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CrN-Ag Self-Lubricating Hard Coatings

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CrN-Ag Self-Lubricating Hard Coatings

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Abstract

CrN-Ag composite films, 2.5-4 μm thick, were deposited by reactive magnetron sputtering on Si and stainless steel substrates in a 0.4 Pa pure nitrogen atmosphere at 500 °C. The layer composition was controlled by the relative power to 7.5-cm-diameter Ag and Cr targets to be 0, 3, 12, and 22 atomic percent Ag. The layers exhibit a dense columnar microstructure where the Ag is homogeneously distributed in the CrN matrix. The coatings were vacuum annealed for $t_a = 5 - 60$ minutes at temperatures ranging from $T_a = 600 - 700^\circ\text{C}$, to study the Ag-lubricant transport to the surface. Ag surface segregation during annealing is negligible for layers with 3 at.% Ag content. However, Ag diffuses to the surface of layers with ≥ 12 at.% Ag and forms particles with diameters ranging, as a function of T_a and t_a , from 50 – 1100 nm. Statistical analyses provide average particle sizes of 110 and 375 nm, and surface particle densities of 2×10^7 and $1.7 \times 10^6 \text{ mm}^{-2}$, for the 12 and 22 % Ag samples, respectively. The Ag diffusive transport occurs 2-3 times faster for the 22% than for the 12%-sample. We attribute the increase in Ag transport as a function of the total Ag concentration to a network of underdense pores that form during deposition due to Ag segregation into nm-size pockets. The pores grow in width and connectivity as the total Ag concentration is increased, leading to a faster Ag-transport at elevated Ag-concentrations. Room temperature micro-scratch tests show that the average friction coefficient decreases from 0.085 to 0.082 to 0.067 to 0.062, while the wear depth decreases from 0.41 to 0.35 to 0.25 to 0.18 μm , for increasing Ag concentrations of 0, 3, 12, and 22 at.%, respectively.

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INTRODUCTION

Transition metal (TM) nitride coatings are of considerable interest due to their high hardness and mechanical strength, chemical inertness, and high-temperature stability. CrN coatings show promise for high temperature applications, as they exhibit good thermal stability [1-3] and oxidation resistance, [4-5] as well as promising tribological properties [6-8]. As a means to further improve the wear resistance of CrN coatings a method of solid lubrication is investigated.

Lubrication at high temperatures (300-1000 °C) presents a considerable challenge to the tribology community [9]. At elevated temperatures, conventional liquid lubricants oxidize or thermally degrade [10] and the most common lattice-layered solid lubricants like graphite and molybdenum disulfide oxidize quickly above ~350 °C [11,12]. In contrast, non-layered solid lubricants including metal oxides (PbO, TiO, NiO, CoMoO₄), inorganic fluorides (CaF₂, BaF₂), and soft noble metals (Ag, Au, Pt) possess stable thermochemistry at elevated temperatures and have been reported to lubricate at high temperatures [13] due to their low shear strength. However, all these materials do have considerable shortcomings and do not correspond to the ideal lubricant, which would be functional from room temperature to ~1100 °C, and would operate in both moist air as well as vacuum. In particular, the fluorites undergo a brittle-to-ductile transition at ~400°C, below which they do not function as a lubricant [14]. In addition, they can become glass-like after melting at high-temperature and are prone to cracking when used again at lower temperatures [12]. The most widely studied oxide lubricant, PbO, is effective at ~400-700 °C but is limited by its reactivity at high temperature and by its shear strength at lower

temperatures [12]. Other oxides are limited in their applicability often because of their abrasive nature and high shear strength at low temperatures. Soft metal coatings exhibit low shear over a large temperature range, however, high wear, plastic deformation, and gross plowing during sliding causes increasing friction and irregular surface topographies [15,16].

Several studies have focused on combining multiple materials in a single coating in an attempt to circumvent the shortcomings of individual high-temperature lubricant materials, with the primary method being to combine a hard, wear resistant phase with a lubricating solid, including composite structures such as Ag/BaF₂-CaF₂ in Cr oxide [9] and Ag in TiC [16], as well as layered structures such as lubricious oxides on metallic and ceramic coatings [10] and MoS₂ over CrN [17], and adaptive coatings that combine lubricating phases which operate at different temperatures [18].

For this study, a composite coating consisting of a hard CrN matrix co-deposited with Ag is investigated. The premise of this coating system is that a solid lubricant layer of silver is present on the surface. As the solid lubricant layer is transferred to the counterface and worn away, Ag diffuses out of the matrix to replenish the surface and maintain a low friction coefficient. The self-lubricating nature of this adaptive coating has the potential to extend the service lifetime of the coating in high and low temperature environments as well as in cyclic temperature use.

EXPERIMENTAL PROCEDURE

CrN-Ag composite coatings were grown in a load-locked multi-chamber UHV stainless-steel dc dual magnetron sputter deposition system with a base pressure of 1.3×10^{-7} Pa (1×10^{-9} Torr). Water-cooled 7.5-

cm-diameter Cr and Ag targets with purities of 99.95% and 99.99%, respectively, were positioned at 12 cm from the substrate at an angle of 45° with respect to the substrate surface normal. The substrates were highly polished 304 stainless steel and Si(001) wafers that were cleaned with successive rinses in ultrasonic baths of trichloroethane, acetone, methanol, and deionized water and blown dry with dry N₂. The wafers were mounted on a molybdenum holder using Pelco colloidal silver paste (Ted Pella, Inc.) and inserted into the sample introduction chamber for transport to the growth chamber where they were heated to the growth temperature, 500 °C, using a resistive heater. 99.999% pure N₂ was further purified using a Micro Torr purifier and introduced through metering valves to reach a constant chamber pressure of 0.4 Pa (3 millitorr), which was measured using a capacitance manometer. Just prior to initiating deposition, the targets were sputter cleaned for 5 minutes while the substrate was covered with a protective shutter. Sputtering was carried out at a constant power of 1 kW to the Cr target, yielding a deposition rate of 50 nm/min. The power to the Ag target was varied from 0 to 80 W to achieve the desired compositions: pure CrN, as well as coatings with 3, 12, and 22 at.% Ag. The substrates were continuously rotated about the polar axis with 50 rpm, in order to obtain optimal coating uniformity. The deposition temperature, including the contribution due to plasma heating, was measured using a pyrometer which was cross-calibrated with a thermocouple within the sample stage.

