Article

Enhancement of sp^3 C Fraction in Diamond-like Carbon Coatings by Cryogenic Treatment

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Abstract: Diamond-like carbon (DLC) coatings deposited onto high-speed-steel surfaces were subjected to deep cryogenic treatment (DCT) at temperatures of -120 to -196 °C to investigate the evolution of microstructure, bonding structure, and mechanical properties. The surface morphology and the bonding structure of the DLC coatings were studied using scanning electron microscopy, transmission electron microscopy, micro-Raman spectroscopy, and X-ray photoelectron spectroscopy. It is found that DCT affects the surface morphology, especially the size and the height of the aggregates. For those DLCs with more than 50% sp^3 C fraction, the sp^2 C $\rightarrow$ sp^3 C transformation occurred in coatings treated at a temperature of -120 to -160 °C; and the maximum fraction of sp^3 C was obtained after treatment at -140 °C. Almost keeping the wear resistance of DLCs, DCT can improve the adhesion strength, and surface hardness. The findings of this study indicate that DCT will be a potential post-treatment method to tune the microstructure and mechanical performance of DLC coatings.

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Keywords: diamond-like carbon; deep cryogenic treatment; phase transformation; microstructure; mechanical performance

1. Introduction

Diamond-like carbon coatings (DLC) have attracted increasing attention because of their excellent performance [1,2]. Their many special characters have found extensive application, including high hardness, solid lubricant, wear resistance, low-temperature field emission, tunable bandgap, wide electrochemical window, a wide range of optical transmission, gas sensitivity and barrier, biocompatibility, and so on [3–10]. DLCs consist of a mixture of sp^3 C and sp^2 C bonded carbon atoms. At present physical and plasma-enhanced chemical vacuum vapor depositing are still the main methods to prepare DLCs in which the energetic C^+ impinges the top surface and implants into the subsurface to create a thermal spike site with high intrinsic stress and high local temperature, thus, stabilize the sp^3 C hybrid [11]. Thus, the sp^3 C fraction can be controlled by varying the depositing parameters, such as bias voltage, working gas, doping species, and even the multiple layer structure [12–17]. The sp^2 C/ sp^3 C bonding ratio plays a crucial role in determining the performance of DLCs [18–20]. Usually, the sp^3 C fraction is responsible for the mechanical performance of DLCs, while the sp^2 C fraction determines the electrical and optical properties. Some post-treatments can also adjust the sp^3 C fraction in carbon materials, for example, annealing [21–23] and high-pressure deforming [24–26]. However, the significant drawbacks of annealing are reduction in the fraction of sp^3 C bonds and hardness degradation, and the high-pressure deforming methods are destructive.

Is there a suitable and non-destructive post-treatment to enhance the sp^3 C fraction to strengthen DLCs? The direct sp^2 C to sp^3 C transformation must overcome a high energy barrier (~ 0.4 eV per atom). From the thermodynamical viewpoint, high pressures and/or temperatures benefit sp^3 C stabilization. Theoretical simulations and experimental studies showed a high contact pressure induced sp^2 C $\rightarrow$ sp^3 C transformation in carbon-based materials [27–31]. When impinged by a C^+ with a chosen kinetic energy, a low substrate temperature enhances the intrinsic stress of the local sites to stabilize the sp^3 C phase [32]. In addition to thermodynamical methods, the sp^2 C to sp^3 C transformation can occur if the energy release from a system is large enough to overcome the above barrier. For example, it is kinetically driven at a low temperature [33]. To explore a non-destructive method to enhance the sp^3 C fraction of DLC, we pay attention to the deep cryogenic treatment (DCT) in this study.

DCT has been extensively used in the machining industry to improve the mechanical performance of alloys by inducing phase transformation and microstructural changes [34–37]. DLCs have been reported to perform well under cryogenic service conditions, e.g., cryogenically treated carbon coatings exhibit significantly improved wear resistance [38–43]. However, there are few comprehensive studies on the effect of DCT on the bonding structure and microstructure of DLCs. We carried out a series of experiments at cryogenic conditions in this study. It was found that the surface morphology and the bonding structure of DLCs varied with the cryogenic temperature. The plausible reason behind them has been provided.

