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Low Frictional MoS_2/WS_2/FineLPN Hybrid Layers on Nodular Iron

Pior Kula [1,2], Robert Pietrasik [1,2,*], Sylwester Pawęta [1,2] and Adam Rzepkowski [1,2]

1 Hart-Tech Ltd., 45 Niciarniana Street, 92-320 Lodz, Poland; p.kula@hart-tech.pl (P.K.); s.paweta@hart-tech.pl (S.P.); adam.rzepkowski@p.lodz.pl (A.R.)

2 Institute of Materials Science and Engineering, Lodz University of Technology, 1/15 Stefanowski Street, 90-924 Lodz, Poland

* Correspondence: robert.pietrasik@p.lodz.pl

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Abstract: The paper presents the new concept of low frictional hybrid composite coatings on nodular cast iron. The structure of it is multilayer and consists of MoS_2 and/or WS_2 nanoinclusions embedded in the iron nitrides' zone and relatively deep hard diffusion zone. It offers a low friction coefficient as well as high wear resistance of coated parts. The details of technology as well as the mechanism of layer's growth have been presented and discussed. The presented technology may be an interesting alternative for chromium-based galvanic coatings of piston rings made of nodular iron using Cr^{6+}.

Keywords: nitriding; low friction; piston ring

1. Introduction

Nodular cast iron is the most popular material used for piston rings. The extremely high and intricate thermal and mechanical load of them [1–4] require the application of advanced solutions, both for a bulk material [5] and surface layer [6,7], as well as for a lubrication regime [1,2,8,9]. In order to improve cooperation between the piston ring and the cylinder sleeve, various coatings are applied. Such coatings include chromium and/or chromium–molybdenum galvanic coatings [10] as well as flame [11] or plasma sprayed [12–16], laser cladded, and PVD/CVD ones [17–19]. The PVD coatings of machining tools [20,21], which are still developed, are generally not applicable for piston ring improvement, due to an adhesive nature of the interface between a coating and the original material. The most common protection of piston rings against scuffing and wear are chromium-based galvanic coatings. However, they are also the most dangerous ones for the employees as well as the natural environment, since Cr^{6+} is used [22].

The nitriding process is also widely used for surface treatment of rings made mainly of steel [17,23]. It improves the friction coefficient of the surface layer as well as its resistance against hydrogen wear both at dry and lubricated regime [24–28]. More intricate is the issue of cast iron nitriding, due to the presence of graphite precipitation in the microstructure [29,30] Recently, the new non-equilibrium, low-pressure nitriding process (FineLPN) has been developed. It may be used for creation of fully controlled phase structure of nitrided case both on steel and cast iron due to dedicated neural network computer support [31].

Layered materials, like MoS_2, WS_2, etc., are well known as efficient solid lubricants [32,33]. They may be used in frictional contacts also at extremely high contact pressures as well as at elevated temperatures. The critical issue with the application of them for the improvement of piston rings frictional performance is the necessity to incorporate of them into a hard and strong matrix of a surface layer. Similar trials of manufacturing of multiphase, gradient surface layers have been presented in numerous papers [10,14,17,18].

The new concept of low frictional hybrid composite coatings [34] on nodular cast iron has been presented in the paper. The structure of it is multilayer and it consists of MoS_2 and/or WS_2 nanoinclusions embedded in iron nitrides zone and relatively deep hard diffusion zone. It offers low friction coefficient, as well as high wear resistance and fatigue strength of coated parts. The details of the multi-stage new technology, as well as mechanism of the layer's growth, have been presented and discussed.

2. Materials and Methods

The substrate material specimens for research were pieces of industrially manufactured piston rings (Φ117.5 mm × 2.68 mm × 4.60 mm) made of S14 grade nodular cast iron. The standardised chemical composition of used cast iron is shown in Table 1.

Table 1. Standardised Chemical Composition of S14 Nodular Cast Iron [% by Weight].