X-ray diffraction (XRD) was completed with a Scintag XDS-2000 system with a Cu K α source and a model GLP 10195/075 detector. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed in a JEOL JSM-840A SEM with a Kevex Instruments model

2003 detector, for both surface plan-views and cross-sectional micrographs.

Vacuum annealing experiments were completed in the above described deposition system at 600 and 700 °C, with a background pressure of less than 1×10^{-5} Pa.

Tribological properties of the coatings were tested using the reciprocating multi-pass scratch method and a 200 micron Rockwell type diamond as the counterface. The testing was carried out with a CSM Instruments Micro-Scratch Tester. The parameters of the test included a stroke of 1.5 mm, a scratch speed of 0.7 mm/sec, and a normal load of 1 N. For each sample, 100 cycles were completed at ambient temperature and a relative humidity of 40-45%. Friction coefficients calculated from the normal and tangential forces were recorded for the first 10 cycles and then recorded at intervals of 10 from cycles 20 – 100.

The relative resistance to wear was determined from the cross-section of the linear wear track, measured using a calibrated Nikon-Lasertec Laser Scanning Confocal Microscope (LSCM), model 1LM21. Both optical and high resolution heightmap images were taken and analyzed with analySIS Pro © imaging software at the center of each wear track. The heightmaps were analyzed to determine the wear profiles of each specimen. The depth and cross-sectional shape of the wear track were measured by taking the horizontal mean of the z-component of the heightmap across the center of the linear wear track.

RESULTS AND DISCUSSION

Coating Composition and Structure

The relative deposition rates of pure CrN and pure Ag, grown in a N₂ atmosphere as a function of dc power, were determined by thickness measurements using SEM cross-

sectional microscopy. Based on these results, the power input to the Ag target was tailored to obtain the desired compositions with a nominal Ag content of 3, 10, and 20 at.%. Post-deposition EDS analyses of surfaces and cross-sections show measured Ag contents of 3, 12, and 22 at.%, in good agreement with the expected compositions from deposition rates. These values correspond to a volume fraction of solid lubricant in the matrix phase of 2.8, 11.1, and 20.5 vol.%, based on CrN and Ag molar volumes of 11.2 and 10.3 cm³/mol, respectively. The CrN within the composite is expected to be stoichiometric, with a Cr-to-N ratio of 1.0, based on the chosen deposition conditions which correspond to those of previous investigations [19-20].

Fig. 1 shows X-ray diffraction θ - 2θ scans from CrN-Ag composite coatings with compositions of 0, 3, 12, and 22 at.% Ag. The only detectable peaks in a scan range from 25 to 65 ° 2θ are from 111 and 002-type reflections, indicating a mixed preferred orientation. The 111 and 002 peaks for pure CrN, at 37.16 and 43.56 ° 2θ , respectively, have a full-widths at half-maximum of 0.54 and 0.24°. The $\sim 2\times$ narrower width of the 002 peak indicates a higher crystalline quality of the 002-oriented columns which can be attributed to the higher adatom mobility on (001) versus (111) surfaces [21]. The scan from the 3%-sample shows the same two peaks, however, the relative 111-peak intensity dropped by a factor of ~ 2 . The plot from the coating with 12 at.% Ag shows a broad shoulder around 37.5°, associated with the convoluted CrN 111 and Ag 111 reflections. The 22%-sample exhibits a Ag 111 peak at 38.08° with a shoulder associated with the CrN 111, and a CrN 002 peak at 43.60° with a shoulder from the Ag 002 reflection at 44.18°.

The XRD analysis clearly shows that the Ag segregates into Ag-grains for

compositions ≥ 12 at.% Ag. The grain size is estimated, based on the width of the Ag 111 peak of the 22%-sample, to be 15 nm. No grain size can be determined for the 12% sample, since the Ag 111 peak is too convoluted with the CrN 111. We expect, based on the negligible solubility of Ag in group VI metals such as Cr and Mo [22], that Ag also segregates in the 3%-coating. However, no conclusion can be made based on the XRD results, since the Ag-grains are likely too small to be detected. The Ag addition to the growth of CrN also affects the preferred CrN texture, which evolves from a 111 and 002 mixed texture to a 002 preferred orientation with increasing Ag content. We attribute this effect to a preferential incorporation of Ag on rough (111) versus smoother (002) surfaces which leads, in turn, to a suppression of the continued growth of the 111-oriented columns for the case of high-Ag-content coatings.

Lubricant transport to the surface

CrN-Ag composite coatings were annealed in order to study the diffusive transport of the Ag to the surface. Fig. 2(a) is a typical plan-view SEM micrograph from a 22%-Ag coating which was annealed at 700 °C for 60 minutes. The Ag that diffused to the surface appears as bright particles in the micrograph. The compositional map, obtained by EDS X-ray dot-mapping from the outlined area, is shown in Fig. 2(b). It confirms that these particles are Ag agglomerates. The dark spots correspond to areas with high Ag concentration while the bright background indicates Cr. The Ag particles are uniformly distributed on the surface with a density of 1.7×10^6 mm⁻² and widths ranging from 100 to 1100 nm, with an average width of 375 nm. That is, these segregated Ag agglomerates are considerably larger, by a factor of 25, than

the Ag grains in the as-deposited layer, which were determined from X-ray peak width analyses to be 15 nm wide.

