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A review of the mechanical properties of 2D transition metal carbides (MXene)-reinforced metal and polymer composites

ABSTRACT

In the modern era, two-dimensional MXenes—commonly known as transition metal carbides, nitrides, and carbonitrides—have emerged as a new class of competitive materials for developing composites across various applications. As a 2D material, MXene-reinforced composites represent an emerging field with significant potential due to their remarkable optical, mechanical, electrical, and electrochemical properties. Additionally, their stability at high temperatures highlights their uniqueness in composite materials. Consequently, MXenes are regarded as revolutionary materials for functional and structural composite applications, offering tunable electrical, thermochemical, and physicomechanical properties. This review examines recent advancements in the use of MXenes as reinforcing elements in metal matrix composites (MMCs) and polymer matrix composites (PMCs), while providing insights for future research in this area.
Keywords: *MXene, MAX phase, metal matrix composite, Ti_3C_2Tx, Tensile property*

1. INTRODUCTION

The complex processes and techniques in tailoring the properties of regular 3D bulk materials discovered the most surprising material known as 2D crystals. Again, the isolation of monolayer graphene flakes by mechanical exfoliation of bulk graphite opened the field of two-dimensional (2D) materials. Since the discovery of graphene, the two-dimensional (2D) materials have proven themselves with their unique electrical, chemical, mechanical, and physical properties [1] over the past decade that make them useful in a wide variety of applications such as sensors, energy storage and conversion, optoelectronics, and catalysis [2]. Since then, many other 2D materials have been discovered, such as transition metal-dichalcogenides (TMDs, e.g., MoS_2), hexagonal boron-nitride (h-BN), and black phosphorous or phosphorene. In 2011, a novel two-dimensional layered nanomaterial family, transition metal carbide known as MXene has drawn the attention of researchers due to their in-plane mechanical stiffness and strength [3,4], high electrochemical activity [4–6], as well as their capacitive and conductive properties [7-9]. MXenes, similar to graphene offer exciting opportunities for sensing applications due to their high specific surface area, excellent electrical conductivity, tuneable surface chemistry, biocompatibility, and ease of processing as compared to other 2D materials [10]. Furthermore, due to inherent properties such as hydrophilicity with a contact angle ranging from 27° to 41° [11], MXenes have a great possibility to be used in reinforced composite materials, especially in energy-related applications such as supercapacitors [12–14], battery electrodes [15–17], and active catalytic materials [18–20]. Furthermore, the strong internal pairing between M-X in MXene causes ample surface terminations, making them a suitable material for metal matrix composites in structural and tribological applications. MXenes have mostly been employed as reinforcing elements in polymeric materials however, limited works have been reported for ceramic and metal matrix composites. This paper consolidates the research based on MXene-reinforced metal matrix composites, polymer matrix composites, and their mechanical properties.

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2. SYNTHESIS OF MXene

The first MXene was discovered by the researchers at Drexel University in 2011, and it was prepared by etching a layer of the MAX phase of Ti_3AlC_2 [21]. From more than 70 types of MAX phases [22,23], about 30 MXene compositions were observed, among which titanium-based MXene, such as Ti_3C_2Tx and Ti_3CTx, has been widely investigated by different authors [24] due to their remarkable specific stiffness and strength. In addition to carbides, other MXene structures having nitrides and carbonitrides are also reported for various applications.

MXenes are created by etching the 'A' element layers from the MAX phase elements (Fig.1) which are denoted as Mn + 1AXn (n = 1 to 4), where 'M' represents a 3d_- 5d-block transition metal (such a Scandium - [Sc], Yttrium - [Y], titanium - [Ti], Zirconium - [Zr], Hafnium - [Hf], Vanadium - [V], Niobium - [Nb], Tantalum - [Ta], Chromium - [Cr], Molybdenum - [Mo], or Tungsten - [W]) mainly the groups 3–6 of the periodic table, 'A' is a group IIIA or IVA element, which are commonly from groups 13–16 of the periodic table (such as Aluminium - [Al], Gallium - [Ga], Indium - [In], Silicon - [Si], Germanium - [Ge], etc.), and 'X' can be either Carbon (C), Nitrogen (N) or both [25].

