

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Tribochemical Conversion of Methane to Graphene and Other Carbon Nanostructures: Implications for Friction and Wear

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Tribochemical Conversion of Methane to Graphene and Other Carbon Nanostructures: Implications for Friction and Wear / Ramirez G.; Eryilmaz O.L.; Fatti G.; Righi M.C.; Wen J.; Erdemir A.. - In: ACS APPLIED NANO MATERIALS. - ISSN 2574-0970. - ELETTRONICO. - 3:8(2020), pp. 8060-8067. [10.1021/acsanm.0c01527]

Availability:

This version is available at: <https://hdl.handle.net/11585/780152> since: 2020-11-12

Published:

DOI: <http://doi.org/10.1021/acsanm.0c01527>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

Giovanni Ramirez, Osman Levent Eryilmaz, Giulio Fatti, Maria Clelia Righi, Jianguo Wen, and Ali Erdemir, *Tribochemical Conversion of Methane to Graphene and Other Carbon Nanostructures: Implications for Friction and Wear*, ACS Applied Nano Materials 2020 3 (8), PP. 8060-8067.

The final published version is available online at:
<https://doi.org/10.1021/acsnm.0c01527>

Rights / License:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

1 Tribochemical Conversion of Methane to Graphene and Other 2 Carbon Nanostructures: Implications for Friction and Wear

3 Giovanni Ramirez, Osman Eryilmaz, Giulio Fatti, Maria Clelia Righi, Jianguo Wen,* and Ali Erdemir*



Cite This: <https://dx.doi.org/10.1021/acsnm.0c01527>



Read Online

ACCESS |



Metrics & More



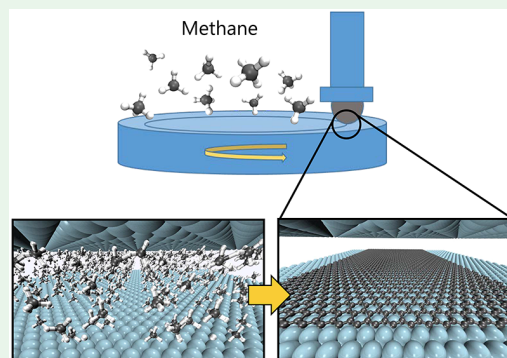
Article Recommendations



Supporting Information

4 **ABSTRACT:** Tribochemistry involves chemical reactions occurring at sliding
5 contact interfaces in the presence of gaseous and/or liquid media. It often leads
6 to the formation of a solid reaction film (also termed boundary film) which
7 controls friction and wear and hence the efficiency and reliability of moving
8 mechanical systems (such as engines). Here we demonstrate tribochemical
9 conversion of methane to graphene, nano-onion, and disordered carbons on
10 the sliding surfaces of Ni-, Cu-, and CuNi-containing VN coatings at
11 atmospheric pressure and room temperature, providing 2–3 orders of
12 magnitude reduction in wear and ~50% reduction in friction compared to
13 those of the uncoated steels. Transmission electron microscopy confirms that
14 graphene forms preferably on metal rich nanoclusters of the composite
15 coatings, while the carbon nano-onions are scattered throughout the carbon
16 tribofilm. Ab initio molecular dynamics simulations elucidate underlying
17 mechanisms involved in the tribochemical conversion of methane to carbon-
18 based nanostructures in support of microscopic observations. These scientific findings may lead to new materials technologies that
19 can use methane as a source for continuous and in situ lubrication. For example, there is an urgent need to curtail the uses of
20 lubricating oils in natural gas compressors and engines as they contaminate the natural gas being compressed or burnt.

21 **KEYWORDS:** tribochemistry, catalysis, carbon nanostructures, friction, wear, thin films/coatings



1. INTRODUCTION

22 Tribochemical reaction films (or tribofilms) are very typical of
23 all interacting surfaces that are in relative motion.¹ These films
24 commonly result from a chemical and/or catalytic response of
25 sliding surface to the reactive gases or liquids present at or in
26 the vicinity of sliding contact interface.² For example, the
27 formation of a phosphate glass-based tribofilm on rubbing
28 surfaces of engine components is extremely important for long
29 life or reliability and is a direct result of tribochemical reactions
30 occurring between sliding surfaces and zinc dialkyl-
31 dithiophosphate (ZDDP) antiwear additive in engine oils.³
32 Likewise, a dramatic reduction of friction (i.e., from ~0.6 to
33 ~0.003) in ta-C and CN_x type carbon coatings in hydrogen
34 environment is due to a tribochemical reaction between
35 surface carbon atoms and hydrogen, creating a fully hydrogen
36 terminated or passivated top surface layer that diminishes
37 adhesion and hence friction during sliding.⁴ Overall, the
38 making and breaking of such tribofilms dominate friction and
39 wear and hence the durability and frictional performance of all
40 moving mechanical systems.

41 Besides these liquid and gaseous species, all kinds of solid
42 lubricants are available^{5,6} for controlling friction and wear. In
43 addition to the traditional graphite, molybdenum disulfide, and
44 boron nitride,⁷ many researchers have confirmed that low-
45 dimensional nanomaterials like fullerenes,⁸ graphene,^{9,10} nano-

tubes,¹¹ and nano-onions, are also very effective in reducing
friction and wear.¹² One major drawback is that mainly
because of their finite thickness or volume, these solids tend to
wear out eventually, and thus high friction and wear prevail
again.

Here we report tribochemical conversion of methane (CH₄)
to graphene, nano-onion, and disordered carbons on the
sliding surfaces of Ni-, Cu-, and CuNi-containing VN coatings
under atmospheric pressure and at room temperature. We
show that these catalytically active coatings enable in-operando
extraction of graphene and other carbon nanostructures
continuously from CH₄, thus providing extraordinary protec-
tion against wear and lowering friction. Obviously there are not
many moving mechanical assemblies that operate in CH₄, but
it is a major constituent of natural gas for power generation
and fueling of transportation systems in which many moving
parts operate in natural gas, including pistons and seal packs of
reciprocating natural gas compressors in pipelines, refueling

