Phase Composition and Crystallite Size Study of Multilayered Transition Metal Films Based on Molybdenum and Chromium Nitrides

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***Abstract*—The paper is focused on the deposition and study of multilayered transition metal nitride films CrN/MoN obtained by vacuum arc deposition (Arc-PVD). Samples have from 12 up to 354 layers with total thickness of 8-15 µm. Bilayer thickness of samples vary in range from 2.2 µ to 40 nm. Films have been studied by scanning electron microscopy (SEM) from cross-section view. Their elemental composition also has been studied by energy-dispersive X-ray spectroscopy (EDS). Characterization of the structure of multilayered CrN/MoN films have been performed using X-ray diffraction (XRD) analysis. Two main phases of cubic CrN and γ-Mo_2N have been identified. Grain size distribution was calculated from XRD analysis data. It was observed the decreasing of average grain size with decreasing of individual layer thickness. This feature of studied films may be important for characterization and prediction of their mechanical properties, such as hardness, elasticity, toughness etc. According to the Hall-Petch strengthening, deposited films with lower values of individual layer thickness may have higher values of hardness and, hence, exhibit better toughness, wear resistance and improved performance of coated tools.**

Keywords—nitrides; structure; X-ray diffraction; grain size; hardness; thin films; cubic phase; multilayer; coatings

I. INTRODUCTION

It is well known that metals as well as the most of discovered nature materials with their intrinsic properties exhaust limits of their bulk-state applications. Engineering, industry and business still need improving of their productivity and efficiency, decreasing of expenses and increasing of quality. For these tasks the instruments, machine details and finished goods must maintain the primary, as-produced, properties, form and state, work adequately and perform specified functions and tasks. It will be not possible if material is damaged, deformed or broken. It is needed to enhance mechanical properties of discussed objects to avoid early failures. A lot of ways have been existed already with individual advantages and disadvantages, but most of them may be merged into two groups focused on direct improvement of entire tool/product's material properties (MAX-phases, alloying, tempering) or on surface modification (ion implantation, surface oxidation, ablation, protective coatings, etc.) [1-19]. Hard coatings are the most efficient in providing the protection from deformation and wear [20-32]. But often hard materials may be brittle and prone to cracking. That's why for protective coatings it is both crucial to have high hardness and toughness. The nitrides of transition metals are the best candidates to occupy the leading positions in satisfying such requirements [33-42]. Their study and development is an actual task of material science and engineering.

Design and characterization of microstructure of material is a key element on the way to produce films with desired mechanical properties. X-ray diffraction (XRD) analysis fits for such kind of problems very well. It is a non-destructive method of structure characterization which allows to get a plenty of necessary information for relatively low costs and short time with no any specific and difficult procedures of sample preparation.

The paper presents results of the study of the structure of multilayered CrN/MoN films which also have been the object of previous studies presented in [43].

II. DEPOSITION AND METHODS OF CHARACTERIZATION

Multilayered CrN/MoN coatings were obtained by vacuum arc deposition (Arc-PVD) using specially designed vacuum-arc unit "Bulat-6M" in atmosphere of nitrogen from two chromium and molybdenum cathodes. Six samples have been deposited during approximately 1 hour per each. Deposition time per one layer varies for samples from 300 to 10 second, which means reducing of individual layer thickness.

Cross-sections of samples deposited on steel substrates have been studied by scanning electron microscopy (SEM) using JEOL JSM-7001F Schottky Emission Scanning Electron Microscope. Elemental composition of layers in samples was analyzed by energy-dispersive X-ray spectroscopy (EDS) using EDAX Genesis X4M unit of FEI Quanta 400 FEG environmental scanning electron microscope. XRD analysis has been performed using Panalytical X'Pert Pro multipurpose diffractometer.

III. Results and Discussion

Multilayer design of coatings, thickness of layers and elemental composition have been studied on cross-section samples. Fig. 1 demonstrates a cross-section view of two

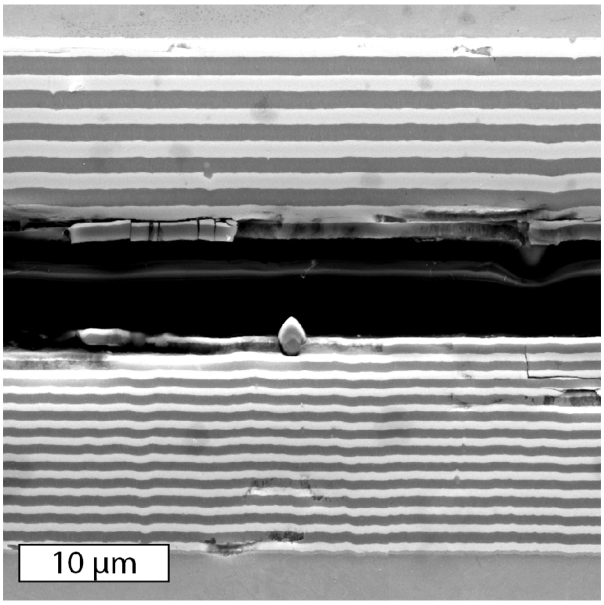

Fig. 1. Cross-section SEM image of multilayered CrN/MoN samples 1 (on the top) and 2 (on the bottom). Samples glued (black area between films) to the "sandwich" due to cross-section preparation process.

