Synthesis and characterization of CrN/Mo$_2$N multilayers and phases of Molybdenum nitride

Robin Abraham Koshy [*], Michael E. Graham [1], Laurence D. Marks [2]

Materials Science and Engineering Department, Northwestern University, Evanston, IL-60208, USA

Available online 15 August 2007

Abstract

CrNx, MoNx, CrOx, MoOx and CrN/Mo$_2$N multilayer films were deposited by reactive sputtering. Characterization of the coatings was carried out using XRD, XPS, optical profilometer, and nano-indentation. The oxidation of the thin films was studied as a function of annealing temperature. Tribological characterization of the Cr$_2$O$_3$ and the Mo-oxides was carried out as a function of annealing temperature. The low friction behavior of MoOx and MoNx was demonstrated. The deposition of CrNx and MoNx was also characterized and multilayer deposition of CrN and Mo$_2$N was carried out. The hardness of Mo$_2$N and CrN and the multilayers were shown to lie in the 20–30 GPa hardness regime. The multilayers are stable up to 500 °C in air and up to 1000 °C in argon. Initial friction testing on the multilayer coatings showed an activated self-lubricating mechanism.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Lubricous oxides; Multilayer coatings; CrN/ Mo$_2$N; In-situ lubrication; Nanolayers; Tool coatings

1. Introduction

Hard coatings for cutting tools have been in use now for thirty years, [1–6] and have evolved from the initial, simple nitride and oxide coatings (such as TiN and Al$_2$O$_3$) applied by CVD and PVD in the 1970s, to more complex, high-performance alloy nitrides (such as TiAlN) employed today. More recently, the interest in green manufacturing has spurred development of coatings for dry machining [7–10]. If tools (coatings) can effectively tolerate high temperatures or can help to reduce the temperatures, then coolant usage can be reduced. If the friction level due to the cutting process can be minimized, then lubricant usage can be reduced along with power requirements. It is proposed to use materials in a nano-layered structure that will be hard, tough, adherent, and lubricious at the service temperature (<1000 °C). The basic system of CrNx and MoNx to form multi (nano)-layered coatings offers some advantages as a starting point. Cr(N) is suggested because of its excellent wear and oxidation resistance to about 800 °C [11,12] and Mo(N) [13] because it is likely to oxidize at about 500 °C, forming its low friction oxide, MoO$_3$. The presumption is that the Mo-oxide will reduce the cutting friction and consequently the heat generated by high-speed contact (relative to a coating without the Mo). Recent research showed that plasma sprayed composites of Cr$_2$O$_3$ and MoO$_3$ benefit from the addition of MoO$_3$ and exhibit a reduction of sliding friction from ∼0.4–0.5 at RT to ∼0.2 at 450 °C (self-mated or against Cr-plated discs) [14]. This approach of using a lubricious oxide has also been explored by others in the cutting tool application, but they chose to explore TiOx [15,16] and VOx [17,18] as the active components. The oxide formation at temperatures above 400 °C appears to offer promise for the approach. In our case, the selected nitrides of Mo and Cr are both hard phases (∼20–30 GPa) and are immiscible in their elemental state up to 800 °C [19]. As a result, if the elemental miscibility gap holds for the corresponding nitrides, the nitrides should retain their layered structure (and strength) at high temperatures. While our interest is in using this multilayer coating, our early work focused on characterizing the individual phases and their behavior and some of this work is presented here. This work was intended to provide insight into which oxides might be formed and how the nitrides and their oxidation products would behave at different temperatures.

* Corresponding author. Tel.: +1 847 275 7597; fax: +1 847 491 7820.
  E-mail addresses: koshy@northwestern.edu (R.A. Koshy),
mgraham@northwestern.edu (M.E. Graham), l-marks@northwestern.edu
(L.D. Marks).
  [1] Tel.: +1 847 491 5436.
  [2] Tel.: +1 847 491 3996.

