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Synthesis and Tribological Properties of WSe₂ Nanorods

Jinghai Yang · Haixia Yao · Yanqing Liu ·
Yongjun Zhang

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Abstract The WSe₂ nanorods were synthesized via solid-state reaction method and characterized by X-ray diffractometer, TEM, and HRTEM. The results indicated the WSe₂ compounds had rod-like structures with diameters of 10–50 nm and lengths of 100–400 nm, and the growth process of WSe₂ nanorods was discussed on the basis of the experimental facts. The tribological properties of WSe₂ nanorods as additives in HVI500 base oil were investigated by UMT-2 multispecimen tribotester. Under the determinate conditions, the friction coefficient of the base oil containing WSe₂ nanorods was lower than that of the base oil, and decreased with increasing mass fraction of WSe₂ nanorods when it was <7 wt.%. Moreover, the base oil with the additives was rather suited to high load and high rotating speed. A combination of rolling friction, sliding friction, and stable tribofilm on the rubbing surface could explain the good friction and wear properties of WSe₂ nanorods as additives.

Keywords WSe₂ nanorods · Growth mechanism · Lubrication additive · Tribological properties · Rotating speed

Introduction

The transition-metal dichalcogenides (including disulfide and diselenium) showed a wide variety of interesting physical properties, such as semiconducting, metallic, superconducting, and magnetic behavior [1–7]. WSe₂ was

an interesting member of the transition-metal dichalcogenides family. It was a semiconductor with a band gap in the range of 1.2–2 eV, which was useful for photovoltaic and optoelectronic applications [8–10]. WSe₂ possessed a layered structure with the metal atoms (W) bonded covalently between the layers of chalcogen atoms (Se), and the remarkable feature of the WSe₂ was highly antiphotocorrosive due to the observation of layered structure, which made it as a strong candidate in the development of high efficiency photoelectrochemical solar cells [11].

In the past few decades, the disulfides, such as MoS₂ and WS₂, had been extensively studied as lubrication additive on reducing friction and wear of rubbing pairs [12, 13]. The friction-and-wear mechanism had been discussed in great detail [14–19]. However, little work focused on the preparation of WSe₂ nanorods, which was similar to the WS₂ nanorods, especially the tribological properties of WSe₂ as lubrication additive.

In this study, we reported a simple and benign method to prepare WSe₂ nanorods using W and Se (mole ratio 1:3) at 800 °C in an argon atmosphere. Moreover, the tribological properties of WSe₂ nanorods as additives in the HVI500 base oil were also investigated.

Experimental

Preparation of WSe₂ Nanorods

All chemicals used in the experiment were from state reagent without any further purification. In a typical procedure, high-purity tungsten, selenium powders (mole ratio W:Se = 1:3), and agate balls with diameter of 8 mm were mixed in an agate jar and mechanically milled with QM-ISP2 apparatus for 50 h at 450 rpm. After ball milling, the

J. Yang (✉) · H. Yao · Y. Liu · Y. Zhang
The Institute of Condensed State Physics, Jilin Normal University, Siping, China
e-mail: jhyang1@jlnu.edu.cn

mixture was pressed into cylindrical pellets with omnipotence tester (CSS44100, ChangChun, China). The pellets were put into a conventional tube furnace, and heated up 800 °C for 1 h followed the argon flow at the rate of about 20 sccm before cooling to the room temperature.

Structural characterization was performed by X-ray diffractometer (XRD) on D/max-2500 copper rotating-anode XRD with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV, 200 mA. The morphology and structure of samples was determined using TEM (JEM-2100HR, Japan) at 200 keV. The composition was characterized by energy dispersive X-ray spectroscopy (EDX, S-570, and Japan).

Tribological Properties of WSe₂ Nanorods as Lubrication Additive

Different mass fractions of WSe₂ nanorods were dispersed in the HVI500 base oil with ultrasonic vibration (1800 W power, 2000 Hz frequency) for 5 h without any active reagent, and then a series of suspended oil samples were obtained. The tribological properties of the base oil containing WSe₂ nanorods and the base oil were investigated using a ball-on-disk mode of UMT multispecimen tribotester at ambient condition. The morphology of the wear scar was examined using a Metallurgical microscope (MBA21000, Japan).