Figure 3 illustrates the accumulation of Ag on the surface as a function of annealing time and temperature from a composite coating with 22 at.% Ag grown on Si(001). The as-deposited layer shown in the micrograph in Fig. 3(a) is relatively uniform, with some roughness related to the columnar microstructure as discussed below. The bright speckles in the micrograph cannot be identified with certainty, but may be due to small (~ 50 nm) Ag aggregates which agglomerate at the surface in the cusps between crystalline columns during the deposition at 500 °C. Fig. 3(b) is from the same coating, after vacuum annealing for 10 minutes at 600 °C. At this stage, Ag agglomerates are clearly observable. Their density is $9.1 \times 10^5 \text{ mm}^{-2}$ and their width ranges from 50 to 400 nm. Statistical analyses from several micrographs equivalent to $100 \mu\text{m}^2$ in total area, provide a value for the average width of the Ag grains of 150 nm. The total amount of Ag on the surface, as determined from the agglomerate size distribution and assuming spherically shaped Ag surface grains, is $1.5 \times 10^{-5} \text{ g/cm}^2$. This value corresponds to 2.4% of the overall Ag content in the 2.5- μm -thick composite coating and corresponds to a continuous Ag layer that would be 15 nm thick. Fig. 3(c) is a plan-view SEM micrograph from the same 22 at.% Ag coating after a 40-minutes anneal at 600 °C. The Ag surface-agglomerates are 60 to 480 nm wide, with an average width of 210 nm. This is 40% larger than for the 10-minute-anneal (Fig. 3b), indicating both a continued Ag diffusion to the surface as well as agglomerate coarsening. The surface grains exhibit distinct shapes and faceting, indicating a relatively large adatom mobility at the annealing temperature $T_a = 600$ °C, which corresponds to a homologous

temperature (T_a/T_m – in K) of 0.71, where the Ag melting point $T_m = 962$ °C. The various grain shapes are attributed to crystalline orientations including 011 (rod), 111 (triangle), and 001 (rounded square). The total amount of Ag on the surface is $2.4 \times 10^{-5} \text{ g/cm}^2$, which corresponds to 3.7% of the Ag in the coating and is 60% more than after a 10-minute anneal. Fig. 3(d) is from the surface of a 22 at.% Ag coating annealed at 700 °C for 60 minutes. The higher annealing temperature leads to larger grains, 100 to 1100 nm wide, which exhibit strong faceting but also show some asymmetric shapes, attributed to coalescence of two or more grains without sufficient time to reacquire equilibrium shape. The Ag coverage is $1.0 \times 10^{-4} \text{ g/cm}^2$ or 16 % of the total Ag content of the coating.

Fig. 4 shows plan-view SEM micrographs from CrN-Ag composite coatings with (a) 12 at.% Ag and (b) 22 at.% Ag. Both coatings were annealed at 700 °C for 60 minutes and are shown with the same magnification to illustrate the strong effect of coating composition on the agglomerate size, distribution, and interparticle spacing. A coating with 3 at.% Ag (not shown) has also been studied. However, no change in surface morphology could be detected by SEM, indicating negligible Ag-transport for such coatings at 700 °C. At 12 at.% Ag (Fig. 4a), the Ag forms surface agglomerates that exhibit a range of particle sizes, from 50 – 270 nm, with an average width of 110 nm and a density of $2 \times 10^7 \text{ mm}^{-2}$. The surface agglomerates of the 22 at.% Ag sample (Fig. 4b) are wider by more than a factor of 3, with an average width of 375 nm. Their density is $1.7 \times 10^6 \text{ mm}^{-2}$, roughly 10 times less than for the 12%-sample. Particle size analyses show that the area densities of Ag on the surfaces are 3.0×10^{-5} and $1.0 \times 10^{-4} \text{ g/cm}^2$ for the 12% and 22%-samples, respectively, corresponding to fractions of 8.4% and 16% of the total Ag content of the

respective coatings. That is, while the 22%-sample contains approximately 2× more Ag than the 12%-sample, the amount of Ag that diffuses to the surface is 4× higher. This indicates that the Ag transport to the surface increases rapidly with increasing Ag content in the coating, in agreement with our observation of negligible Ag transport during a 700-°C-anneal of a coating with 3 at.% Ag. We attribute the increased Ag transport to a higher connectivity of diffusion pathways, as discussed below. A similar mechanism has been reported previously [16].

Fig. 5 is a cross-sectional SEM micrograph of an as-deposited 2.5-μm-thick CrN-Ag composite coating with 22 at.% Ag grown on Si(001). The coating exhibits a dense columnar microstructure with a column width ranging from 25 – 50 nm, in good agreement with the feature size, ~50 nm, observed in the plan-view micrograph from the same sample shown in Fig. 3(a). The surface roughness exhibits a maximum peak-to-valley height difference of ~30 nm. At the imaging resolution, no Ag agglomerates can be detected on the surface or in the coating. This is in agreement with the SEM surface micrograph and the XRD peak-width analysis, showing that the Ag grains in the as-deposited 22%-coating are only ~15 nm wide and below the detection limit of the SEM.

We expect that the columnar grain boundaries offer a preferential diffusion path to the surface. In particular, some Ag may segregate during deposition to open columnar grain boundaries to form Ag-filled channels that are up to ~15 nm in width, as indicated by XRD. During annealing, the Ag-filled boundaries become the preferential diffusion paths for Ag transport to the surface. The rate for Ag transport depends strongly on the width and connectivity of the paths which increases with increasing Ag content, as observed in our experiments. The

22 at.% Ag coating contains efficient diffusion paths, resulting in considerable Ag transport to the surface and between adjacent Ag-rich regions to form large surface agglomerates. At a reduced Ag concentration of 12 at.%, the boundary regions are narrower and less connected, resulting in a reduced rate of transport, particularly between adjacent columnar regions. At a Ag concentration of 3%, the formation of surface agglomerates is absent as the diffusion paths are expected to be discontinuous.

The SEM investigations presented in Figs. 2-5 show that annealing of the CrN-Ag composite coatings results in Ag transport to the surface. This process is exactly what is envisioned for the CrN-Ag self-lubricating coating system. During ideal coating operation, the Ag distributes evenly across the surface and across the counterface material as sliding contact progresses. When wear during operation removes Ag from the surface, the depleted regions will be replenished with Ag that diffuses to the top surface during medium-to-high temperature operation. The optimal Ag concentration will depend on the application parameters like operating temperature and wear-rate. For example, at high operating temperatures, it may be desirable to limit the Ag transport to the surface by providing only limited diffusion paths, as observed in the 12% Ag sample. Another advantage of the 12% over the 22% coating may be the smaller closely-spaced agglomerates which provide good surface coverage at a lower level of Ag per surface area. In contrast, the higher total Ag concentration in the 22%-coating yields lower friction and wear at room temperature, as shown in the following.