C	Si	Mn	P	S	Cr
3.6–4.0	2.1–3.3	0.2–0.5	0.3	Max. 0.05	Max. 0.2

According to the industrial technology, the rings have been hardened to obtain the matrix microstructure of tempered martensite free of carbide precipitations. The ca. 2 µm of micro-particles diameter of tungsten disulphide and molybdenum disulphide have been used as low frictional reinforcing phases. The creation of a low friction surface layer was multi-stage and the process has been conducted as follows. First, the slurry 1 g of MoS_2 or MoS_2 + WS_2 suspended in 10 mL of C_3H_7OH + 1 mL of $C_5H_{11}OH$ has been prepared. Then, it has been used for the uniform spray coating of piston rings specimens. After the natural drying, the coated specimens have been annealed at 300 °C for 1 h in an inert N_2 atmosphere to sinter the cladded particles and to adhere them to the metallic substrate. Next, such preliminary prepared green compacts were thermo-chemically treated by FineLPN low-pressure nitriding [31] or alternatively, additionally treated by gas sulphonitriding in an active atmosphere containing ammonia gas and sulphur vapors [35]. Two options A and B of the multi-stage surface engineering process have been conducted and compared. The technological schedule and parameters of them are presented in the Table 2.

Table 2. Technological Details of Compared Processes Options.

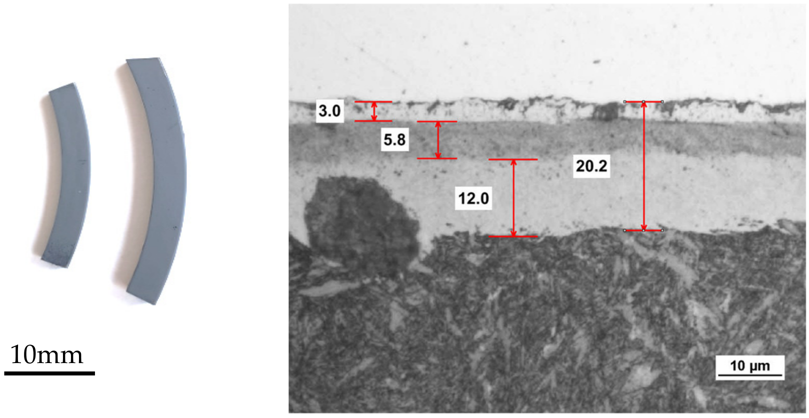
Option A	Option B
Low frictional particles—MoS_2 + WS_2	Low frictional particles—MoS_2
Sintering—300 °C, 1 h, N_2	Sintering—300 °C, 1 h, N_2
Two-stage thermochemical treatment —FineLPN – 8 h, 540 °C, 40–60 mbar —Gas Sulphonitriding – 4 h, 540 °C, sulphur evaporation at 180 °C	One-stage thermochemical treatment —Fine – 12 h, 540 °C, 40–60 mbar

The cross-section microstructures of specimens were observed having used the optical microscope Nikon MA200 (Nikon Instech Co., Ltd., Tokyo, Japan). The microstructure and chemical composition of surface layers were investigated also by using the scanning electron microscope (SEM) JEOL JSM-6610 LV (JEOL Ltd., Tokyo, Japan) equipped with the energy dispersion spectroscope (EDS) X-MAX 80 Oxford Instruments (Oxford Instruments Group, Abingdon, UK).

Dry friction tribological tests at oscillating movement have been conducted using ball on disc tribometer SRV Optimol Instruments Prüftechnik (Optimol Instruments Prüftechnik GmbH, Munich, Germany). The parameters of tests were as follows: 20 N regular load, 1 mm stroke, 20 Hz frequency, 1800 s total time of test, at temperature of 25 °C. Dry friction coefficient has been registered during the test, and the maximum depth of frictional tracks has been measured after it alike. Three specimens were investigated for each option. The average values of frictional coefficient have been determined from all plots' courses (total duration 5400 s). The average values of the maximum depth of frictional tracks as well as the standard deviation of results have been calculated too.

