Thermal stability and mechanical properties of sputtered Chromium-Molybdenum-Nitride (CrMoN) coatings

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ABSTRACT

Purpose: The purpose of paper is to determinate thermal stability and mechanical properties of sputtered chromium-molybdenum-nitride (CrMoN) coatings.
Design/methodology/approach: We have deposited 1.8 m-thick ternary $Cr_{0.5}Mo_{0.5}N_{1.0}$ films on a CoCrMo alloy using a RF dual magnetron sputtering system, with Cr and Mo targets and N_2 as the reactive gas. These films were subjected to various thermal treatments in Ar, air, and microwave plasma. The hardness, Young's modulus, surface roughness, microstructure, and composition of films were studied by nanoindentation, AFM, x-ray diffraction, and x-ray photoelectron spectroscopy.
Findings: The as-prepared CrMoN films consist of an amorphous Cr-rich nitride matrix with Mo-rich nitride crystalline grains, about 15 nm in size. These films are thermally stable up to 600ºC in air. Thermal annealing in the air at 800ºC resulted in an increase in surface roughness and hardness, due to film oxidation, with Cr_2O_3 as the main crystalline phase. Plasma treatment in a H_2/N_2 gas mixture, at 800ºC, did not lead to grain growth. Instead, the existing grains were reduced to about 10 nm and a new nanocrystalline phase has been formed. This leads to a decrease in the surface roughness, and an increase in the film hardness. In addition, we have further modified the film properties through a combined thermal treatment process. Thermal annealing in the air at 800ºC, followed by microwave plasma treatment at 800ºC resulted in a film with decreased surface roughness, and improved mechanical properties. Reversing the order of the thermal treatments resulted in a further decrease in surface roughness, but it shows a reduction in the mechanical properties.
Research limitations/implications: The present investigation was carried out with only one composition, $Cr_{0.5}Mo_{0.5}N_{1.0}$, of ternary thin-film system.
Originality/value: The combination of thermal and plasma treatments can be used to control the microstructure, surface topography, and mechanical properties of ternary CrMoN films. Such post-deposition treatments can further improve the materials properties for desired application, and to produce new nanocomposite materials with technologically important combination of properties.
Keywords: Heat treatment; Hardness; Surface morphology; CrMoN coatings

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1. Introduction

The CoCrMo alloy system is still a material of choice for many articulating biomedical implants, and the improvement of their performance is important. The methods to increase the hardness and corrosion resistance of metallic implants include nitrogen ion implantation, thermal diffusion, and deposition of hard coatings. Many of these innovations have not been proven to be successful in clinical applications. For example, nitrogen ion implantation increases the surface hardness and wettability. However, the ion-implanted surface layer is less than a micrometer in thickness, which may quickly get worn through. Thermal diffusion hardening of the metallic surface can produce a thicker surface layer than ion implantation, but scratching and oxidative wear are still possible. Among the surface modification methods used, a significant improvement of CoCrMo implant performance has been obtained with TiN, CrN, CrCN coatings in various combinations, and with nanocrystalline structure [1, 2]. Transition metal nitrides, mainly based on titanium and chromium, display a wide spectrum of interesting physical properties, which make them useful materials for a variety of different applications, such as protective coatings against wear and corrosion [3-5]. Ternary Cr-X-N (X=Ti, Al, Si, C, B, Ta, Nb, Ni.) [6-17] coatings were explored as an evolutionary step from CrN coatings. For example, ternary Cr-Mo-N coatings demonstrated superior properties tailored through two binary coatings of CrN and MoN [18].

In this paper, we investigated CrMoN ternary coatings prepared by RF-magnetron sputter deposition on CoCrMo alloy substrates. Such a ternary system is compositionally close to the substrate and may have the potential for improving the performance of CoCr alloy-based articulating implants when compared to binary CrN or MoN coating systems. The resulting 1.8 μm-thick films were also subjected to various thermal treatments to explore their stability, and the evolution of the microstructure and properties. The resulting crystallinity, surface morphology, and mechanical properties of the ternary films were determined and analyzed.

