Serbian Tribology Society

SERBIATRIB ‘23

18th International Conference on Tribology

Faculty of Engineering
University of Kragujevac

Kragujevac, Serbia, 17 – 19 May 2023

APPLICATION OF MXENE NANOSHEETS FOR IMPROVING MACHINE ELEMENTS PROPERTIES

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Abstract: Due to a growing energy problems in the last decades, different ideas and methods for saving energy and efficiency improvement become more and more requested. Taking into account that almost half of the energy losses in machines and mechanisms occur in frictional processes thus the importance of improving tribology performances in different machine elements is rather clear.

Machine elements such as gears, rolling and sliding bearings in various applications are usually operating with different lubricants in order to reduce friction and wear of their contacting surfaces. Besides surfaces in contact cannot be conventionally lubricated due to legal and environmental restrictions or physical limitations, in applications in food, textile, paper or medical industry as well as limitations due to ultra-clean conditions, extreme temperatures, radiation or vacuum, solid lubricants gain more and more attention due to the possibility to maintain essential lubrication properties. MXenes are a novel class of new two-dimensional materials, derived from well established MAX phases such as Ti_3AlC_2, which have the ability for a wide use in fields and applications due to their unique structure and properties. The distinct structure, low shear resistance, and easy-to-modify ability endow MXenes with particularly superior lubrication potentials. Authors of the paper present an overview synthesis and variety of MXenes, their mechanical and frictional properties dealing with ideas for possible applications in several machine elements aimed to reduce friction, wear rate and improve their performances making longer working life.

Keywords: Machine elements, MXenes, solid lubricants, coatings, tribology performances

1. INTRODUCTION

With a change of the world and the level of technological achievements since the beginning of the 21st century, new challenges in society and science have arisen due to the growing need for energy and the limitation of fossil fuel use due to regulations aimed to protect the environment. Industrial growth and the necessity to increase productivity require the use of different types of machines and mechanical systems, which have many moving parts and, consequently, interaction surfaces. Controlling friction and wear on surfaces where objects interact significantly impacts the durability, dependability, precision, and efficiency of machines and the parts that make them up. Around 23% of the world's energy goes towards overcoming tribological contact, 20% account for friction, and 3% are attributed to remanufacturing worn parts as a result of wear and wear-related problems. Energy losses due to friction and wear might possibly be decreased by

40% over the course of 15 years and by 18% over the short term by using new surfaces, materials, and lubrication technologies in automobiles, machines, and other equipment around the world [1]. The three main lubrication regimes are boundary, mixed, and hydrodynamic [2]. The fluid film method of lubricating sliding parts uses mineral-based oil, which is still used the most globally in terms of volume [1]. As our concern for the environment grows, the use of synthetic oils will undoubtedly increase. The performance of synthetic lubricants can be superior to that of traditional mineral-based oils. As a result of their reduced volatility and greater thermal stability, they often have a longer service life, which is advantageous for the environment [3]. Due to the negative environmental effects of these types of lubricants during production, usage, and disposal after use, rigorous environmental regulation is rapidly restricting their use. In many applications, including those involving food, paper, the medical industry, and space missions, as well as ultra-clean conditions, high or low temperatures, vacuum, and a particular environment, conventional fluid lubricants are rendered ineffective and solid lubricants are used instead [4]. Instead of liquid and grease-type lubricants, a greater proportion of solid lubricants is anticipated to be utilized in future tribosystems as a result of environmental concerns and more demanding operating conditions [5]. There are four major categories of solid lubricant materials: carbon-based materials such as graphite and diamond-like carbon (DLC), transition metal dichalcogenide (TMDs) compounds like MoS_2, soft metals, and polymers such as polytetrafluoroethylene (PTFE). Most of these materials can be applied on tribological components, such as machine parts, as thin films and coatings to reduce friction and wear, besides PTFE and its composites [6]. While bulk material must fulfill requirements for stiffness, strength, and formability, coatings are applied as a thin surface layer that is the carrier of all functional qualities such as tribological, chemical, and thermal. Improved wear resistance and decreased friction from applied coatings, which result in lower energy consumption and, in some circumstances, the removal of lubrication and cooling phases, are additional benefits beyond lifetime extension [7]. Because of their excellent tribological performance resulting from their distinct chemical and physical properties, two-dimensional layered-structured materials, such as graphene [8], have attracted enormous interest as solid lubricants and lubrication nano-additives [9]. In recent years, significant advances in synthetic techniques have enabled the production of an increasing number of 2D materials beyond graphene [10], such as transition metal dichalcogenides, graphitic carbon nitride, layered metal oxides, hexagonal boron nitride, black phosphorous [11], and a newly discovered large family of 2D materials named early, "MXenes".