Results and Discussions

Characterization of WSe₂ Nanorods

The XRD pattern of WSe₂ nanorods is illustrated in Fig. 1a. All peaks were indexed to the hexagonal WSe₂ (JCPDS No. 38-1388), which indicated the high purity of the obtained WSe₂ nanorods. Figure 1b shows the shifted (002) peak caused by the crystal defects and strains [20]. Moreover, all peaks were not obviously widened from XRD pattern. The EDS results gave a W:Se ratio about 1:2, so the sample was confirmed to be WSe₂.

Figure 2 shows the TEM patterns of WSe₂ nanorods. Figure 2a indicated that the diameters of WSe₂ nanorods were from 10 to 50 nm, and the lengths were hundreds of nanometers. At the same time, Fig. 2a also reveals that the nanorods have a sharp top and unsmooth trunk, which is different from the WS₂ nanorods obtained by self-transformation process [21]. Further observation showed the top of the short nanorods joined at different angles as shown in Fig. 2a (area f, e). The special structure might be due to the unsaturated dangling bonds of the top, which combined with each other under a high temperature. Figure 2b displays a single WSe₂ nanorod with diameter of 6 nm. The HRTEM image shows the d-spacing between two adjacent

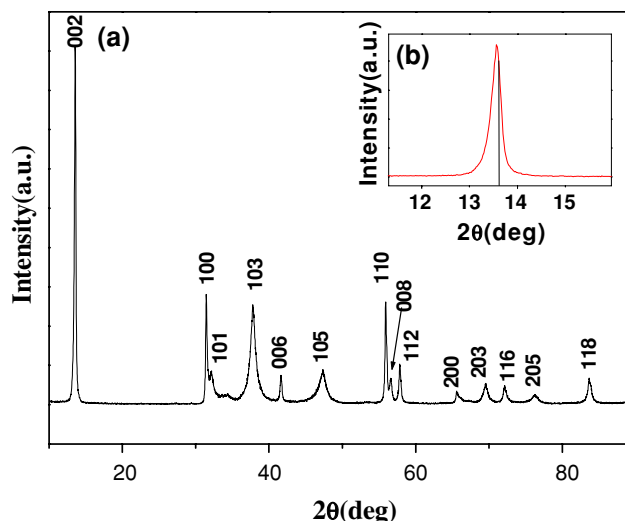


Fig. 1 XRD pattern of the WSe₂ nanorods

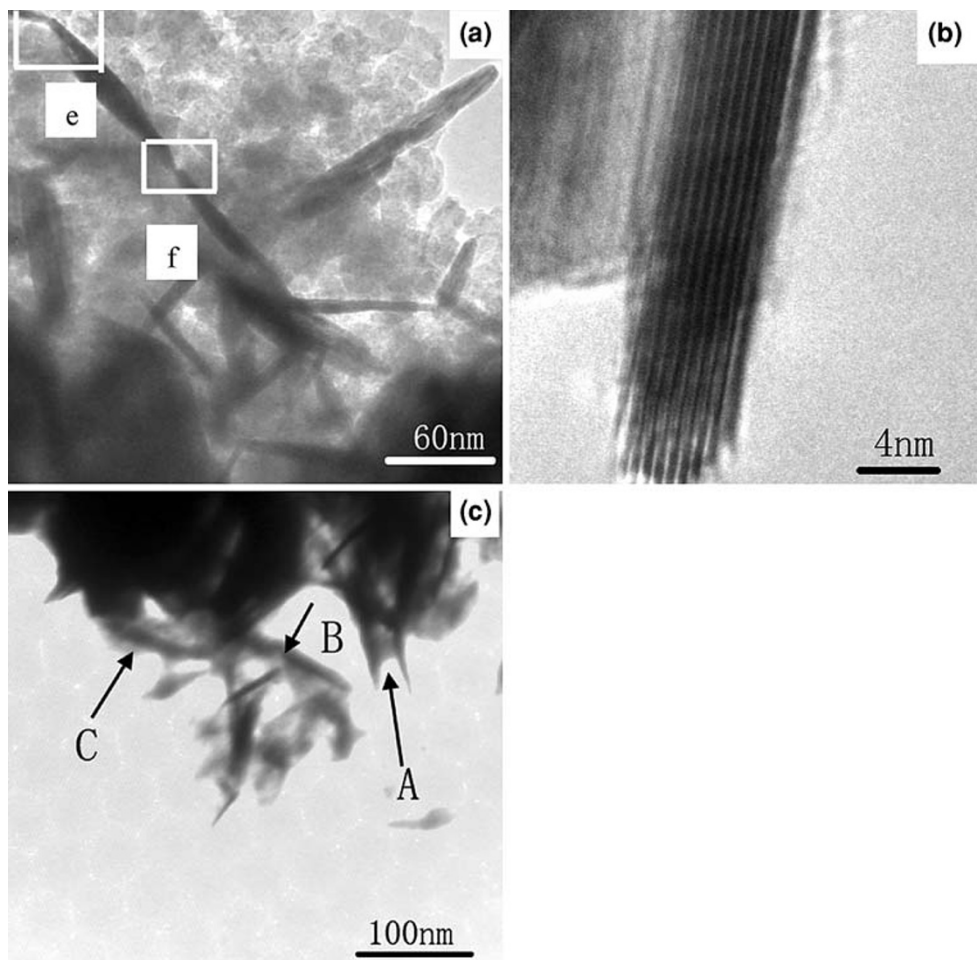
layers was 6.54 Å corresponding to the (002) plane. Moreover, different folding stages of samples were observed at regions marked A, B, and C (Fig. 2c), the WSe₂ nanorods were formed at last.

