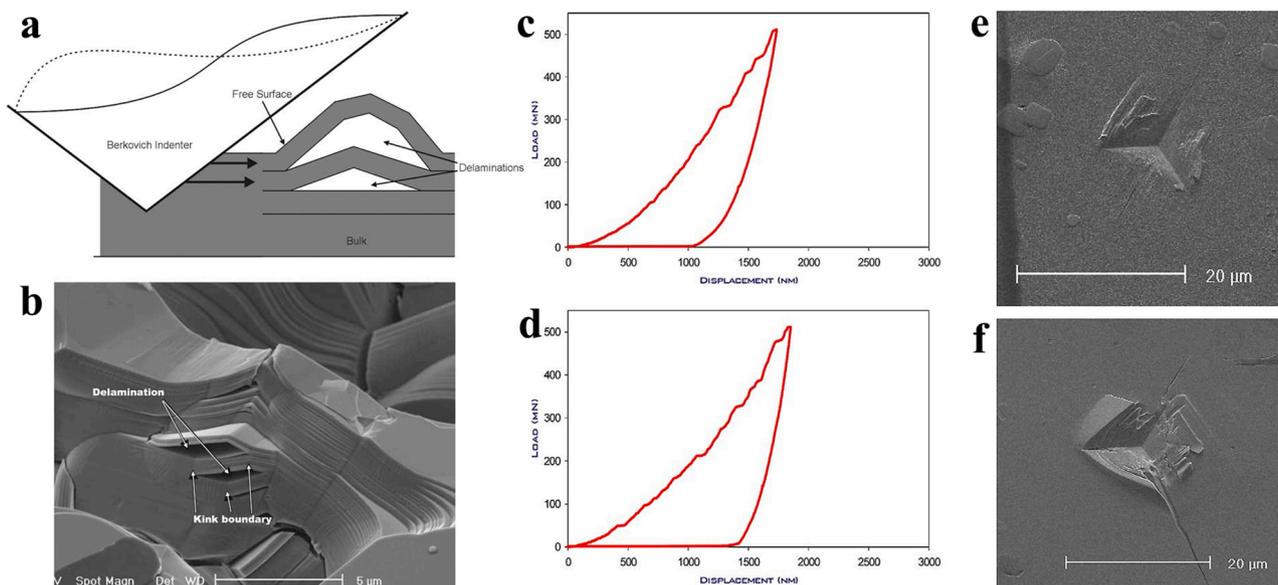
Material	Preparation method	Grain size ( $\mu\text{m}$ )	f001 on TS	Vickers hardness (GPa)	Flexural strength (MPa)	Fracture toughness ( $\text{MPa}\cdot\text{m}^{1/2}$ )	Thermal conductivity ( $\text{W}/(\text{m}\cdot\text{K})$ )	Electrical conductivity ( $\times 10^6 \Omega^{-1}\cdot\text{m}^{-1}$ )
$\text{Ti}_2\text{AlN}$ [153]	EFSPS	$\sim 5$	0.80	10.4 (TS, 49 N)	–	–	20.5 (// c-axis)	4.08 (// c-axis)
				7.9 (SS, 49 N)	735 (// c-axis)	8.5 (// c-axis)	32.3 ( $\perp$ c-axis)	2.47 ( $\perp$ c-axis)
$\text{Ti}_2\text{AlC}$ [23]	HP	$\sim 1$	0.74	7.9 (TS, 10 N)	626 ( $\perp$ c-axis)	8.2 ( $\perp$ c-axis)	–	–
				6.8 (SS, 10 N)	–	–	–	–
				8.1 (TS, 1 N)	–	–	–	–
$\text{Ti}_3\text{AlC}_2$ [165]	MA & SPS	$\sim 5$	–	9.1 (SS, 1 N)	1261 (// c-axis)	13.1 (// c-axis)	14.6 (// c-axis)	1.01 (// c-axis)
				7.4 (TS, 100 N)	1005 ( $\perp$ c-axis)	14.6 ( $\perp$ c-axis)	25.3 ( $\perp$ c-axis)	0.83 ( $\perp$ c-axis)
				5.8 (SS, 100 N)	–	–	–	–
$\text{Ti}_3\text{AlC}_2$ [166]	SPS	$\sim 3$	0.69	5.9 (TS, 10 N)	–	–	–	–
$\text{Ti}_3\text{SiC}_2$ [22]	MA & PLS	$\sim 5$	0.97	7.0 (SS, 10 N)	623 (// c-axis)	5.9 (// c-axis)	–	–
$\text{Ti}_3\text{SiC}_2$ [167]	SPS	$\sim 5$	0.60	–	843 (// c-axis)	6.6 (// c-axis)	–	–
				–	978 (// c-axis)	7.3 (// c-axis)	–	–
$\text{Ti}_3\text{SiC}_2$ [159]	MA & SPS	$\sim 2$	0.95	8.7 (TS, 9.8 N)	–	–	–	–
				7.3 (SS, 9.8 N)	–	–	–	–
				10.4 (TS, 0.245 N)	881 (// c-axis)	14.1 (// c-axis)	14.1 (// c-axis)	0.49 (// c-axis)
$\text{Nb}_4\text{AlC}_3$ [164]	MA & SPS	$\sim 5$	$\sim 1$	12.4 (SS, 0.245 N)	789 ( $\perp$ c-axis)	9.3 ( $\perp$ c-axis)	21.1 ( $\perp$ c-axis)	0.81 ( $\perp$ c-axis)
				7.0 (TS, 49 N)	–	–	–	–
				4.9 (SS, 49 N)	–	–	–	–