2. Materials and Methods

2.1. Substrate Treatment

Substrate coupons included EM 35 high speed steel disks with Φ 20.5 mm $\times$ 5 mm size and single-crystal Si wafers. The Si wafer substrate were without any treatment. EM35 alloy commercially from Eramet Group (Paris, France) is with composition of 0.93% C, 0.3% Mn, 0.35% Si, 4.1% Cr, 5.0% Mo, 6.2% W, 1.9% V, and balance Fe. The different groups and their processing steps are listed in Table 1. Quenching was performed by heating the samples in a VUQ-557H-10 furnace (Find-Shine Vacuum Tech. Co., Ltd., Shengyang, China) at 1170 °C for 15 min followed by cooling using nitrogen gas. Tempering was carried out thrice in a VPT-557H furnace (Find-Shine Vacuum Tech. Co., Ltd., Shengyang, China) at 560 °C for 1 h. The cooling and the heating rates during DCT were maintained at 5 °C /min using a cooling box (Cryometal-50, Aisike Instrum. Co., Ltd., Wuxi, China). Cryo-treat-I (-180 °C for 6 h) was used to stabilize the microstructure of the EM35 alloy (similar detail seen in [34]).

Table 1. Specimen groups and their processing steps.

Group	Pre-Treat				DLC Coat	Post-Treat
	Substrate	Quenching	Tempering	Cryo-Treat-I		Cryo-Treat-II
EM-0	EM35	YES	YES	YES	YES	NO
EM-T	EM35	YES	YES	YES	YES	YES (at T)
Si-0	Si wafer	NO	NO	NO	YES	NO
Si-T	Si wafer	NO	NO	NO	YES	YES (at T)

2.2. DLC Deposition and Post-Treatment

After those substrate EM 35 coupons treated above and Si wafers were mirror polished, orderly cleaned in ethanol and deionized water to remove surface contaminants, and dried using N_2 stream, they are put into the vacuum chamber of Hauzer Flexicoat 850 PECVD system (IHI Corporation, Venlo, The Netherlands). The deposition processing steps are presented in Table 2. Prior to depositing the a-C:H top layer, a Cr+WC interlayer was prepared using WC and Cr targets (99.99 at.%) connected to DC power sources in the presence of a carrier gas (argon, 99.999% pure). Then, the a-C:H was immediately deposited

in the vacuum chamber by the method of pulsed-DC PECVD with 40 kHz frequency and 740 V bias voltage, using acetylene (99.999 at.%) as the gas precursor. The thickness of the top a-C:H layer was 1.6–1.9 μm .

Table 2. Summary of a-C:H film deposition parameters.

Item	Item Parameter
Substrate cleaning	Base pressure 5×10^{-3} Pa; voltage bias 200 V; Ar gas flow rate 250 sccm; duration 90 min
Cr + WC interlayer	Target power 5 kW; heating 150 °C; duration 50 min
a-C:H layer	Bias voltage 740 V; coil current 2 A; C ₂ H ₂ gas flow rate 250 sccm; heating 300 °C; duration 80 min; work pressure 0.8–1 Pa

After the DLC deposition, the Cryo-treat-II step in Table 1 was carried out for some specimens at different temperatures, i.e., −120, −140, −160, −180 and −196 °C for 6 h. The Si wafer specimens with or without DLC were only used to measure the residual stress in the coatings.

2.3. Microstructure Characterization

Scanning electronic microscopy (SEM; Sigma 300, Zeiss Group, Oberkochen, Germany) and 300 kV transmission electron microscopy (TEM; Titan3 Themis G2, Thermo Fisher Scientific, Waltham, MA, USA) studies were conducted to analyze the microstructure of the DLC samples. The hybridization of carbon was determined by micro-Raman spectroscopy using a 532-nm laser (LabRAM Arami, Horiba Scientific, Palaiseau, France) and X-ray photoelectron spectroscopy (XPS) at an incident photon energy of 1486.6 eV (Thermo K-Alpha+, Thermo Fisher Scientific, Waltham, MA, USA). The XPS instrument was calibrated using Au4f^{7/2} core-level electron binding energy (84.00 eV) as the standard. Prior to each measurement, the specimen surface was etched for 60 s using Ar ions with 2 keV energy and a current density of 1 mA/mm². The Shirley method was used for background subtraction and the data analysis was performed using the XPS Peak 4.1 software, using the Gaussian–Lorentzian (G–L) with a 20% L mode.

