



Editorial

# The Promise of 2D Nanolaminated Materials as Protective Solid-State Lubricants

Andy Nieto

Department of Mechanical and Aerospace Engineering, Naval Postgraduate School, Monterey, CA 93943, USA; andy.nieto@nps.edu

Received: 16 December 2019; Accepted: 16 December 2019; Published: 2 January 2020



Lubricants are an important part of any tribological system. The ability to reduce friction and effectively dissipate heat are important mechanisms needed in reducing wear and frictional heating. Lubricants are typically in the liquid state, the most common being oil-based liquids. Liquid lubricants are external to the tribological mating surfaces, and must be stored and supplied externally. As such, loss-of-lubrication conditions can occur when problems in lubrication storage or delivery occur. Damage can be gradual from wear or corrosion, or can be severe and acute—for example, due to impact damage from kinetic strikes in military applications, foreign object damage in commercial/military aviation, or roadway debris in automotive applications. The ability to survive loss-of-lubrication conditions provides a level of robustness and reliability that can offer substantial benefits from energy efficiency to prevention of loss of life. Developing materials with intrinsic lubrication mechanisms is a promising approach for developing low friction materials that require little or no external liquid-phase lubrication.

Two-dimensional (2D) nanomaterials have found promising uses as composite fillers in polymer, metal, and ceramic matrix composites [1,2]. Some 2D materials such as graphene have found direct uses in tribological applications as protective surface layers [3,4]. This has brought forth the concept of using 2D nanolaminated materials as protective solid-state lubricants. While the use of nanofluids has already put into practice this concept, it still relies on storage and delivery of the lubricant. Nanomaterials have other favorable attributes that makes it logical to incorporate them directly into materials as a secondary phase or reinforcement. Nanocomposite materials can be endowed with in situ solid-state lubrication by the effective distribution of protective 2D nanomaterials throughout the primary or matrix material.

Graphene reinforcements, particularly reduced graphene oxide (rGO) and graphene nanoplatelets (GNPs), have proven adept at providing ceramic matrix composites (CMCs) with enhanced fracture toughness, along with improvements in functional properties such as thermal and electrical conductivity [1]. The improvement in fracture toughness has an immediate benefit in improving wear resistance in ceramics as crack formation and subsequent propagation can quickly accelerate wear. Increases in wear resistance of up to 75% have been reported [5]. The fine scale of reinforcement provided by GNPs enhances localized energy dissipation, toughness, and wear resistance even during microscratch tests utilizing loads as low as 100 mN and scratch distances of 50  $\mu\text{m}$  [6]. In addition to the intrinsic toughening reinforcement, GNPs have enhanced wear resistance by the in situ formation of a protective and lubricating tribofilm [7]. The gradual wear of the ceramic composite leads to the ejection of GNP particulates (that are loosely adhered to the ceramic matrix by design). These GNP particulates become exposed to high shear forces and frictional heat that promotes edge-to-edge bonding and the formation of a continuous or near continuous (dependent on filler loading in the CMC) tribofilm. The diffusion barrier and high mechanical properties of graphene are believed to impart the film with protective properties, whereas the weak interlayer forces enable it to serve as a solid lubricant. Characteristics of the protective graphene films have been found to be dependent on CMC composition and the severity of wear conditions [8,9]. In this Special Issue, Siddaiah et al. [10]

have investigated the effect of graphene reinforcements on the surface energy of electrodeposited Ni-graphene composite coatings. The low surface energy of the coatings is believed to contribute to a reduction in the embedment of third-body abrasive particles from the wear process, thereby reducing wear and friction.