3. Results and Discussion

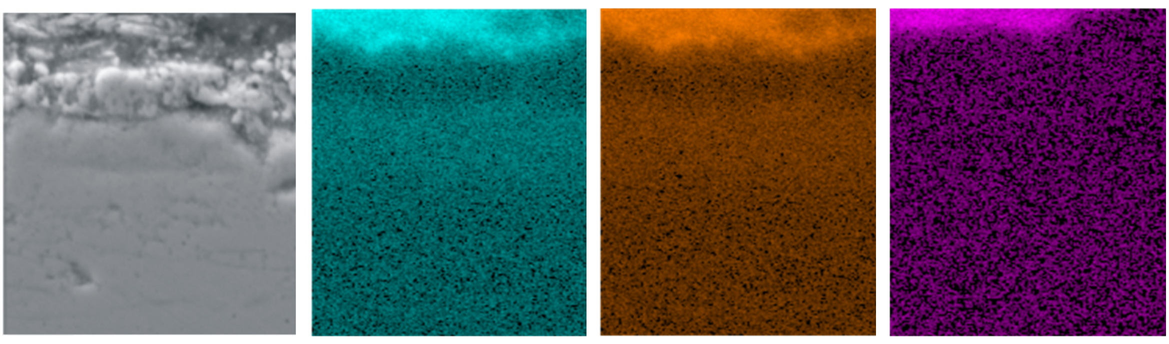
The external appearance of piston rings specimens after spray coating and preliminary annealing are shown in Figure 1a. The metallic surface has been homogenously coated by a tight coating of low frictional particles which adhere themselves strong enough, and also to the substrate. An exemplary final microstructure cross-section of the obtained hybrid low frictional layer is presented in Figure 1b. It consists of the following subzones: an externally grown compound zone containing low-friction particles of MoS_2 and optionally WS_2 embedded in iron nitrides ε − 3 µm, white iron nitrides zone (−17.8 µm), partially containing FeS fine inclusions (−5.8 µm), and relatively deep (−154 µm) dark diffusive zone in the original microstructure. Such a multizone gradient structure of the surface layer should be beneficial from the point of view of frictional and antiwear properties of piston rings made of nodular cast iron.



(**a**) (**b**)

Figure 1. (**a**) External appearance of samples after spray coating and preliminary annealing. Sintering parameters: temperature: 300 °C, time: 2 h ramp 5 °C/min withstand for 1 h in N atmosphere; (**b**) Exemplary cross section of final microstructure of hybrid layer – option A.

SEM cross sections and EDS pictures are presented in Figures 2 and 3 for layers options A and B, respectively.



10 µm Sulfur S Lα1 Molybdenum Mo Lα1 Tungsten W Lα1

Figure 2. SEM Cross Sections and corresponding EDS maps of S, Mo and W distribution for layer option A.

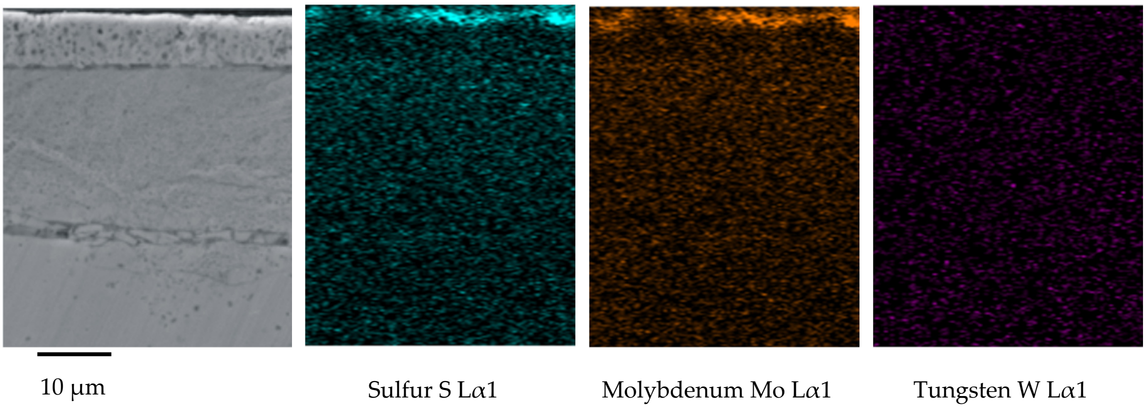
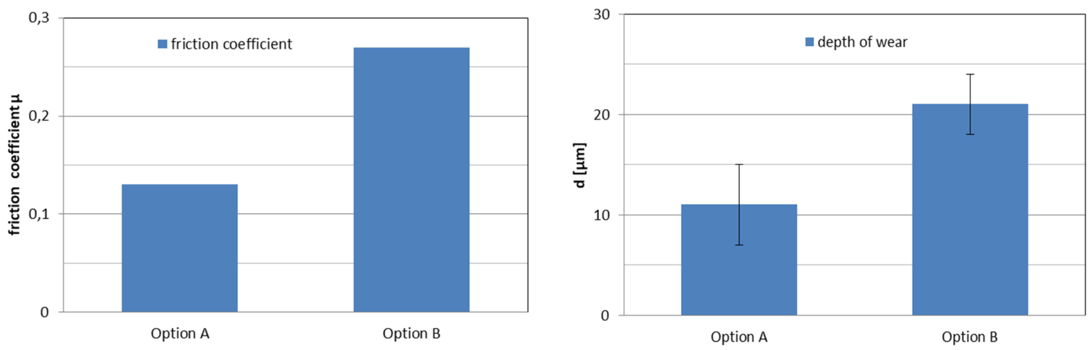


Figure 3. SEM Cross Sections and corresponding EDS of S, Mo and W distribution maps for layer option B.