The reported growth mechanism in literatures [22, 23], especially the solid-state reaction of MoS₂ nanostructure, gave us much inspiration toward understanding the formation of WSe₂ nanorods. Under the high temperature conditions, Se quickly evaporated and simultaneously reacted with W. This rapid reaction might lead to supersaturation and fast nucleation. Thus, numerous nuclei of WSe₂ were initially formed in the vapor phase. When the initial clusters grew to the critical size, they began to form crystal flakes. Because of the instability of unsaturated dangling bonds, crystalline sheets began folding, and the dangling bonds of self-terminated planes stabilized into spherical or cylindrical crystal shapes. Thin-folded flakes could directly roll up and adopt the rod-like structure (Fig. 2c).

Effect of WSe₂ Nanorods on Tribological Properties

Figure 3 shows the friction coefficient as a function of time with 2 N load and 150 rpm rotating speed. The average friction coefficient of 7 wt.% WSe₂ nanorods (Fig. 3b) was close to 0.063, whereas it was 0.116 for the HVI500 base oil (Fig. 3a). That meant the addition of WSe₂ nanorods to the base oil resulted in nearly 50% reduction for the friction coefficient of the base oil. The wear scar of plate after rubbing is shown in Fig. 4a (the base oil) and Fig. 4b (the base oil containing WSe₂ nanorods). It could easily be found from Fig. 4a that wear scar has evidently rough, thick, and deep furrows and the width of about 0.18 mm. Compared to the wear scar of the base oil, the wear scar

Fig. 2 **a** TEM image of WSe₂ nanorods. **b** HRTEM image of single WSe₂ nanorod. **c** TEM image of WSe₂ layers at different folding stages



was flat and smooth, and the width was only 0.06 mm as in Fig. 4b. For other materials, such as MoS₂ micrometer spheres [24], the lowest friction coefficient was only 0.08, and the wear scars of MoSe₂ and WS₂ [25] have evidently

thick and deep furrows different from that of the WSe₂ nanorods we synthesized.

Figure 5a shows the friction coefficient as a function of concentration of the WSe₂ nanorods from 2 to 7 wt.% at 200 N load and 300 rpm rotating speed. For any mass fraction <7 wt.%, the friction coefficient of the base oil containing WSe₂ nanorods was lower than that of the base oil, and decreased with increasing mass fraction of the additives. Figure 5b shows the impact of rotating speed and load for the base oil containing 7 wt.% WSe₂ nanorods. Obviously, under low rotating speed, the friction coefficient at low load was lower than that at high load. But under high rotating speed, the friction coefficient at high load decreased. In other words, the base oil containing the additives was rather suitable for high loads and high rotating speeds.

