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Review

Tribofilm Formation As a Result of Complex Interaction at the Tool/Chip Interface during Cutting

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Abstract: Tribofilms are dynamic structures that form at the interface during frictional sliding. These films play a significant role in friction control, particularly under heavy loaded/high temperature conditions, such as those found at the cutting tool/chip interface. The thermodynamic aspects of tribofilm formation are discussed here. Thermodynamic analysis of entropy production during friction shows that there are two types of tribofilms that affect the wear behavior of a cutting tool: (1) tribofilms forming as a result of the surface modification of the cutting tools with further tribo-oxidation; and (2) tribofilms that form as a result of material transfer from the contacting frictional body (the workpiece) during the tool/chip interaction. Experimental examples are presented, outlining the beneficial role of both types of tribofilms.

Keywords: tribofilms; cutting tool; thermodynamic analysis

1. Introduction

The frictional behavior of contacting surfaces depends strongly on the formation of tribofilms at the interface. Comprehensive reviews on tribofilms have been previously published [1,2]. As stressed in these articles, the importance of tribofilms is frequently underestimated. Researchers, mechanical designers and material developers have repeatedly drawn the wrong conclusions, since their models of tribological materials were too simplistic [1].

Tribofilms, being self-organized patterns [3–5], form as a result of (1) the transformation (structural/chemical) of an existing surface layer through interaction with the environment [2–7]; or (2) material transfer from the counter body (due to chips sticking to the tool rake surface) with the further formation of a modified layer on top of the original surface [1]. Tribofilms carry out protective, thermal barrier and lubricating functions.

Various features of tribofilms (or secondary structures, *i.e.*, generated during friction) were intensively studied [6–17]. The tribofilms generated during friction can be divided into lubricating [6] and hard ceramic tribo-phases [7]. A relationship was proven to exist between tribofilm formation and self-organization during friction [18]. The thermodynamical aspect of tribofilm formation has been outlined in [18,19].

According to the principle of "dissipative heterogeneity" [8], there occurs a phenomenon of the structural adaptation of tribo-materials, which leads to the concentration of the larger part of the interactions between frictional bodies within the thin layer of the tribofilms (secondary structures, SS) [7,12]. The depth of the layer can be an order of magnitude (or even magnitudes) lower than that typically associated with damage phenomena [12].

One of the most heavily-loaded tribo-systems known is found in manufacturing tooling applications [20]. The tool-workpiece tribo-system works under heavy (up to 5 GPa) loads and high (1200 °C and above) temperature conditions [20,21]. The major portion of the energy of friction during machining transforms to heat and dissipates through various channels (via chip removal, into the workpiece, into the environment, and so on [22]). However, an appreciable fraction of frictional energy is accumulated within the tribofilm layer [8]. Therefore, the tribofilm layer can be considered as a steady-state zone, where intensive energy dissipation and accumulation is happening, which decisively affects wear resistance under severe/extreme operational conditions.

The goal of this paper is to perform thermodynamic analysis of tribofilms formation for specific conditions of cutting considering various ways that they may be generated at the cutting tool-workpiece interface. Based on the results of such an analysis, some ways to control friction are outlined by means of the proper selection and development of tooling materials for specific machining applications to improve the wear resistance of the cutting tools.

2. Results and Discussion

2.1. Thermodynamics of Tribofilms

To understand the mechanisms of tribofilm formation, consideration of the self-organizing process during friction has to be made based on the thermodynamic analysis of the cutting tool-workpiece tribo-system [4].

As shown in detail in [9], the change of entropy of a frictional body (dS) is:

$$\mathrm{d}S = \mathrm{d}S_\mathrm{i} + \mathrm{d}S_\mathrm{e} + \mathrm{d}S_\mathrm{m} + \mathrm{d}S_\mathrm{f} - \mathrm{d}S_\mathrm{w} \quad (1)$$

After differentiation with respect to time, Equation (1) in a stationary condition will look like:

$$\mathrm{d}S/\mathrm{d}t = 0 = \mathrm{d}S_\mathrm{i}/\mathrm{d}t + \mathrm{d}S_\mathrm{e}/\mathrm{d}t + \mathrm{d}S_\mathrm{m}/\mathrm{d}t + \mathrm{d}S_\mathrm{f}/\mathrm{d}t - \mathrm{d}S_\mathrm{w}/\mathrm{d}t$$

or:

$$\mathrm{d}S_\mathrm{w}/\mathrm{d}t = \mathrm{d}S_\mathrm{i}/\mathrm{d}t + \mathrm{d}S_\mathrm{e}/\mathrm{d}t + \mathrm{d}S_\mathrm{m}/\mathrm{d}t + \mathrm{d}S_\mathrm{f}/\mathrm{d}t \quad (2)$$

For the cutting tool-chip interface, this equation should be slightly modified:

$$\mathrm{d}S_\mathrm{w}/\mathrm{d}t = \mathrm{d}S_\mathrm{i}/\mathrm{d}t + \mathrm{d}S_\mathrm{e}/\mathrm{d}t \pm \mathrm{d}S_\mathrm{m}/\mathrm{d}t - \mathrm{d}S_\mathrm{f}/\mathrm{d}t$$

where:

$\mathrm{d}S_\mathrm{i}/\mathrm{d}t$—the entropy production as a result of the distribution of heat and other flows within a body;

$\mathrm{d}S_\mathrm{e}/\mathrm{d}t$—the flow of entropy due to external interactions, which could change due to the transition of heat from a frictional surface with a higher temperature into a body (the cutting tool) with a lower temperature, resulting in an entropy increase;

$\mathrm{d}S_\mathrm{m}/\mathrm{d}t$—the change of entropy due to the formation of chemical compounds on the tool surface due to the entropy of the matter transferred from the contacting frictional body (the workpiece). In the case of the tool-chip interaction, it can be either positive, due to cutting tool-chip interactions with the further formation of seizure zones or build-ups that tend to break away and eventually cause deep surface damage [23], or negative when the material transformed to the tool surface either forms lubricants (MnS for example) or interacts with the environment (tribo-oxidation), forming lubricating tribofilms [1,23];

$\mathrm{d}S_\mathrm{f}/\mathrm{d}t$—the change of entropy due to tribofilm formation as a result of the surface modification of the cutting tools with further tribo-oxidation;

$\mathrm{d}S_\mathrm{w}/\mathrm{d}t$—the change of entropy due to the wear process (the "−" sign is used in the Equation 2, because the products of the wear process leave the frictional body with their own entropy). The change of entropy, $\mathrm{d}S_\mathrm{f}/\mathrm{d}t$, could be negative if non-equilibrium processes are occurring on the surface and the entropy of a frictional body is reduced (which is typical for cutting tools [24,25]), or it could be positive if there are equilibrium processes [9]. However, the sum of these terms, *i.e.*, $\mathrm{d}S_\mathrm{i}/\mathrm{d}t + \mathrm{d}S_\mathrm{f}/\mathrm{d}t > 0$, is the general entropy production [18]. As follows from (2), lower entropy production corresponds to a lower $\mathrm{d}S_\mathrm{w}/\mathrm{d}t$ value. Bearing in mind that entropy is an additive value, we can consider that the lower $\mathrm{d}S_\mathrm{w}/\mathrm{d}t$, the lower the wear rate. Therefore, the entropy production decrease leads to wear rate reduction. Non-equilibrium processes on the surface ($\mathrm{d}S_\mathrm{f}/\mathrm{d}t < 0$) and the formation of lubricating tribofilms due to material transfer from the workpiece with its further tribo-oxidation ($\mathrm{d}S_\mathrm{m}/\mathrm{d}t < 0$), with all other conditions being equal, can also lead to a wear rate decrease.

It has been found that there are two types of tribofilms that are formed on the frictional body as a result of structural modification and interaction with the environment: (1) super-ductile and lubricating films [12]; and (2) tribo-ceramics with thermal barrier properties and increased hardness and strength [10,24,26,27,30–39]. Tribofilms (SS) of the first type (SS-I) are observed as a result of structural activation marked by an increase in the density of atomic defects at the surface. Tribofilms are supersaturated solid solutions formed by reaction with elements from the environment (most often, oxygen). In these secondary structures, the material may be super-plastic (due to a nano-scale grained or amorphous-like structure) [6,7]. Secondary structures of this type mostly promote energy dissipation during friction.

Tribofilms (SS) of the second type (SS-II or tribo-ceramics containing a higher content (%) of elements, such as oxygen) are primarily formed by thermal activation processes. The SS-IIs are usually non-stoichiometric compounds [6,7]. Secondary structures of this type exhibit mostly surface protective properties due to their high thermodynamic stability, thermal barrier properties and high hot hardness [12–14]. The adaptation of the tribo-system, in this case, relies on a low intensity chemical interaction with the workpiece, the beneficial heat distribution on the friction surface and the high hardness of the tribofilms. This results in a low entropy production during friction and, obviously, a decrease in the wear rate. On the other hand, the destruction of these hard films could be prevented by proper surface engineering of the substrate material, which ensures effective support of the tribofilms during friction. Depending on their chemical composition, tribo-oxides can also provide high temperature lubricating properties that benefit energy dissipation [4].