2.4. Mechanical Performance Characterization

Friction tests were performed using a pin-on-disk instrument (SFT-2M, Zhongke Kaihua Co., Ltd., Lanzhou, China) by applying a normal load of 40 N in air at 25 °C and 40% relative humidity, and an alumina ball with a diameter of 4 mm was used as the pin. The wear volume was measured using a light-interference profiler (RTEC UP Dual Model, Rtec Instruments, San Jose, CA, USA).

The hardness was measured using a nanoindenter (Anton Paar TTX-NHT3, Anton Paar GmbH, Graz, Austria) by applying a load of 5 mN at a rate of 10 mN/min. For each specimen, the average hardness value over six tests was considered as the hardness of the coatings. The adhesion strength was estimated using a scratch instrument with a diamond stylus tip of radius 200 μm (MFT-4000, Zhongke Kaite, Lanzhou, China). A maximum load of 100 N was applied at a rate of 100 N/min for a scratch length of 5 mm. The adhesion was characterized by the critical load which induced the first detachment of the film. For each specimen, four tests were performed.

The residual stress in the coating deposited on the Si wafer was analyzed using a film stress instrument (FST1000, Supro Instruments, Shenzhen, China) and the Stoney's Equation (1) [13,14,23]. In this formula, E is the Young's modulus of the Si wafer, h_s is the thickness of the silicon wafer, ν is the Poisson ratio of the Si wafer, h_f is the thickness of the film, R_0 is the radius of curvature of the Si wafer before film deposition, and R is the radius of curvature after film deposition. The residual stress was then taken as the average of the values for the three specimens with the same surface treatment.

$$\sigma(x, y) = Eh_s^2(1/R_0 - 1/R) / [6h_f(1 - \nu)]. \quad (1)$$

3. Results

3.1. Microstructure

All DLC-coated specimens were prepared in the same heat. The top surface morphology of specimen EM-0 without DCT is shown in Figure 1a, which presents smooth appearance with tens' nanometer of cauliflower-like aggregates. The surface morphology changes significantly after DCT, and the aggregates with different sizes and heights are observed in Figure 1b–f. Many pinhole-like defects exist at the boundaries of the aggregates in Figure 1d. In this study, the size and the height of the aggregates vary inconsistently with the DCT temperature; smooth (Figure 1b,e) and rough (Figure 1c,d) surface morphology images are observed. DCT process leads to shrinkage and even elimination of various defects, smoothening the surface of DLC or graphite-like carbon (GLC) films [38,39]. Sometimes an unusual large submicrometer sp^2 C-enriched aggregates could be produced when DLCs depositing onto a 20–100 K cryogenic substrate using pulsed laser [44], and it is unlike this study. If only considering the shrinkage effect induced by DCT, it is difficult to interpret the surface morphology change in this study. This result probably relates to phase transformation during DCT, and it will be discussed in the next sections.

Figure 1. SEM images of top-surface morphologies of different specimens (a–f).

The cross-sectional TEM images of specimens EM-0 and EM-140 are presented respectively in Figure 2a and (Figure 2b), indicating that the coatings are intact, and no microcracks are formed after DCT. There is no locally ordered region formation in the cryogenically treated coating in the high-resolution TEM (HRTEM) image (Figure 2c).

Figure 2. TEM images of the cross-sections (a,b) and plan-view HRTEM image (c).

3.2. Chemical Bonding

The raw and fitted peaks of C 1s spectra of different specimens are shown in Figure 3a–f. The standard core level binding energies (BE) of sp^2 C=C, sp^3 C–C, and C–O bonds are 284.4 ± 0.2 , 285.2 ± 0.2 and 286.5 ± 0.3 eV, respectively [6,12,19]. During fitting, the fitted BE deviated slightly from the above ideal value probably due to the collective effect of the chemical environment, defect density, together with residual stress [17]. It is shown that the area of sp^3 C–C and sp^2 C=C varies a little with DCT temperature.