Received: June 3, 2020

Accepted: July 16, 2020

Published: July 16, 2020

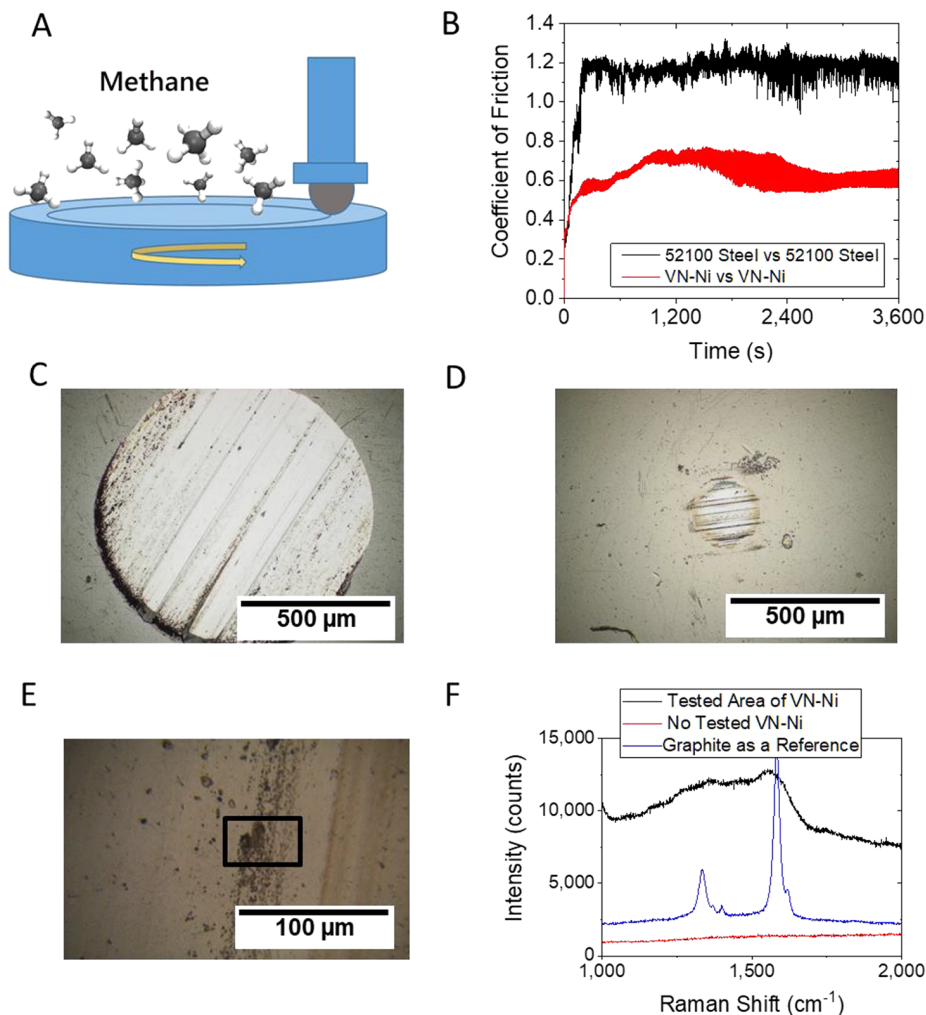


Figure 1. Comparison of friction and wear behaviors in ball-on-flat tests. (A) Schematic illustration of test method and environment. (B) Friction coefficient of uncoated AISI 52100 steel sliding against the same material compared with that of VN-Ni-coated AISI 52100 steel sliding against the same material in 960 bar of CH₄ gas. (C) Size of wear scar formed on uncoated AISI 52100 steel ball in CH₄. (D) Size of wear scar formed on VN-Ni-coated AISI 52100 steel ball in CH₄. (E) SEM image of wear track on VN-Ni-coated surface with blackish wear debris layer. (F) Raman spectra obtained from the area denoted with a black rectangle showing broad D and G bands located in the same position as the ones corresponding to the graphite used as a reference.

64 stations, and the fuel injectors of natural gas-powered
 65 engines.¹³ Therefore, the results of our study are not only
 66 scientifically significant but also have the capacity of positively
 67 influencing these fields by leading to more efficient, durable,
 68 and cost-effective industrial practices. In particular, enabling
 69 hydrocarbon molecules of natural gas to provide a composite
 70 carbon tribolayer on a self-replenishing or self-healing manner
 71 is very attractive.

2. RESULTS

72 **2.1. Friction and Wear Performance.** Details of the
 73 coating deposition procedure, structural, chemical, and
 74 mechanical characterization of resultant coatings as well as
 75 the tribological test methodology and conditions are provided
 76 in the [Supporting Information](#) (see Figures S1–S3). Under the
 77 test configuration illustrated in [Figure 1a](#), the friction
 78 coefficient of a steel ball sliding against the steel flat in CH₄
 79 goes up very quickly to a value of 1.2 and remains relatively
 80 constant until the end of the 2 h long test ([Figure 1b](#)). When
 81 the same test was repeated with a VN-Ni-coated test pair, the
 82 friction coefficient was reduced by nearly 50%. More

remarkably, the wear volume loss on the coated ball side was
 reduced by more than 2 orders of magnitude (i.e., 245 times;
 see [Figures 1c,d](#)), going from $7.7 \times 10^{-12} \text{ m}^3$ when steel vs
 steel surfaces were tested ([Figure 1c](#)) down to $3.14 \times 10^{-14} \text{ m}^3$
 for the VN-Ni vs VN-Ni test case ([Figure 1d](#)). The wear
 damage on the uncoated 52100 steel flat was also very
 extensive, as a very wide and deep wear groove had formed,
 while on the VN-Ni-coated flat side, the wear damage was hard
 to discern ([Figure 1e](#)). Additional supporting results (obtained
 from two other coatings: VN-CuNi and VN-Cu) further
 confirmed the unusual wear reducing abilities of these
 composite coatings in the presence of CH₄ ([Figure S4](#)).

2.2. Characterization of Sliding Surfaces. Upon close
 examination of the sliding surfaces of VN-Ni-coated test pairs
 with a microscope, we noticed some blackish wear debris
 particles or patches at or near the rubbing surfaces of both the
 ball and flat surfaces, as highlighted with the rectangles in
[Figures 1d,e](#). Also, in [Figure 1f](#), the Raman spectra of these
 black deposits display a signature that overlaps with the D and
 G bands of crystalline graphite (which was used as a
 reference). These results suggest that the blackish debris that