Room Temperature Tribological Performance

Fig. 6 is a plot of the friction coefficient μ , determined by multi-pass micro-scratch measurements, for CrN-Ag composite coatings with 0, 3, 12, and 22 at.% Ag deposited on stainless steel substrates. The plot also includes a 12%-sample which has been annealed at 700 °C for 60 minutes, comparable to that shown in Fig. 4(a). Fig. 6(a) is a plot over the full 100 cycles while Fig. 6(b) shows the first 10 cycles. The pure CrN coating, as well as the 3% and as-deposited 12% Ag coatings show a drop in μ for the first ten cycles, followed by a continuous increase up to the total measured 100 cycles. The initial decrease in friction for these samples is attributed to the transfer of material to the counterface as has been previously reported [23]. As sliding wear progresses, the depth of penetration of the diamond gradually increases, which both widens the linear wear track and increases the plowing stress in front of the counterface. This increase in measured tangential force increases the calculated friction coefficient. The friction of the 22 at.% Ag sample remains relatively constant throughout the test, with μ increasing slightly from 0.04 to 0.06. That is, the composite coating with 22 at.% Ag exhibits a friction coefficient that is 2× smaller over the entire testing range (all cycles), clearly demonstrating the lubricating effect of Ag in CrN. The 12% Ag annealed sample shows an initially low μ -value, comparable to that of the 22% Ag sample, but as the testing continues, μ approaches that of the as-deposited 12% Ag sample. This behavior is attributed to Ag surface agglomerates, as shown in Fig. 4(a), which initially provide a high level of lubrication. However, as wear progresses, this Ag solid lubricant surface-layer is depleted and the counterface material comes into contact with the bulk

coating. Since only the surface is significantly affected by the annealing, the friction coefficient approaches that of the 12% coating in the as-deposited condition. The result on the 12% annealed coating indicates that this composite may show promising tribological performance at high operating temperatures where Ag transport to the surface will replenish the solid lubricant layer and maintain a low friction coefficient. The excellent Ag surface coverage of this coating after annealing, as discussed above, adds to the promising properties of this coating.

Fig. 7 shows the cross-sections of the wear tracks from CrN-Ag composite coatings as determined using LSM. The wear-track in the pure CrN coating after 100 scratch cycles is 0.40 μm deep. The track-depth decreases to 0.33, 0.25, and 0.19 μm as 3, 12, and 22% Ag is added to the coating, respectively. This result is in good agreement with the decreasing friction coefficient with increasing Ag-content, as shown in Fig. 6. The lower tangential force experienced in the higher Ag content samples leads to a lower plowing stress, which, in turn, reduces the wear rate. The reduced wear even at relatively high Ag contents indicates that the mechanical integrity of the CrN matrix is maintained and the added Ag continues to provide enhanced lubrication.

CONCLUSIONS

Composite coatings consisting of a CrN matrix and an embedded Ag solid lubricant were co-deposited via reactive magnetron sputtering. Film compositions are controlled by the power to the Ag target. X-ray diffraction shows that pure CrN coatings exhibit a mixture of 111 and 002 oriented grains. However, co-deposition of Ag leads to a 002 preferred orientation due to a suppressed growth on the rougher 111

surfaces. Segregation within the columnar microstructure leads to a phase separation of the CrN matrix and the Ag solid lubricant.

Annealing experiments demonstrate that Ag is mobile in the CrN matrix for coatings with ≥ 12 at.% Ag. The Ag diffuses to the surface and forms uniformly distributed agglomerates which increase in size with annealing time, annealing temperature, and Ag content of the coating. The diffusive transport increases rapidly with Ag content. This is attributed to a higher connectivity of Ag-filled grain boundary regions which are expected to form between crystalline CrN columns and to offer an ideal segregation and diffusion path for Ag.

The coating with the highest Ag content (22 at.%) exhibits the lowest friction coefficient and the best wear resistance at room temperature. The initial friction during scratch testing of 12%-Ag coatings is reduced by prior annealing. This is due to the presence of solid lubricant agglomerates on the surface. These results promise that the envisioned replenishment of the solid lubricant surface layer via diffusive transport through the CrN matrix is feasible and that CrN-Ag composite coatings may exhibit excellent high temperature wear resistance.

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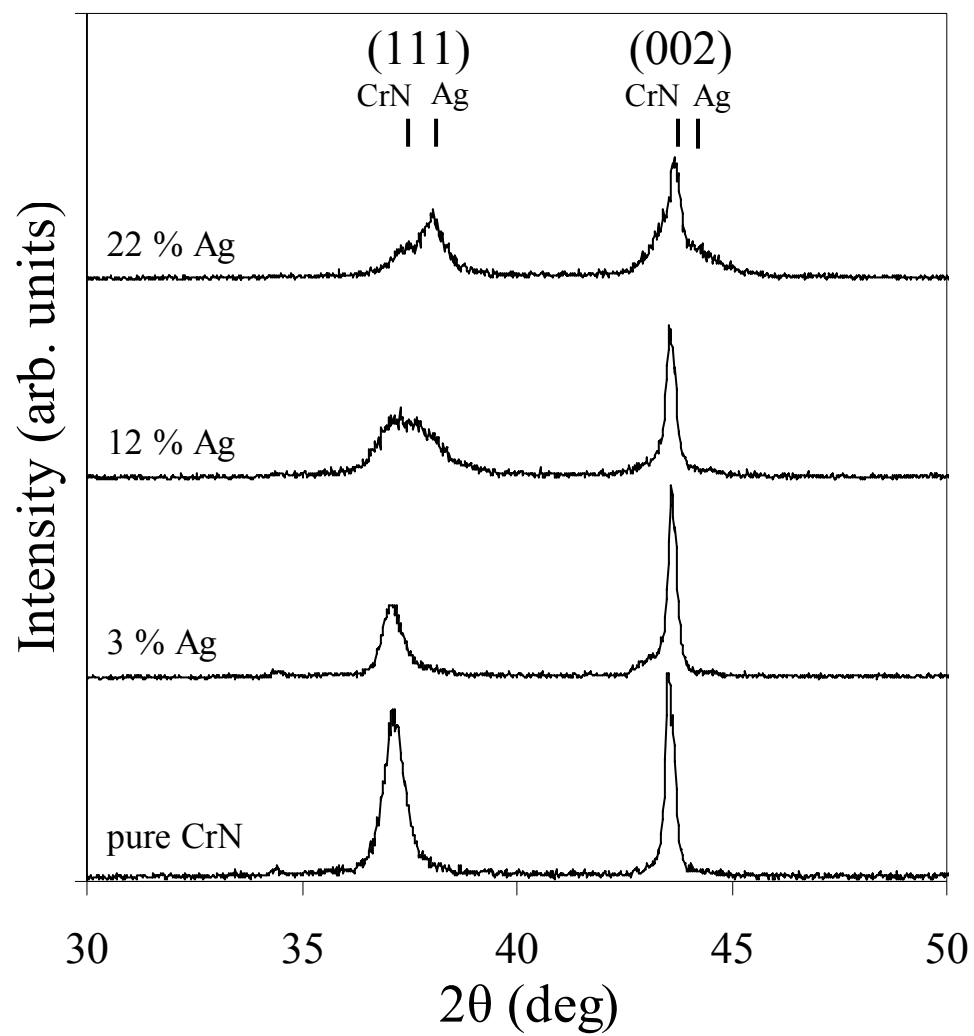