Figure 3. (a–f): C 1s XPS spectra of different specimens.

Raman spectra varied with DCT temperature, as shown in Figure 4a, where the dot line linking those peak points deviated nonlinearly from the straight line. It meant microstructure change induced by DCT at different temperature. The so-called G peak and D peak, fitted based on two Gaussian curve shapes, lay at around 1580 and 1360 cm^{-1}

respectively [17,45]. The G peak the D peak can be fitted [20,29,30]. The G peak is due to all sp^2 C sites, and the D peak is only due to six-fold ring sp^2 C sites [11]. Thus, the G peak position and the intensity ratio (I_D/I_G) depend inversely on the content of sp^3 C, number of chain-like sp^2 C sites; and relate to cluster size, residual stress, and disorder degree [20,44,46].

Figure 4. Raman spectra (a), I_D/I_G and sp^2/sp^3 bond ratios (b) of specimens with the cryogenic temperature.

The variations of I_D/I_G and sp^2/sp^3 bond ratios with the DCT temperature are shown in Figure 4b. The sp^2 C=C $\rightarrow$ sp^3 C–C transformation takes place in the specimens treated at temperatures of -120 to -160 °C. This result was surprising, so we repeated these tests three times. Every time EM-140 specimen exhibits the highest fraction of sp^3 C; which can reach approximately 4% more than EM-0 without DCT. The temperature dependence of I_D/I_G ratio differs from that of sp^2 C/ sp^3 C bond ratio at temperatures below -180 °C, which may be partly attributed to the different depth resolutions of XPS and Raman techniques, as well as the different contributions from surface dangling bonds [23,29]. The C–O bond fraction differs in different DCT coatings in Figure 4, which were probably produced by the chemical absorption of O_2 and H_2O in the environment. The background signal of XPS spectra intensified when some kinds of pencil lead was wet etched [45], probably it was due to the similar chemical absorption.

3.3. Mechanical Properties

The macro-residual stress in the DLCs after DCT is similar to that in the untreated DLC (Figure 5a). The adhesion of all the specimens except EM-196 is improved, as shown in Figure 5b. Specimen EM-140 exhibits the highest hardness in Figure 5c. The variation of hardness with DCT temperature agree with the above change of I_D/I_G and sp^2/sp^3 bond ratios. Because specimens with or without DCT kept almost the same residual stress, and the nano-indentation depth was less than 1/8 thickness of the DLC coatings, thus, the hardness improvement of EM-140 surely was responsible for sp^3 C fraction enhancement [2,12,20]. One hand, the mechanical and micro-structural change of EM 35 alloy substrate induced by DCT [34,35,37] provided strong support for the coating; another hand, the sp^2/sp^3 C ratio of the coating affected the interface strength between DLC and the interlayer.

The friction curves and wear volumes of the specimens are shown in Figure 6a,b, respectively. The steady-state friction coefficient of EM-0 is 0.08; the other specimens exhibit higher or lower values, c.f., 0.1 for EM-196, and 0.08 for EM-140. Because the sp^3 C fraction the hardness differs a little for these coatings, friction coefficient seems positively related to the surface roughness under high load 40 N. From Figure 1 the surface roughness can be ranked in the order: EM-180 < EM-140 < EM-120 < EM-0 < EM-160 < EM-196. The asperity on the surface affects the effective contact Hertz stress [23,29]. The factors that

influence the friction performance of DLCs include surface morphology, adhesion, and hardness [1,2,7,46]. Contrasting with EM-0, cryogenic treatment almost holds the wear resistance of DLCs. Probably rough surface and higher sp^2 C in the EM-196 coating, the tribofilm could be formed easily, which presented the minimum wear volume. Detailed analyses of these factors will be carried out in our future work.

Figure 5. Residual stress (a), adhesion strength (b), and hardness (c) of specimens subjected to different treatments.

Figure 6. Friction coefficient (a) and wear volume (b) of specimens subjected to different treatments.