Other 2D nanomaterials that show promise as solid-state lubricants are the ternary transition metal carbides, nitrides (MAX phases) [11,12], and borides (MAB phases) [13,14]. These materials exhibit intrinsic energy-dissipating mechanisms, and ductility and machinability similar to metals, along with refractory and oxidative properties similar to those of conventional ceramic materials. The incorporation of MAX phases has shown promise in enhancing the wear resistance and friction behavior of polymeric and metal matrix composites [15–18]. The numerous MAX- and MAB-phase compositions make them promising candidates for developing tailored tribofilms for the specific matrix material or tribocouple. In this Special Issue, Tran et al. [19] implement this approach to wear reduction through the use of multilayered Ni-MAX-based composites. Layers consisted of either pure Ni or Ni-Al, interspersed with Ni-Ti<sub>3</sub>SiC<sub>2</sub> composites, where the volume fraction of the MAX phase within the layer varied from 10%–40 vol %. The effect of chemistry, layer thickness, and reinforcement fraction on wear and triboactive behavior is detailed by Tran et al. [19].

As with other nanocomposites, a challenge in dispersing secondary particles remains. Inducing favorable tribo-reactions often requires higher contents of the secondary phase in order to generate a sufficiently robust tribolayer than can impact the wear and friction behavior. Dispersion of secondary phases is often most efficient using wet dispersions rather than solid-state powder processing. This makes processes such as slip casting and emerging slurry-based additive manufacturing (AM) techniques promising for enabling higher contents of reinforcements that can provide more protective and robust tribolayers. 2D nanomaterials are especially suited to processing techniques that promote or necessarily form layered structures, as it allows facile attainment of preferential layering of the 2D nanomaterials parallel to the microstructural layers or laminates. The unique functional properties of 2D materials may also be harnessed to promote the efficacy of AM techniques where full densification is often a challenge.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The author declares no conflict of interest.

## References

1. Nieto, A.; Bisht, A.; Lahiri, D.; Zhang, C.; Agarwal, A. Graphene reinforced metal and ceramic matrix composites: A review. *Int. Mater. Rev.* **2017**, *62*, 241–302. [[CrossRef](#)]
2. Li, B.; Zhong, W.H. Review on polymer/graphite nanoplatelet nanocomposites. *J. Mater. Sci.* **2011**, *46*, 5595–5614. [[CrossRef](#)]
3. Berman, D.; Erdemir, A.; Sumant, A.V. Few layer graphene to reduce wear and friction on sliding steel surfaces. *Carbon* **2013**, *54*, 454–459. [[CrossRef](#)]
4. Marchetto, D.; Held, C.; Hausen, F.; Wählich, F.; Dienwiebel, M.; Bennewitz, R. Friction and Wear on Single-Layer Epitaxial Graphene in Multi-Asperity Contacts. *Tribol. Lett.* **2012**, *48*, 77–82. [[CrossRef](#)]
5. Kim, H.J.; Lee, S.M.; Oh, Y.S.; Yang, Y.H.; Lim, Y.S.; Yoon, D.H.; Lee, C.; Kim, J.Y.; Ruoff, R.S. Unoxidized Graphene/Alumina Nanocomposite: Fracture- and Wear-Resistance Effects of Graphene on Alumina Matrix. *Sci. Rep.* **2014**, *4*, 5176. [[CrossRef](#)] [[PubMed](#)]
6. Nieto, A.; Zhao, J.M.; Han, Y.H.; Hwang, K.H.; Schoenung, J.M. Microscale tribological behavior and in vitro biocompatibility of graphene nanoplatelet reinforced alumina. *J. Mech. Behav. Biomed. Mater.* **2016**, *61*, 122–134. [[CrossRef](#)] [[PubMed](#)]
7. Zhang, C.; Nieto, A.; Agarwal, A. Ultrathin Graphene Tribofilm Formation During Wear of Al<sub>2</sub>O<sub>3</sub>-Graphene Nanoplatelet Composites. *Nanomater. Energy* **2016**, *5*, 1–9. [[CrossRef](#)]
8. Li, H.; Xie, Y.; Li, K.; Huang, L.; Huang, S.; Zhao, B.; Zheng, X. Microstructure and wear behavior of graphene nanosheets-reinforced zirconia coating. *Ceram. Int.* **2014**, *40*, 12821–12829. [[CrossRef](#)]