layers with limited constraint for plate-like grains parallel to the sample surface, as shown in Fig. 24(a). Therefore, the elastic recovery for plate-like grains perpendicular to the surface is larger than that parallel to the surface, that is, the energy consumption during the loading-unloading process is higher for plate-like grains parallel to the surface, as shown in Fig. 24(c) and (d). Plastic deformation for plate-like grains perpendicular to the surface is mainly *via* delamination, as shown in Fig. 24(e), where the delamination between plate-like grains occurs from bottom-left to top-right. Plastic deformation for plate-like grains parallel to the surface is mainly *via* kink band formation, as shown in Fig. 24(f), where much kink band pile-up is observed around the indentation, also indicating that kink band formation is more easily to occur for plate-like grains parallel to the surface. As a result, the nano-indentation hardness for plate-like grains parallel to the surface

(4.9 GPa) is lower than that for plate-like grains perpendicular to the surface (7.3 GPa).

Similar to the nano-indentation results for plate-like  $\text{Ti}_3\text{SiC}_2$  grains with different orientations, The Vickers hardness of textured bulk MAX phases also varies greatly along different directions, as shown in Table 4. The hardness measured under a low load on the sample surface perpendicular to the *c*-axis orientation, which is called the top surface (TS), is normally lower than the hardness measured on the sample surface parallel to the *c*-axis orientation, which is called the side surface (SS) [164–166]. However, a high load can result in a higher hardness on TS than on SS, which is attributed to the irreversible plastic deformation (delamination, crack deflection, etc.) on SS [159,164,165].

For textured bulk MAX phases, crack formation and propagation along layers (perpendicular to the *c*-axis orientation) requires breaking



**Fig. 24.** (a) delamination and kink band formation caused by a nano-indentation on plate-like  $\text{Ti}_3\text{SiC}_2$  grains parallel to the sample surface; (b) kink bands observed in a porous  $\text{Ti}_3\text{SiC}_2$  bulk sample; (c) and (d) load-displacement curves for nano-indentations on plate-like  $\text{Ti}_3\text{SiC}_2$  grains perpendicular and parallel to the surface, respectively; (e) and (f) morphologies of nano-indentations corresponding to (c) and (d), respectively.

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of the weak M—A bonds, which is much easier than fracture parallel to the *c*-axis orientation which requires breaking of the stronger M—X bonds and AA— bonds, leading to a higher flexural strength and fracture toughness along the *c*-axis orientation [22,23,165,167], as shown in Table 4.