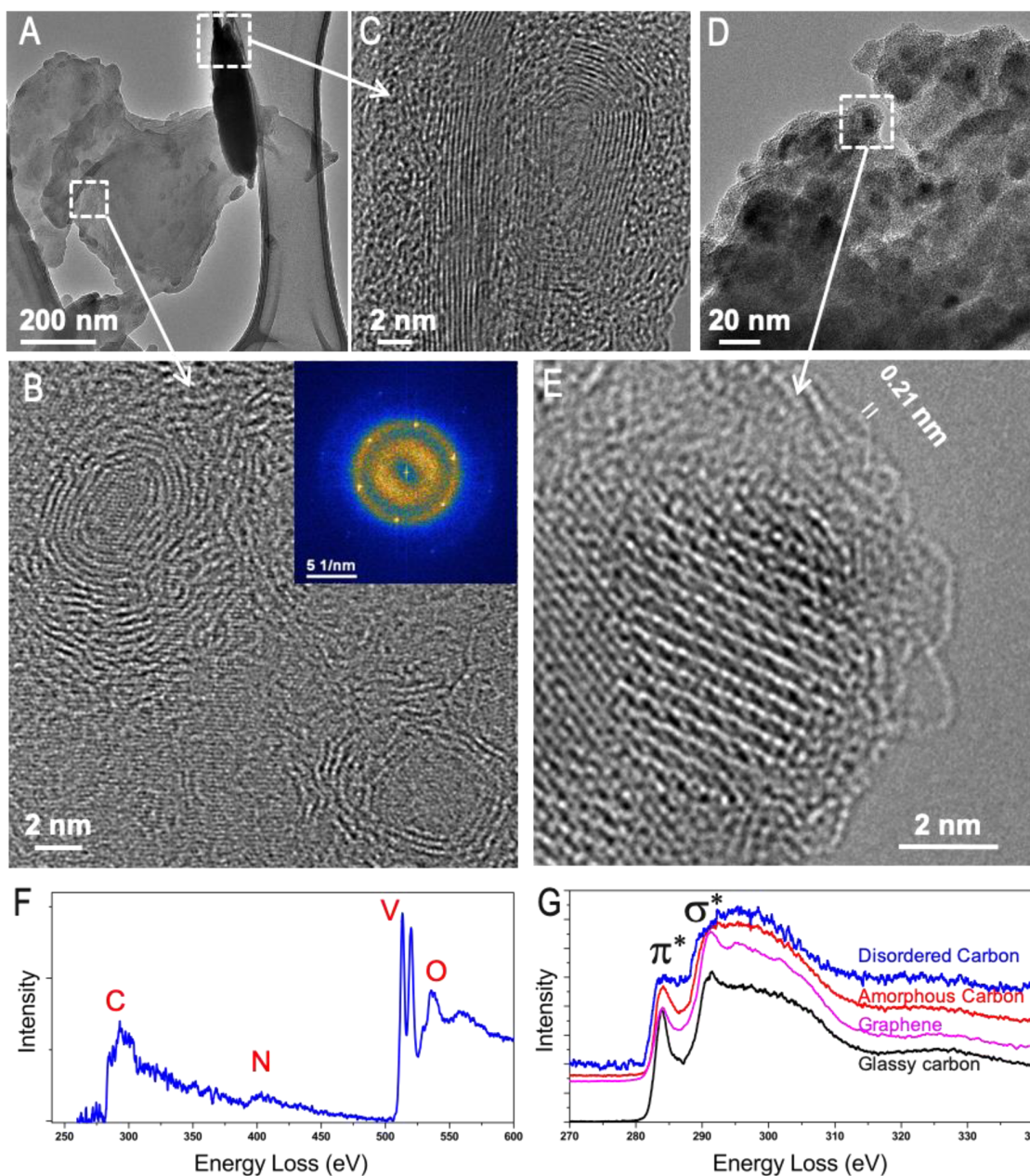


Figure 2. TEM study of debris particles. (A) Low-magnification and (B) HRTEM images of large graphene sheet with scattered carbon nano-onions. (C) TEM image showing side view of carbon nano-onions attached on a graphene sheet (about 10 layers). (D) Low-magnification and (E) HRTEM images of agglomerated nanoparticles wrapped with highly disordered carbon. (F) EELS spectrum from agglomerated debris showing almost no N. (G) EELS spectra of carbon K-edge of disordered carbon compared with glassy carbon (standard), graphene (from image B), and amorphous carbon on the TEM grid.

104 was detected on and around the rubbing surfaces of the coated
 105 ball and flat samples had a structural chemistry that is
 106 analogous to that of the reference material graphite. Overall,
 107 the results in Figure 1 clearly show that the VN-Ni coating
 108 provided much lower wear in CH₄, and this improvement was
 109 most likely due to the formation of a carbon-rich tribofilm
 110 derived from the CH₄ gas during sliding experiment (Figure
 111 1a). Results from VN-CuNi and VN-Cu (presented in Figure
 112 S4) were similar and in support of the findings shown in Figure
 113 1. Specifically, remarkable improvements in their friction and
 114 wear performance were also associated with the formation of a
 115 blackish tribofilm on or near their rubbing surfaces.

We recovered a portion of the debris particles from the area 116
 highlighted with the rectangle in Figure 1e using a metallic tip 117
 and placed it onto a copper grid for transmission electron 118
 microscopy (TEM). The TEM images in Figure 2 show two 119
 major types of debris: graphene with carbon nano-onions 120
 (Figures 2a–c) and an agglomeration of numerous nano- 121
 particles wrapped by highly disordered graphitic carbon 122
 (Figures 2d,e). The first type is mainly a large graphene 123
 sheet ranging from 500 nm to several micrometers in size, as 124
 shown in Figure 2a. High-resolution transmission electron 125
 microscopy (HRTEM) showed that the graphene sheets are 126
 composed of a single layer (Figure 2b) to about 10 layers 127
 (Figure 2c). Single-layer graphene was confirmed by an 128

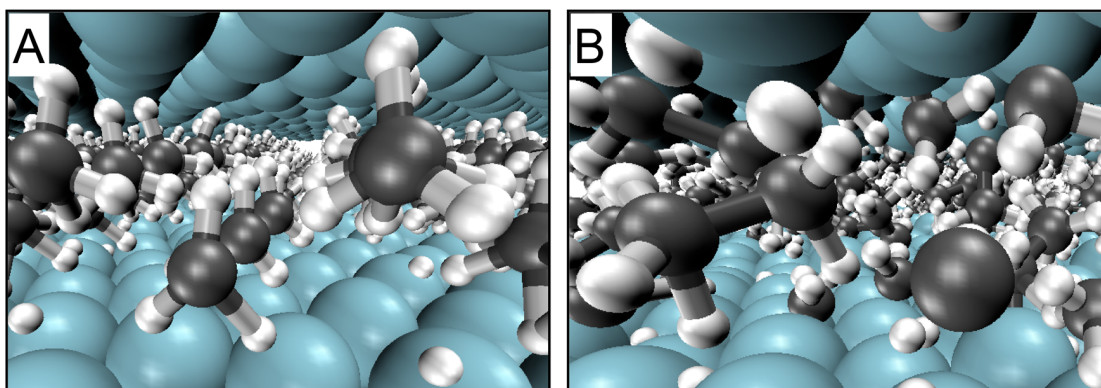


Figure 3. AIMD simulation of methane molecules confined at Ni interface during sliding. (A) Initial system configuration with undissociated methane molecule. (B) Snapshot acquired after ~ 2 ps of AIMD at constant load and shear velocity: the molecules started dissociating and H atoms diffusing below the surfaces. The full simulation movie ([Movie S1](#)) is available as [Supporting Information](#).

129 HRTEM image at broken edges (see [Figure S5](#)). Carbon nano-
 130 onions with diameters of 5–10 nm were scattered on the
 131 graphene sheet, as highlighted in [Figures 2b,c](#), throughout the
 132 examined area. These carbon nano-onions are hollow in the
 133 center, and no other crystalline form of carbon structure is
 134 observed. Compositional analyses by energy-dispersive X-ray
 135 spectroscopy (EDS) and electron energy-loss spectroscopy
 136 (EELS) showed that the nano-onions are composed of
 137 graphene with a small amount of Ni and V (see [Figure S5](#)).
 138 The small amounts of Ni and V could act as catalysts for the
 139 growth of graphene and carbon nano-onions.

3. DISCUSSION

140 Results presented above demonstrate that the VN-Ni coating
 141 can convert CH_4 into graphene, carbon nano-onion, and
 142 disordered carbon, all of which are known for their favorable
 143 antifriction and antiwear properties.^{8,9,12} Specifically, friction
 144 was reduced by 50%, and the wear was reduced by a factor of
 145 245 (other systems tested, i.e., VN-CuNi and VN-Cu, have
 146 also exhibited remarkable reductions in wear (as much as 3
 147 orders of magnitude) as presented in [Figure S4](#)). As is evident
 148 from [Figure 1b](#), the reduction in friction is not as dramatic as
 149 in wear. This is mainly due to the incomplete coverage of
 150 sliding surfaces with a continuous layer of graphene and other
 151 carbon forms. Specifically, because of their very soft nature,
 152 they are prevented from thickening into a continuous tribofilm
 153 under the influence of high contact pressure and shear forces
 154 exerted on them. Instead, they are ejected from the interface
 155 and accumulated around the edges of the wear scar and track
 156 as highlighted with rectangles in [Figures 1d,e](#). In addition, the
 157 shear properties of graphene and other carbon nanostructures
 158 are not as favorable in nitrogen and methane.