2. Experimental details

2.1. Sample preparation

CrMoN coatings were prepared using a RF dual magnetron sputtering system (NORDIKO 3500-13.56 MHz) with two 4-in targets of Cr and Mo, at ENSAM. The nitrogen flow was adjusted in these deposition experiments to a saturation limit. The target voltages were varied to change the sputtering rate and to modify the composition of the CrMoN layers. Chromium and Molybdenum targets were co-sputtered at an optimized sputtering rate to yield uniform 1.8 μm thick films of desired $Cr_{0.5}Mo_{0.5}N_{1.0}$ composition on polished CoCrMo biomedical alloy substrates. The substrate temperature during the deposition was about 200°C. A representative SEM image of the resulting $Cr_{0.5}Mo_{0.5}N_{1.0}$ is shown in Fig. 1.

2.2. Thermal treatments

Once the films were deposited, several samples underwent various *ex-situ* thermal treatments. These treatments included furnace annealing in the air, argon, and microwave plasma processing in H_2/N_2 gas mixture. The latter treatment is used as an initial step in preparing the substrate for nanocrystalline diamond (NCD) deposition in a CVD process, and it was important to understand the behaviour of CrMoN film as a potential interlayer for NCD. The furnace annealing of the samples in the air and Ar was conducted at temperatures up to 800°C. Microwave plasma annealing in a H_2/N_2 gas mixture (typical pre-treatment procedure for the deposition of nanodiamond films) was performed at 600 W power; this leads to a substrate temperature of 800°C. The gas pressure and flow rates were set at 30 mTorr, 10 sccm for H_2, and 36 sccm for N_2, respectively. In addition, two combinatorial thermal treatments were conducted: (i) the sample was annealed in the air at 600°C, with subsequent annealing in the H_2/N_2 microwave plasma at 800°C; and (ii) the sample was annealed in the H_2/N_2 microwave plasma at 800°C, with subsequent annealing in the air at 800°C.

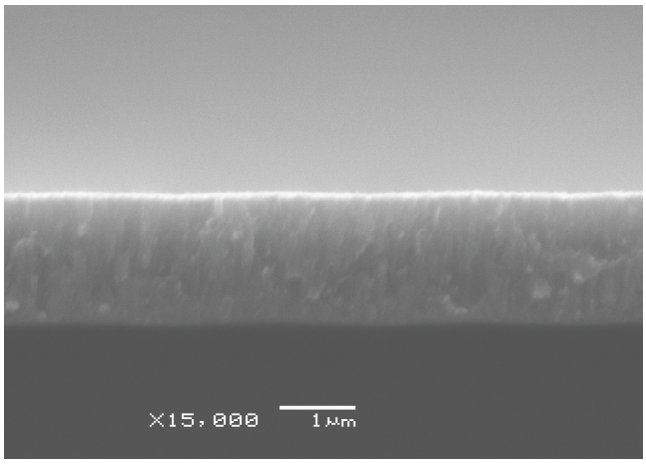


Fig. 1. A cross-sectional scanning electron micrograph of the as-prepared $Cr_{0.5}Mo_{0.5}N_{1.0}$ coating

2.3. Characterisation

After deposition and thermal processing, the films underwent various characterisation techniques to determine the physical changes induced by the thermal treatments. For crystallinity, the films were analyzed by x-ray diffraction (XRD). The surface morphology was studied with atomic force microscopy (AFM). The chemical analysis was performed with x-ray photoelectron spectroscopy (XPS). Finally, the elastic parameters were determined by nanoindentation.

A Philips X'pert thin film X-ray diffractometer with Cu Kα radiation (operated at 45 kV and 40 mA, wavelength 0.15406 nm) was used to determine the structure and phase composition of the coatings. The mean size of crystallites was determined with Lorentzian fitting of the major peaks in the X-ray diffraction (XRD) spectrum and Scherrer equation.

Atomic force microscopy (AFM, Veeco Topometrix Explorer) was employed in contact mode at normal laboratory conditions to obtain the surface morphology images of the coatings. V-shaped high resonance frequency silicon nitride cantilevers with a pyramidal tip of 50 nm radius and force constant of 0.032 N/m were used.