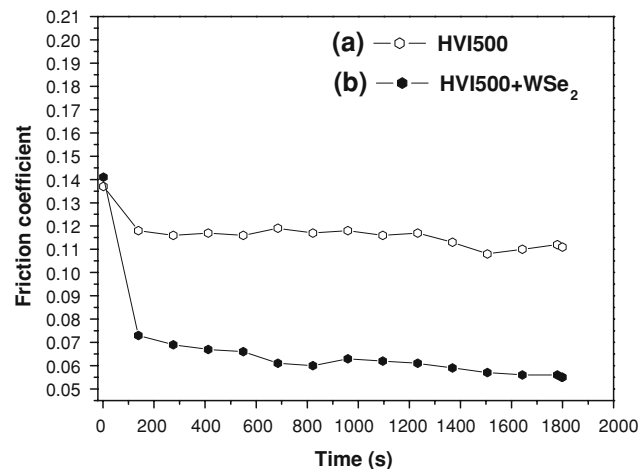


Fig. 3 Variation of friction coefficients for the HVI500 base oil and the HVI500 base oil containing 7 wt.% WSe₂ nanorods

From the above results, WSe₂ nanorods as lubrication additive could improve tribological properties of the base oil. A rolling friction mechanism could explain the excellent tribological properties of nanoparticles as lubrication additive. In this study, the effect WSe₂ nanorods as lubrication additive could be attributed to the molecule bearing

Fig. 4 The wear scar of plate: **a** HVI500 base oil, **b** HVI500 base oil containing WSe₂ nanorods

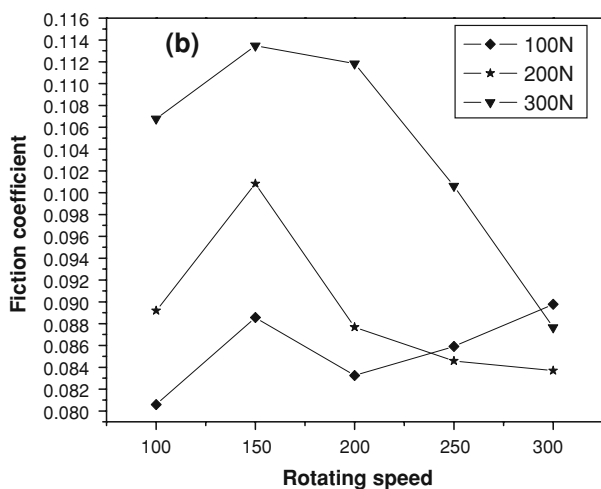
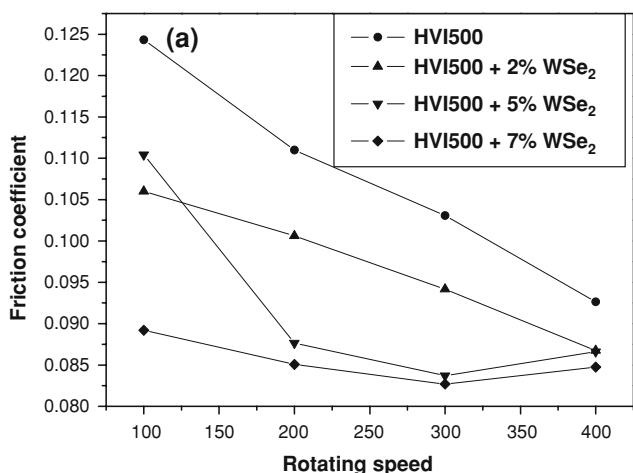
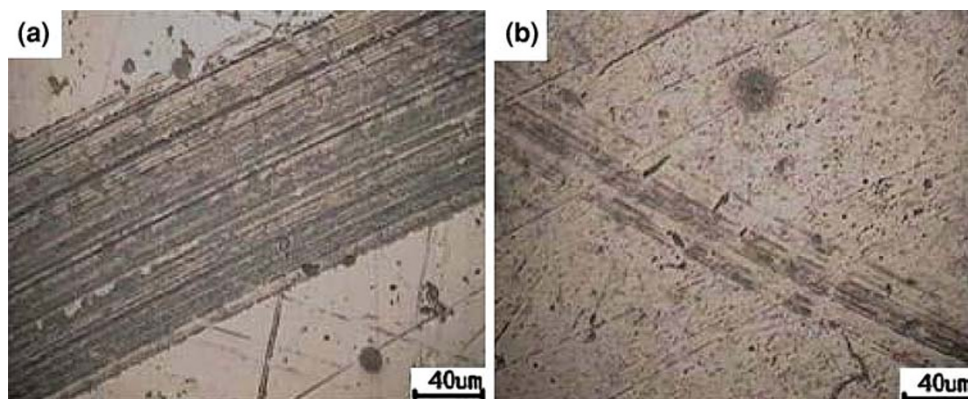