159 We believe that the Ni, Cu, and CuNi are most likely acting
 160 as catalysts for the tribochemical conversion of CH_4 into
 161 graphene, nano-onion, and disordered carbon (since such
 162 carbon structures were only found in and around the sliding
 163 contact areas). Ni and Cu are used extensively in the synthesis
 164 of graphene, nanotubes, and nano-onions by chemical vapor
 165 deposition (CVD) at high temperatures.¹⁴ The specific steps
 166 involved in the catalytic conversion of hydrocarbon gases into
 167 graphene by CVD method using Ni, Cu, and other transition
 168 metals are well-documented.^{15–18} Briefly, these studies have
 169 suggested that partially filled d-orbitals of Ni (or Cu) enable
 170 them to adsorb hydrocarbon molecules first and then facilitate
 171 their dehydrogenation. Liberated carbon atoms are free to

migrate throughout the surface (as well as bulk) and eventually
 172 come together to form the planar sheets of carbon as in
 173 graphene.¹⁴ Also, vanadium nitride probably contributed to the
 174 catalytic dehydrogenation of CH_4 to some extent, despite its
 175 catalytic activity being much lower than that of transition
 176 metals,^{19–21} as is confirmed by means of ab initio calculations
 177 in [section 3.1](#). However, VN presents high resistance to
 178 thermal degradations because of its high thermal stability and
 179 thus helps prevent film fracture and due to thermal stresses.²²
 180

In our case, there was no similarity to the traditional CVD
 181 synthesis route, rather a situation involving two VN-Ni (or
 182 VN-Cu, VN-CuNi)-coated solid surfaces pressed against one
 183 another in relative motion in the presence of CH_4 at ambient
 184 pressure and temperature. Yet, these rubbing surfaces were
 185 able to extract graphene and other carbon nanostructures in a
 186 continuous manner from the methane gas and thereby enable
 187 ultrahigh resistance against wear. In an attempt to understand
 188 the molecular-level mechanisms of tribochemical conversion of
 189 CH_4 to mentioned carbon nanostructures at sliding contact
 190 interfaces, we concentrated on VN-Ni-coated test pairs and
 191 conducted *ab initio* molecular dynamic simulation on them as
 192 discussed below.
 193

Because of the very complex nature of the physical,
 194 chemical, and tribological events taking place at a sliding
 195 contact interfaces, understanding the exact mechanisms by
 196 which graphene, carbon nano-onion, and disordered graphitic
 197 carbons are derived from CH_4 on VN-Ni and other surfaces
 198 (i.e., VN-Cu and VN-CuNi) will be rather challenging. In
 199 particular, determining time and spatial resolutions of events
 200 leading to the formation of such carbonaceous nanostructures
 201 is deemed impossible with currently available tribological
 202 methods. However, it is conceivable that under the tribological
 203 contact configuration shown in [Figure 1a](#) and conditions
 204 described in the [Supporting Information](#) (i.e., a high-pressure
 205 mechanical shearing action combined with transient high flash
 206 heating of real contact spots²³) the tribochemical extraction of
 207 such carbon nanostructures from CH_4 may become feasible.
 208 Specifically, the high-pressure rubbing action continuously
 209 creates nascent surface atoms^{24–26} of the catalyst metals (Ni,
 210 Cu, and NiCu) which enhance catalytic and hence the
 211 tribochemical activity toward methane in the surrounding
 212 environment. As mentioned above, both Ni and V are well-
 213 known catalysts used previously in the synthesis of graphene
 214 and carbon nanotubes by high-temperature CVD meth-
 215 ods.^{15–18} Their lower activation energy for dissociative
 216

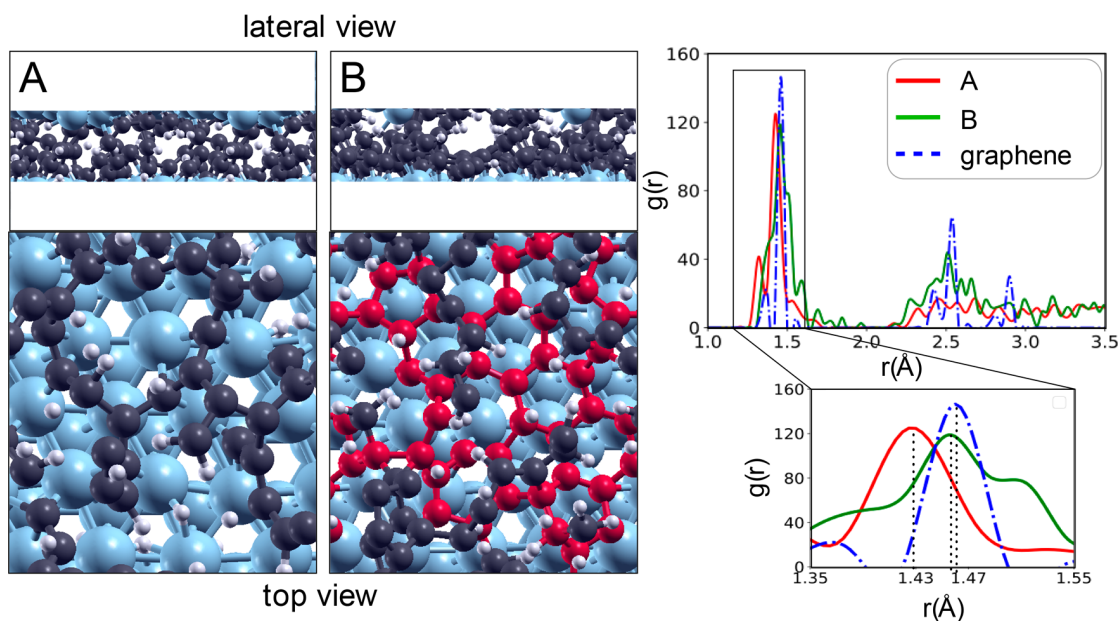


Figure 4. First stages of tribologically induced graphene formation. Snapshots acquired during AIMD simulations of dehydrogenated methane molecules confined at Ni interfaces in concentrations corresponding to 50% (A) and 100% (B) coverages of the Ni interface. (A) In a first stage the C atoms bind to each other in interconnected chains that form a disordered, low-density film. (B) Load and shear stresses applied promote the rehybridization of C atoms and the formation of sp^2 planar structures as the graphene flake highlighted in green. (C) The corresponding radial distribution functions for C–C bonds are represented by red and green lines, respectively, while the dashed-dot blue line indicates the radial distribution function of a nondefective graphene layer commensurate with the Ni (111) surface. The full simulation movies (Movies S2 and S3) are available as [Supporting Information](#).

217 extraction of carbon from methane and hence facilitate the
 218 formation of such carbon materials. In the following section,
 219 we present the results from *ab initio* molecular dynamics
 220 (AIMD) simulations to provide further insight into the
 221 atomistic mechanisms that govern the tribochemically induced
 222 formation of carbon nanostructures.