X-ray photoelectron spectroscopy was used to determine the electronic and chemical states of the components within the system. Incident x-rays are absorbed by different chemical species. Both surface and depth profile information were collected on a Kratos Analytical Axis 165 XPS system equipped with the monochromatic Al Kα tube at 17 mA and 10 kV. The resultant photoelectrons were collected with hybrid lens at pass energy of 20 eV. The Ar-ion sputter etch gun was set at 10 mA and 3 kV. The base pressure of the system below $5x10^{-7}$ Pa, with an Argon pressure of $1.1x10^{-5}$ Pa during the measurement and etch cycles. At each scan depth, we collected seven different scans: a full survey, and a scan the Co *2p*, Cr *2p*, O *1s*, N *1s*, C *1s*, and Mo *3d* peaks.

Nanoindentation hardness and Young's modulus of CrMoN ternary films were measured by using a Nanoindenter XP (MTS Systems Corporation, Oak Ridge TN) system. The system was calibrated by using silica samples for a range of operating conditions. Silica nanoindentation modulus and hardness were calculated as 70.5 GPa and 9.1 GPa, respectively, before the experiments with the samples. A Berkovich diamond indenter with total included angle of 142.3° was used for all the measurements. The maximum indentation depth was 250 nm. A 10 seconds hold time at maximum load and 50 second at 10% of maximum load during unloading was used in order to minimize thermal drift and creep effects. The data set was processed using the proprietary software (TestWorks 4, MTS Systems Corporation) to produce load-displacement curves, and the mechanical properties were calculated using the Oliver and Pharr method.

3. Results and discussion

The CrMoN films are stable with no visible changes in the microstructure and properties during furnace thermal treatments up to 600°C in both Ar and air. However, when the temperature is increased to 800°C, significant changes are observed.

In the XRD patterns shown in Fig. 2, we can clearly see the changes in the crystalline structure and phase composition of the samples with different thermal treatments. The black line in Fig. 2a represents the original as-deposited sample; the red line in Fig. 2b is the sample annealed in the air at 800°C; and the green line in Fig. 2c is the sample annealed in microwave plasma at 800°C.

Based on the XRD peak positions and the XPS data, it was suggested that in the original untreated sample, the structure can be described as a nanocrystalline Mo-rich ternary nitride phase with about 15 nm grain size dispersed in a predominantly amorphous Cr-rich nitride matrix. In the air annealed sample (Fig.2b), we see the development of Cr_2O_3 crystallites as the dominant phase, while the proposed nanocrystalline ternary phase is still mainly preserved. This has been confirmed by the XPS data. When the thermal treatment was performed in microwave plasma, a secondary nanocrystalline phase was formed in addition to the existing ternary phase as shown in Fig. 2c. This new phase could not be identified through the JCPDS database. Interestingly, the calculated grain size for both co-existing phases in plasma-treated sample is about the same, about 10 nm. The analysis of the XPS spectra recorded for the different depths across the film, coupled with the XRD results, suggest that this new phase is a metal-rich quaternary Cr-Mo-C-N where the amount of nitrogen is small when compared with the as-deposited sample. Indeed, the H_2/N_2 plasma treatment resulted in substantial depletion of nitrogen in the original ternary film and contamination of the sample with carbon. It was also proposed that the new phase could form, at least partially, at the expense of the original nanocrystalline ternary phase in the coating. This could lead to a reduction in the grain size and/or partial decomposition of the original nanocrystalline ternary phase.