4. Discussion

The surface morphology is determined by the bombardment energy and the hydrogen content of the DLC [17,47]. The change in the surface morphology after DCT is not only due to the cooling contraction, but also due to phase transformation. Based on the hybrid structure analysis in Section 3.2, it shows that the sp^2 C $\rightarrow$ sp^3 C transformation can be fulfilled under a combination of suitable cryogenic temperature and original DLC microstructure. Owing to the presence of large amounts of unbonded H in the coating [14,17], it is expected that H_2 outdiffuses during cooling. This may have resulted in the formation of pinhole-like defects in EM-160.

High pressure deformation, high pressure torsion, and high contact pressure of friction can result in phase transformation of carbon materials to enhance the sp^3 C fraction [26–28,30]. According to the carbon P–T phase [32], after overcoming the energy barrier (−0.4 eV per carbon atom [33]), the pressure required to stabilize the diamond phase decreases with decrease in temperature. Recently the bulk ta-C could be synthesized at room temperature by pressing the glassy carbon (sp^2 C) if the pressure was more than 8.5 GPa [25]. In this study the macro residual compressive stress in DLCs was approximately 1.8 GPa (Figure 5a), which is not enough to promote sp^2 C $\rightarrow$ sp^3 C transformation.

In order to plausibly interpret the phase transformation induced by DCT, we propose that the following conditions need to be satisfied to realize sp^2 C $\rightarrow$ sp^3 C. First, very

high pressure should be created at local sites in the coatings. Second, the release of elastic energy must be greater than the energy barrier. In the present study, the fraction of sp^3 C bond in the as-deposited DLCs is more than 50% (Figure 4b). This results in the formation of a rigid network of sp^3 C bonds. If sp^2 C=C clusters embedded in the rigid network slide under strain, the confinement from the rigid network generates high local pressure. During DCT, the mismatch between the rigid network and the clusters provides the needed local strain if the rigid network is stiff enough. In summary, the prerequisites to realize the sp^2 C $\rightarrow$ sp^3 C transformation are: (1) enough stiffness of the rigid network of sp^3 C bonds; and (2) suitable strain range in the clusters. The above-mentioned requirements are fulfilled when the DLCs are treated at temperatures of -120 to -160 °C. The very high local pressure at temperatures lower than -160 °C collapses the rigid network; the local pressure is too low when treated at temperatures higher than -120 °C. In addition, the sp^3 CH_n fraction in a DLC will affect the rigidity of the sp^3 C network, and influence the sp^2 C to sp^3 C transformation. Verification of the above hypothesis is undergoing by molecular dynamic simulation and systematical experiments.

5. Conclusions

The effects of DCT at temperatures of -120 to -196 °C on the microstructure, bonding structure, and mechanical properties of DLCs were investigated. DCT affects the surface morphology, especially the size and the height of the aggregates. The hardness of DLC improves after treatment at -140 °C due to sp^2 C $\rightarrow$ sp^3 C transformation. DCT at suitable conditions is beneficial for enhancing the fraction of sp^3 bonded carbon and the surface hardness of DLC. Thus, DCT will be a potential method for tuning the microstructure and mechanical properties of DLCs.

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References

1. Vetter, J. 60 years of DLC coatings: Historical highlights and technical review of cathodic arc processes to synthesize various DLC types, and their evolution for industrial applications. *Surf. Coat. Technol.* **2014**, *257*, 213–240. [\[CrossRef\]](#)
2. Bewilogua, K.; Hofmann, D. History of diamond-like carbon films—From first experiments to worldwide applications. *Surf. Coat. Technol.* **2014**, *242*, 214–225. [\[CrossRef\]](#)
3. Birney, R.; Cumming, A.; Campsie, P.; Gibson, D.; Hammond, G.; Hough, J.; Martin, I.; Reid, S.; Rowan, S.; Song, S.; et al. Coatings and surface treatments for enhanced performance suspensions for future gravitational wave detectors. *Class. Quantum Grav.* **2017**, *34*, 235012. [\[CrossRef\]](#)
4. Saha, B.; Toh, W.; Liu, E.; Tor, S.; Hardt, D.; Lee, J. A review on the importance of surface coating of micro/nano-mold in micro/nano-molding processes. *J. Micromech. Microeng.* **2016**, *26*, 013002. [\[CrossRef\]](#)
5. Markwitz, A.; Leveneur, J.; Gupta, P.; Suschke, K.; Futter, J.; Rondeau, M. Transition metal ion implantation into diamond-like carbon coatings: Development of a base material for gas sensing applications. *J. Nanomater.* **2015**, *2015*, 706417. [\[CrossRef\]](#)
6. Son, M.; Zhang, T.; Jo, Y.; Kim, K. Enhanced electrochemical properties of the DLC films with an arc interlayer, nitrogen doping and annealing. *Surf. Coat. Technol.* **2017**, *329*, 77–85. [\[CrossRef\]](#)