223 3.1. Tribochemical Mechanism by Means of *Ab Initio*

224 **Calculations.** First, we evaluated the catalytic capability of the
 225 Ni and VN substrates in promoting the CH_4 dehydrogenation
 226 by means of *ab initio* static calculations. The results of this
 227 study, which are reported as [Supporting Information](#) (Figures
 228 S10–S12), are in agreement with the literature in the case of
 229 Ni,^{27–30} while we are not aware of any previous study for VN.
 230 The reaction energies calculated for methane dissociation on
 231 Ni (111) and VN (100) surfaces, which are the most stable
 232 surfaces for these materials, correspond to 0.02 and 0.89 eV,
 233 respectively. Therefore, at ordinary conditions, the full
 234 dehydrogenation reaction, $CH_4 = C_{ads} + 4H_{ads}$, is not
 235 energetically favorable. However, the molecular confinement,
 236 mechanical stresses applied, and high temperatures present at
 237 the tribological interface can promote the dehydrogenation
 238 reaction at a very high rate, as shown by the *ab initio* molecular
 239 dynamic (AIMD) simulation of CH_4 molecules confined at
 240 sliding Ni interfaces, as described in the following.

241 In the AIMD simulations, both the electronic and the ionic
 242 degrees of freedom were considered. This approach is essential
 243 to obtain an accurate description of the chemical processes
 244 occurring under conditions of enhanced reactivity. The first set
 245 of simulations aimed at identifying the mechanisms of carbon
 246 release from CH_4 molecules, while subsequent simulations,
 247 where the concentration of interfacial carbon was increased,
 248 were aimed at monitoring in real time the formation of carbon
 249 nanostructures assisted by mechanical stresses.

The initial system configuration, shown in [Figure 3A](#),²⁵⁰ contained a concentration of CH_4 molecules such that the
 251 number of C atoms corresponded to 25% of the Ni interfacial
 252 atoms. A normal pressure of 5 GPa was applied, and the upper
 253 surface was moved at constant velocity of 200 m/s along the
 254 $[11\bar{2}]$ direction. The temperature of the Ni surfaces was kept
 255 constant at 1000 K, while the intercalated molecules were left
 256 free to evolve without any temperature control. The high
 257 temperature is chosen to model the flash temperatures that,
 258 depending on the ratio between the real contact area and the
 259 apparent contact area, can rise up to thousands of kelvin.^{31,32}
 260 However, the comparison with AIMD simulations performed
 261 at 300 K, while leaving unchanged the other setup parameters,
 262 which are presented in the [Supporting Information](#) (Figure
 263 S12), shows that the temperature plays a secondary role in the
 264 dehydrogenation process, which is to be attributed mainly to
 265 molecular confinement under load and shear stresses.²⁶⁶

As can be seen from the atom trajectories ([Movie S1](#)), the
 267 dehydrogenation process started immediately after the
 268 beginning of the dynamic simulation: H atoms detach from
 269 CH_4 molecules as soon as they come into contact with the
 270 clean Ni surfaces. This result indicates that molecular
 271 dissociation, which is energetically unfavorable at the open
 272 surface, can be easily promoted at the tribological interface.
 273 The molecular confinement under load and shear dramatically
 274 reduces the activation time for molecular dissociation, as
 275 previously found for water molecules confined at diamond
 276 interfaces^{33–35} and organophosphorus additives at iron
 277 interfaces.³⁶²⁷⁸

The simulation then indicated H diffusion into the Ni bulk,
 279 which leads to an increase of carbon concentration at the
 280 interface. This is consistent with the above-described
 281 experimental observation of newly formed carbon nanostructures
 282 almost H free. After ~ 2 ps, around 20% of the H atoms
 283

284 had been expelled from the interface and diffused into the bulk.
285 At the same time, more than half of the carbon atoms were
286 adsorbed on the surfaces, where they tend to capture other C
287 atoms, forming small hydrocarbon groups, C_nH_x with $n \leq 3$
288 (Figure 3B).

289 After ~ 3 ps from the beginning of the simulation, the
290 interfacial concentration of H atoms decreased by more than
291 50% with respect to the initial value, and all the C atoms
292 present at the interface become bonded either to surface Ni
293 atoms or to other C atoms in short carbon chains, C_n with $n \geq$
294 2. Reactive carbon intermediates, C_m , have been also identified
295 during the thermal decomposition of CH_4 on Ni(111) by the
296 in-operando technique of near-ambient-pressure X-ray photo-
297 electron spectroscopy.³⁷ Not observed were Ni_2C reconstruc-
298 tion and other carbide structures, which are often found during
299 graphene growth on Ni (111). The origin of some differences
300 with the structures observed during graphene growth may be
301 related to the presence of a countersurface: the coordination of
302 molecular fragments during the decomposition process is
303 always higher at the interface than at the open surface, and this
304 may for example limit the subsurface diffusion of carbon.

305 Figure 4 shows two snapshots acquired during AIMD
306 simulations containing increased concentrations of C atoms,
307 corresponding to 50% (A) and 100% (B) coverages of the Ni
308 interface. The full adatom trajectories are presented in Movie
309 S2 and Movie S3. In a first stage, we observed the formation of
310 carbon chains, the length of which increased during the
311 simulation until every interfacial C atom had been included
312 into a chain branch (Figure 4A). The chains became cross-
313 linked, forming a disordered film of low density. The applied
314 load and shear smeared out this film, reducing more and more
315 its thickness. During this rubbing process, the carbon atoms
316 change their hybridization and start to form planar rings that
317 constitute the first seeds for graphene growth. Indeed, we
318 observed the formation of a graphene flake upon further
319 increase of C coverage (Figure 4B). The shift of the peak of the
320 C–C radial distribution functions from ~ 1.43 to ~ 1.47 Å
321 (Figure 4C) clearly indicates the rehybridization from sp to sp^2
322 that accompanies the structural change from interconnected
323 carbon chains to 2D structures. The similarity of the $g(r)$
324 function calculated for the structure in Figure 4B (green
325 continuum line), which also presents a second peak, and the
326 $g(r)$ calculated for a nondefective graphene layer commensu-
327 rate to the Ni(111) surface (blue dashed-dotted line) provides
328 a further evidence that graphene is being formed during the
329 simulation under the tribological conditions.

330 Recently, it was shown that carbon-based tribofilms can also
331 be derived from a variety of carbon-based liquids including
332 synovial fluids that lubricate joints, poly(α -olefin) (PAO)
333 which is a base oil used in the making of synthetic lubricants,
334 and palm methyl ester (PME) which is a biodiesel fuel
335 extracted from palm oil. Specifically, it was reported that a
336 graphitic tribofilm forms on the rubbing surfaces of metal-on-
337 metal (MOM) hip replacements (which are made of cobalt,
338 chrome, and molybdenum),³⁸ MoN-Cu coatings³⁹ lubricated
339 by a PAO oil, and AISI 304 stainless steel lubricated by PME.⁴⁰
340 MOM is suspected to derive graphitic tribofilm from protein
341 molecules through the catalytic effects of Co and Mo, while in
342 the cases of MoN-Cu and AISI 304 stainless steel, Cu and Ni
343 present in their structures, respectively, are believed to help in
344 the extraction of carbon-rich tribofilms from the PAO and
345 PME molecules.