2. SYTNTHESIS AND PROPERTIES

This class of transition metal carbides, nitrides, and carbonitrides named MXenes was discovered by a group of researchers from Drexel University, Philadelphia [12]. The universal chemical formula is $M_{n+1}X_nT_x$ (n = 1 to 4). Transition metal atoms (Ti, V, Nb, Zr, Ta, or Mo) are denoted with M, X represents carbon or nitrogen, with abundant surface terminations T_x such as –F, -OH, O, or –Cl on the outermost exposed M layer [13].

2.1 Synthesis of MXenes

Top-down and bottom-up methods are the two primary strategies used for the synthesis of 2D MXenes. Although the bottom-up method focuses on the development of MXenes from atoms or molecules, the top-down process corresponds to the exfoliation of huge crystal quantities into single-layered MXene sheets [6]. Based on literature [14], the process of MXene production is described, which is usually done in three steps. The synthesis of multilayer MXene precursors is the initial stage. The majority of experimentally realized MXenes come from MAX phases. MAX phases are chemically denoted by $M_{n+1}AX_n$, for which the M-X layers found in MXenes are sandwiched by one layer of group 11–16 A-element atoms [13]. By soaking MAX phase in certain acids and breaking M-A bonds, MXenes are separated from MAX phase. It is possible to break M–A bonds in several MAX phases because they are weaker than the ionic and/or covalent interaction that exists between M and X atoms. This chemical reaction must take place in an etchant that can dissolve the reaction products [15]. The etchants can be broadly separated into two groups: salts containing fluorine ions (NH_3F, KF, LiF, or NaF) and acidic solutions containing fluoride ions (HF, a mixture made of LiF and HCl, or NH_4HF_2) [16]. Finally, the delaminated single- to few-layer MXene sheets are produced from the exfoliated multilayer MXene sheets.

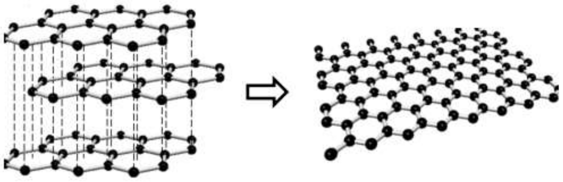

Figure 1. Mechanical exfoliation techniques are used to create 2D materials.

Based on this name, MXene is created by combining "MX" to emphasize the loss of an A layer from the parent MAX phase and "ene" for its 2D character similar to graphene [13]. First MXene $Ti_3C_2T_x$ was synthesized by immersing Ti_3AlC_2 powder in 50% concentrated HF acid at room temperature for 2 hours [12]. Although HF has shown to be a highly effective etchant for the selective removal of aluminum, it is extremely corrosive and has serious health and environmental concerns, which should be taken into account when producing MXene [15]. A careful control of the etching conditions is necessary to completely convert the MAX phase to MXene during the etching process. Typically, the M and n atoms in the chemical formula $M_{n+1}AX_n$ should modify the etching conditions. The fluorine ion concentration in the etching solution as well as the etching period should be increased as the M-A bond energies increase with the M atomic number. Larger fluorine ion concentrations and etching times are also necessary for larger n values. Additionally, a higher temperature is required if the etchant loses acidity. As a result, in addition to acid solutions, salts that include fluorine ions can also be used as etchants to create MXenes, however, the latter should be accompanied by a much higher etching temperature [16].

2.2 Mechanical properties of MXenes

For mechanical applications of MXene such as in tribology or structural composites, desired physical properties are tunable Tx towards varying lubrication or stiffness, controllable MXene thickness, minimal defects, and a large surface area, among others. For these purposes, HF etching is the most often used synthesis technique, while additional options include alkali etching, halogen etching, and Lewis acid molten salt etching [14]. The mechanical properties of MXenes play a major role in their effective use. The mechanical characteristics of MXenes are mainly determined by the presence of strong M-N and M-C bonds. The surface terminations M-O, M-OH, M-F, or M-CL also have an impact on the characteristics, however M-X bonds are more important in terms of mechanical properties [17]. Using the stiffness of M-X bonds, mechanical parameters such as Young's modulus can be predicted [18]. Bond stiffness between M and C tends to grow as the group member of M employed in transition carbides increases [17]. Surface terminations with a -O termination have a very high stiffness, however, surface terminations with -F and -OH terminations have a lower elastic stiffness than -O [19]. The strength and hardness of $M_{n+1}X_nT_x$ for functionalized MXene increase with decreasing n, and the Youngs modulus decreases [20]. When compared to carbide-based MXenes, nitride-based MXenes have a higher Youngs modulus [21]. According to experimental studies published in [22], the elastic modulus of bare Tin+1Cn drops from 604 GPa to 454 GPa and 479 GPa for n = 1, 2, and 3. The results of an experiment on $Ti_3C_2T_x$ show that it has a 2D stiffness of 326 +/- 29 Nm^{-1} and a failure strength of 5.2% of its elastic modulus. Mechanical properties are examined on thin films. The MXene flake size, quality, orientation of the individual flakes, film thickness, and fabrication procedure all affect the mechanical properties of Ti3C2Tx films [17].