Fig. 5 Variation of friction coefficient as a function of rotating speed for **a** the HVI500 base oil and the HVI500 base oil containing 2, 5, 7 wt.% WSe₂ nanorods at 200 N, **b** the HVI500 base oil containing 7 wt.% WSe₂ nanorods for 30 min

mechanism of rolling friction and sliding friction of the WSe₂ nanorods between the rubbing surfaces. In addition, rotating speed was very important in the experimental process. Under low rotating speed, the stability of liquid lubricant reduced, the load almost acted on protruding part

of rubbing surfaces. When the load was increased, the lubricant film became unstable and easily splintered, the friction coefficient became high, as shown in Fig. 5b. But with the increase of rotating speed, the oil film became more and more stable, which could not only bear the load of the steel balls but also prevented any direct contact between the two rubbing surfaces. Moreover, when the shape of nonmaterial was destroyed at high load and high rotating speed, exfoliation of nonmaterial layer filled the rough contact surface and formed a stable thin film with base oil, which could decrease friction and wear happening on the rubbing surfaces.

Conclusions

WSe₂ nanorods of 10–50 nm in diameters and 100–400 nm in lengths were prepared successfully by solid-state reaction of the tungsten and selenium powders. The HVI500 base oil with addition of WSe₂ nanorods showed the best friction-and-wear properties. Tribological experiments indicated that the effect of WSe₂ nanorods as lubrication additive could be attribute to the molecule-bearing mechanism of rolling friction and the sliding friction of the WSe₂ nanorods between the rubbing surfaces. Moreover, a stable film on the rubbing surface could not only bear the load of the steel ball but also prevent any direct contact between the two rubbing surfaces.

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References

- N.D. Boscher, C.J. Carmalt, I.P. Parkin, *J. Mater. Chem.* **16**, 122 (2006). doi:10.1039/b514440j