2. Experimental details

The samples were prepared by sputter deposition in a closed-field dual cathode unbalanced magnetron system. The cryo pumped system has a base pressure of 4×10^{-7} Torr and includes a high vacuum load lock chamber. There are two vertically mounted 12.8×40.6 cm planar magnetron cathodes facing each other on opposite sides of the substrate holder and 10 cm from the substrates. The hexagonal substrate holder is just large enough to eliminate the cross contamination from the other cathode. The substrate holder can be rotated at 5–15.2 rpm to produce nano-layered materials with controlled layer thickness. All coatings were 1 to 1.5 μm thick. The substrates were single crystal Si (001), glass sides and polished M50 tool steel discs. Sapphire substrates were used in cases where high temperature anneals were to be carried out. Prior to deposition the samples were cleaned in an ultrasonic bath of methanol. All reactive sputter depositions were carried out under a total pressure of 4 mTorr of argon and nitrogen. A −50 V bias was applied on the substrate and the substrate temperatures due to plasma heating were generally in the 150 °C–200 °C range. The oxidation anneals were carried out in air and held at the highest temperature for 2 h with a heat up rate of 5 °C/min. The annealing tests on the multilayers were carried out in argon and held at the highest temperature for 2 h with a heat up rate of 5 °C/min. The CETR micro-tribometer is used to measure the coefficient of friction (COF) at room temperatures, while a CSEM high temperature tribometer is used for high temperature tests. Both tribometers are the "pin on disc" type. Room temperature friction tests on the nitrides and oxides of both Mo and Cr were carried out using a steel ball (52100 steel, 3 mm dia, 20–25 gm load.) run on the rotating coated M50 steel flat (25.4 mm dia). High temperature friction tests on the multilayers were carried out using a sapphire ball (3 mm dia, 40 gm load). The linear velocity is kept constant at 1 cm/s by adjusting the rotation speed in all tests. X-ray diffraction (XRD) was carried out using a Scintag XDS diffractometer having an unfiltered Cu–Kα radiation source operated at 40 kV and 20 mA. Coating hardness was determined using a CSIRO, UMIS-2000 nano-indenter fitted with a Berkovich diamond tip. The indentations depths are kept within 10% of the coating thickness. The film thickness on the Si substrate was measured using a Dektak 3030ST profilometer at the edge of a masked section of the substrate. XPS phase identification of CrNx phases was done using a Omnicon ESCAPROBE. It is equipped with single channeltron detection and a twin-anode X-ray source (Al/Mg anode, 400 W). All XPS spectra were referenced to the C 1s line of hydrocarbon-type carbon. SEM characterization was carried out on a LEO-Gemini 1525.

3. Results and discussions

3.1. Molybdenum oxide films

Molybdenum oxide (MoO_3) is the phase that, we propose, will be formed at high temperature from the MoNx in the coating. MoO_3, formed from the oxidation of MoNx [14,20–22] is known to be a lubricous phase and would provide reduced friction. Initially, Mo-oxide films were deposited directly by reactive sputtering and analyzed to determine the phases that were likely to appear as oxidation products. The oxide samples were then annealed in air at several different temperatures to determine their stability of its oxides at different temperatures. This also allowed us to study any physical changes that might occur to the oxides as a result of heating (up to 600 °C). Following these treatments and characterization, we tested the sliding friction.