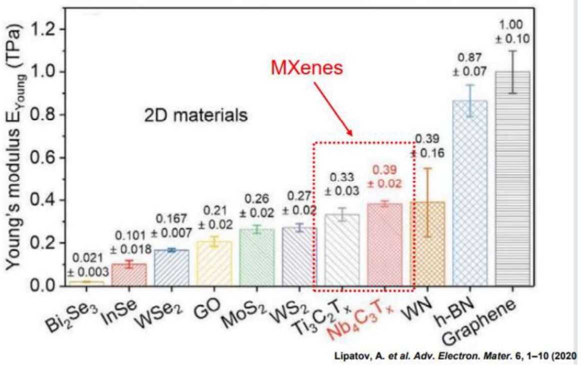

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Figure 2. MXenes demonstrate the highest effective Young's modulus for processable 2D materials.

The tensile strength of $Ti_3C_2T_x$ layers layered randomly is as low as 40 MPa [23]. A tensile strength of 568 MPa is achieved by a highly oriented film with a thickness of around 940nm that was created by blade coating [24]. Although it has elastic capabilities that are two to three times less than those of graphene, its maximum bending characteristics of 1050 GPa support its use as a composite reinforcing material. In contrast to graphene, MXene has exceptional capacity to interact with polymer matrix [25]. By creating composites with polymers, MXenes mechanical characteristics are experimentally improved. The tensile and compressive strengths, flexibility, and toughness of MXene can all be improved by adding various types of polymers [16].

2.3 Tribological properties of MXenes

MXene properties such as low shear resistance between adjacent layers due to weak secondary inter-layer bonding make them particularly promising to be used for tribological purposes [17]. Less than 5% of MXene's publications, out of more than 3000 published so far, deal with their mechanical and tribological applications [26]. Currently, they have been applied as liquid lubricant additives, solid lubrication coatings, and reinforcement phases in composites.

The effect of temperature and applied pressure on the friction and adhesion forces of Ti3C2 MXene was investigated by the authors in [27]. The findings demonstrated that high temperatures would reduce friction and adhesion while high pressure would increase friction and adhesion forces. Nb2C MXene was investigated in [28] and shows reduced friction and adhesive force under the same circumstances as Ti_3C_2. The lack of coatings is a result of easy oxidation, poor substrate adherence, low durability, and poor environmental adaptation. The most effective way to compensate for the shortage is to combine MXene with other materials. Based on their MXene properties, they show great potential as additives in liquid lubricants, both oil-based and water-based. They have a lot of potential as additives in liquid lubricants, both oil- and water-based. The demands of industrial manufacturing cannot be met by pure liquid lubricants; consequently, efficient additives must be added. To enhance the friction and wear performance of paraffin, poly-(alpha)-olefins, and other base oils, multilayer powders have been utilized [17]. 2D Ti3C2 was employed as an additive in paraffin base oil by researchers in [31]. With 1.0 wt% Ti3C2, there is a decrease in COF and anti-wear characteristics.

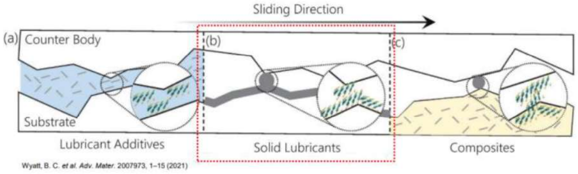

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Figure 3. MXenes can be used as lube. additives, solid lubricant coating, or as reinforcement phase in composite materials.

In addition to using MXenes in oils, the authors in [32] added them as additives to water, which reduced COF by around 20% at a Ti3C2 concentration of 5 wt %. Polymer coatings are frequently utilized because of their inexpensive cost, quick preparation, and effective results. Application is hampered by some mechanical characteristics, such as low wear resistance, creep resistance, and weak fatigue strength [33]. Adding MXene nanoparticles is an effective way to improve their mechanical properties. Ti_3C_2 MXene nanosheets were utilized as a reinforcement phase in the polymer matrix by the authors in [33]. Using Ti_3C_2 and ultrahigh molecular weight polyethylene, they produced a composite.