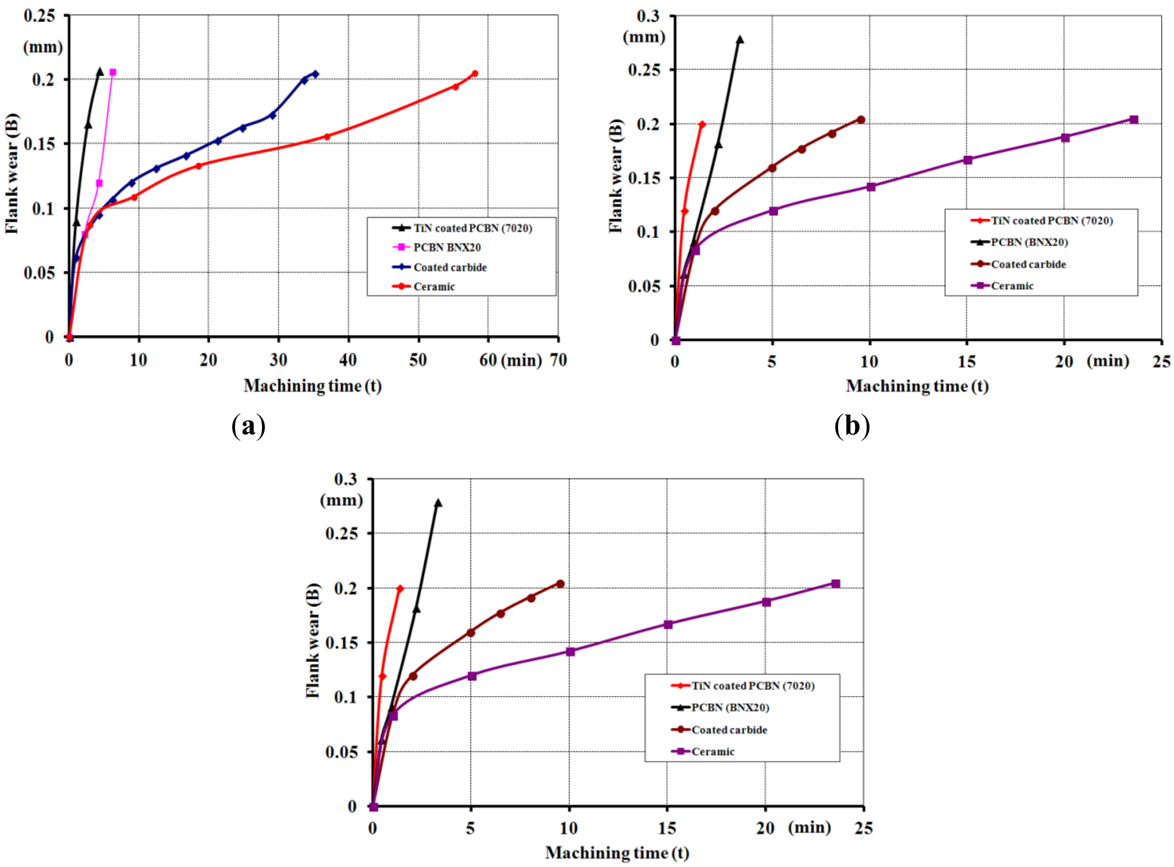
2.2. Experimental Examples of Tribofilm Formation

In relation to the Equation (2), two examples are presented illustrating the beneficial role of both types of tribofilms. The films have been formed as a result of (1) the surface modification of the cutting tool material [17,44,45]; and (2) due to the transfer from the workpiece with further tribo-oxidation [1,46].

Example 1: Figure 1 shows cutting tool life data during hard turning of HSS (T 15) with the hardness of HRC 52 [31]. Under aggressive cutting conditions (a speed above 100 m/min), ceramic inserts, (Al_2O_3 + TiC) followed by a coated carbide tool with an intermediate ceramic (Al_2O_3) layer show the best tool life when compared to two types of PCBN (low content PCBN and PVD TiN-coated PCBN). This is related to a number of different beneficial characteristics of the ceramic and coated carbide inserts, including the ability to form protective alumina tribofilms on the friction surface, as confirmed by Raman data presented in Figure 2 [31]. Similar results of the surface modification of the cutting tool were presented elsewhere [4,17]. A major feature of these protective tribofilms is their ability to accumulate frictional energy.

As is shown in Figure 2, the addition of material transferred from the workpiece along with further tribo-oxidation results in a small, but well-defined and sharp peak at 420 cm^{-1} associated with the formation and/or promotion in the surface of Al_2O_3 (Spectrum 3) due to tribo-oxidation of the tool surface. Raman spectra were coupled to EDX analysis (Figure 3) in order to confirm the formation of alumina.

Figure 1. Machining time *vs.* flank wear for the four different cutting tools at (**a**) 20 m/min; (**b**) 100 m/min; and (**c**) 200 m/min. CT1, CBN; CT2, with TiN PVD coating; CT3, mixed alumina ceramic (Al_2O_3 (70%) + TiC (30%)); CT4, TiC/TiCN/Al_2O_3/TiN coating on a carbide insert; the feed and the depth of the cut were kept constant at 0.05 mm/rev and 0.15 mm, respectively [31].



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

Figure 2. SEM micrograph (**a**) of CT3 used in the 100 m/min test and Raman spectra (**b**) of numerically-labeled regions [31].