3.1.1. Phase characterization

The reactive sputtering was carried out in an atmosphere of 0.3 mTorr oxygen and a total pressure of 4 mTorr (O_2+Ar), on an M50 substrate with a substrate bias of −50 V. The XRD results confirmed that we deposited MoO_2 and Mo_4O_{11}. Annealing the coating at 250 °C formed MoO_3 and Mo_4O_{11} as the predominant phases. Further annealing to 550 °C sharpened and intensified the peaks, but MoO_3 becomes the dominant phase. There are peaks that can be possibly identified with other phases such as Mo_8O_{23}/Mo_9O_{27} but the identification is still somewhat uncertain, via XRD, due to nearly overlapping peak positions for some of these complex phases. Annealing increased the surfaces roughness from 25 nm in the deposited coating to 100 nm and 350 nm at 550 °C and 600 °C respectively. Hardness was a low 3–4 GPa and it is likely that the oxide was weakly adhered to the substrate in addition to being very weak itself [23]. The higher value of hardness occurred after annealing at the highest temperature, which is indicative of some stress relief and recrystalization.

3.1.2. Tribological behavior of Mo-oxide films

Sliding wear tests on the Mo-oxide surfaces demonstrates that the combination of MoO_2 and Mo_4O_{11} as deposited shows a low COF value of less than 0.15. While it is expected that the MoO_3 surface would exhibit low friction [20–22] it was unclear what to expect from the other oxides such as MoO_2, which are stable to relatively high temperature. As the film is annealed, the friction plots get noisier, apparently due to structural changes in the oxide. When annealed at about 550 °C, where the oxide is predominantly MoO_3, the friction is again a stable value of about 0.1–0.12 [Fig. 1].
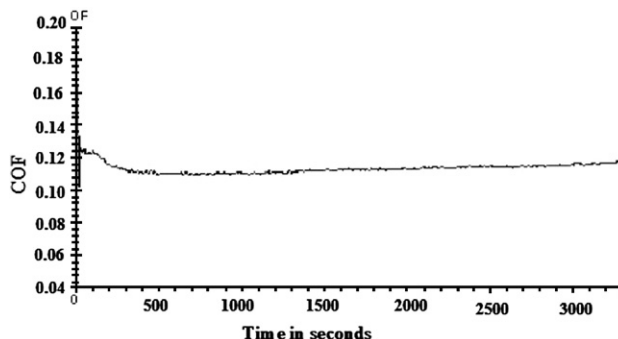

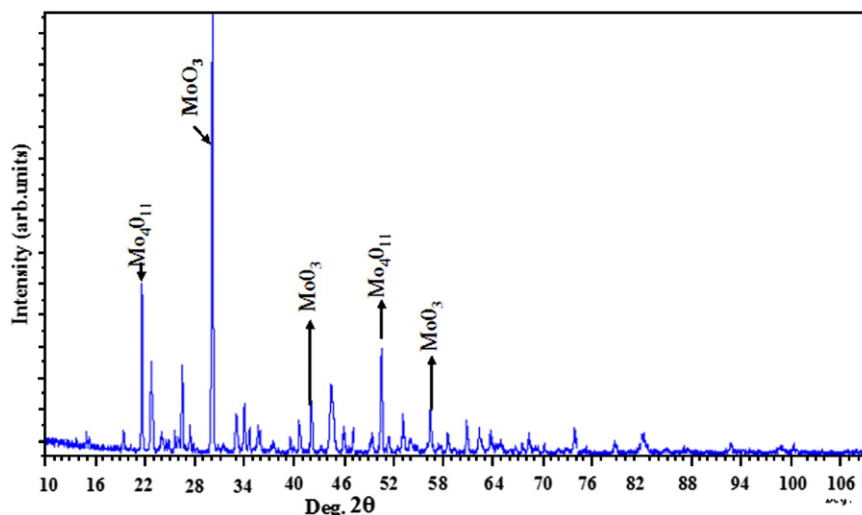Fig. 1. Friction plot for 550 °C-annealed Mo-oxide (MoO_3).

Fig. 2. XRD pattern for Mo-Nx deposited on M50 and annealed at 650 °C.