Figure 1. Periodic table elements that form MAX phase [26]

2D materials can be synthesized by two techniques, one is the bottom-up approach that after chemical deposition produces thin film of high quality on various substrate and second is top-down method which includes exfoliation of layered solids that may be mechanical or chemical. The top-down approach is mostly used for the synthesis of 2D MXene and it consists of numerous processes such as precursor, etching and exfoliation. Various MXenes have been synthesized by acid etching (HF etching) at room temperature to different temperatures by regulating the concentration of HF and reaction time. The first discovered two-dimensional (2D) MXene was $Ti_3C_2T_X$ (Tx represents the terminal groups such as hydroxyl (-OH), oxide (-O) or fluorine (-F), x is the number of terminal groups) and obtained by etching of Al with hydrofluoric acid (HF) solution from the layered hexagonal ternary carbide, Ti_3AlC_2, at room temperature (Fig -2).

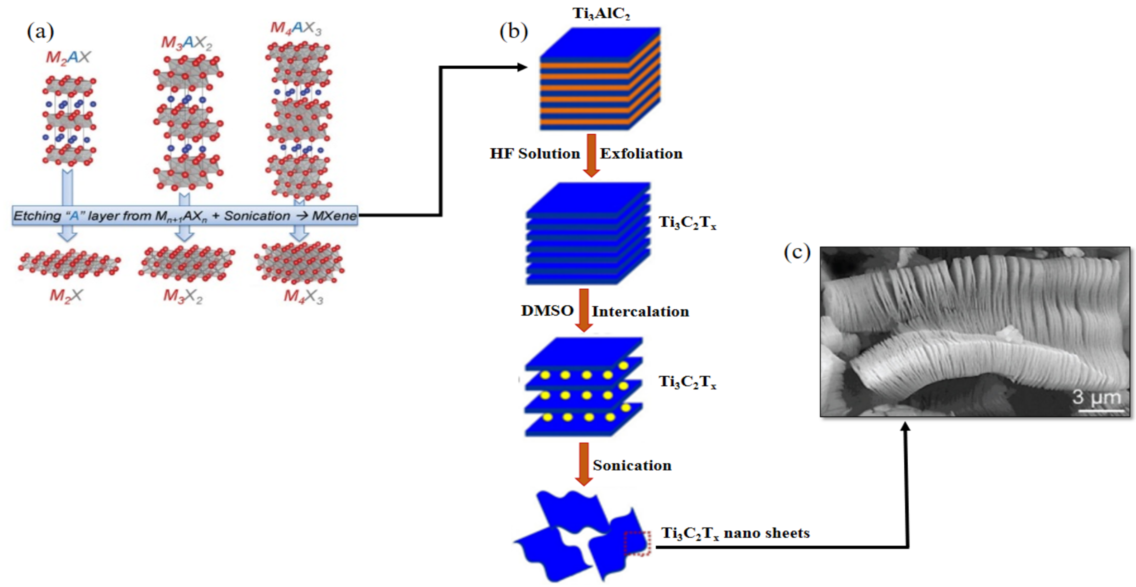

Figure 2. Pictorial illustration of (a) structures of typical M_2A_X, M_3AX_2, M_4AX_3 phases [22], (b) Synthesis of $Ti_3C_2T_x$ [23], (c) SEM micrograph of $Ti_3C_2T_x$ after HF treatment [24]

The HF etching process to dissociate the M-A bond in M_n+1AX_n phases with Al can be described with the following reactions:

$$M_{n+1}AX_n + 3HF \rightarrow M_{n+1}X_n + AlF_3 + 1.5H_2 \quad (1)$$

$$M_{n+1}X_n + 2H_2O \rightarrow M_{n+1}X_n (OH)_2 + H_2 \quad (2)$$

$$M_{n+1}X_n + 2HF \rightarrow M_{n+1}X_nF_2 + H_2 \quad (3)$$

According to Eqs. (2) and (3), the surface terminations are formed due to the combination of –OH and –F during the etching of Al, resulting in the functionalization of the M layers.