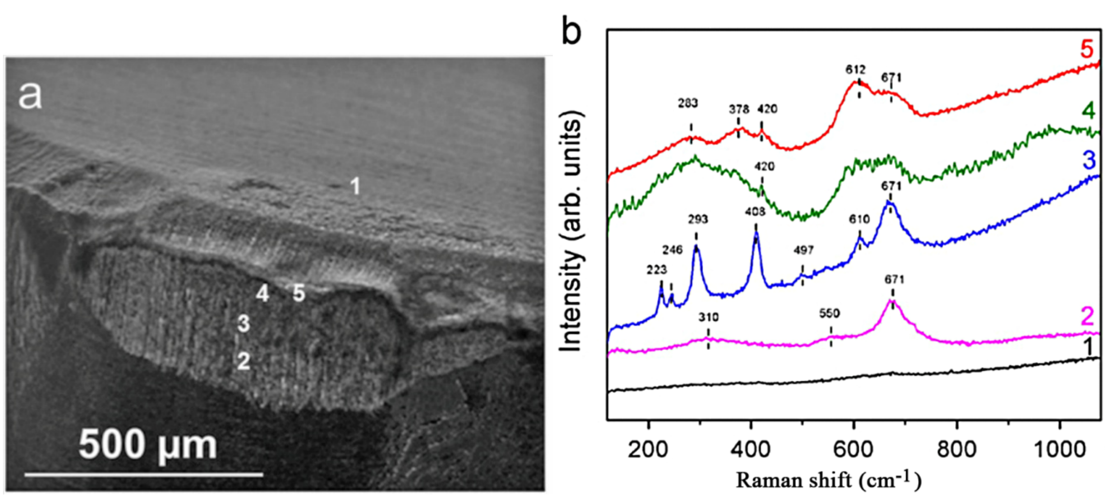


Figure 3. SEM micrograph (**a**) of CT3 used in the 100 m/min test and EDS spectra (**b**) of numerically-labeled regions; ♦ corresponds to typical gold energy [31].

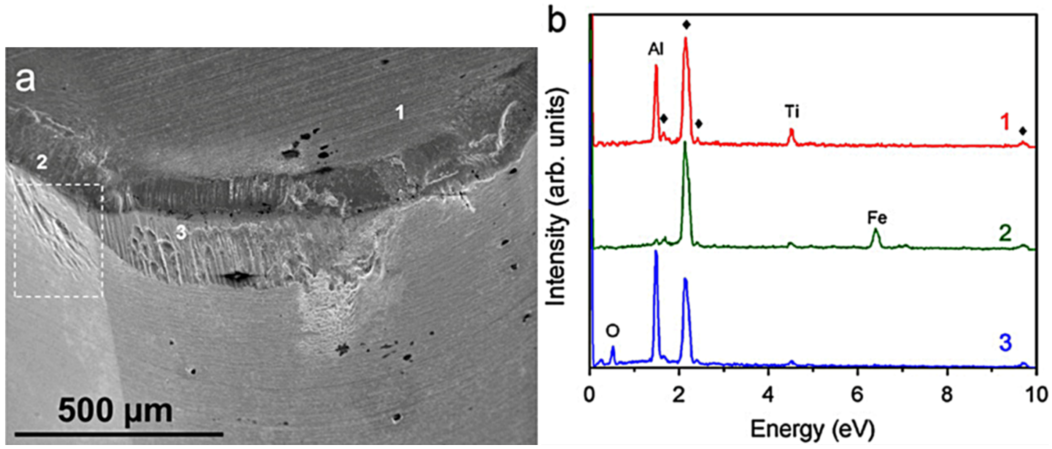
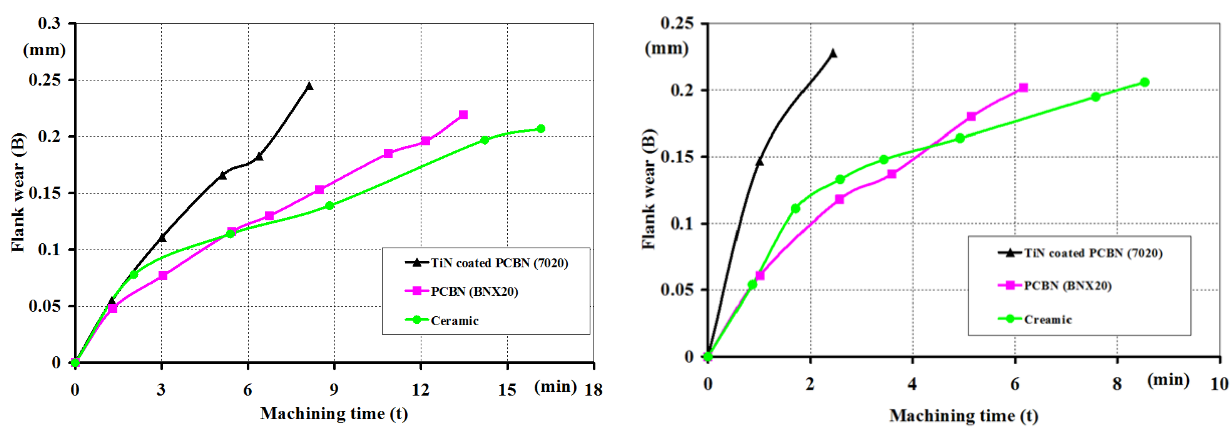


Figure 3 shows the SEM image and EDS spectra of a ceramic tool. EDS analysis of the cutting tool shows the presence of titanium and aluminum (Spectrum 1). Depending on the studied zone, different elements are identified. Spectrum 2 reveals the presence of iron and titanium, and Spectrum 3 (at the beginning of the trailing zone) shows a large peak corresponding to aluminum and oxygen.