4. CONCLUSIONS

Our test results demonstrate that tribochemistry can play a
major role in the friction and wear behavior of sliding surfaces.
Specifically, under the high-pressure shearing condition
described in our study, VN-Ni, VN-Cu, and VN-CuNi coatings
can convert CH_4 molecules into graphene, nano-onion, and
disordered graphite, which in turn reduce friction (by as much
as 50%) and wear by 2–3 orders of magnitude (see Figure 1
and Figure S4). High catalytic reactivity of Ni and Cu in the
composite coatings promotes tribochemistry and hence
conversion of CH_4 to a carbon-based tribofilm consisting of
graphene, nano-onion, and disordered carbons. Transmission
electron microscopy (Figure 2) showed that graphene is
preferably formed on and around the VN-Ni clusters, while
nano-onions and highly disordered graphite were scattered
throughout the carbon tribofilm. *Ab initio* MD simulations
(Figures 3 and 4, Figures S10–S12, and Movies S1–S3)
revealed the mechanism by which carbon nanostructures are
extracted from CH_4 molecules. These simulations showed that
the conversion of CH_4 to 2D graphene and nano-onions
occurs by a catalytic process involving first the dehydrogen-
ation of CH_4 on Ni followed up by C atoms forming chains of
an amorphous carbon network of low atomic density. Under
the influence of high contact pressure and shear forces, some of
the amorphous carbon network sandwiched between the Ni
surfaces undergoes rehybridization and subsequent conversion
to sp^2 planar structures. These newly formed sp^2 -bonded
hexagonal rings nucleate the first graphene flakes. Once such
graphene-rich tribofilms are formed on sliding surface, wear is
reduced dramatically (as much as 3 orders of magnitude).^{40–42}
Overall, our study demonstrates the critical role of
tribochemistry in the extraction of low-shear and highly
protective carbon tribofilms from CH_4 and hence the
reduction of friction and wear. Such carbon-based protective
tribofilms could be utilized and produced on demand in
natural gas compressors and engines, eliminating the use of oils
that contaminate natural gas and diminish the need for
frequent oil change continuous resupply.

5. MATERIALS AND METHODS

Test materials used in this study included coated steel balls rubbing
against coated flats made from AISI 52100-grade through-hardened
ball bearing steel (nominal hardness, 58–62 Rockwell C). Prior to the
deposition of Ni-, Cu-, and CuNi-containing VN coatings, Ar sputter
ion etching is conducted to remove the surface contaminants.
Subsequently, a V bonding layer (120 nm thick) was deposited first
on the steel substrate by using a dual magnetron sputtering system.
The nanocomposite coatings were deposited from high-purity targets
(i.e., V (99.95%) and Cu, Ni (99.99%). For example, to prepare the
VN-Ni nanocomposite coatings (containing ~ 9.5 at. % of nickel),
4000 W (9 W/cm^2) and 225 W (5.1 W/cm^2) were applied on V and
Ni targets, respectively. The substrate temperature was kept constant
at 325 °C. The total working pressure was fixed at 0.4 Pa in a mixture
of Ar/ N_2 (120 sccm/80 sccm, respectively).

As the next step, a crystallographic phase analysis was performed of
the composite coatings (about 1 μm thick) by using an X-ray
diffractometer (Bruker D2 Phaser) with the monochromatized Cu $K\alpha$
radiation. The hardness and elastic modulus of the coatings were
measured by a nanoindenter (Hysitron Triboindenter TI-950) with a
Berkovich diamond probe. Different loads (0.5–12 mN) were used to
evaluate the hardness/elastic modulus as a function of the penetration
(h_c) to avoid the influence of the substrate mechanical properties. The
Oliver–Pharr⁴³ method was used to calculate the hardness and the
elastic modulus of the coatings. The surface roughness of the as-

407 received and coated surfaces was measured by a Bruker Contour GT
408 white light 3D profilometer.

409 Sliding experiments were performed with a high-vacuum
410 tribometer using a ball-on-disk setup, in which a stationary steel
411 ball (9.5 mm in diameter) was pressed against a rotating disc (50.8
412 mm and 6.35 mm thick) under mean Hertz pressures of ~ 0.6 GPa.
413 Both coated and uncoated balls were tested against the coated/
414 uncoated steel flats in the presence of atmospheric pressure methane
415 at room temperature. The sliding contact surfaces of ball and flat
416 specimens had a nominal surface roughness of $0.02 \mu\text{m}$ RMS. Prior to
417 the tribological tests, all test samples were cleaned by acetone and
418 isopropanol solvents in an ultrasonic bath for 5 min. The pure
419 methane gas was bled into the vacuum chamber after evacuating it
420 down to 10^{-4} Pa levels until reaching 0.9 atm (~ 91 MPa). The
421 experiment was performed at room temperature. The normal load on
422 top of the stationary ball was 2 N (which would create a peak Hertz
423 pressure of ~ 0.6 GPa), and the sliding speed was 0.1 m/s, so that the
424 rubbing surfaces would have been under severe contact conditions at
425 all times. The total sliding distance accumulated during the tests was
426 360 m. The friction force generated during the sliding ball and flat
427 surfaces was continuously monitored and recorded throughout the
428 tests using a data acquisition system and later converted to the friction
429 coefficients for the entire test cycle.

430 The wear volumes on the ball and disk samples were assessed with
431 the help of optical microscopy; specifically, the wear scars and tracks
432 were imaged by an Olympus STM6 microscope. The amount of wear
433 was calculated by using the standard wear volume equations based on
434 the wear scar diameter measured by the microscope.

435 The tribofilms were analyzed by confocal Raman microscopy
436 (inVia Reflex, Renishaw, Inc.) using appropriate light sources with a
437 wavelength of 633 nm to determine the nature of the tribochemical
438 films that formed on the rubbing surfaces during sliding. The Raman
439 instrument was calibrated with an internal silicon reference, and the
440 spectra were recorded in the range $1000\text{--}2000 \text{ cm}^{-1}$. Highly oriented
441 pyrolytic graphite (Ted Pella, lacey carbon) was used as a reference.

442 Density functional theory calculations were performed within the
443 generalized gradient approximation in the Perdew–Burke–Ernzerhof
444 parametrization.⁴⁴ The ionic species were described by ultrasoft
445 pseudopotentials, and the electronic wave functions expanded in
446 plane waves.⁴⁵ A kinetic energy cutoff of 25 Ry (200 Ry) was used to
447 truncate the expansion of the wave functions (charge density) on the
448 basis of test calculations on the bulk properties of the considered
449 materials. The static calculations were performed by means of
450 periodic supercells containing a vacuum region 15 Å thick and a slab
451 with (2×2) in-plane size and three layers thickness. The in-plane size
452 of the cell was increased to a $4 \times 3\sqrt{3}$ cell, corresponding to 24 atoms
453 per layer, in dynamic calculations. Although nickel is known to be
454 ferromagnetic, we did not consider the spin polarization to avoid a
455 dramatic increase of the computational workload of the *ab initio*
456 molecular dynamics simulations, where the reaction paths are mainly
457 governed by the mechanical stresses applied. This computational
458 choice is also justified by previous works on C/CH_x chemisorption
459 and CH₄ dehydrogenation on Ni.^{27,28,30}

460 *Ab initio* molecular dynamics simulations were performed in the
461 Born–Oppenheimer scheme using a home-modified version of the
462 program included in the Quantum Espresso package that permits the
463 user to simulate tribological conditions. In particular, a constant load
464 and a constant relative velocity of the two surfaces have been
465 modeled. We controlled the temperature of the two sliding slabs
466 (excluding the translational motion), while leaving the temperature of
467 the intercalated molecules free to evolve.