3. MXENE-REINFORCED METAL - MATRIX COMPOSITES

Particle-reinforced metal - matrix composites (MMCs) are an important class of composite material that have drawn much more attention due to their low density, low cost, and easy fabrication characteristics. MMCs mainly consists of lightweight metals (Al, Mg, Li) as the matrix element and ceramic particles as reinforcements. As a consequence, properties of the soft metal matrix, such as yield strength, fatigue, and corrosion resistance are possible to improve significantly with the inclusion of hard ceramic nanoparticles [25] which makes the MMCs compatible material for various structural and tribological applications. Similar to the other commercially available ceramic and carbon nanoparticles such as SiC, Al_2O_3, Graphene platelets, and carbon nanotubes, MXene has also shown exceptional mechanical and electrical properties. Also, the stability of MXenes at higher temperatures i.e. more than 1000 °C proves its potential to provide a nanolamellar transition metal carbide reinforcing material for metals with high melting points [27]. Additionally, being a functional filler, its potential cannot be neglected for matrix composites (MMCs).

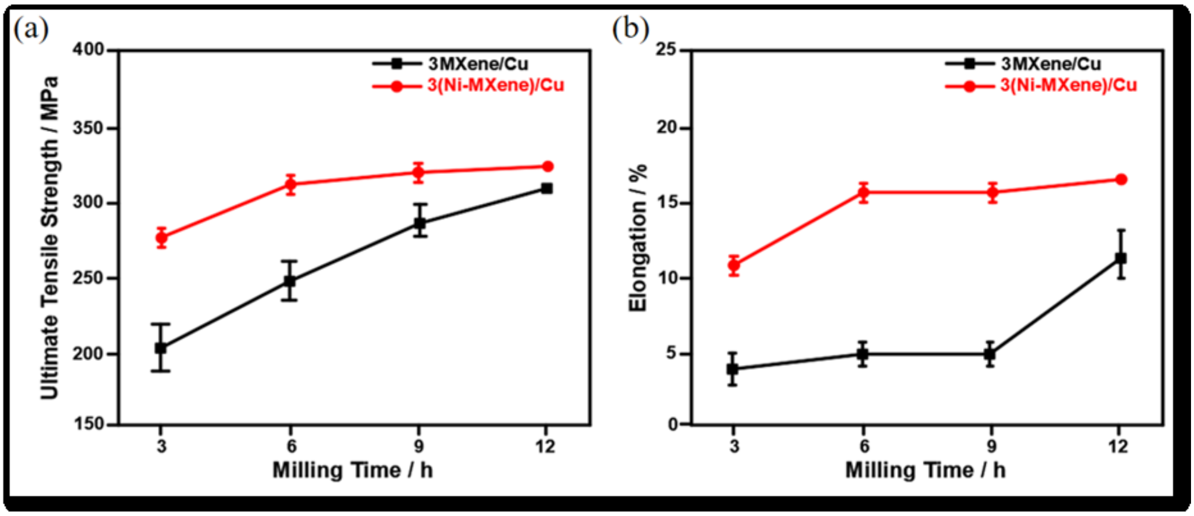

Figure 3. The UTS and elongation of 3(Ni-MXene)/Cu composites, (a) the variation of UTS with the milling time, (b) the variation of elongation with the milling time [31]