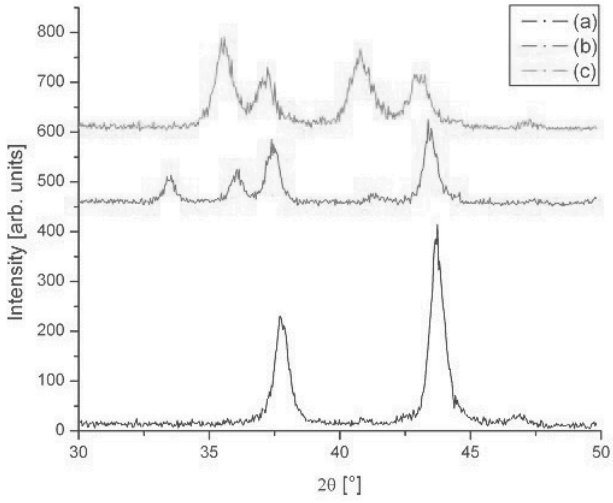


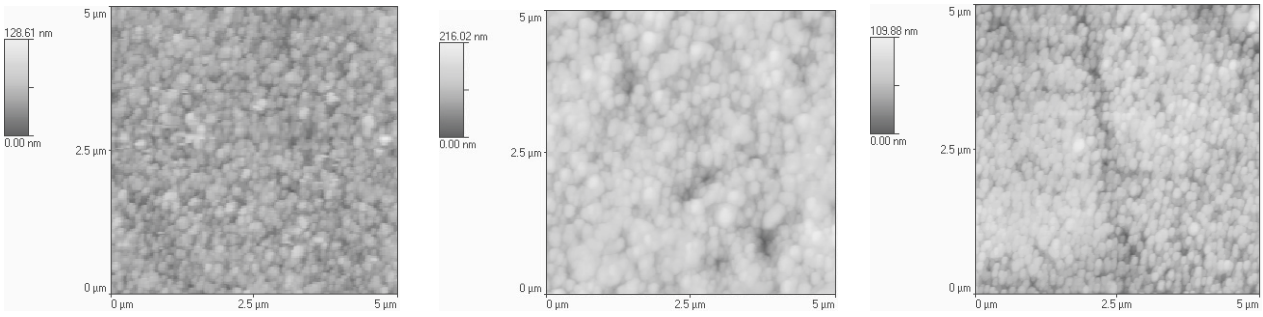
Fig. 2. X-ray diffraction patterns of (a) as-deposited CrMoN ternary film, (b) annealed in the air at 800°C, and (c) annealed in H_2/N_2 microwave plasma at 800°C

Table 1 above summarizes the elastic and roughness parameters for the samples subjected to different post-deposition treatments. While the thermal treatments result in a substantial increase of both the hardness and Young's modulus of the material, the observed trends in surface topography changes demonstrate the need for optimisation in the post-deposition treatment process, to obtain a combination of high hardness and low roughness which is critical for the application of such material in articulating implant components.

The surface roughness of the fabricated films was found to be in the nanoscale range. However, the thermal treatment changes the surface topography as the result of stress, grain growth, and phase transformations. The representative AFM 5x5 μm^2 images of the surface topography for the CrMoN samples exposed to different treatments are shown in Fig. 3. The surface roughness increases significantly due to the growth of a chromium oxide crystalline phase when the sample is annealed in the air. The plasma annealing does not change the surface roughness, but microcracks are often observed in the film (e.g., in AFM image in Fig. 3c) as the result of thermal stress.

Table 1.
Hardness, Young's modulus, roughness Ra and RMS parameters after different thermal treatments

Treatment	Hardness(GPa)	Modulus(GPa)	Roughness(Ra)nm	RMS(nm)
Original	9	200	11.1	14.1
Annealing in the air at 800°C	15	280	20.3	25.6
Annealing in mw plasma at 800°C	11	190	12.0	15.1
Annealing in the air at 600°C+mw plasma	10	225	10.7	13.4
Annealing in mw plasma air at 800°C	7	175	30.0	40.1



a) Original b) Annealing in air at 800°C c) Annealing in mw plasma at 800°C

Fig. 3. Atomic Force Microscopy (AFM) results of CrMoN coatings under different treatments

The results of nanoindentation tests show that the hardness of the original sample is relatively low, about 9 GPa. However, thermal processing resulted in significant changes in both the hardness and the Young's modulus of the samples. The sample annealed in the air at 800°C showed an increase in the hardness by 50 percent. Unfortunately, this sample also shows an increase in surface roughness, as shown in Figure 3b. For the microwave plasma annealed sample, the surface roughness was comparable to the untreated sample. However, the hardness only showed a modest increase of about 20 percent. Fig. 4 is a representative graph of the hardness versus the nanoindentation depth for these samples.