2. N.D. Boscher, C.J. Carmalt, I.P. Parkin, *Eur. J. Inorg. Chem.* **10**, 1255 (2006). doi:[10.1002/ejic.200500857](https://doi.org/10.1002/ejic.200500857)
3. T. Tsuneta, T. Toshima, K. Inagaki, T. Shibayama, S. Tanda, S. Uji, M. Ahlskog, P. Hakonen, M. Paalanen, *Curr. Appl. Phys.* **3**, 473 (2003). doi:[10.1016/j.cap.2003.07.002](https://doi.org/10.1016/j.cap.2003.07.002)
4. Z. Salman, D. Wang, K.H. Chow, M.D. Hossain, S.R. Kreitzman, T.A. Keeler, C.D.P. Levy, W.A. MacFarlane, R.I. Miller, G.D. Morris, T.J. Parolin, H. Saadaoui, M. Smadella, R.F. Kiefl, *Phys. Rev. Lett.* **98**, 167001 (2007). doi:[10.1103/PhysRevLett.98.167001](https://doi.org/10.1103/PhysRevLett.98.167001)
5. F. Soto, H. Berger, L. Cabo, C. Carballeira, J. Mosqueira, D. Pavuna, P. Toimil, F. Vidal, *Physica C* **460**, 789 (2007). doi:[10.1016/j.physc.2007.04.032](https://doi.org/10.1016/j.physc.2007.04.032)
6. Z. Zhou, R. Jin, G. Eres, D. Mandrus, V. Barzykin, P. Schlottmann, Y.-S. Hor, Z. Xiao, J.F. Mitchell, *Phys. Rev. B* **76**, 104511 (2007). doi:[10.1103/PhysRevB.76.104511](https://doi.org/10.1103/PhysRevB.76.104511)
7. S.Y. Hu, Y.C. Lee, J.L. Shen, K.W. Chen, K.K. Tiong, Y.S. Huang, *Solid State Commun.* **139**, 176 (2006). doi:[10.1016/j.ssc.2006.05.027](https://doi.org/10.1016/j.ssc.2006.05.027)
8. K.S. Tiefenbacher, V. Eyert, C. Pettenkofer, W. Jaegermann, *Thin Solid Films* **380**, 221 (2000). doi:[10.1016/S0040-6090\(00\)01510-8](https://doi.org/10.1016/S0040-6090(00)01510-8)
9. A.H. Reshak, S. Auluck, *Physica B* **393**, 88 (2007). doi:[10.1016/j.physb.2006.12.065](https://doi.org/10.1016/j.physb.2006.12.065)
10. A.H. Reshak, S. Auluck, *Phys. Rev. B* **68**, 195107 (2003). doi:[10.1103/PhysRevB.68.195107](https://doi.org/10.1103/PhysRevB.68.195107)
11. J. Jebaraj Devadasan, C. Sanjeeviraja, M. Jayachandran, *Mater. Chem. Phys.* **77**, 397 (2002). doi:[10.1016/S0254-0584\(02\)00095-0](https://doi.org/10.1016/S0254-0584(02)00095-0)
12. Y. Feldman, G.L. Frey, M. Homyonfer, R. Tenne, *J. Am. Chem. Soc.* **118**, 5632 (1996). doi:[10.1021/ja9602408](https://doi.org/10.1021/ja9602408)
13. L. Rapoport, V. Leshchinsky, M. Lvovsky, I. Lapsker, Yu Volovik, R. Tenne, *Tribol. Int.* **35**, 47 (2002). doi:[10.1016/S0301-679X\(01\)00094-9](https://doi.org/10.1016/S0301-679X(01)00094-9)
14. L. Rapport, Y. Bilik, Y. Feldman, M. Homyonfer, S.R. Cohen, R. Tenne, *Nature* **387**, 791 (1997). doi:[10.1038/42910](https://doi.org/10.1038/42910)
15. L. Rapoport, O. Nepomnyashchy, I. Lapsker, A. Verdyan, A. Moshkovich, Y. Feldman, R. Tenne, *Wear* **259**, 703 (2005). doi:[10.1016/j.wear.2005.01.009](https://doi.org/10.1016/j.wear.2005.01.009)
16. L. Rapoport, O. Nepomnyashchy, I. Lapsker, A. Verdyan, Y. Soifer, R. Popovitz-Biro, R. Tenne, *Tribol. Lett.* **19**, 143 (2005). doi:[10.1007/s11249-005-5095-2](https://doi.org/10.1007/s11249-005-5095-2)
17. R. Tenne, L. Margulis, M. Genut, G. Hodes, *Nature* **60**, 444 (1992). doi:[10.1038/360444a0](https://doi.org/10.1038/360444a0)
18. M. Chhowalla, G.A.J. Amaratunga, *Nature* **407**, 164 (2000). doi:[10.1038/35025020](https://doi.org/10.1038/35025020)
19. W.G. Sawyer, A. Thierry, T.A. Blanchet, *Wear* **225**, 581 (1999). doi:[10.1016/S0043-1648\(99\)00020-4](https://doi.org/10.1016/S0043-1648(99)00020-4)
20. L. Joly-Pottuza, F. Dassenoya, M. Belina, B. Vachera, J.M. Martin, N. Fleischer, *Tribol. Lett.* **18**, 477 (2005). doi:[10.1007/s11249-005-3607-8](https://doi.org/10.1007/s11249-005-3607-8)
21. L.L. Zhang, J. Xu, H.M. Wu, Y.Z. Yang, *Mater. Sci. Eng. A* **454**, 487 (2007). doi:[10.1016/j.msea.2006.11.072](https://doi.org/10.1016/j.msea.2006.11.072)
22. X.L. Li, J.P. Ge et al., *Chem. Eur. J.* **10**, 6163 (2004). doi:[10.1002/chem.200400451](https://doi.org/10.1002/chem.200400451)
23. X.L. Li, Y.D. Li, *Chem. Eur. J.* **9**, 2726 (2003). doi:[10.1002/chem.200204635](https://doi.org/10.1002/chem.200204635)
24. X.D. Zhou, D.M. Wu et al., *Tribol. Int.* **40**, 863 (2007)
25. T. Kubart, T. Polcar et al., *Surf. Coat. Technol.* **193**, 230 (2005). doi:[10.1016/j.surfcoat.2004.08.146](https://doi.org/10.1016/j.surfcoat.2004.08.146)