multilayer films prepared for sample study as a sandwich. Dark field between coatings is the glue used during cross-section sample preparation. Image demonstrate shape interface between alternating layers and shows good quality of Arc-PVD coatings. Top layer of films demonstrated in Fig. 1 have several exfoliations caused by cutting and mechanical polishing of samples during cross-section preparation.

Measured total thickness of each sample varies between 8-15 μm. Period (bilayer) thickness was 2.3, 1,2, 0.6, 0.1 and 0,04 μm for sample 1, 2, 3, 4, 5 and 6, respectively.

Elemental composition analysis by EDS have been performed on cross-section samples separately for CrN and MoN layers. Energy-dispersive X-ray spectra of sample 1 with period thickness of 2.3 μm is shown in Fig. 2. Spectrum of CrN layer and MoN layer taken separately are shown in Fig. 2(a) and Fig. 2(b) respectively.

EDS analysis of sample 1 has demonstrated elemental composition of CrN layer as following: 51 at.% of Cr, 43 at.% of N; for MoN layer the elemental composition was 67 at.% of Mo, 23 at.% N. 6-7 at.% of oxygen has been detected in studied multilayer films. It should be noted that EDS technique is not sensitive enough for light elements as nitrogen or oxygen as well as has low resolution of energy peaks. Thus, EDS may not give relevant results in Cr/N or Mo/N ratios with high quality and precision. Wavelength-dispersive X-ray spectroscopy (WDS) better fits for such kind of tasks and elements.

Structure of multilayered Arc-PVD CrN/MoN films has been studied using XRD (Cu Kα1 radiation) $\theta/2\theta$ scan. Spectra of studied samples in range $2\theta = 32\text{-}47°$ is presented in Fig. 3.

Two main phases have been identified in CrN/MoN multilayer coatings: cubic CrN phase and cubic γ-Mo_2N phase (structural type NaCl). Diffraction peaks observed on experimental patterns are very broad due to the overlapping of diffraction peaks from CrN and γ-Mo_2N phases. It happens due to the multilayer structure of studied films and due to the similar crystal structure of layers. X-ray beam penetrates the material deep enough to expose several layers and, hence, obtained diffraction pattern has contribution from several multilayered films. This way, presented experimental patterns are the integral spectra of CrN and γ-Mo_2N phases, which have very similar positions of diffraction peaks.

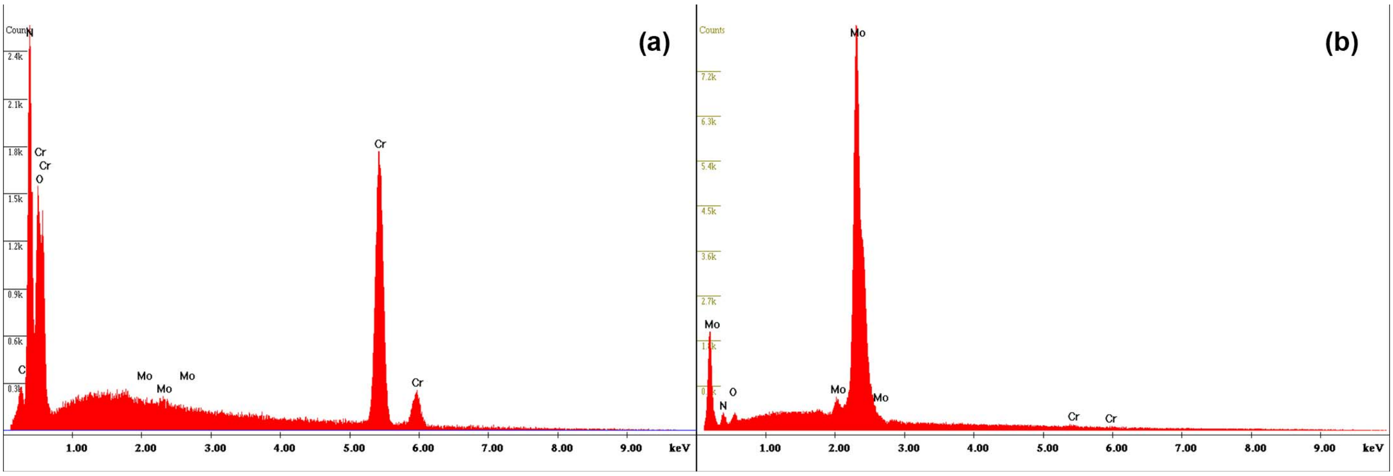

Fig. 2. Energy-dispersive X-ray spectra for multilayered CrN/MoN film, sample 1: (a) CrN layer, (b) MoN layer (taken from cross-section view).