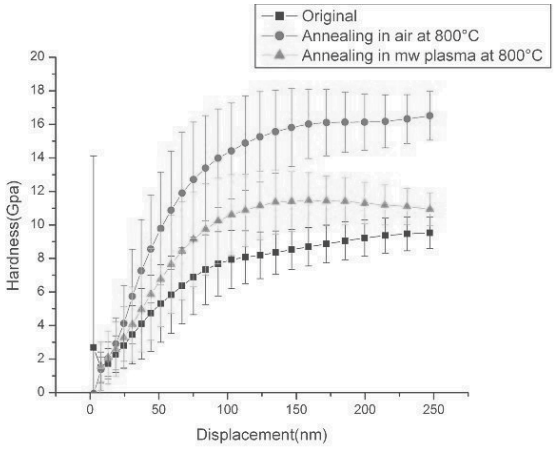


Fig. 4. Nanoindentation results of CrMoN coatings after the annealing treatment in the air and mw plasma at 800°C in comparison with the as-deposited sample

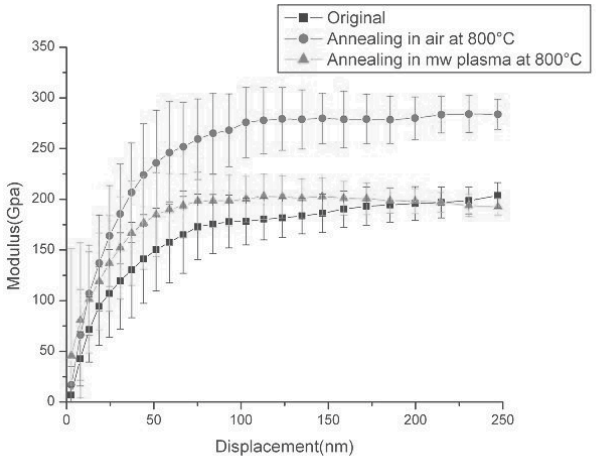


Fig. 5. Modulus results of CrMoN coatings after the annealing treatment in the air and mw plasma at 800°C in comparison with the as-deposited sample

In Figure 5, we can see a representative graph of the modulus results of the two thermal treatments in comparison with the untreated sample. From this, we can see the modulus of the air annealed sample increased about 33 percent with respect to the untreated sample. The modulus of the plasma annealed sample shows no significant change with respect to the untreated sample. Following the discussion above, a combinatorial post-deposition processing was proposed as the pathway for further modification of the microstructure and properties of the ternary CrMoN films;

in addition, this approach may lead to a better understanding of the observed phenomena.