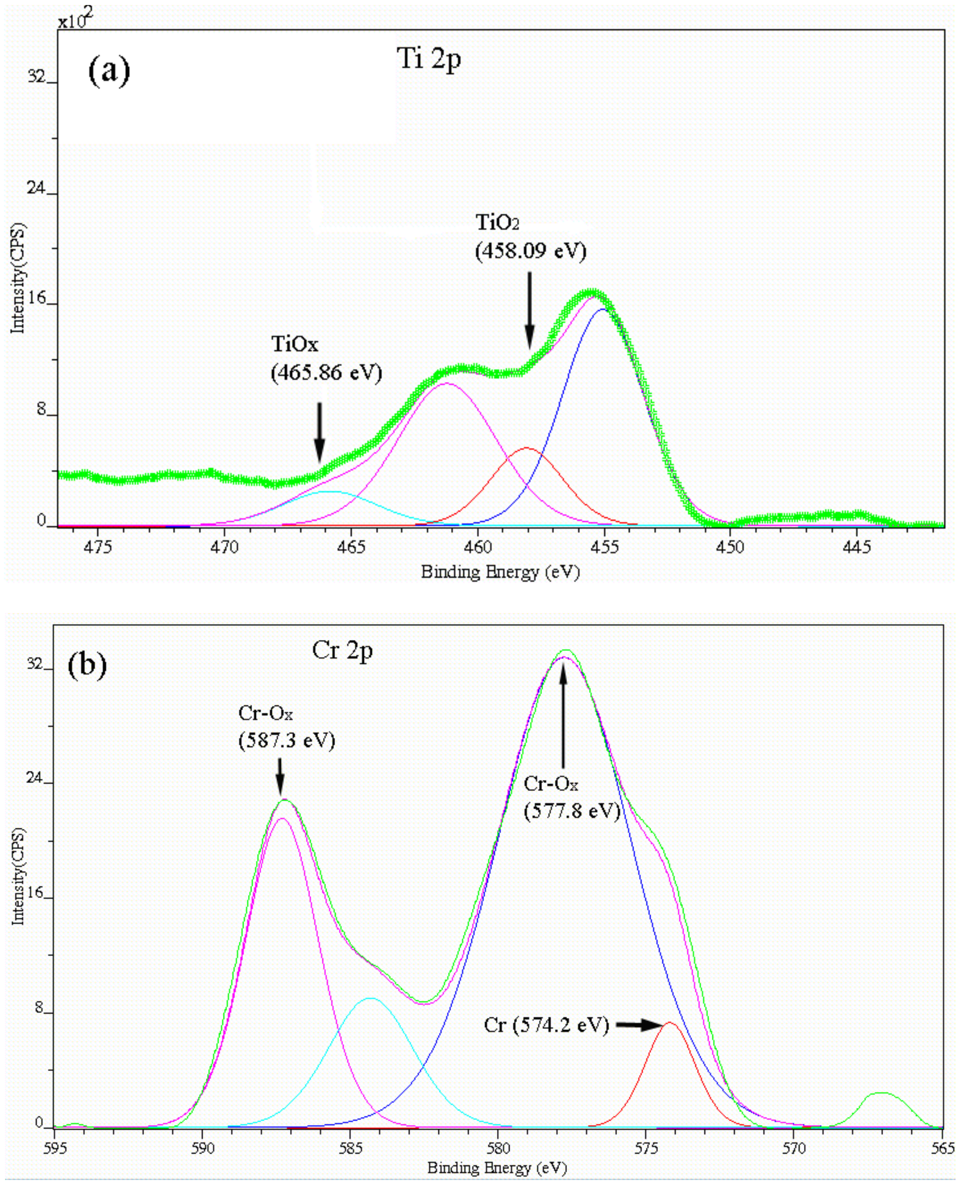
Example 2: Figure 4 presents the tool life data during hard turning of D 2 steel with a hardness of HRC 52 [46]. The same ceramic insert mentioned in Example 1 also shows the best tool life in comparison to TiN-coated and uncoated PCBN. This is associated with a number of characteristics of the ceramic tool, including its ability to promote the formation of high temperature lubricating Cr-O tribofilms on the friction surface, as confirmed by XPS studies of the worn tools (Figure 5) [46]. Formation of such tribofilms promotes energy dissipation during friction, which benefits tool life [1,4]. The formation of these tribofilms is caused by material transfer from the counter body (workpiece), along with further tribo-oxidation at the tool surface [1]. A major feature of these high temperature lubricating tribofilms is their ability to dissipate the energy of friction.

Figure 4. Wear curves at different cutting speeds using the different tool materials: (**a**) v_c = 100 m/min and (**b**) v_c = 175 m/min; a_p = 0.06 mm, f = 0.05 mm/rev, $r_ε$ = 1.2 mm [46].