As stated in Section 5.1, ball milling of synthesized bulk MAX phases to form fine plate-like grains is needed to prepare highly textured bulk MAX phases. The ball milling process could introduce some oxygen into these plate-like grains, resulting in the formation of oxides during sintering. Such homogeneously distributed nano-sized oxide particles in the MAX phase matrix could play a role in strengthening as well as toughening by crack deflection and blunting [165,170]. Fig. 25 shows the crack propagation paths perpendicular and parallel to the *c*-axis orientation of a textured Ti<sub>3</sub>AlC<sub>2</sub> bulk sample prepared by slip casting in a magnetic field using ball milled Ti<sub>3</sub>AlC<sub>2</sub> powders and subsequent SPS. The white particles are Al<sub>2</sub>O<sub>3</sub> formed by the oxidation of Al, which deflect and blunt cracks along both directions. The nano-laminated structure itself also leads to a zigzag crack propagation path through layers, as shown in Fig. 25(a). Due to these Al<sub>2</sub>O<sub>3</sub> particles, textured Ti<sub>3</sub>AlC<sub>2</sub> bulk samples possess high flexural strength (> 1000 MPa) and fracture toughness (> 13 MPa·m<sup>1/2</sup>) along both directions, as shown in Table 4.

### (2) Thermal conductivity and electrical conductivity

Due to the mixed covalent-ionic-metallic nature of chemical bonds in MAX phases, both electrons and phonons contribute to their thermal conduction. The thermal conductivity of a MAX phase can be estimated according to Eq. (19) [171,172]:

$$k = k_e + k_{ph} \quad (19)$$

where  $k_e$  and  $k_{ph}$  are the contributions of electrons and phonons to the thermal conductivity, respectively.  $k_e$  can be estimated according to the Wiedmann-Franz law [171,172]:

$$k_e = L_0 \sigma T \quad (20)$$

where  $L_0$  is the classic Lorenz number equaling to  $2.45 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ , and  $\sigma$  is the electrical conductivity at the temperature  $T$ .

The anisotropy in the electrical conductivity varies strongly between different MAX phases due to their different densities of states (DOS) around the Fermi level. For example, textured Ti<sub>3</sub>AlC<sub>2</sub> has a higher electrical conductivity parallel to the *c*-axis orientation [165], while textured Nb<sub>4</sub>AlC<sub>3</sub> has a higher electrical conductivity perpendicular to the *c*-axis orientation [164]. For Nb<sub>4</sub>AlC<sub>3</sub>, Nb *d* electrons mainly contribute to the DOS around the Fermi level, while Al electrons do not have significant contribution to the DOS around the Fermi level due to the "scooping effect" caused by Nb *d* states, resulting in a higher electrical conductivity along layers [173]. For Ti<sub>3</sub>AlC<sub>2</sub>, the number of Ti<sub>II</sub> 3d

states, which are around the Fermi level and mainly contribute to electrical conduction, increases significantly by the introduction of Al, thus Ti<sub>3</sub>AlC<sub>2</sub> has a higher electrical conductivity along the stacking direction of Ti—Al bonds, *i.e.*, the *c*-axis orientation [174].

Unlike the electrical conductivity, the thermal conductivity parallel to the *c*-axis orientation of textured bulk MAX phases is always lower than that perpendicular to the *c*-axis orientation, even for Ti<sub>2</sub>AlN and Ti<sub>3</sub>AlC<sub>2</sub> which possess a higher electrical conductivity along the *c*-axis orientation [153,164,165], as shown in Table 4. Such phenomenon is attributed to the phonon contributions to the thermal conduction of MAX phases. For example, according to the Wiedmann-Franz law, the phonon contributions of Ti<sub>2</sub>AlN and Ti<sub>3</sub>AlC<sub>2</sub> to their total thermal conductivity are both around 50 % at room temperature [175]. Phonon conduction is faster along layers than through layers due to the strong M—X and AA— bonds in layers and the weak M—A bonds between layers. Besides, there are more grain boundaries along the *c*-axis orientation, which can cause more serious phonon scattering. Therefore, textured bulk MAX phases always possess a higher thermal conductivity perpendicular to the *c*-axis orientation.