Figure 1. XRD θ - 2θ scans from CrN-Ag composite coatings containing 0, 3, 12, and 22 at.% Ag. The expected positions for CrN and Ag 111 and 002 reflections are indicated.

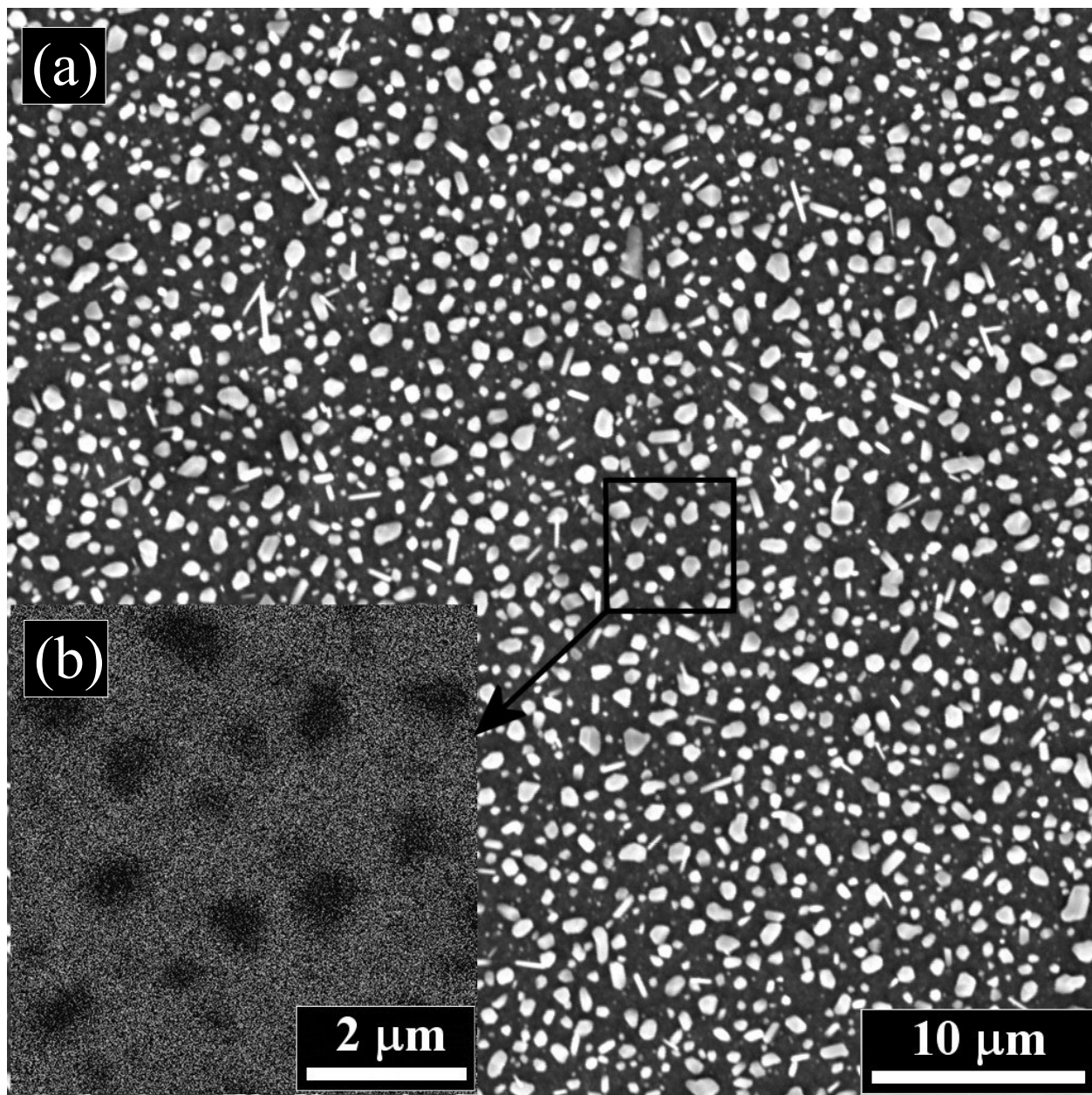


Figure 2. (a) Secondary electron micrograph and (b) corresponding higher magnification EDS X-ray dot map from a surface of a CrN-Ag composite coating with 22 at.% Ag that was annealed for 60 minutes at 700°C. The composition map is obtained from the outlined area and shows Ag as dark and Cr as bright dots.