The analysis of SEM pictures and EDS maps confirmed the incorporation phenomenon of low frictional particles MoS_2 and WS_2 into the structure of outer zone of hybrid layers.

The probable incorporation mechanism of them is the growth of ε iron nitrides during FineLPN and sulphonitriding processes outside of the original metallic surface due to reciprocal diffusion of iron ions through cationic defects in nitrides structure [35]. After the B process, the outer compound zone that contains sulphur and molybdenum is relatively shallow and tight (Figure 2). The application of additional sulphonitriding process after FineLPN treatment (option A) causes an important thickening as well as structural loosening of composite's outer zone that contains numerous and very fine inclusions of low frictional particles MoS_2 and WS_2, which are embedded in ε-nitrides porous matrix. That porous composite outer zone based on ε – iron nitrides matrix should be beneficial from a tribological point of view for both dry [25] and liquid friction conditions [26,36]. Additionally, a relatively deep (ca. 150 μm) and relatively hard (up to 700 HV) diffusive zone should decrease the development of frictional contact area and protect a nodular iron against hydrogen wear [24].

The low frictional and antiwear properties for optimized structure of hybrid layer (option A) have been confirmed by dry friction and oscillation tribological tests. The results of them are presented in Figure 4.



(**a**) (**b**)

Figure 4. (**a**) Comparison of friction coefficients obtained during tribological tests; (**b**) Comparison of the maximum depth of frictional tracks.

The specimens treated in the hybrid process according to the schedule and parameters of option A have shown an extremely low value of dry friction coefficient, 0.13, which is two-fold than the non-optimum layers, e.g., those treated to the schedule and parameters of option B (Figure 4). Also, the linear wear results after tribological tests have been twice as less for specimens treated according to the parameters A. That low frictional effect is the result of layered microstructure of numerous and relatively deep distributed MoS_2 and WS_2 inclusions. They have been incorporated relatively deep into hard ε – iron nitrides matrix. Therefore, they are durable structural sources of solid lubricant for long frictional action in piston rings – engine cylinders systems.

The obtained tribological test results allow to conclude that optimized hybrid layers contain both MoS_2 and WS_2 low frictional inclusions, and are well aerated by double thermo-chemical treatment (FineLPN + sulphonitriding). Thus, such new technology may represent an interesting alternative to replace and exclude the chromium-based galvanic coatings using Cr^{6+} from the manufacturing of piston rings made of nodular iron.

4. Conclusions

- The new hybrid, multistage technology—that consists of following stages: slurry coating, drying, sintering, FineLPN low pressure nitriding, and sulphonitriding thermochemical treatments—may be an interesting alternative for chromium-based galvanic coatings of piston rings made of nodular iron using Cr^{6+}.
- The optimum tribological properties of hybrid layers have been obtained for option of two low frictional particles MoS_2 and WS_2 and additional sulphonitriding heat treatment for important thickening, as well as the structural loosening of outer composite zone.
- The extremely low dry friction coefficient (0.13) and low linear wear have been revealed for the optimum hybrid layer, which were ca. twice as less in comparison to the benchmark technological solutions.
- The optimised low frictional effect is the result of a layered microstructure composed of numerous MoS_2 and WS_2 inclusions, which are and relatively deeply distributed in a hard ε – iron nitrides matrix.