3.2. Chromium oxide films

Cr_2O_3 is the expected product of CrNx oxidation and is known to be hard and abrasive [14]. The authors felt it was important to understand and confirm mechanical and friction properties of the oxide, since this could give some insight into the wear processes in the multilayers and the role played there by the Cr_2O_3 formed there. Cr_2O_3 films were reactively sputtered, on an M50 substrate at various partial pressures of oxygen and a total pressure of 4 mTorr ($O_2 + Ar$) with a substrate bias of −50 V. Hardness of the as deposited sample was about 25 GPa which on annealing at 200 °C dropped to 15 GPa. Further annealing lead to an increase in hardness to 18 GPa, 20 GPa and 30 GPa at temperatures of 250 °C, 400 °C and 600 °C respectively. The drop in hardness initially on annealing could be indicative of stress relief as defects migrate to free surfaces or interfaces. Friction tests on the coating shows that Cr_2O_3 removes material from the ball fairly rapidly and a "steady state" condition is reached quite rapidly. The COF value appears in the 0.6–0.7 range which is consistent with published results [14]. The friction value has a component of metal on metal sliding involved since metal–metal sliding lies in the 0.6 to 0.8 range. Metal transfer is confirmed via EDS and optical microscopy.

3.3. Mo-nitride films

Since molybdenum nitride is one of the constituents in our multilayer coating, it is necessary to explore the oxidation process on the MoNx films. The different phases of MoNx were reactively sputtered at different partial pressures of nitrogen forming Mo-Nx, β-Mo_2N and γ-Mo_2N. At low partial pressures of 0.3 mTorr N2 a coating of Mo-N_x is formed (Mo bcc structure with nitrogen incorporated into the lattice). At intermediate partial pressures of (1–2 mTorr) β-Mo_2N (hexagonal) was deposited and at partial pressures of 2 mTorr and above γ-Mo_2N (tetragonal) was deposited. This is in good agreement with literature [24].

3.3.1. Heat treating in air

The oxidation products and oxidation temperatures of Mo_2N have been well characterized by researchers [21,23,25]. We report the annealing results on Mo-Nx since it showed the lowest COF at room temperatures. Annealing Mo-Nx showed that the MoO_2 phase and possibly the Mo_4O_{11} phase appear first, but up to 400 °C, the dominant structure is still Mo-Nx. At 650 °C, we observed nearly complete oxidation with a dominant MoO_3 peak and Mo_4O_{11} [Fig. 2]. Many of the unlabeled peaks are from the oxidation products of M50 substrate.

3.3.2. Tribological behavior of MoNx films

We found that the Mo-N_x film exhibits a lower friction coefficient of 0.16 to 0.18, [Fig. 3] (the horizontal line in the figure assists in reading the COF level). Other nitride phases such as β-Mo_2N and γ-Mo_2N showed a COF ~0.7. Friction testing on annealed Mo-Nx sample in air (held at 400 °C for 1 h) indicates a friction coefficient around 0.12. Though our XRD data does not indicate any oxidation products, there is a marked
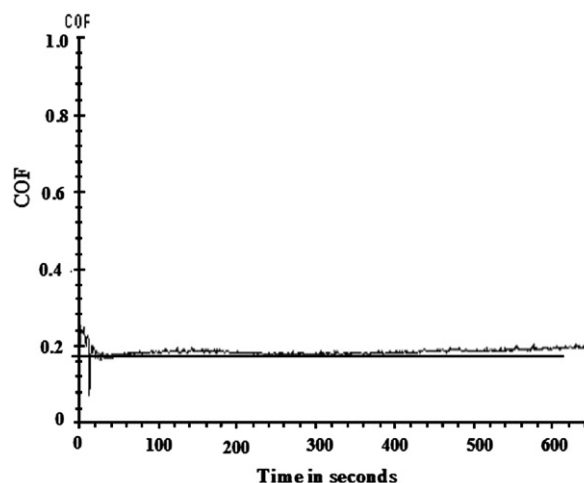