High surface area, excellent hydrophilicity, and the presence of abundant elements such as Ti, C, and N enable MXenes to possess unique mechanical properties [28]. MXene has been reinforced into commercial metals and their alloys namely Copper, Aluminium, and Magnesium by various powder metallurgy techniques such as ball milling and spark plasma sintering (SPS) followed by hot extrusion. It has been reported that the inclusion of MXenes of 2 wt% to 5 wt% in metal and ceramic matrix composites improves the tensile fracture toughness, flexural strength, and hardness by 40%, 300%, 150%, and 300%, respectively [29,30]. From the findings of researchers, it has been observed that MXene (Ti_3C_2Tx) reinforced metals either Aluminium or copper composites show a linear relationship between the ultimate tensile strength (UTS) and the wt% of MXene. In addition, the ultimate tensile strength (UTS) of MMCs reinforced with MXene tend to be further improved with increasing the wt% of MXene. Furthermore, it has been reported that the transformation in the ultimate tensile strength (UTS) is also a function of the ball milling time. For MXene-reinforced copper composites, UTS increases linearly with increasing the milling time. As the milling time increased from 3 to 12 h, the UTS of the MXene/Cu composites of 3 wt% increased from 202 MPa to 314 MPa whereas the UTS of MXene/AL composites with the same weight percentage and milling time of 10 h achieved UTS of 148 MPa. Thus, it can be analyzed from the finding that MXene has the potential to strengthen metal matrix effectively by a multiple strengthening mechanism such as wt% of MXene and ball milling time which eventually enhances the strength of the MMCs. One adverse impact of MXenes has been observed that the UTS of MXenes reinforced metal matrix composites show a decreasing tendency with an increase in milling time after a certain limit because of the serious agglomeration of MXene particles at 5 wt% for copper matrix. Hence, it can be indicated that the pristine MXene has a poor wettability with the Cu matrix because of the surface functional groups. It has been reported that when MXene/Cu composites are hybridized with Ni, the wettability of Cu matrix element improves by inter diffusion of Cu and Ni elements at the interface and subsequently it diffuses to the inside of the agglomerated MXene particles, which effectively improves the tensile properties of the composites [31]. Including the ultimate tensile strength (UTS), the elongation percentage has also been improved for the metal matrix composites with an increase in MXenes wt%. But for MMcs and hybridized MMCs, the milling time maintains the linear relation which can be observed in Fig. 3. The metals and alloys adopted as matrix material by different authors whose work has been reported in this work is listed in Table 1. The potentiality of MXenes in improving the mechanical properties of ZK61 alloy has also been reported.

Table 1. Mechanical properties of MMCs with MXene

Name of Metal	Weight %	UTS, (MPa)	Elongation (%)	Hardness, (VHN)	References
Al	0.5	110	11.1	31.61	25
	1	119	12.6	34.67	
	2	138	14.2	42.8	
	3	148	15.3	53	
Cu	1	202	20	70	26
	3	314	11.1	98	
	5	354	6	111	
Magnesium Alloy (ZK61)	0.5	305	17	64.3	27
	1	227	5.3	77.8	
Ni-Cu	3	325	16.1	101.67	32

It has been reported that in MXenes reinforced metal matrix composites, the surfaces of $Ti_3C_2T_x$ nanosheets are terminated with Ti or functional groups such as –OH, –O, and –F which enhances the wettability between $Ti_3C_2T_x$ and the metal. Subsequently, it helps in homogeneous distribution of $Ti_3C_2T_x$ (Fig. 2a and 2b) and the formation of strong interfacial bonding in the composites causing improved mechanical properties.

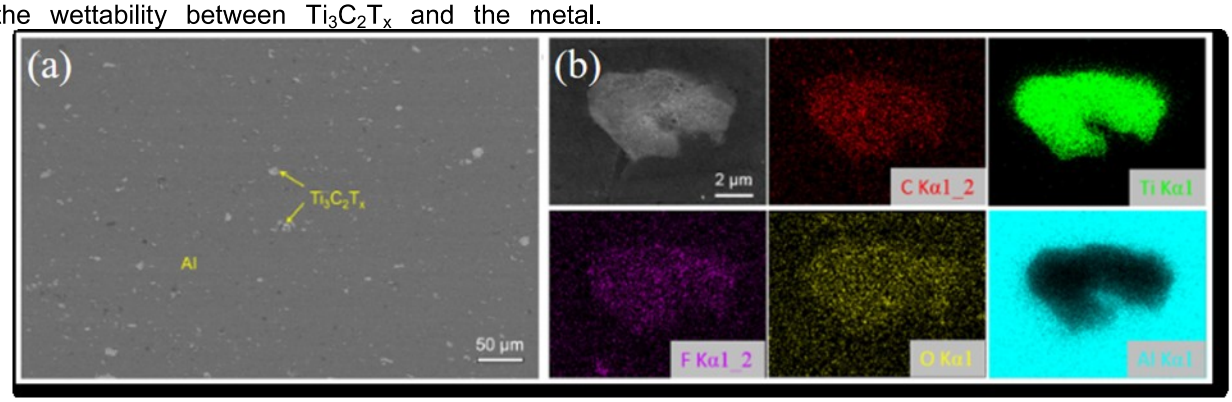

Figure 4. Pictorial illustration of (a) SEM micrograph of the polished surface of 3 wt% $Ti_3C_2T_x$ /Al composite. (b) EDS maps for the distribution of C, Ti, F, O and Al [24]