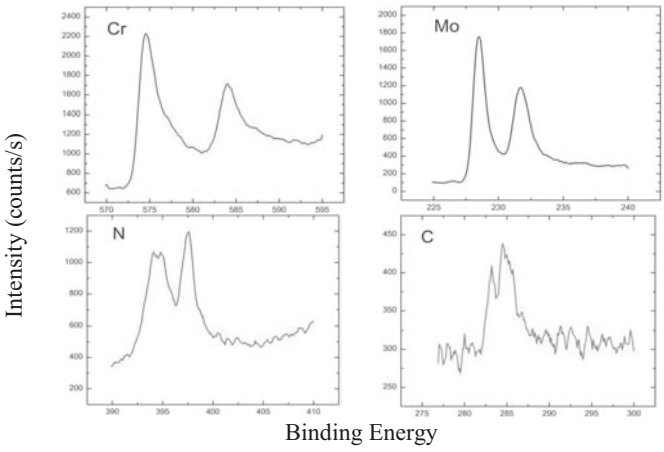


Fig. 6. XPS results of original as-deposited CrMoN coating

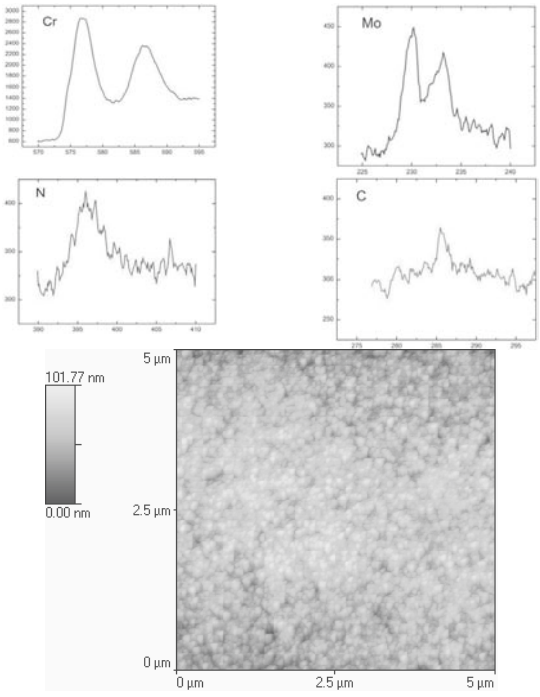


Fig. 7. XPS and AFM results after a combination treatment of annealing in the air at 600°C plus mw plasma at 800°C

In particular, the origin, structure, and composition of the secondary phase observed after the plasma treatment needs to be clarified.

Figure 6 shows the XPS spectra recorded after 30 min sputter etching of the as-deposited CrMoN sample. The composition of the sample was found to be uniform throughout the film thickness. Some carbon and oxygen impurities were found; and the carbon was partially present in a carbide form. After the H_2/N_2 plasma treatment, oxygen content was below the detection limit, and nitrogen content was significantly reduced.

However, the amount of metal-carbon bonding increased. The new secondary nanocrystalline phase was formed in this process as discussed above. On the other hand, when plasma treatment was performed with an initially oxidized sample (air oxidation at 600°C which neither forms chromium oxide nor induces phase changes), the loss of nitrogen was reduced and a very small amount of the secondary phase was observed.

This treatment resulted in a slight increase of the sample hardness and a reduction in the surface roughness, while maintaining a significant percentage of the initial phase. The XPS spectra and AFM image of the surface topography of the CrMoN sample exposed to sequential treatment in the air and plasma, respectively, are shown in Figure 7.

4. Conclusions

We have successfully deposited $Cr_{0.5}Mo_{0.5}N_{1.0}$ coatings on CoCrMo-alloy substrates, using RF reactive magnetron sputtering. These films were subjected to various thermal treatments. There are no significant changes observed in the film properties for thermal treatments in the air or argon up to 600 ºC. Films annealed in the air at 800 ºC, show the oxidation, as confirmed with both XRD and XPS. The dominant phase is Cr_2O_3, and the degree of oxidation depends on the annealing time. The thermal treated films show an increase in both hardness and Young's modulus, but there is a corresponding increase in grain size and surface roughness. Films treated in Argon at 800 ºC, show a smaller increase in hardness, with an increase in grain size and surface roughness. However, films annealed in microwave plasma at 800ºC, in an H_2/N_2 gas mixture, show a slight increase in the mechanical properties, but with a decrease in surface roughness, and grain size. The drawback is the possibility of crack formation in the film, due to increased thermal stress. In addition, this process leads to the formation of a new, presumably ternary or quaternary, nanocrystalline phase.

Furthermore, we treated samples with a combinatorial thermal process to further understand the observed trends. For films annealed in the air at 600ºC, with subsequent annealing in H_2/N_2 microwave plasma at 800ºC, there is a slight increase in the mechanical parameters of the film, with a slight decrease in surface roughness. By reversing the order of thermal treatments, we observe a significant reduction in the grain size. However, the resultant mechanical properties are substantially declined, and the surface roughness increased.

In this paper, we have successfully demonstrated the use of thermal treatments to control grain size, surface morphology, and mechanical properties in $Cr_{0.5}Mo_{0.5}N_{1.0}$ coatings on CoCrMo substrates. These simple processing techniques may be used for further improvement of the surface characteristics of nanocomposite coatings on biomedical implants. However, further research is necessary to understand the underlying physical processes involved. As a result, we plan to continue this research with various compositions of CrMoN coatings, and a wider range of thermal treatments.

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Additional information

The results of this investigation were presented as a poster at the International Conference on Vacuum and Plasma Surface Engineering 2009, held jointly with the International Workshop on Science and Application of Nanoscale Diamond Materials, in Hejnice, Czech Republic.

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