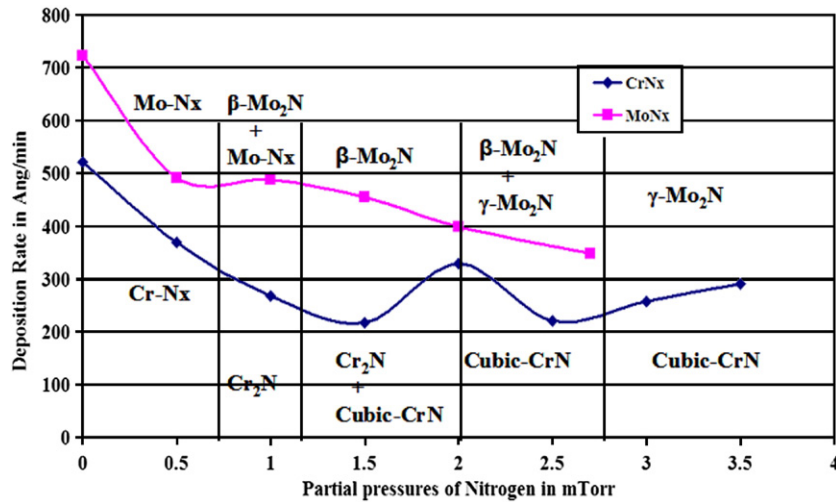Fig. 3. Friction trace for as-deposited MoNx coating.

Fig. 4. Deposition rates and Phase regions of CrNx and MoNx.

difference in the nature of the friction curve. The curve is markedly noisier with indication of early breakdown and a gradual increase of friction to 0.6–0.7, suggesting a possible loss of the coating. It appears that the transformation from the nitride to the oxide might not yield a surface quite as stable (mechanically) as the as-deposited oxides, but the resultant friction is still quite low. The properties of Mo-Nx suggest that it is not very hard (12 GPa), whereas we know that MoNx films can be deposited with hardness values in the 20–30 GPa range [13].

3.4. Deposition of phases of MoNx and CrNx

The powers on the chromium and molybdenum cathodes were set at 2.1 kW and 3.5 kW respectively. The total pressure was held constant at a 4 mTorr pressure ($Ar+N_2$) and the substrate bias was a constant −50 V. It is critical to understand the effect of nitrogen partial pressures on the formation of the nitrides since the reactivity of Cr and Mo to nitrogen is different [Fig. 4]. Varying the partial pressure of nitrogen allows us to characterize the deposition rates of the different phases of both CrNx and MoNx. The deposition rates control the relative thickness of the two phases. XPS was carried out to determine the exact phases of chromium nitride at intermediate nitrogen partial pressure, since an XRD analysis failed in identifying the phases present because of peak broadening and overlap. The $Cr\ 2p_{3/2}$ in the 1.0 mTorr to 2.0 mTorr range of reactive sputtering pressure can be decomposed into two components from Cr_2N (576.24 eV compared to reference value of 576.1 eV) and CrN (575.24 eV compared to the reference value of 575.5 eV). With increasing partial pressure the peak shifts from the Cr_2N to the CrN peak. The CrN peak location is in better agreement with reference values than those described in literature. [26,27]. In the case of Mo at partial pressures of less than ∼0.8 mTorr of nitrogen, we have Mo-Nx, the bcc phase with nitrogen incorporated into its lattice. At intermediate nitrogen partial pressures of around 1 mTorr we have a mixed phase of Mo-Nx and Mo_2N. At pressures of 1.5 mTorr of nitrogen, we have the hardest phase

of β-Mo_2N. At higher partial pressures of 2 mTorr and above we have the γ-Mo_2N phase forming, initially in combination with the β-Mo_2N and at higher partial pressures it exists as the predominant phase [24]. Similar phase regions of Cr-Nx (solid solution of nitrogen in Cr), Cr_2N and CrN are depicted in Fig. 4. The vertical line shown in Fig. 4 depicts approximate phase regions. This is in good agreement with similar studies in literature [12,13].