### (3) Oxidation resistance

Due to the layered structure of MAX phases, the defect migration along layers is much easier than that through layers, as discussed in Section 3.1. Therefore, the oxidation process of MAX phases is anisotropic. Song et al. [176] studied the anisotropic oxidation rates of HP-ed Ti<sub>3</sub>AlC<sub>2</sub> bulk samples by oxidizing their fresh fracture surfaces containing grains with different orientations at 1373 K in air for different time. Firstly, nano oxide particles mainly containing Al<sub>2</sub>O<sub>3</sub> form preferentially on the ledges of fractured plate-like Ti<sub>3</sub>AlC<sub>2</sub> grains (Fig. 26(a)), which demonstrates that defect formation and migration for Al is much easier than that for Ti and defect migration along layers is much easier than that through layers, as discussed in Section 3.1. These nano Al<sub>2</sub>O<sub>3</sub> particles on ledges tend to spread (Fig. 26(b)) to form an Al<sub>2</sub>O<sub>3</sub> layer with a thickness of about 100 nm (Fig. 26(c)). The Al<sub>2</sub>O<sub>3</sub> layer thickens with some fine faceted TiO<sub>2</sub> particles formed on it (Fig. 26(d)). Prolonged oxidation results in the formation of a porous layer composed of loose Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> particles between the dense Al<sub>2</sub>O<sub>3</sub> layer and the Ti<sub>3</sub>AlC<sub>2</sub> matrix (Fig. 26(e, f)). The compositions of the multilayer oxide film are demonstrated in the EDS line scan (Fig. 26(g, h)). The outside faceted particles are TiO<sub>2</sub>, beneath which is the initial Al<sub>2</sub>O<sub>3</sub> film with a small amount of TiO<sub>2</sub>, and the porous layer containing Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> is adjacent to the Ti<sub>3</sub>AlC<sub>2</sub> matrix. Fig. 26(i–l) shows the schematic diagrams of the oxidation process. Firstly, nano Al<sub>2</sub>O<sub>3</sub> particles form on the ledges of plate-like Ti<sub>3</sub>AlC<sub>2</sub> grains (Fig. 26(i)), which spread and form a dense Al<sub>2</sub>O<sub>3</sub> layer with some nucleation of TiO<sub>2</sub> between them (Fig. 26(j)). The oxide layer grows both inwards (the oxygen diffuses through the oxide layer and reacts with Al atoms and small amount Ti atoms which have diffused outwards from the Ti<sub>3</sub>AlC<sub>2</sub> matrix to the interface,