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References

1. Williams, J. Boundary lubrication and friction. In *Engineering Tribology*; Cambridge University Press: Cambridge, UK, 2005; pp. 348–380. [CrossRef]
2. Neville, A.; Morina, T.; Haque, M.; Voong, M. Compatibility between tribological surfaces and lubricant additives—How friction and wear reduction can be controlled by surface/lubes synergies. *Tribol. Int.* **2007**, *40*, 1680–1695. [CrossRef]
3. Ostapski, W. Analysis of thermo-mechanical response in an aircraft piston engine by analytical, FEM, and test-stand investigations. *J. Therm. Stress.* **2011**, *34*, 285–312. [CrossRef]
4. Zabala, B.; Igartua, A.; Fernández, X.; Priestner, C.; Ofner, H.; Knaus, O.; Nevshupa, R. Friction and wear of a piston ring/cylinder liner at the top dead centre: Experimental study and modeling. *Tribol. Int.* **2017**, *106*, 23–33. [CrossRef]
5. Yamagata, H. *The Science and Technology of Materials in Automotive Engines*; Woodhead Publishing Limited: Cambridge, UK, 2005.
6. Chida, C.; Okano, M. Piston Ring. U.S. Patent US10385971B2, 20 August 2019.
7. Esser, P.K. Coated Piston Ring Having A Protective Layer. U.S. Patent Application US2019/0100836A1, 4 April 2019.

8. Sherrington, I.; Smith, E.H. Experimental methods for measuring the oil-film thickness between the piston-rings and cylinder-wall of internal combustion engines. *Tribol. Int.* **1985**, *18*, 315–320. [CrossRef]
9. Ali, M.K.A.; Hou, X.; Mai, L.; Cai, Q.; Turkson, R.F.; Chen, B. Improving the tribological characteristics of piston ring assembly in automotive engines using Al_2O_3 and TiO_2 nanomaterials as nano-lubricant additives. *Tribol. Int.* **2016**, *103*, 540–554. [CrossRef]
10. Bindumadhavan, P.N.; Makesh, S.; Gowrishnkar, N.; Wah, H.K.; Prabhakar, O. Aluminizing and subsequent nitriding of plain carbon low alloy steels for piston ring applications. *Surf. Coat. Tech.* **2000**, *127*, 251–258. [CrossRef]
11. Babu, M.V.; Kumar, R.K.; Prabhakar, O.; Shankar, N.G. Simultaneous optimization of flame spraying process parameters for high quality molybdenum coatings using Taguchi methods. *Surf. Coat. Tech.* **1996**, *79*, 276–288. [CrossRef]
12. Li, Y.; Dong, S.; He, P.; Yan, S.; Li, E.; Liu, X.; Xu, B. Microstructure characteristics and mechanical properties of new-type FeNiCr laser cladding alloy coating on nodular cast iron. *J. Mater. Process. Tech.* **2019**, *269*, 163–171. [CrossRef]
13. Zhou, Y.X.; Zhang, J.; Xing, Z.G.; Wang, H.D.; Lv, Z.L. Microstructure and properties of NiCrBSi coating by plasma cladding on gray cast iron. *Surf. Coat. Tech.* **2019**, *361*, 270–279. [CrossRef]
14. Arps, J.H.; Page, R.A.; Dearnaley, G. Reduction of wear in critical engine components using ion-beam-assisted deposition and ion implantation. *Surf. Coat. Tech.* **1996**, *84*, 579–583. [CrossRef]
15. Dahm, K.L.; Dearnley, P.A. Novel plasma-based coatings for piston rings. *Tribol. Ser.* **2002**, *40*, 243–246.
16. Karamış, M.B.; Yıldızlı, K.; Çakırer, H. An evaluation of surface properties and frictional forces generated from Al–Mo–Ni coating on piston ring. *Appl. Surf. Sci.* **2004**, *230*, 191–200. [CrossRef]
17. Kula, P.; Dybowski, K.; Lipa, S.; Batory, D.; Sawicki, J.; Wołowiec, E.; Klimek, L. Hybrid surface layers, made by nitriding with DLC coating, for application in machine parts regeneration. *Arch. Mater. Sci. Eng.* **2013**, *60*, 32–37.
18. Lin, J.; Wei, R.; Bitsis, D.C. Development and evaluation of low friction TiSiCN nanocomposite coatings for piston ring applications. *Surf. Coat. Tech.* **2016**, *298*, 121–130. [CrossRef]
19. Friedrich, C.; Berg, G.; Broszeit, E.; Rick, F.; Holland, J. PVD Cr_xN coatings for tribological application on piston rings. *Surf. Coat. Tech.* **1997**, *97*, 661–668. [CrossRef]
20. Fernández-Abia, A.I.; Barreiro, J.; Fernández-Larrinoa, J.; López de Lacalle, L.N.; Fernández-Valdivielso, A.; Pereira, O.M. Behaviour of PVD coatings in the turning of austenitic stainless steels. *Proc. Eng.* **2013**, *63*, 133–141. [CrossRef]
21. Rodriguez-Barrero, S.; Fernández-Larrinoa, J.; Azkona, I.; López de Lacalle, L.N.; Polvorosa, R. Enhanced performance of nanostructured coatings for drilling by droplet elimination. *Mater. Manuf. Process.* **2016**, *31*, 593–602. [CrossRef]
22. Prado, F.E.; Hilal, M.; Chocobar-Ponce, S.; Pagano, E.; Rosa, M.; Prado, C. Chapter 6—Chromium and the plant: A dangerous affair? In *Plant Metal Interaction*; Ahmad, P., Ed.; Elsevier: Amsterdam, The Netherlands, 2016; pp. 149–177.
23. Dayanç, A.; Karaca, B.; Kumruoğlu, L.C. Plasma nitriding process of cast camshaft to improve wear resistance. *Acta Phys. Pol. A* **2019**, *135*, 793–799. [CrossRef]
24. Kula, P. The comparison of resistance to "hydrogen wear" of hardened surface layers. *Wear* **1994**, *178*, 117–121. [CrossRef]
25. Kula, P. The "self-lubrication" by hydrogen during dry friction of hardened surface layers. *Wear* **1996**, *201*, 155–162. [CrossRef]
26. Kula, P.; Pietrasik, R.; Wendler, B.; Jakubowski, K. The effect of hydrogen in lubricated frictional couples. *Wear* **1997**, *212*, 199–205. [CrossRef]
27. Gawronski, Z.; Sawicki, J. Technological surface layer selection for small module pitches of gear wheels working under cyclic contact loads. *Mater. Sci. Forum* **2006**, *513*, 69–74. [CrossRef]
28. Sawicki, J.; Gorecki, M.; Kaczmarek, Ł.; Gawronski, Z.; Dybowski, K. Increasing the durability of pressure dies by modern surface treatment methods. *Chiang. Mai. J. Sci.* **2013**, *40*, 886–897.
29. Writzl, V.; Rovani, A.C.; Pintaude, G.; Lima, M.S.F.; Guesser, W.L.; Borges, P.C. Scratch resistances of compacted graphite iron with plasma nitriding, laser hardening, and duplex surface treatments. *Tribol. Int.* **2020**, *143*, 106081. [CrossRef]