Comparing Ti_3C_2 with pure ultrahigh molecular weight polyethylene, the COF is lowered by 31%. MXenes are also used on metal matrices to enhance tribological characteristics. In [34], self-lubricating Ti3C2 nanosheet/copper composite coatings with various Ti3C2 concentrations were examined. The 26-Ti3C2/Cu composite, which exhibits the lowest COF and wear rate among all the content coatings, was synthesized by the authors.

3. APPLICATION IN MACHINE ELEMENTS

Possibilities for applications in machine elements are based on the fact that MXenes can be used as lubricant additives, solid lubricant coatings, or as reinforcement phases in composite materials. Results in tribological properties from previous done long-term tests show reduced microstructural changes, following with a few results of MXenes as a solid lubricant in thrust ball bearings.

The first experiment on MXene tribological coating was conducted in [29]. A 200-nm-thick Ti_3C_2 coating was prepared on a copper disk, and results showed a coefficient of friction of 0.15 for an applied load of 0.5 N and 0.19 for a 1.0 N load. In the paper [4], when a Ti_3C_2 coating was placed on ball bearings, frictional torque, normal force, and cumulative wear distance were detected on the stationary shaft mounting under uniform load application. The housing washer mounting constantly rotated at 1000min^{-1}. The applied axial force resulted in initial maximum Hertzian pressures of 800MPa in the ball / raceway contact.

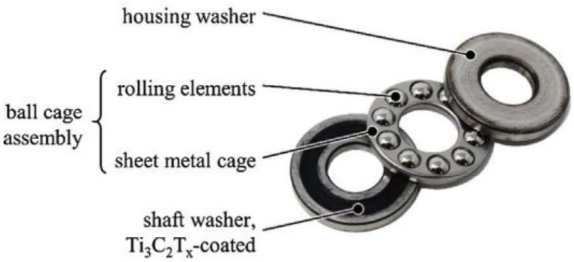

Figure 4. Tested thrust ball bearing 51201, [4]

The maximum service life of the bearing has been reached when the measured frictional torque increased to a value of 1.3 Nm due to successive wear.

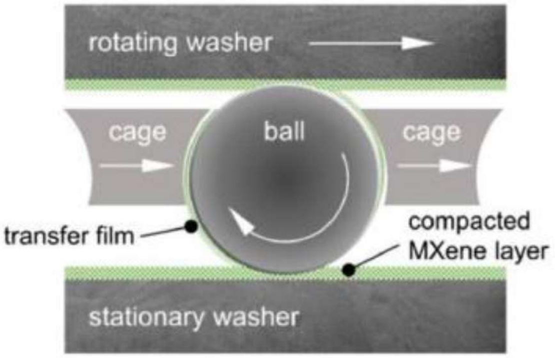

Figure 5. Tested ball cage coated assembly [4]

Impressive MXene qualities in terms of friction and anti-wear were demonstrated by these tests. Compared to the uncoated reference, this corresponded to a reduction of frictional torque by a factor of 3.2, which was attributed to the self-lubricating behaviour of the MXene nanosheets and the potential formation of a beneficial tribo-film consisting of densified MXene nanosheets. The use of MXene in industrial production was evaluated, and it was found that it had a lower COF and wear rate compared with standard bearings. Same authors continued with experiments with rolling bearings and showed reduction of wear and extended service life compared to MoS2 and diamond-like carbon materials in [30]. Besides some already completed investigations in rolling bearing applications, the authors are still dealing with the idea of applying the advantages of MXenes lubrication mechanisms, pointing out some unexplored research fields, and then putting forward possible solutions and prospects for future research focused on sliding bearing applications and possible gearing surfaces. The basic idea is to apply MXenes in different ways, aiming improve the performance of self-lubricating sliding bearings:

- MXenes as a component in mixture for porous sinter bearings production.
- Coatings in contact layers for composites.
- Contact layer for polymer bearings.

4. CONCLUSION

For the first time, accurate material characterization and tribological experiments were used to assess the influence of $Ti_3C_2T_x$-

nanosheets on energy efficiency and operating time when used as a solid lubricant in highly loaded rolling-sliding contacts of machine elements. A reduction of the frictional torque by a factor of up to 3.2, an extension of the service life by about 2.1 times, and a decrease of the linear cumulative wear rate by up to 2.9 compared to uncoated references were observed. These results were already comparable to those from various reports in the literature on graphene, amorphous carbon coatings, or advanced transition metal dichalcogenides.

It is doubtless that MXene nanosheets can significantly reduce friction, thus leading to significantely enhanced long-lasting wear life [35], especially when applied as solid lubricants, which could make them applicable in most of machine elements exploitation.

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