9. Belmonte, M.; Ramírez, C.; Gonzalez-Julian, J.; Schneider, J.; Miranzo, P.; Osendi, M.I. The beneficial effect of graphene nanofillers on the tribological performance of ceramics. *Carbon* **2013**, *61*, 431–435. [[CrossRef](#)]
10. Siddaiah, A.; Kumar, P.; Henderson, A.; Misra, M.; Menezes, P.L. Surface Energy and Tribology of Electrodeposited Ni and Ni–Graphene Coatings on Steel. *Lubricants* **2019**, *7*, 87. [[CrossRef](#)]
11. Radovic, M.; Barsoum, M.W. MAX phases: Bridging the gap between metals and ceramics. *Am. Ceram. Soc. Bull.* **2013**, *92*, 20–27.
12. Sun, Z.M. Progress in research and development on MAX phases: A family of layered ternary compounds. *Int. Mater. Rev.* **2011**, *56*, 143–166. [[CrossRef](#)]
13. Bai, Y.; Sun, N.; Li, N.; Kong, F.; Qi, X.; He, X.; Wang, R.; Zheng, Y. High-temperature mechanical properties and thermal shock behavior of ternary-layered MAB phases  $\text{Fe}_2\text{AlB}_2$ . *Int. J. Refract. Met. Hard Mater.* **2019**, *80*, 151–160. [[CrossRef](#)]
14. Ade, M.; Hillebrecht, H. ChemInform Abstract: Ternary Borides  $\text{Cr}_2\text{AlB}_2$ ,  $\text{Cr}_3\text{AlB}_4$ , and  $\text{Cr}_4\text{AlB}_6$ : The First Members of the Series  $(\text{CrB}_2)_n\text{CrAl}$  with  $n = 1, 2, 3$  and a Unifying Concept for Ternary Borides as MAB-Phases. *Inorg. Chem.* **2015**, *46*, 6122–6135. [[CrossRef](#)] [[PubMed](#)]
15. Wang, S.; Zhu, S.; Cheng, J.; Qiao, Z.; Yang, J.; Liu, W. Microstructural, mechanical and tribological properties of Al matrix composites reinforced with Cu coated  $\text{Ti}_3\text{AlC}_2$ . *J. Alloys Compd.* **2017**, *690*, 612–620. [[CrossRef](#)]
16. Gupta, S.; Habib, M.A.; Dunnigan, R.; Kaabouch, N.; Ghosh, S. Synthesis and Characterization of  $\text{Ti}_3\text{SiC}_2$  Particulate-Reinforced Novel Zn Matrix Composites. *J. Mater. Eng. Perform.* **2015**, *24*, 4071–4076. [[CrossRef](#)]
17. Gupta, S.; Hammann, T.; Johnson, R.; Riyad, M.F. Tribological Behavior of Novel  $\text{Ti}_3\text{SiC}_2$  (Natural Nanolaminates)-Reinforced Epoxy Composites during Dry Sliding. *Tribol. Trans.* **2014**, *58*, 560–566. [[CrossRef](#)]
18. Mahesh, K.; Balanand, S.; Raimond, R.; Mohamed, A.P.; Ananthakumar, S. Polyaryletherketone polymer nanocomposite engineered with nanolaminated  $\text{Ti}_3\text{SiC}_2$  ceramic fillers. *Mater. Des.* **2014**, *63*, 360–367. [[CrossRef](#)]
19. Tran, Q.; Fuka, M.; Dey, M.; Gupta, S. Synthesis and Characterization of Novel  $\text{Ti}_3\text{SiC}_2$  Reinforced Ni-Matrix Multilayered Composite-Based Solid Lubricants. *Lubricants* **2019**, *7*, 110. [[CrossRef](#)]



© 2020 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).