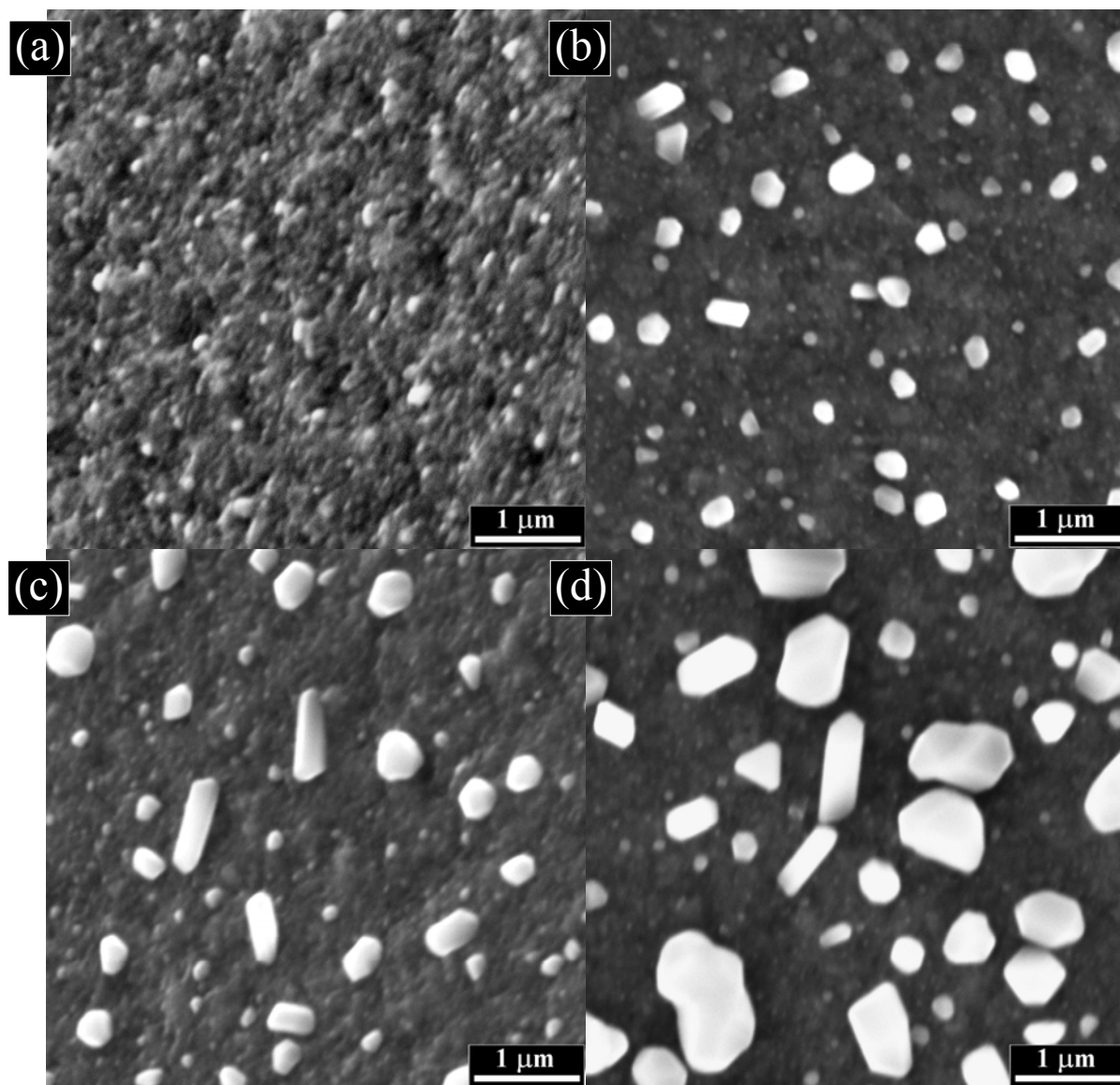


Figure 3. Plan-view SEM micrographs from a 22 at.% Ag specimen (a) as-deposited, (b) annealed for 10 min. at 600 °C, (c) annealed for 40 min. at 600 °C, and (d) annealed for 60 min. at 700 °C.