3.5. Nanostructured multilayered films

Nanolayered films [Fig. 4] were deposited via reactive sputtering at an intermediate partial pressure of 1.5 mTorr. The total pressure was held at a constant 4 mTorr ($Ar+N_2$) and the substrate bias was a constant −50 V. Sapphire substrates were used in samples that were annealed to high temperatures. The chromium and molybdenum targets were set at powers of 2.1 kW and 3.5 kW. This is the regime where the hardest phase of β-Mo_2N and a combination of CrN and Cr_2N are formed, with CrN being the dominant phase. Different nanolayer periods were synthesized at different rates of rotation of the substrate holder. The hardness of the films were in excess of 25 GPa making them suitable for tool coatings [Fig. 5]. Our low angle XRD studies showed strong large order multiple
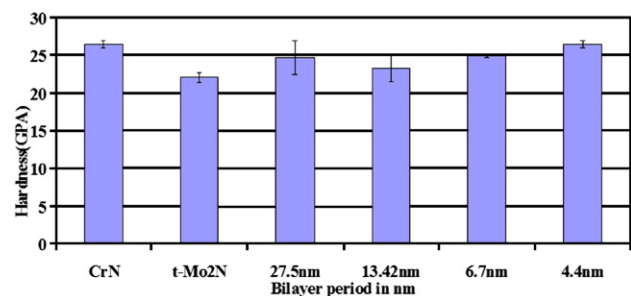

Fig. 5. Hardness vs. periodicity for CrN/Mo_2N multilayers and for CrN and Mo_2N films.
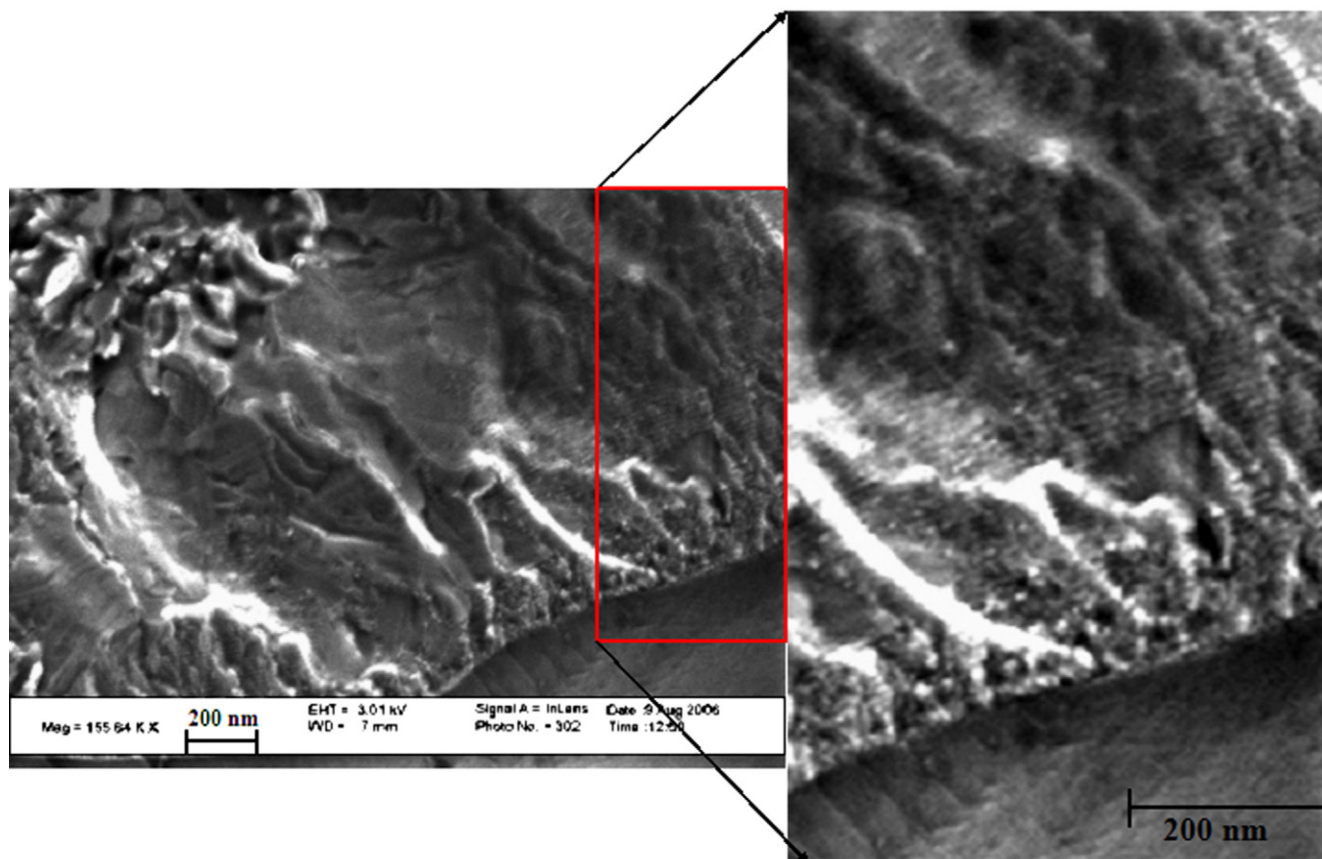
Fig. 6. Cross-sectional SEM micrograph of the multilayer coating annealed to 1000 °C on a sapphire wafer.