468 ■ ASSOCIATED CONTENT

469 **SI** Supporting Information

470 The Supporting Information is available free of charge at
471 <https://pubs.acs.org/doi/10.1021/acsanm.0c01527>.

472 Coating characterization (Figures S1–S3); tribological
473 characterization (Figure S4); tribofilm characterization
474 (Figures S5–S9); computational results (Figures S10–

S12); captions for Movies S1–S3; supplementary
References (1–9) (PDF)
Movie S1 (MP4)
Movie S2 (MP4)
Movie S3 (MP4)

515 ■ AUTHOR INFORMATION

516 Corresponding Authors

517 **Ali Erdemir** – Energy Systems Division, Argonne National
518 Laboratory, Argonne, Illinois 60439, United States;
519 Email: aerdemir@tamu.edu

520 **Jianguo Wen** – Center for Nanoscale Materials, Argonne
521 National Laboratory, Argonne, Illinois 60439, United States;
522 orcid.org/0000-0002-3755-0044; Email: jwen@anl.gov

523 Authors

524 **Giovanni Ramirez** – Energy Systems Division, Argonne
525 National Laboratory, Argonne, Illinois 60439, United States;
526 orcid.org/0000-0003-0985-1605

527 **Osman Eryilmaz** – Energy Systems Division, Argonne National
528 Laboratory, Argonne, Illinois 60439, United States

529 **Giulio Fatti** – Department of Physics, Informatics and
530 Mathematics, University of Modena and Reggio Emilia, 41125
531 Modena, Italy; orcid.org/0000-0001-7000-7310

532 **Maria Clelia Righi** – Department of Physics and Astronomy,
533 University of Bologna, 40127 Bologna, Italy

534 Complete contact information is available at:
535 <https://pubs.acs.org/10.1021/acsanm.0c01527>

536 Notes

537 The authors declare no competing financial interest.

538 ■ ACKNOWLEDGMENTS

539 Funding at Argonne National Laboratory was provided by The
540 U.S. Department of Energy, Office of Energy Efficiency and
541 Renewable Energy, Vehicle Technologies and Advanced
542 Manufacturing Offices under Contract DE-AC02-
543 06CH11357. ~~The U.S. Department of Energy, Office of~~
544 ~~This work was performed, in part, at the Center for Nanoscale Materials, a U.S. Department of Energy~~
545 ~~Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science,~~
546 ~~under Contract No. DE-AC02-06CH11357.~~

547 M.C.R. acknowledges support by the University of Modena
548 and Reggio Emilia through the FAR project and by the
549 European Union through the MAX Centre of Excellence
550 (Grant No. 676598). We thank Dave Gosztola for his support
551 with the Raman measurements at the Center of Nanoscale
552 Materials, Argonne National Laboratory.

553 ■ REFERENCES

- 554 (1) Hsu, S. M.; Zhang, J.; Yin, Z. The Nature and Origin of
555 Tribochemistry. *Tribol. Lett.* **2002**, *13* (2), 131–139.
- 556 (2) Kajdas, C.; Hiratsuka, K. Tribochemistry, Tribocatalysis, and the
557 Negative-Ion-Radical Action Mechanism. *Proc. Inst. Mech. Eng., Part J.*
558 **2009**, *223* (6), 827–848.
- 559 (3) Spikes, H. The History and Mechanisms of ZDDP. *Tribol. Lett.*
560 **2004**, *17* (3), 469–489.
- 561 (4) Erdemir, A.; Eryilmaz, O. Achieving Superlubricity in DLC Films
562 by Controlling Bulk, Surface, and Tribochemistry. *Friction* **2014**, *2*
563 (2), 140–155.
- 564 (5) Donnet, C.; Erdemir, A. Historical Developments and New
565 Trends in Tribological and Solid Lubricant Coatings. *Surf. Coat.*
566 *Technol.* **2004**, *180–181*, 76–84.
- 567 (6) Sutor, P. Solid Lubricants: Overview and Recent Developments.
568 *MRS Bull.* **1991**, *16* (05), 24–30.