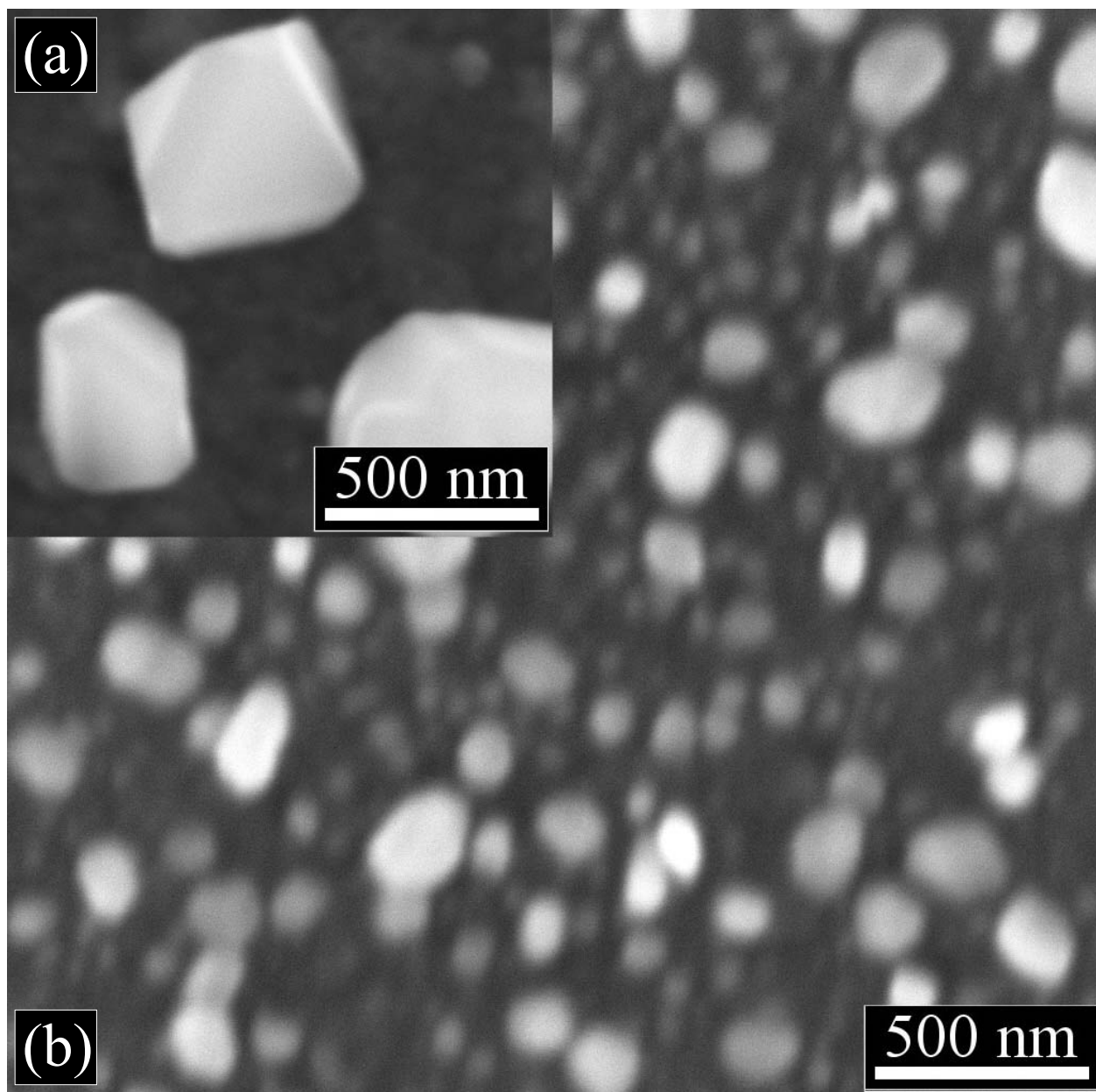


Figure 4. SEM micrographs (same magnification) of composite coatings annealed for 60 minutes at 700 °C with (a) 12 at.% Ag and (b) 22 at.% Ag.

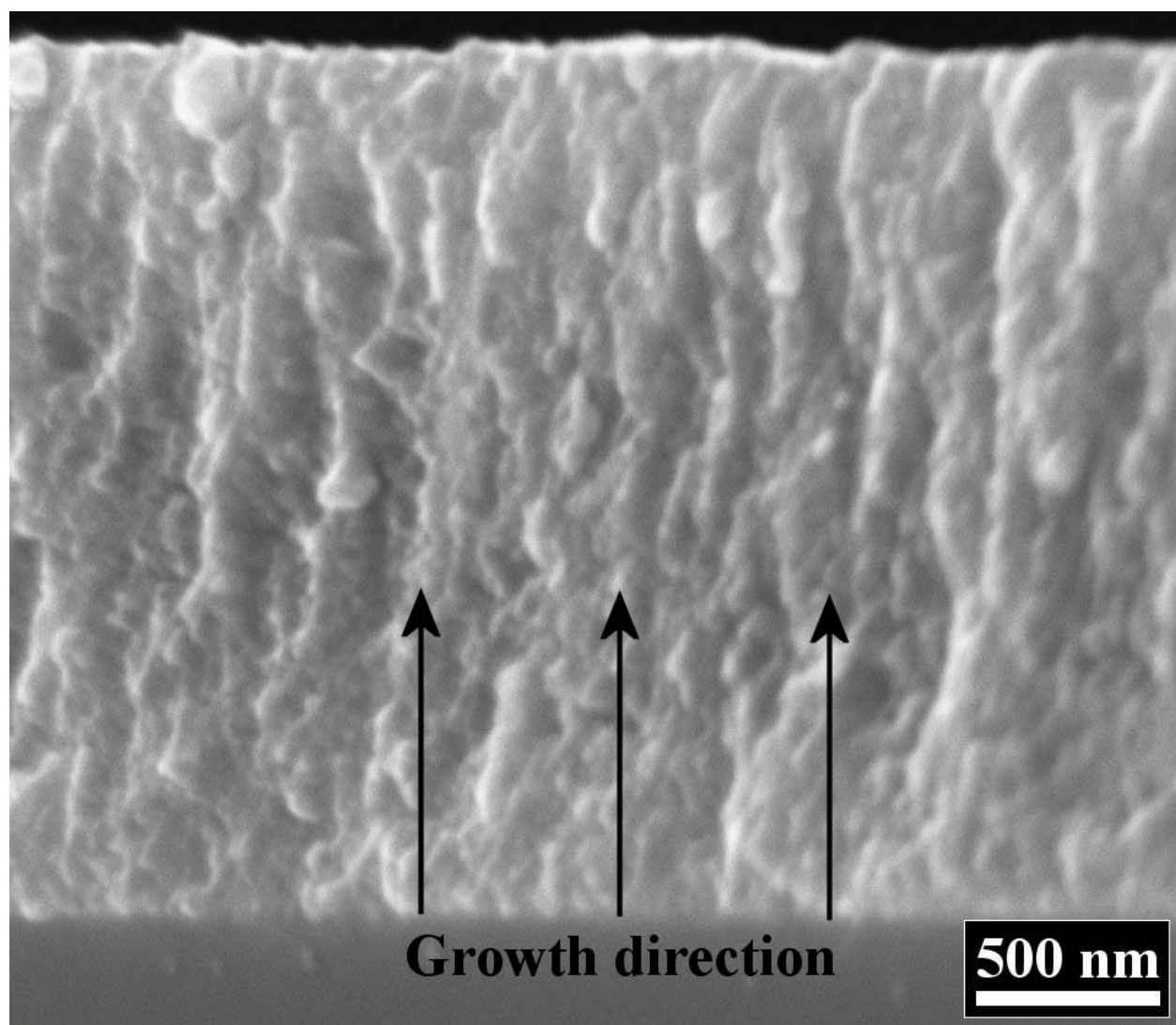


Figure 5. Fracture cross-section of an as-deposited CrN-Ag composite coating with 22 at.% Ag grown on Si(001).