reflections indicative of a sharp interface. A series of high temperature anneals were carried out to understand the temperature effects on the interface and the coatings in general. These anneals were carried out in an atmosphere of argon with the sample held at high temperature (200 °C, 400 °C, 600 °C, 1000 °C) for 2 h. Low angle XRD shows strong interaction peaks to several orders indicating that the interface is stable to 600 °C. Low angle XRD on the sample at 1000 °C indicates a loss of these fringes. SEM imaging of the cross section of these annealed coatings shows that the layers are still intact at 1000 °C [Fig. 6] and the loss of low angle XRD fringes is likely due to an increase in surface roughness, since low angle XRD is extremely sensitive to surface roughness.

3.5.1. Friction tests

Sliding tests on the multilayer films were carried out on the high temperature CSEM Tribometer using a sapphire ball. A 40 gm load is applied with the sample rotated relative to the ball such that the ball maintains a linear velocity of 1 cm/s. The film tested had a CrN/Mo2N bilayer period of 13.4 nm with a layer ratio of 3:2 (Mo_2N:CrN). The friction initially increases from a value of about 0.4 at room temperature, to a high of about 1.0 at 300 °C, and then drops to a steady value of about 0.55 when tested at 600 °C. These tests indicate that the friction behaves much in the same way as in the case of VNx additions [28]. The authors believe that the oxidation of the nitride phase is responsible for the low friction seen in the test. Preliminary XPS studies on the wear debris obtained at 550 °C indicate the presence of the Mo $3d_{3/2}$ at 233 eV. This peak is MoO_3 and is consistent with literature [14].

4. Conclusion

Deposition of the nitrides and oxides of Cr and Mo were carried out. The low friction behavior of MoO_3 was demonstrated. The various oxidation products of Mo were characterized. Cr was shown to form a hard and stable Cr_2O_3 .A complete deposition rate and phase characterization of the CrNx and MoNx was carried out .A hardness test of the nano-layered coatings showed them to be in the hardness realm of ∼25 GPa. This is the high hardness regime suitable for a tool coating. Deposition of nano-layered Mo_2N/CrN was carried out. The nano-layered structure was shown to be intact up to 1000 °C. A high temperature friction test on the coating shows an in-situ activated lubricating mechanism. XPS analysis of the wear debris at high temperature shows the presence of MoO_3.