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

Figure 5. Photoelectron spectra of the (**a**) Ti 2p and (**b**) Cr 2p region taken from the worn rake surface of a ceramic tool [46].



It is worth noting that the tribofilms studied are closely related to the generic concept of the tribological compatibility of the cutting tool-workpiece tribo-system. Tribological compatibility is related to the capacity of two surfaces to adapt to each other during friction, providing wear stability to the two components of the specific tribo-system, for the longest period of time [11]. The goal is to achieve stable tool service and a predictable rate of wear with a given set of operating parameters. In this interpretation, as was outlined above, compatibility implies an integrated optimization, both from an engineering (minimal wear rate) and physical (self-organizing) point of view [4,5,11,19]. The tribological compatibility of the tool-workpiece tribo-system could be achieved, in particular, by the proper selection of the tooling materials, such as hard/lubricating PVD coatings [47]. Alternatively, it could be realized by the promotion of beneficial tribofilms formation, as a result of material transfer to the cutting tool surface from the workpiece, as is shown in Figure 4.

3. Conclusions

The results show that each type of tribofilm, either formed due to the structural/chemical modification of the tooling material or due to the material transfer from the counter body with further tribo-oxidation, can lead to the improvement of tool life if it exhibits the ability to accumulate or dissipate the energy of friction.

It is time to understand that the frictional surface becomes strongly modified either by the change of the original material, or due to the transfer of material from the counter body. Therefore, tribological materials should be tuned to achieve optimum properties after these transformations. Friction control by means of beneficial tribofilm formation makes it possible to improve the wear resistance of the tool-workpiece tribo-couple. To perform this task, the proper selection and development of tooling materials or coatings have to be adjusted for specific machining applications. Simultaneous optimization of machining parameters could be also very beneficial.

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Author Contributions

German S. Fox-Rabinovich, paper writing, thermodynamic modeling; Iosif Gershman, thermodynamic modeling; Mohamed A. El Hakim, cutting test performance and planning; Mohamed A. Shalaby, cutting test performance and tool wear evaluation; James E. Krzanowski, XPS analysis; Stephen Veldhuis, cutting tests supervision.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Jacobson, S.; Hogmark, S. Tribofilms—On the crucial importance of tribologically induced surface modification. In *Recent Developments in Wear Prevention, Friction and Lubrication*; Nikas, G.K., Ed.; Research Signpost: Kerala, India, 2010; p. 19.
2. Morina, A.; Neville, A. Tribofilms: Aspects of formation, stability and removal. *J. Phys. D Appl. Phys.* **2007**, *40*, 5476–5487.
3. Fox-Rabinovich, G.S. Adaptive hard coatings design based on the concept of self-organization during friction. In *Encyclopedia of Tribology*; Wang, Q.J., Chung, Y.-W., Eds.; Springer: London, UK, 2013; pp. 16–23.

4. Bushe, N.; Gershman, I. Tribological compatibility and nanotribological characteristics. In *Self-Organization during Friction: Advance Surface Engineered Materials and Systems Design*; Fox-Rabinovich, G.S., Totten, G., Eds.; CRC Press, Taylor and Francis Group: Boca Raton, NW, USA, 2006.
5. Fox-Rabinovich, G.S. Principles of friction control for the surface engineered materials. In *Self-organization during Friction: Advanced Surface Engineered Materials and Systems Design*; Fox-Rabinovich, G.S., Totten, G., Eds.; CRC Press, Taylor and Francis Group: Boca Raton, NW, USA, 2006; pp. 3–13.
6. Kostetsky, B.I. Structural-energetic adaptation of materials at friction. *Frict. Wear* **1985**, *6*, 201–212.
7. Kostetsky, B.I. An evolution of the materials' structure and phase composition and the mechanisms of the self-organizing phenomenon at external friction. *Frict. Wear***1993**, *14*, 773–783.
8. Bershadskiy, L.I. On self-organizing and concept of tribosystem self-organizing. *Frict. Wear* **1992**, *8*, 1077–1094.
9. Gershman, J.S.; Bushe, N.A. Thin films and self-organization during friction under the current collection conditions. *Surf. Coat. Technol.* **2004**, *186*, 405–411.
10. Fox-Rabinovich, G.S.; Yamamoto, K.; Beake, B.D.; Gershman, I.S.; Kovalev, A.I.; Aguirre, M.H.; Veldhuis, S.C.; Dosbaeva, G.; Endrino, J.L. Hierarchical adaptive nano-structured PVD coatings for extreme tribological applications: The quest for non-equilibrium states and emergent behavior. *Sci. Technol. Adv. Mater. (STAM)* **2012**, *13*, doi:10.1088/1468-6996/13/4/043001.
11. Bushe, N.A.; Kopitko, V.V. *Compatibility of Rubbing Surfaces*; Nauka: Moscow, Russia, 1981.
12. Kostetsky, B.I. *Friction, Lubrication and Wear in Machines*; Technika: Kiev, Ukraine, 1970.
13. Ivanova, V.S.; Bushe, N.A.; Gershman, I.S. Structure adaptation at friction as a process of self-organization. *Frict. Wear* **1997**, *18*, 74–79.
14. Kostetskaya, N.B. Structure and Energetic Criteria of Materials and Mechanisms Wear-Resistance Evaluation. Ph.D. Thesis, Kiev State University, Kiev, Ukraine, 1985.
15. Kostetskaya, N.B. Mechanisms of deformation, fracture and wear particles forming during the mechanical-chemical friction. *Frict. Wear* **1990**, *16*, 108–115.
16. Ivanova, V.S. Fracture synergetic and mechanical properties. In *Synergetic and Fatigue Fracture of Metals*; Nauka: Moscow, Russia, 1989; pp. 6–27.
17. Kabaldin, Y.G.; Kojevnikov, N.V.; Kravchuk, K.V. HSS cutting tool wear resistance study. *Frict. Wear* **1990**, *11*, 130–135.
18. Gershman, I.S.; Bushe, N.A. Fundamentals of Non-Equilibrium Thermodynamics and Self-organization at Friction. In *Self-organization during Friction: Advanced Surface Engineered Materials and Systems Design*; Fox-Rabinovich, G.S., Totten, G., Eds.; CRC Press, Taylor and Francis Group: Boca Raton, NW, USA, 2006; pp. 13–59.
19. Gershman, I.S.; Bushe, N.A. Compatibility of tribo-systems. In *Self-organization during Friction: Advanced Surface Engineered Materials and Systems Design*; Fox-Rabinovich, G.S., Totten, G., Eds.; CRC Press, Taylor and Francis Group: Boca Raton, NW, USA, 2006; pp. 59–81.
20. Bouzakis, K.D.; Michailidis, N.; Scordaris, G.; Bouzakis, E.; Biermann, D.; M'Saoubi, R. Cutting with coated tools: Coating technologies, characterization methods and performance optimization. *CIRP Ann. Manuf. Technol.* **2012**, *61*, 703–723.