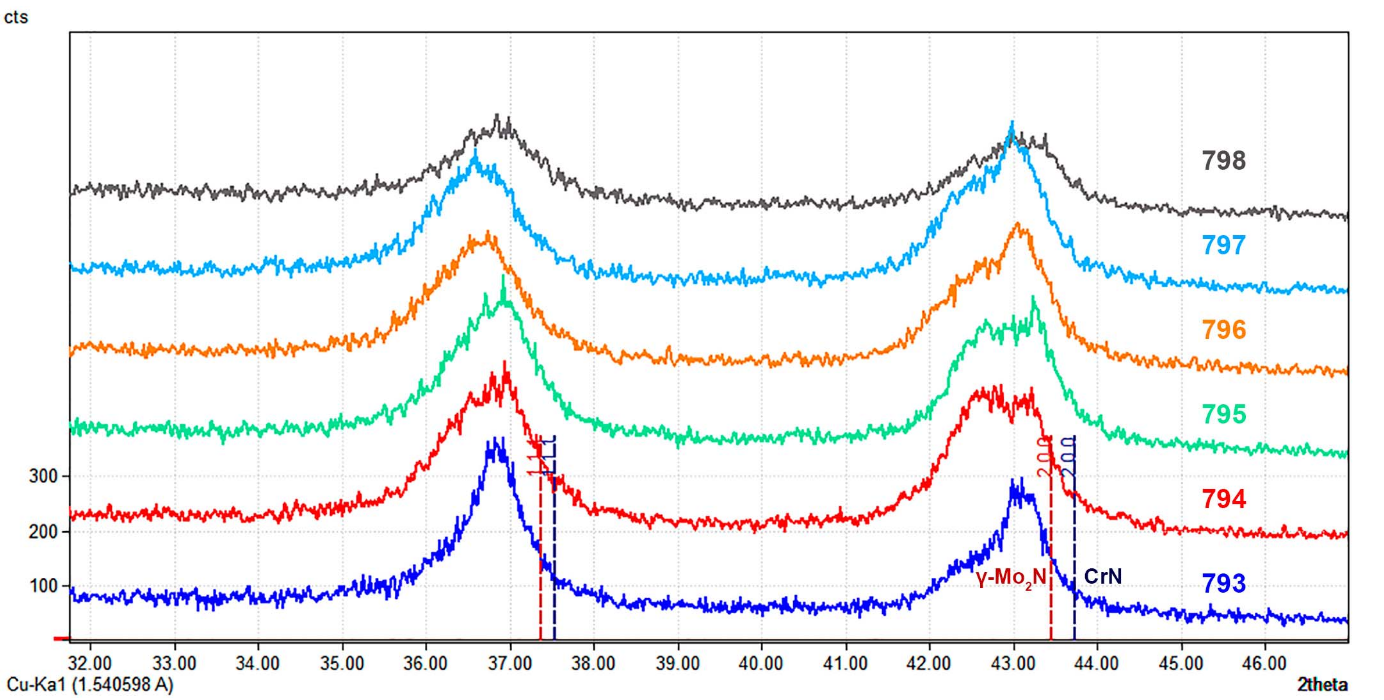

Fig. 3. X-ray diffraction spectra of multilleyered CrN/MoN films for samples 1-6 (spectra 793-798 respectively) and defined diffraction peaks positions for (111) and (200) reflections of cubic CrN and γ-Mo_2N phases.

From the diffraction spectra, it is seen that experimental diffraction peaks are shifted to the side of lower angles and, hence, larger interplanar distances and lattice constants, which may point on the present of compressive stresses in plane parallel to the surface. Calculated grain size distribution has shown the decrease of average grain size from 14 to 8 nm with the reduce of individual layer thickness.

IV. Conclusions

The elemental composition, micro- and nanostructure of the deposited Arc-PVD multilayered transition metal nitride

CrN/MoN films have been studied. It was observed, that coatings consist mainly of cubic CrN and γ-Mo_2N phases (structural type NaCl), their stoichiometry corresponds to the results of EDS elemental composition analysis. But limitations of EDS technique don't allow completely rely on obtained results and the confirmation by other methods of elemental composition study is necessary. XRD patterns demonstrate the presence of compressive stresses in deposited coatings. The decrease of grain size in samples has been observed while the thickness of individual layer reduces. It may be very important for prediction and evaluation of mechanical properties of studied films due to possible phenomena of Hall-Petch strengthening. This way obtained films would be interesting as hard protective or decorative coatings in plenty of fields of research or industry.

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