Acknowledgements

References

[1] P.Eh. Hovsepian, W.-D. Munz, Vacuum 69 (2003) 27.

[2] J. Patscheider, T. Zehnder, M. Diserens, Surf. Coat. Technol. 146–147 (2001) 201.

[3] A. Erdemir, M. Halter, G.R. Fenske, Wear 205 (1997) 236.

[4] A.A. Voevodin, J.S. Zabinski, Thin Solid Films 370 (2000) 223.

[5] K.L. Strong, J.S. Zabinski, Thin Solid Films 406 (2002) 174.

[6] E. Lugscheider, O. Knotek, K. Bobzin, S. Barwulf, Surf. Coat. Technol. 133–134 (2000) 362.

[7] S. Paldey, S.C. Deevi, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. 342 (2003) 58.

[8] W.-D. Münz, J. Vac. Sci. Technol., A 4 (1986) 2717.

[9] A. Hörling, L. Hultman, M. Odén, J. Sjölén, L. Karlsson, J. Vac. Sci. Technol., A 20 (2002) 1815.

[10] J. Musil, H. Hruby, Thin Solid Films 365 (2000) 104.

[11] S. Hofmann, H. Jehn, Werkst. Korros. 41 (1990) 756.

[12] P. Hones, R. Sanjines, F. Levy, Surf. Coat. Technol. 94–95 (1997) 398.

[13] Peter Hones, Nicolas Martin, Manfred Regula, Francis Lévy, J. Phys. D: Appl. Phys. 36 (2003) 1023.

[14] I.W. Lyo, H.-S. Ahn, D.-S. Lim, Surf. Coat. Technol. 163–164 (2003) 413.

[15] Aizawa, T. Mitsuo, A. Yamamoto, S. Sumitomo, T. Muraishi, Wear 259 (2005) 708.

[16] A. Mitsuo, S. Uchida, S. Yamamoto, T. Aizawa, Surf. Coat. Technol. 188 (2004) 630.

[17] G. Gassner, H. Mayrhofer, K. Kutschej, Mitterer, M. Kathrein, Tribol. Lett. 17 (2004) 751.

[18] R. Franz, J. Neidhardt, B. Sartory, Kaindl, R. Tessadri, Polcik, V.H. Derflinger, C. Mitterer, Tribol. Lett. 23 (2006) 101.

[19] M. Venkatraman, J.P. Neumann, in: H. Baker (Ed.), ASM Handbook, Alloy Phase Diagrams, vol. 3, ASM International, 1992, p. 2.155.

[20] M. Urgen, O.L. Eryilmaz, A.F. Cafir, E.S. Kayali, B. Nilufer, Y. Isik, Surf. Coat. Technol. 94–95 (1997) 501.

[21] N. Solak, F. Ustel, M. Urgen, S. Aydin, A.F. Cakir, Surf. Coat. Technol. 174–175 (2003) 713.

[22] T. Suszko, W. Gulbinki, J. Jagielski, Surf. Coat. Technol. 194 (2005) 319.

[23] Zhengwei Li, Yedong He, Wei Gao, Oxid. Met. 53 (2000) 577.

[24] Paul J. Rudnik, Michael E. Graham, William D. Sproul, Surf. Coat. Technol. 49 (1991) 293.

[25] T. Suszko, W. Gulbinki, J. Jagielski, Surf. Coat. Technol. 200 (2006) 6288.

[26] A. Conde, A.B. Cristóbal, G. Fuentes, T. Tate, J. de Damborenea, Surf. Coat. Technol. 201 (2006) 3588.

[27] S. Han, J.H. Lin, G.H. Wang, H.C. Shih, Surf. Coat. Technol. 57 (2003) 1202.

[28] P.H. Mayrhofer, P.Eh. Hovsepian, C. Mitterer, W.-D. Munz, Surf. Coat. Technol. 177–178 (2004) 341.