21. Ning, L.; Veldhuis, S.C.; Yamamoto, K. Investigation of wear behavior and chip formation for cutting tools with nano-multilayered TiAlCrN/NbN PVD coating. *Int. J. Mach. Tools Manuf.* **2008**, *48*, 656–665.
22. Astakhov, V.P. *Tribology of Metal Cutting*; Elsevier: London, UK, 2006.
23. Wright, P.; Trent, E. *Metal Cutting*, 4th ed.; Butterworth-Heinemann: Boston, MA, USA, 2000.
24. Fox-Rabinovich, G.S.; Kovalev, A.I.; Veldhuis, S.C.; Shuster, L.S.; Gershman, I.S. Surface Engineered Tool Materials for High Performance Machining. In *Self-organization during Friction: Advanced Surface Engineered Materials and Systems Design*; Fox-Rabinovich, G.S., Totten, G., Eds.; CRC Press, Taylor and Francis Group: Boca Raton, NW, USA, 2006; pp. 231–297.
25. Mah, T.I.; Mazdiyasni, K.S. Mechanical properties of mullite. *J. Am. Ceram. Soc.* **1983**, *66*, 699–703.
26. Hulse, C.O.; Pask, J.A. Analysis of deformation of fireclay refractory. *J. Am. Ceram. Soc.* **1966**, *49*, 312–318.
27. Lessing, P.A.; Gordon, R.S.; Mazdiyasni, K.S. Creep of polycrystalline mullite. *J. Am. Ceram. Soc.* **1975**, *58*, doi:10.1111/j.1151-2916.1975.tb19585.x.
28. Osendi, M.I.; Baudín, C. Mullitematerials: Microstructural evolution. *J. Eur. Ceram. Soc*. **1996**, *16*, 217–224.
29. Aksay, I.A.; Dabbs, D.M.; Sarikaya, M. Mullite for structural, electronic and optical applications. *J. Am. Ceram. Soc.* **1991**, *74*, 2343–2358.
30. Hynes, A.P.; Doremus, R.H. High-temperature compressive creep of polycrystallinemullite. *J. Am. Ceram. Soc.* **1991**, *74*, 2469–2475.
31. El Hakim, M.A.; Abad, M.D.; Abdelhameed, M.M.; Shalaby, M.A.; Veldhuis, S.C. Wear behavior of some cutting tool materials in hard turning of HSS. *Tribol. Int.* **2011**, *44*, 1174–1181.
32. Fox-Rabinovich, G.; Kovalev, A.; Aguirre, M.H.; Yamamoto, K.; Gershman, I.; Rashkovskiy, A.; Endrino, J.L.; Beake, B.; Veldhuis, S.; Dosbaeva, G.; *et al*. Evolution of self-organization in nano-structured PVD coatings under extreme tribological conditions. *Appl. Surf. Sci.* **2014**, *297*, 22–32.
33. Fox-Rabinovich, G.S.; Endrino, J.L.; Agguire, M.H.; Beake, B.D.; Veldhuis, S.C.; Kovalev, A.I.; Gershman, I.S.; Yamamoto, K.; Losset, Y.; Wainstein, D.L.; *et al*. Mechanism of adaptability for the nano-structured TiAlCrSiYN-based hard PVD coatings under extreme frictional conditions. *J. Appl. Phys.* **2012**, *111*, doi:10.1063/1.3693032.
34. Beake, B.D.; Fox-Rabinovich, G.S.; Losset, Y.; Yamamoto, K.; Agguire, M.H.; Veldhuis, S.C.; Endrino, J.L.; Kovalev, A.I. Why can TiAlCrSiYN-based adaptive coatings deliver exceptional performance under extreme frictional conditions? *Faraday Discuss.* **2012**, *156*, 1–11.
35. Kovalev, A.; Wainstein, D.; Rashkovskiy, A.; Fox-Rabinovich, G.; Veldhuis, S.; Agguire, M.; Yamamoto, K. Investigation of electronic and atomic structure of tribofilms on the surface of cutting tools with TiAlCrSiYN and multilayer TiAlCrSiYN/TiAlCrN coatings during machining of hardened steels. *Surf. Interface Anal.* **2010**, *42*, 1368–1372.