7. Fan, X.; Xue, Q.; Wang, L. Carbon-based solid-liquid lubricating coatings for space applications—A review. *Friction* **2015**, *3*, 191–207. [\[CrossRef\]](#)
8. Yu, Q.; Chen, X.; Zhang, C.; Luo, J. Influence factors on mechanisms of superlubricity in DLC films: A Review. *Front. Mech. Eng.* **2020**, *6*, 65. [\[CrossRef\]](#)
9. Nakaya, M.; Uedono, A.; Hotta, A. Recent progress in gas barrier thin film coatings on PET bottles in food and beverage applications. *Coatings* **2015**, *5*, 987–1001. [\[CrossRef\]](#)
10. Voevodin, A.; Zabinski, J. Nanocomposite and nanostructured tribological materials for space applications. *Compos. Sci. Technol.* **2005**, *65*, 741–748. [\[CrossRef\]](#)
11. Robertson, J. Diamond amorphous carbon. *Mater. Sci. Eng.* **2002**, *37R*, 129–281. [\[CrossRef\]](#)
12. Almeida, L.; Souza, A.; Costa, L.; Rangel, E.; Manfrinato, M.; Rossino, L. Effect of nitrogen in the properties of diamond-like carbon (DLC) coating on Ti6Al4V substrate. *Mater. Res. Express* **2020**, *7*, 065601. [\[CrossRef\]](#)
13. Zhang, D.; Li, S.; Zuo, X.; Guo, P.; Ke, P.; Wang, A. Structural and mechanism study on enhanced thermal stability of hydrogenated diamond-like carbon films doped with Si/O. *Diam. Relat. Mater.* **2020**, *108*, 107923. [\[CrossRef\]](#)
14. Peng, J.; Yang, M.; Zeng, J.; Su, D.; Liao, J.; Yick, M. Influence of nitrogen doping on the thermal stability of hydrogenated amorphous diamond coating. *Thin Solid Films* **2020**, *709*, 138188. [\[CrossRef\]](#)
15. Wang, J.; Pu, J.; Zhang, G.; Wang, L. Architecture of superthick diamond-like carbon films with excellent high temperature wear resistance. *Tribol. Int.* **2015**, *81*, 129–138. [\[CrossRef\]](#)
16. Braak, R.; May, U.; Onuseit, L.; Repphun, G.; Guenther, M.; Schmid, C.; Durst, K. Accelerated thermal degradation of DLC-coatings via growth defects. *Surf. Coat. Technol.* **2018**, *349*, 272–278. [\[CrossRef\]](#)
17. Peng, J.; Yang, M.; Bi, J.; Sheng, R.; Li, L. Hydrogen existence state of a hydrogenated amorphous carbon coating and its thermal stability. *Diam. Relat. Mater.* **2019**, *99*, 107535. [\[CrossRef\]](#)
18. Yamamoto, S.; Kawana, A.; Ichimura, H.; Masuda, C. Relationship between tribological properties and sp^3/sp^2 structure of nitrogenated diamond-like carbon deposited by plasma CVD. *Surf. Coat. Technol.* **2012**, *210*, 1–9. [\[CrossRef\]](#)
19. Muguruma, T.; Iijima, M.; Kawaguchi, M.; Mizoguchi, I. Effects of sp^2/sp^3 ratio and hydrogen content on in vitro bending and frictional performance of DLC-coated orthodontic stainless steels. *Coatings* **2018**, *8*, 199. [\[CrossRef\]](#)
20. Li, A.; Li, X.; Wang, Y.; Lu, Z.; Wang, Y.; Zhang, G.; Wu, Z. Investigation of mechanical and tribological properties of super-thick DLC films with different modulation ratios prepared by PECVD. *Mater. Res. Express* **2019**, *6*, 086433. [\[CrossRef\]](#)
21. Takabayashi, S.; Okamoto, K.; Nakatani, T. Influence of post-annealing on a diamondlike carbon film analyzed by Raman spectroscopy. *Surf. Interface Anal.* **2018**, *50*, 441–447. [\[CrossRef\]](#)
22. Grenadyorov, A.; Solov'yev, A.; Oskomov, K.; Oskirko, V.; Semenov, V. Thermal stability of anti-reflective and protective a-C:H:SiO_x coating for infrared optics. *Appl. Surf. Sci.* **2020**, *510*, 145433. [\[CrossRef\]](#)