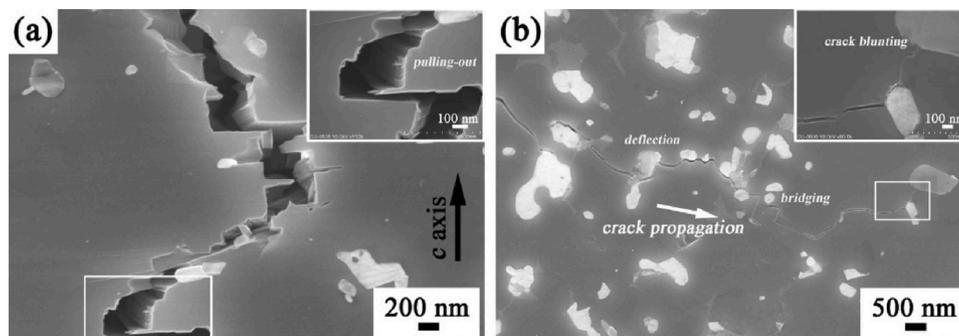
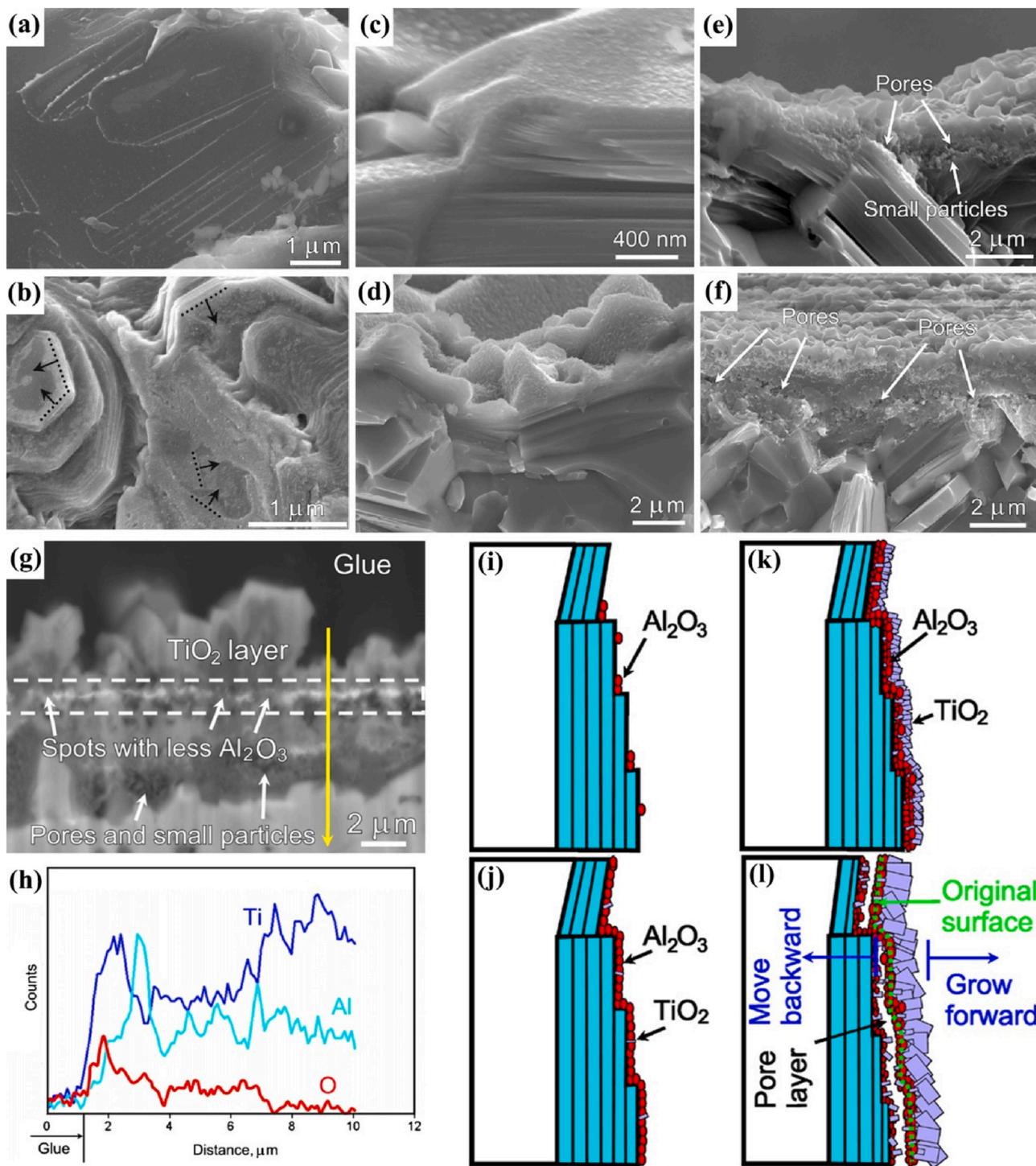


Fig. 25. Crack propagation paths along different directions of a textured Ti<sub>3</sub>AlC<sub>2</sub> bulk sample containing 15 vol.% Al<sub>2</sub>O<sub>3</sub>: (a) parallel to the *c*-axis orientation on SS; (b) perpendicular to the *c*-axis orientation on TS.

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**Fig. 26.** Characterization of  $\text{Ti}_3\text{AlC}_2$  bulk samples with fresh fracture surfaces oxidized at 1373 K in air for different time: (a) and (b) fracture surfaces oxidized for 20 s and 180 s, respectively; (c–f) cross-sections of fracture surfaces oxidized for (c) 180 s, (d) 360 s, (e) 600 s and (f) 900 s, respectively; (g) and (h) polished cross-sections of fracture surfaces oxidized for 900 s and the elemental concentrations from EDS line scan along the yellow line, respectively; (i–l) schematic diagrams of (i) nucleation of  $\text{Al}_2\text{O}_3$  on the ledges of fractured plate-like  $\text{Ti}_3\text{AlC}_2$  grains, (j) formation of the  $\text{Al}_2\text{O}_3$  layer and nucleation of  $\text{TiO}_2$  at  $\text{Al}_2\text{O}_3$  grain boundaries, (k) inward growth of the  $\text{Al}_2\text{O}_3$  layer and outward growth of the  $\text{TiO}_2$  layer, and (l) formation of the porous oxide layer due to further volume loss caused by oxidation, respectively.