36. Fox-Rabinovich, G.S.; Yamamoto, K.; Beake, B.D.; Kovalev, A.I.; Aguirre, M.H.; Veldhuis, S.C.; Dosbaeva, G.K.; Wainstein, D.L.; Biksa, A.; Rashkovskiy, A. Emergent behavior of nano-multilayered coatings during dry high speed machining of hardened tool steels. *Surf. Coat. Technol.* **2010**, *204*, 3425–3435.
37. Kovalev, A.; Wainstein, D.; Fox-Rabinovich, G.; Veldhuis, S.; Yamamoto, K. Features of self-organization in nanostructuring PVD coatings on a base of polyvalent metal nitrides under severe tribological conditions. *Surf. Interface Anal.* **2008**, *40*, 881–884.
38. Fox-Rabinovich, G.S.; Veldhuis, S.C.; Dosbaeva, G.K.; Yamamoto, K.; Gershman, I.S.; Kovalev, A.; Beake, B.D.; Shuster, L.S. Nano-crystalline coating design for extreme applications based on the concept of complex adaptive behavior. *J. Appl. Phys.* **2008**, *103*, doi:10.1063/1.2904907.
39. Fox-Rabinovich, G.; Kovalev, A.; Gershman, I.; Korshunov, S.; Veldhuis, S.; Beake, B.; Endrino, J.; Wainstein, D.L. Features of self-organization in ion modified nano-crystalline PVD AlTiN coatings under severe tribological conditions. *JAP* **2007**, *102*, doi:10.1063/1.2785947.
40. Biksa, A.; Yamamoto, K.; Dosbaeva, G.; Veldhuis, S.C.; Fox-Rabinovich, G.S.; Wagg, T.; Elfizy, A.; Shusterd, L.S. Wear behavior of adaptive nano-multilayered AlTiN/MexN PVD coatings during machining of aerospace alloys. *Tribol. Int.* **2010**, *43*, 1491–1499.
41. Fox-Rabinovich, G.S.; Yamamoto, K.; Kovalev, A.I.; Veldhuis, S.C.; Ning, L.; Shuster, L.S. Wear behavior of adaptive nano-multilayered TiAlCrN/NbN coatings under dry high performance machining conditions. *Surf. Coat. Technol.* **2008**, *202*, 2015–2022.
42. Fox-Rabinovich, G.S.; Yamamoto, K.; Veldhuis, S.C.; Kovalev, A.; Shuster, L.S.; Ning, L. Self-adaptive wear behavior of nano-multilayered TiAlCrN/WN coatings under severe machining conditions. *Surf. Coat. Technol.* **2006**, *201*, 1852–1860.
43. Fox-Rabinovich, G.S.; Yamamoto, K.; Veldhuis, S.C.; Kovalev, A.; Dosbaeva, G.K. Tribological Adaptability of TiAlCrN PVD Coatings under High Performance Dry Machining Conditions. *Surf. Coat. Technol.* **2005**, *200*, 1804–1813.
44. Hovsepian, P.E.; Luo, Q.; Robinson, G.; Pittman, M.; Howarth, M.; Doerwald, D. TiAlN/VN superlattice structured PVD coatings: A new alternative in machining of aluminium alloys for aerospace and automotive components. *Surf. Coat. Technol.* **2006**, *201*, 265–270.
45. Mayrhofer, P.H.; Mitterer, C.; Hultman, L.; Clemens, H. Microstructural design of hard coatings. *Prog. Mater. Sci.* **2006**, *51*, 1032–1114.
46. Shalaby, M.A.; El Hakim, M.A.; Abdelhameed, M.M.; Krzanowski, J.E.; Veldhuis, S.C.; Dosbaeva, S.C. Wear mechanisms of several cutting tool materials in hard turning of high carbon-chromium tool steel. *Tribol. Int.* **2014**, *70*, 148–154.
47. Veldhuis, S.C.; Dosbaeva, G.K.; Yamamoto, K. Tribological compatibility and improvement of machining productivity and surface integrity. *Tribol. Int.* **2009**, *42*, 1004–1010.