23. Peng, J.; Liao, J.; Yang, M.; Liao, J.; Bi, J. Effect of annealing treatment on the tribological performance of hydrogenated amorphous diamond coatings doped with nitrogen. *Ceram. Intern.* **2021**, *47*, 13423–13431. [\[CrossRef\]](#)
24. Durandurdu, M. Formation of a very high-density amorphous phase of carbon and its crystallization into a simple cubic structure at high pressure. *Comput. Mater. Sci.* **2021**, *200*, 110822. [\[CrossRef\]](#)
25. Tan, L.; Sheng, H.; Lou, H.; Cheng, B.; Xuan, Y.; Prakapenka, V.; Greenberg, E.; Zeng, Q.; Peng, F.; Zeng, Z. High-pressure tetrahedral amorphous carbon synthesized by compressing glassy carbon at room temperature. *J. Phys. Chem. C* **2020**, *124*, 5489–5494. [\[CrossRef\]](#)
26. Edalati, K.; Horita, Z. Phase transformations during high-pressure torsion (HPT) in titanium, cobalt and graphite. *IOP Conf. Ser.: Mater. Sci. Eng.* **2014**, *63*, 012099. [\[CrossRef\]](#)
27. Li, X.; Wang, A.; Lee, K. Insights on low-friction mechanism of amorphous carbon films from reactive molecular dynamics study. *Tribol. Int.* **2019**, *131*, 567–578. [\[CrossRef\]](#)
28. Bai, Y.; Yu, Z.; Liu, R.; Li, N.; Yan, S.; Yang, K.; Liu, B.; Wei, D.; Wang, L. Pressure-induced crystallization and phase transformation of para-xylene. *Sci. Rep.* **2017**, *7*, 5321. [\[CrossRef\]](#)
29. Manimunda, P.; Al-Azizi, A.; Kim, S.; Chromik, R. Shear-induced structural changes and origin of ultralow friction of hydrogenated diamond-like carbon (DLC) in dry environment. *ACS Appl. Mater.* **2017**, *9*, 16704–16714. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Fukumasu, N.; Bernardes, C.; Ramirez, M.; Trava-Airoldi, V.; Souza, R.; Machado, I. Local transformation of amorphous hydrogenated carbon coating induced by high contact pressure. *Tribol. Int.* **2018**, *124*, 200–208. [\[CrossRef\]](#)
31. Chen, L.; Liu, K.; Wei, X.; Lu, Z.; Ren, N.; Zhang, G.; Xue, Q. Enhancement in the tribological properties of Cr/DLC multilayers in methane: Structural transformation induced by sliding. *SN Appl. Sci.* **2019**, *1*, 1483. [\[CrossRef\]](#)
32. Kalinichenko, A.; Perepelkin, S.; Strel'nitskij, V. Dependence of intrinsic stress and structure of ta-C film on ion energy and substrate temperature in model of the non-local thermoelastic peak. *Diam. Relat. Mater.* **2010**, *19*, 996–998. [\[CrossRef\]](#)
33. Esmeryan, K.; Castano, C.; Bressler, A.; Abolghasemibizaki, M.; Fergusson, C.; Roberts, A.; Mohammad, R. Kinetically driven graphite-like to diamond-like carbon transformation in low temperature laminar diffusion flames. *Diam. Relat. Mater.* **2017**, *75*, 58–68. [\[CrossRef\]](#)
34. Liao, J.; Li, L.; Peng, J.; Gao, J. Effects of deep cryogenic treatment on the microstructure and friction performance of M35 high-speed steel. *J. Phys. Conf. Ser.* **2020**, *1676*, 012098. [\[CrossRef\]](#)
35. Jovicevic-Klug, P.; Jenko, M.; Jovicevic-Klug, M.; Batic, B.; Kovac, J.; Podgornik, B. Effect of deep cryogenic treatment on surface chemistry and microstructure of selected high-speed steels. *Appl. Surf. Sci.* **2021**, *548*, 149257. [\[CrossRef\]](#)