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forming  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) and outwards (Ti atoms diffuse outwards and react with the oxygen, forming  $\text{TiO}_2$ ) (Fig. 26(k)). When the volume loss of the  $\text{Ti}_3\text{AlC}_2$  matrix caused by oxidation cannot be compensated by these oxides growing inwards, a porous oxide layer forms between the initial dense  $\text{Al}_2\text{O}_3$  layer and the  $\text{Ti}_3\text{AlC}_2$  matrix (Fig. 26(l)).

As the oxidation rates along different crystal directions of MAX phases are different, the oxidation resistance of textured bulk MAX phases should be anisotropic. Xu et al. [177] studied the anisotropic oxidation resistance of textured  $\text{Ti}_3\text{AlC}_2$  bulk samples prepared by MA and subsequent SPS. For temperatures below 1373 K, the weight gain of

both TS and SS proceeds in a parabolic manner against the oxidation time, indicating a good oxidation resistance (Fig. 25(a, b)). For temperatures higher than 1473 K, the weight gain of TS increases dramatically against the oxidation time, while the good oxidation resistance of SS is maintained. The oxide layer on TS mainly contains  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  after oxidation below 1373 K (Fig. 27(c, d)), which is similar to the research of Song et al. [176]. Although  $\text{Al}_2\text{O}_3$  contributes to the oxidation resistance of TS below 1373 K, compared with the dense  $\text{Al}_2\text{O}_3$  layer on SS (Fig. 27(g, h)), the porous oxide layer on TS is beneficial to the diffusion of oxygen and Al/Ti atoms, resulting in a much thicker oxide layer on TS than on SS. For TS and temperatures higher than 1473 K,  $\text{Al}_2\text{O}_3$  almost completely reacted with  $\text{TiO}_2$ , leading to the formation of a more porous oxide layer composed of  $\text{Al}_2\text{TiO}_5$  and  $\text{TiO}_2$  (Fig. 27(e, f)). For SS, the dense  $\text{Al}_2\text{O}_3$  layer can be maintained at temperatures lower than 1473 K, while a large amount of  $\text{Al}_2\text{TiO}_5$  is formed after oxidation at 1573 K for 20 h (Fig. 27(j)). Microstructural observations prove that the oxide layer on TS after oxidation at 1373 K for 20 h is porous, while the oxide layer on SS after oxidation at 1473 K for 20 h is composed of dense  $\text{Al}_2\text{O}_3$  grains with very few small and closed pores (Fig. 27(k–n)). The better oxidation resistance of SS than TS of textured  $\text{Ti}_3\text{AlC}_2$  bulk samples is attributed to the faster diffusion of Al atoms along layers than that through layers, leading to the rapid formation of a dense  $\text{Al}_2\text{O}_3$  layer on SS which significantly slow down the further oxidation of the  $\text{Ti}_3\text{AlC}_2$  matrix under SS.

## 6. Summary and outlook

This review paper summarizes the formation mechanisms, the defect structure and its relation to the self-healing performance and radiation tolerance, solid solutions and how this can be used to tailor properties,

texture formation and finally the anisotropy in properties of MAX phases. The following points are summarized:

- (1) To obtain MAX phases with a high purity, the elemental A content in the starting materials, the synthesis temperature and holding time need to be adjusted considering the vaporization of the A element and the formation of intermediate phases during the synthesis process. Besides, the introduction of intermediate phases  $\text{M}_x\text{X}_y$  in the starting materials can lower the formation temperature of MAX phases and improve the purity.
- (2) The formation energies of intrinsic point defects vary depending on the compositions of MAX phases. For most MAX phases, the formation energies of  $\text{A}_{\text{FP}}$  and  $\text{X}_{\text{FP}}$  are lower than that of  $\text{M}_{\text{FP}}$ . The formation energies of  $\text{M}_{\text{A}}\text{-A}_{\text{M}}$  anti-site pairs are much lower than those of  $\text{M}_{\text{X}}\text{-X}_{\text{M}}$  and  $\text{A}_{\text{X}}\text{-X}_{\text{A}}$  anti-site pairs, which is in correspondence with the fact that the M–A bonds are relatively weaker than the M–X bonds. The weaker MA–bonds also promote the formation and migration of defects along the A layers, making the  $\text{M}_{n+1}\text{A}$  block act as a defect sink. MAX phases with higher electronegative differences between M and A atoms tend to possess higher formation energies of  $\text{M}_{\text{A}}\text{-A}_{\text{M}}$  anti-site pairs, which are strongly related to their radiation tolerance. Besides, as the self-healing performance of MAX phases depends on the oxidation of the A element, which would leave A vacancies in MAX phases, the theoretical calculation of the stability of MAX phases with A vacancies can provide important guidance on their application as self-healing materials.
- (3) The configurations of M alloyed  $\text{M}_{n+1}\text{AX}_n$  phase solid solutions can be either ordered or disordered, which are determined by the formation enthalpy, the relationship between the order-disorder