- 533 (7) Bowden, F. P.; Young, J. E. Friction of Diamond, Graphite, and
534 Carbon and the Influence of Surface Films. *Proc. R. Soc. London A*:
535 *Math. Phys. Eng. Sci.* **1951**, *208* (1095).
- 536 (8) Guo, W.; Yin, J.; Qiu, H.; Guo, Y.; Wu, H.; Xue, M. Friction of
537 Low-Dimensional Nanomaterial Systems. *Friction* **2014**, *2* (3), 209–
538 225.
- 539 (9) Berman, D.; Erdemir, A.; Sumant, A. V. Approaches for
540 Achieving Superlubricity in Two-Dimensional Materials. *ACS Nano*
541 **2018**, *12* (3), 2122–2137.
- 542 (10) Berman, D.; Erdemir, A.; Sumant, A. V. Graphene: A New
543 Emerging Lubricant. *Mater. Today* **2014**, *17* (1), 31–42.
- 544 (11) Zhang, R.; Ning, Z.; Zhang, Y.; Zheng, Q.; Chen, Q.; Xie, H.;
545 Zhang, Q.; Qian, W.; Wei, F. Superlubricity in Centimetres-Long
546 Double-Walled Carbon Nanotubes under Ambient Conditions. *Nat.*
547 *Nanotechnol.* **2013**, *8* (12), 912–916.
- 548 (12) Erdemir, A.; Donnet, C. Tribology of Diamond-like Carbon
549 Films: Recent Progress and Future Prospects. *J. Phys. D: Appl. Phys.*
550 **2006**, *39* (18), R311–R327.
- 551 (13) Smil, V. Natural Gas : Fuel for the 21st Century.
- 552 (14) Zhang, Y.; Zhang, L.; Zhou, C. Review of Chemical Vapor
553 Deposition of Graphene and Related Applications. *Acc. Chem. Res.*
554 **2013**, *46* (10), 2329–2339.
- 555 (15) Kozlov, S. M.; Viñes, F.; Görling, A. Bonding Mechanisms of
556 Graphene on Metal Surfaces. *J. Phys. Chem. C* **2012**, *116* (13), 7360–
557 7366.
- 558 (16) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.;
559 Ahn, J.-H.; Kim, P.; Choi, J.-Y.; Hong, B. H. Large-Scale Pattern
560 Growth of Graphene Films for Stretchable Transparent Electrodes.
561 *Nature* **2009**, *457* (7230), 706–710.
- 562 (17) Reina, A.; Jia, X.; Ho, J.; Nezich, D.; Son, H.; Bulovic, V.;
563 Dresselhaus, M. S.; Kong, J. Large Area, Few-Layer Graphene Films
564 on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Lett.*
565 **2009**, *9* (1), 30–35.
- 566 (18) Patera, L. L.; Africh, C.; Weatherup, R. S.; Blume, R.; Bhardwaj,
567 S.; Castellarin-Cudia, C.; Knop-Gericke, A.; Schloegl, R.; Comelli, G.;
568 Hofmann, S.; Cepek, C. *In Situ* Observations of the Atomistic
569 Mechanisms of Ni Catalyzed Low Temperature Graphene Growth.
570 *ACS Nano* **2013**, *7* (9), 7901–7912.
- 571 (19) Kwon, H.; Choi, S.; Thompson, L. T. Vanadium Nitride
572 Catalysts: Synthesis and Evaluation For n-Butane Dehydrogenation. *J.*
573 *Catal.* **1999**, *184* (1), 236–246.
- 574 (20) OYAMA, S. Kinetics of Ammonia Decomposition on
575 Vanadium Nitride. *J. Catal.* **1992**, *133* (2), 358–369.
- 576 (21) Ramanathan, S.; Oyama, S. T. New Catalysts for Hydro-
577 processing: Transition Metal Carbides and Nitrides. *J. Phys. Chem.*
578 **1995**, *99* (44), 16365–16372.
- 579 (22) Franz, R.; Mitterer, C. Vanadium Containing Self-Adaptive
580 Low-Friction Hard Coatings for High-Temperature Applications: A
581 Review. *Surf. Coat. Technol.* **2013**, *228*, 1–13.
- 582 (23) Lim, S. C.; Ashby, M. F. Wear-Mechanism Maps. *Acta Metall.*
583 **1987**, *35* (1), 1–24.
- 584 (24) Mori, S.; Yoshida, M. Decomposition of Aromatic Compounds
585 on Cut Nickel Surface. *Tribol. Trans.* **1988**, *31* (1), 128–132.
- 586 (25) Mori, S. Adsorption of Benzene on the Fresh Steel Surface
587 Formed by Cutting under High Vacuum. *Appl. Surf. Sci.* **1987**, *27* (4),
588 401–410.
- 589 (26) Lu, R.; Kobayashi, K.; Nanao, H.; Mori, S. Deactivation Effect
590 of Tricresyl Phosphate (TCP) on Tribochemical Decomposition of
591 Hydrocarbon Oil on a Nascent Steel Surface. *Tribol. Lett.* **2009**, *33*
592 (1), 1–8.
- 593 (27) Klinke, D. J.; Wilke, S.; Broadbelt, L. J. A Theoretical Study of
594 Carbon Chemisorption on Ni(111) and Co(0001) Surfaces. *J. Catal.*
595 **1998**, *178* (2), 540–554.
- 596 (28) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. Methane
597 Activation and Dehydrogenation on Nickel and Cobalt: A Computa-
598 tional Study. *Surf. Sci.* **1995**, *324* (2–3), 345–356.
- 599 (29) Abild-Pedersen, F.; Lytken, O.; Engbæk, J.; Nielsen, G.;
600 Chorkendorff, I.; Nørskov, J. K. Methane Activation on Ni(1 1 1):
Effects of Poisons and Step Defects. *Surf. Sci.* **2005**, *590* (2–3), 127–
137.
- (30) Watwe, R. M.; Bengaard, H. S.; Rostrup-Nielsen, J. R.;
Dumesic, J. A.; Nørskov, J. K. Theoretical Studies of Stability and
Reactivity of CH_x Species on Ni(111). *J. Catal.* **2000**, *189* (1), 16–
30.
- (31) Kalin, M. Influence of Flash Temperatures on the Tribological
Behaviour in Low-Speed Sliding: A Review. *Mater. Sci. Eng., A* **2004**,
374 (1–2), 390–397.
- (32) Kong, J.; Xiong, D.; Li, J.; Yuan, Q.; Tyagi, R. Effect of Flash
Temperature on Tribological Properties of Bulk Metallic Glasses. *Tribol.*
Lett. **2009**, *35* (3), 151–158.
- (33) An, W.; Zeng, X. C.; Turner, C. H. First-Principles Study of
Methane Dehydrogenation on a Bimetallic Cu/Ni(111) Surface. *J.*
Chem. Phys. **2009**, *131* (17), 174702.
- (34) Zilibotti, G.; Corni, S.; Righi, M. C. Load-Induced Confinement
Activates Diamond Lubrication by Water. *Phys. Rev. Lett.* **2013**,
111 (14), 146101.
- (35) Kajita, S.; Righi, M. C. A Fundamental Mechanism for Carbon-
Film Lubricity Identified by Means of Ab Initio Molecular Dynamics.
Carbon **2016**, *103*, 193–199.
- (36) Loehlé, S.; Righi, M. Ab Initio Molecular Dynamics Simulation
of Tribochemical Reactions Involving Phosphorus Additives at Sliding
Iron Interfaces. *Lubricants* **2018**, *6* (2), 31.
- (37) Shibuta, Y.; Arifin, R.; Shimamura, K.; Oguri, T.; Shimojo, F.;
Yamaguchi, S. Ab Initio Molecular Dynamics Simulation of
Dissociation of Methane on Nickel(1 1 1) Surface: Unravelling
Initial Stage of Graphene Growth via a CVD Technique. *Chem. Phys.*
Lett. **2013**, *565*, 92–97.
- (38) Liao, Y.; Pourzal, R.; Wimmer, M. A.; Jacobs, J. J.; Fischer, A.;
Marks, L. D. Graphitic Tribological Layers in Metal-on-Metal Hip
Replacements. *Science* **2011**, *334* (6063), 1687–1690.
- (39) Erdemir, A.; Ramirez, G.; Eryilmaz, O. L.; Narayanan, B.; Liao,
Y.; Kamath, G.; Sankaranarayanan, S. K. R. S. Carbon-Based
Tribofilms from Lubricating Oils. *Nature* **2016**, *536* (7614), 67–71.
- (40) Fuadi, Z.; Adachi, K.; Muhammad, T. Formation of Carbon-
Based Tribofilm Under Palm Methyl Ester. *Tribol. Lett.* **2018**, *66* (3),
88.
- (41) Restuccia, P.; Righi, M. C. Tribochemistry of Graphene on Iron
and Its Possible Role in Lubrication of Steel. *Carbon* **2016**, *106*, 118–
124.
- (42) Marchetto, D.; Restuccia, P.; Ballestrazzi, A.; Righi, M. C.;
Rota, A.; Valeri, S. Surface Passivation by Graphene in the Lubrication
of Iron: A Comparison with Bronze. *Carbon* **2017**, *116*, 375–380.
- (43) Oliver, W. C.; Pharr, G. M. An Improved Technique for
Determining Hardness and Elastic Modulus Using Load and
Displacement Sensing Indentation Experiments. *J. Mater. Res.* **1992**,
7 (06), 1564–1583.
- (44) Perdeu, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient
Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–
3868.
- (45) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.;
Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo,
I.; Dal Corso, A.; de Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.;
Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-
Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.;
Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.;
Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M.
QUANTUM ESPRESSO: A Modular and Open-Source Software
Project for Quantum Simulations of Materials. *J. Phys.: Condens.*
Matter **2009**, *21* (39), 395502.