36. Dhokey, N.; Hake, A.; Kadu, S.; Bhoskar, I.; Dey, G. Influence of cryoprocessing on mechanism of carbide development in cobalt-bearing high-speed steel (M35). *Metall. Mater. Trans. A* **2014**, *45*, 1508–1516. [[CrossRef](#)]
37. Gavriljuk, V.; Theisen, W.; Sirosh, V.; Polshin, E.; Kortmann, A.; Mogilny, G.; Petrov, Y.; Tarusin, Y. Low-temperature martensitic transformation in tool steels in relation to their deep cryogenic treatment. *Acta Mater.* **2013**, *61*, 1705–1715. [[CrossRef](#)]
38. Kong, Y.; Chen, Q.; Wang, L. Microstructures and tribological properties of GLC coated 100Cr6 bearing steels. *Mater. Res. Express* **2017**, *4*, 116404. [[CrossRef](#)]
39. Zhao, Y.; Nie, C.; Jin, Y.; Zhu, W.; Liu, X.; Nie, Y. Effect of cryogenic treatment on friction and wear property of DLC film/304 stainless steel. *Adv. Mater. Res.* **2014**, *900*, 767–772. [[CrossRef](#)]
40. Wang, J.; Jia, Q.; Yuan, X.; Wang, S. Experimental study on friction and wear behaviour of amorphous carbon coatings for mechanical seals in cryogenic environment. *Appl. Surf. Sci.* **2012**, *258*, 9531–9535. [[CrossRef](#)]
41. Aggleton, M.; Burton, J.; Taborek, P. Cryogenic vacuum tribology of diamond and diamond-like carbon films. *J. Appl. Phys.* **2009**, *106*, 013504. [[CrossRef](#)]
42. Gradt, T.; Borner, H.; Schneider, T. Low temperature tribometers and the behaviour of ADLC coatings in cryogenic environment. *Tribol. Intern.* **2001**, *34*, 225–230. [[CrossRef](#)]
43. Ostrovskaya, Y.; Strelnitskij, V.; Kuleba, V.; Gamulya, G. Friction and wear behaviour of hard and superhard coatings at cryogenic temperatures. *Tribol. Intern.* **2001**, *34*, 255–263. [[CrossRef](#)]
44. Hu, A.; Alkhesho, I.; Duley, W.; Zhou, H. Cryogenic graphitization of submicrometer grains embedded in nanostructured tetrahedral amorphous carbon films. *J. Appl. Phys.* **2006**, *100*, 084319. [[CrossRef](#)]
45. Knápek, A.; Sobola, D.; Burda, D.; Danhel, A.; Mousa, M.; Kolarík, V. Polymer graphite pencil lead as a cheap alternative for classic conductive SPM probes. *Nanomaterials* **2019**, *9*, 1756. [[CrossRef](#)]
46. Tambe, N.; Bhushan, B. Nanoscale friction-induced phase transformation of diamond-like carbon. *Scr. Mater.* **2005**, *52*, 751–755. [[CrossRef](#)]
47. Catena, A.; McJunkin, T.; Agnello, S.; Gelardi, F.; Wehner, S.; Fischer, C. Surface morphology and grain analysis of successively industrially grown amorphous hydrogenated carbon films (a-C:H) on silicon. *Appl. Surf. Sci.* **2015**, *347*, 657–667. [[CrossRef](#)]