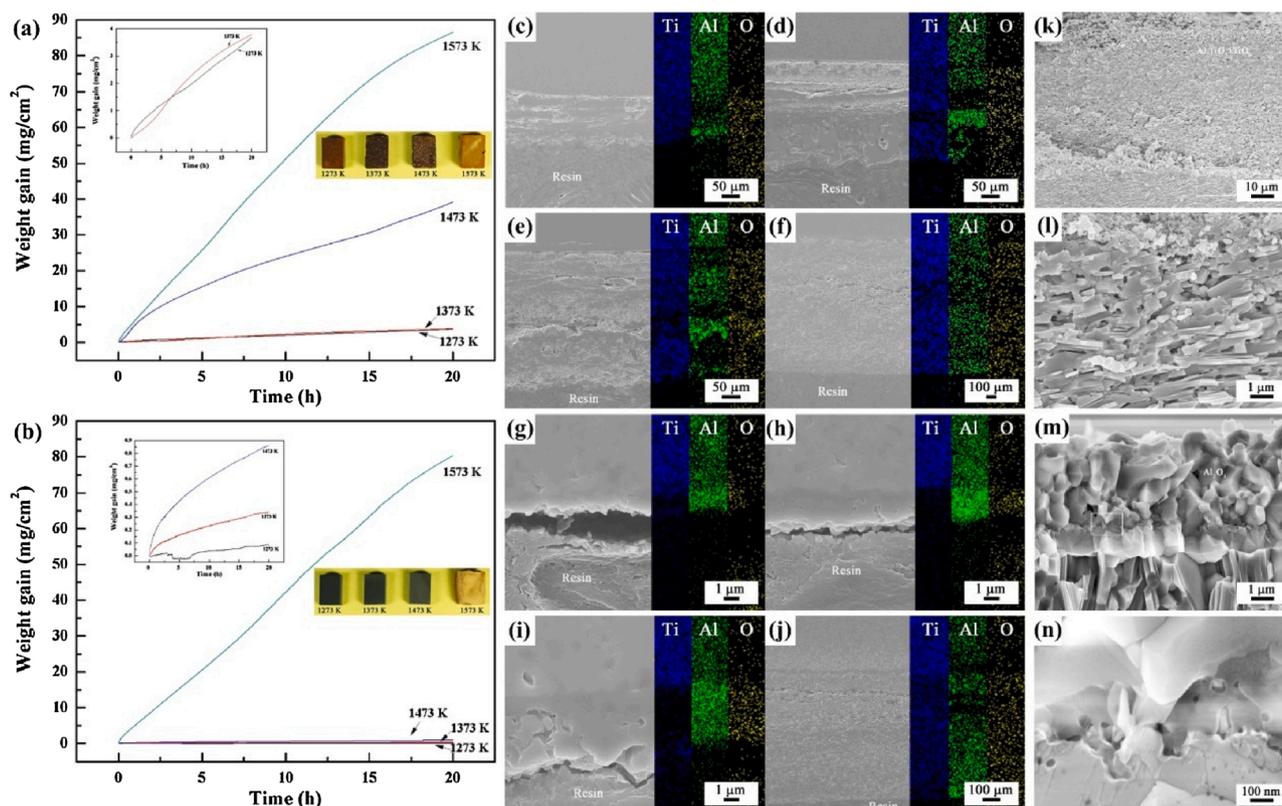


Fig. 27. Characterization of textured  $\text{Ti}_3\text{AlC}_2$  bulk samples oxidized at different temperatures in a flowing mixture gas ( $\text{N}_2$  and  $\text{O}_2$  with a volume ratio of 78:22) for 20 h: (a) and (b) weight gain per unit surface area vs. oxidation time at different temperatures for TS and SS, respectively; (c–f) polished cross-sections of TS oxidized at (c) 1273 K, (d) 1373 K, (e) 1473 K and (f) 1573 K, respectively; (g–j) polished cross-sections of SS oxidized at (g) 1273 K, (h) 1373 K, (i) 1473 K and (j) 1573 K, respectively; (k) and (l) cross-sections of TS oxidized at 1373 K; (m) and (n) cross-sections of SS oxidized at 1473 K. Reproduced with permission from Ref. [177], © 2018 Elsevier Ltd.

transformation temperature ( $T_{\text{disorder}}$ ) and the synthesis temperature of solid solutions. MAX phase solid solutions can be used to tailor their mechanical properties, physical properties, oxidation resistance, etc. Whether a MAX phase solid solution employs solid solution strengthening/toughening or not seems like to be strongly influenced by the change rate of the lattice parameter  $c$  with the change of the content of alloying atoms in the MAX phase solid solution ( $c_{\text{CR}}$ ), which needs to be verified by further experiments. Similar to their mechanical properties, no simple linear relationship exists for the CTEs of MAX phase solid solutions and their end members, which reflect the average bonding strength. For the electrical conductivity, alloying atoms on the M-site have a more significant solid solution scattering effect, while alloying atoms on the A-site only lead to slight scattering, which is attributed to the fact that the electrical conduction in MAX phases is mainly driven by the transition metal atoms. Some alloying atoms can introduce magnetic properties to MAX phases which do not normally show magnetic properties.

- (4) Textured bulk MAX phases can be prepared by pressure-assisted sintering (HP and SPS) and magnetic alignment (MA) followed by sintering. The anisotropy in the hardness of textured MAX phases varies for different loads due to the easier kink band formation on TS under lower loads and the irreversible plastic deformation on SS under higher loads. The preferential orientation of plate-like grains in textured MAX phases results in zigzag crack propagation paths through layers, giving them a high toughness. The anisotropy in the electrical conductivity could be different for different MAX phases, which is determined by the DOS at the Fermi level. While the thermal conductivity parallel to the  $c$ -axis orientation of textured MAX phases is always lower than that perpendicular to the  $c$ -axis orientation due to the contribution of phonon conduction. For MAX phases with a good oxidation resistance (e.g.,  $\text{Ti}_{n+1}\text{AlC}_n$ ), texturing gives them a better oxidation resistance on SS due to the faster diffusion of A atoms along layers which results in the faster formation of a protective dense oxide scale on SS.

Although much research progress has been achieved in the field of MAX phase synthesis and properties, there are still some issues which need to be solved or more deeply investigated. The stability of MAX phases with A vacancies, which can provide important guidance on their application as self-healing materials, need to be widely studied. Theoretical basis needs to be given to judge whether a MAX phase solid solution employs solid solution strengthening/toughening or not ( $c_{\text{CR}}$  is proposed as a basis for judgment in this review, which needs to be verified by further experiments). The magnetic properties of MAX phases and their solid solutions are also an area to be further studied, especially tailoring magnetic properties by controlling the atomic configuration, the composition of multiple alloying elements, the temperature, the magnetic field or the applied pressure. For textured MAX phases which possess improved properties along specific directions, ball milling of synthesized bulk MAX phases, which usually introduces some oxygen into the raw powders, is usually needed to prepare highly textured MAX phases. Although the formed oxide particles usually play a role of strengthening and toughening by crack deflection and blunting, they are harmful to thermal and electrical conduction due to their scattering effect, which needs to be solved for textured MAX phases used in heat sinks or electrical parts. Therefore, more effective texturing techniques for MAX phases need to be developed.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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