4. MXene-REINFORCED POLYMER - MATRIX COMPOSITES

Polymeric materials have been widely used in recent decades due to their distinct characteristics, including affordability, low weight, and ease of manufacturing. Nevertheless, the limited mechanical and tribological characteristics of polymeric materials have hindered their extensive utilization. For instance, polymeric coatings are primarily employed as protective coatings for metallic substrates due to their exceptional corrosion resistance. Nevertheless, its wear resistance is compromised when subjected to tribological environments. Hence, several methods have been implemented to enhance the mechanical and tribological properties of polymeric composites [33–36]. Incorporating nanoparticles into the matrixes of polymeric composites is an option to improve their tribological performance. Moreover, the extensive utilization of fillers in polymers for the purpose of creating high-performance composite materials with enhanced characteristics may be traced back to the 1960s [37]. Nevertheless, it was only in the late 1980s and early 1990s that nanoparticles were first utilized as additives to create a novel category of materials called nano-composites (NCs). This breakthrough was made possible by Toyota's research on nylon/clay hybrids [38]. The difference between regular composites and nano-composites lies in the fact that in nano-composites, the filler has at least one dimension on the nano-scale, usually less than 100 nm. So far, polymer composites have been enhanced by using many kinds of nano-materials, including one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nano-materials [39–44]. Research has shown that 2D nano-materials, such as Graphene, MoS_2, clay nanoparticles, and others, have distinctive shape and characteristics that make them promising reinforcements for polymeric matrices [45–48].

Thermosetting polymers are commonly utilized as the matrix for composite materials in various applications due to their benefits, such as the ease of incorporating reinforcements, particularly nanoparticles, into their matrix [49–51]. Thus far, there have been efforts to integrate MXenes into thermosetting polymers. This section examines the effects of incorporating MXene into thermosetting composites on their mechanical, tribological, thermal, corrosion, and electrical properties.

5. SUMMARY

Since 2011, MXenes have demonstrated properties that make them suitable for a broad range of applications, from structural components to highly sensitive energy storage devices. Although studies have explored the use of MXenes as reinforcement materials in metal and polymer matrix composites, numerous challenges and opportunities for further experimental validation remain. The mechanical, tribological, piezoelectric, and electrically conductive properties of MXenes, particularly when combined with various transition metals, carbon or nitrogen, and surface group compositions, hold great promise for tailoring MXenes for specific applications in metal matrix composites. Additionally, the exceptional stability of MXenes' transition metal carbide and nitride core at temperatures exceeding 1000°C makes them a highly promising 2D nanomaterial for reinforcing composites intended for high-temperature applications. It is expected that MXenes will emerge as the primary nanomaterial reinforcement for composites, meeting the high-temperature demands of future metal and polymer matrix composite materials.

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IZVOD

PREGLED MEHANIČKIH SVOJSTVA 2D PRELAZNIH METALNIH KARBIDA (MXene) OJAČANIH METALA I POLIMERA KOMPOZITA

U ovoj modernoj eri, dvodimenzionalni MXeni, poznatiji kao karbidi prelaznih metala, nitridi i karbonitridi, evoluirali su kao nova klasa konkurentnih materijala za razvoj kompozita za različite primene. Budući da su 2D materijali, kompoziti ojačani MXenes-om postaju novo polje sa značajnim potencijalom zbog svog izvanrednog optičkog, mehaničkog, električnog i elektrohemijskog ponašanja. Štaviše, njegova stabilnost na visokim temperaturama pokazuje njegovu jedinstvenost u oblasti kompozita. Kao rezultat toga, MXene se smatra revolucionarnim materijalom za primenu funkcionalnih i strukturnih kompozita sa podesivim električnim termohemijskim i fizičko-mehaničkim svojstvima. U ovom izveštaju razmatramo nedavni razvoj MXene-a kao elementa za ojačavanje u kompozitima metalne matrice (MMC) kao i kompozitima sa polimernom matricom (PMC) i pružamo perspektivu za buduća istraživanja u ovoj provinciji.

Ključne reči: *MXene, MAX faza, kompozit metalne matrice, Ti3 C2 Tk, zatezna svojstva*

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