30. Ampaw, E.K.; Arthur, E.K.; Badmos, A.Y.; Obayemi, J.D.; Adewoye, O.O.; Adetunji, A.R.; Olusunle, S.O.O.; Soboyejo, W.O. Sliding wear characteristics of pack cyanided ductile iron. *J. Mater. Eng. Perform.* **2019**, *28*, 7227–7240. [CrossRef]
31. Wołowiec-Korecka, E.; Kula, P.; Pawęta, S.; Pietrasik, R.; Sawicki, J.; Rzepkowski, A. Neural computing for a low-frictional coatings manufacturing of aircraft engines' piston rings. *Neur. Comput. Appl.* **2019**, *31*, 4891–4901. [CrossRef]
32. Watanabe, S.; Noshiro, J.; Miyake, S. Tribological characteristics of WS_2/MoS_2 solid lubricating multilayer films. *Surf. Coat. Tech.* **2004**, *183*, 347–351. [CrossRef]
33. Wong, K.C.; Lub, X.; Cotter, J.; Eadie, D.T.; Wong, P.C.; Mitchell, K.A.R. Surface and friction characterization of MoS_2 and WS_2 third body thin films under simulated wheel/rail rolling–sliding contact. *Wear* **2008**, *264*, 526–534. [CrossRef]
34. Kula, P.; Pietrasik, R.; Paweta, S.; Patent Office of the Republic of Poland. Low-friction layer from Nanocomposite Gradient Material and Method for Producing It. Poland Patent PL233113B1, 30 September 2019.
35. Kocemba, I.; Szynkowska, M.I.; Mackiewicz, E.; Goralski, J.; Rogowski, J.; Pietrasik, R.; Kula, P.; Kaczmarek, L.; Jóźwik, K. Adsorption of gas-phase elemental mercury by sulphonitrided steel sheet. Effect of hydrogen treatment. *J. Hazard Mater.* **2019**, *368*, 722–731. [CrossRef]
36. Liskiewicz, G.; Kula, P.; Neville, A.; Pietrasik, R.; Morina, A.; Liskiewicz, T. Hydrogen influence on material interaction with ZDDP and MoDTC lubricant additives. *Wear* **2013**, *297*, 966–971. [CrossRef]