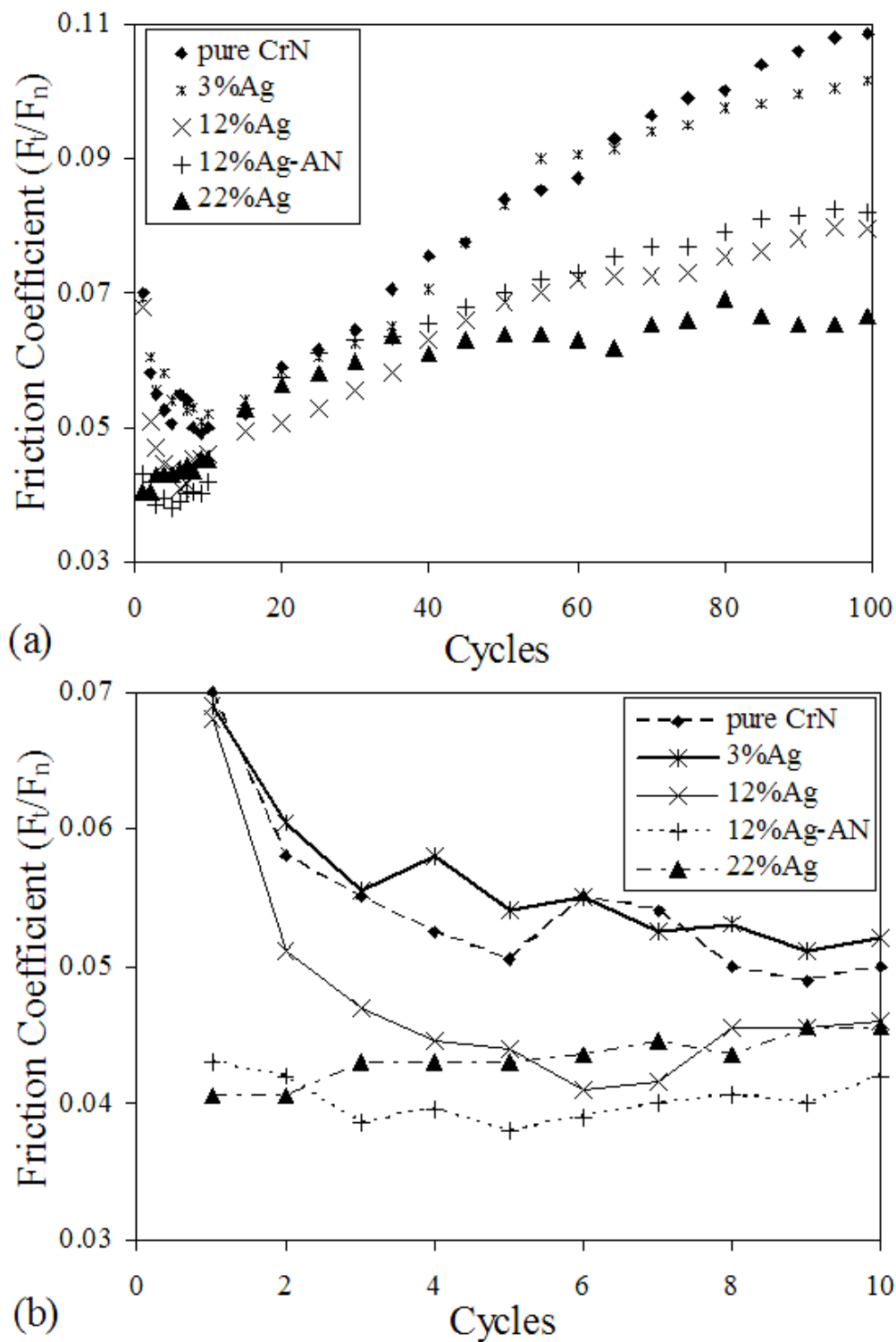


Figure 6. Plot of friction coefficients versus # of cycles during multi-pass micro-scratch tests on CrN-Ag composite coatings with 0, 3, 12, and 22 at.% Ag and an annealed 12%-coating. (a) shows the data from 100 cycles and (b) from the first 10 cycles.

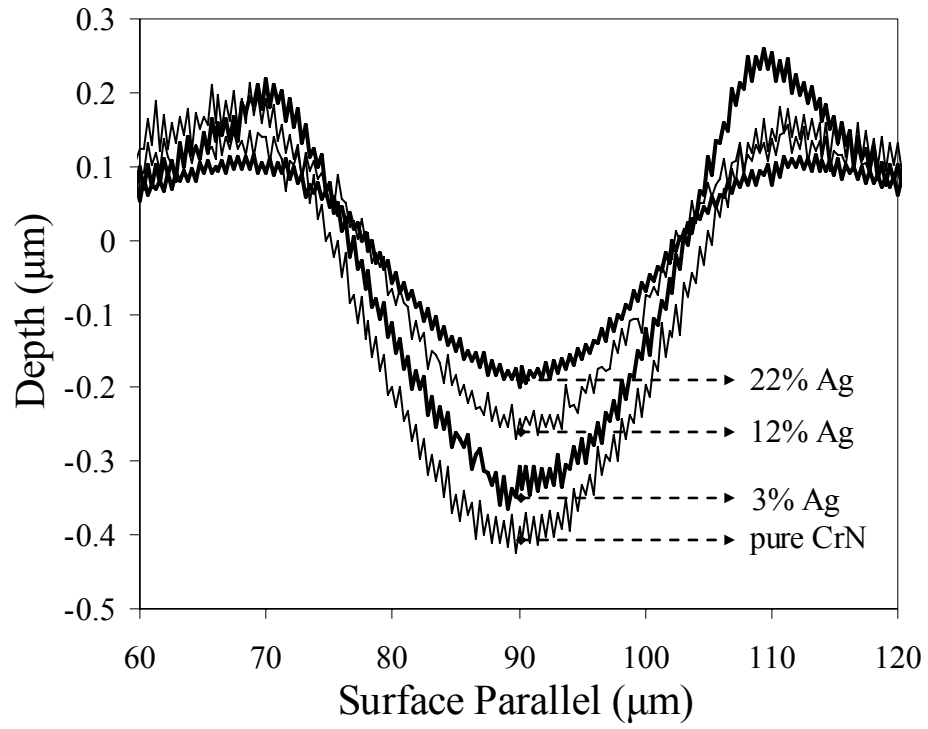


Figure 7. Wear-track cross-sections from CrN-Ag composite coatings with 0, 3, 12, and 22 at.% Ag.