INFLUENCE OF MONOLAYERS THICKNESSES RATIO ON STABILITY OF STRUCTURE AND PHASE COMPOSITION OF CrN/SiN_x MULTILAYERED COATINGS UNDER AIR ANNEALING

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Multilayered CrN/SiN_x coatings are formed using the method of magnetron sputtering by the sequential sputtering of Cr and Si_3N_4 targets upon a variation in the thickness of an individual layer from 2 to 5 nm at a substrate temperature of 450°C. X-ray diffraction analysis demonstrates that multilayered CrN/SiN_x coatings consist of nanocrystalline CrN layers with the preferred orientation (002) and amorphous SiN_x layers. The lattice parameters of the metal nitride phase for the CrN/SiN_x films are greater than for monolytic CrN layers. As wavelength dispersive X-ray spectrometry of the film composition and scanning electron microscopy of the surface have shown, the multilayered CrN/SiN_x coatings are more resistant to high-temperature oxidation (in the temperature range of 400–950°C) in comparison with the CrN coatings. This resistance does not essentially depend on the ratio of the thickness of the CrN individual layer to that of the SiN_x individual layer. The stability of CrN/SiN_x system is compared with the earlier obtained results for ZrN/SiN_x system. In general, CrN/SiN_x coatings are significantly more stable than ZrN/SiN_x coatings under the conditions of high-temperature oxidation.

Keywords: multilayer coatings, chromium nitride, silicon nitride, oxidation stability.

Introduction

Thin films on the basis of nitrides of transitional metals (TM) have became widespread in the industry as solid protective coatings.

At the present, the development of multilayer film structures is widely used for increasing their resistance to high-temperature oxidation as well as for improvement in the mechanical properties [1-3].

The studies show that the degree of mutual diffusion of the components of individual single layers through the interface between layers is an important factor, which affects the physical and mechanical characteristics of multilayer coatings. For example, a large difference in the characteristics of TM_1/TM_2 multilayer systems from $Metal_1/Metal_2$ systems was mentioned in the work [4]. It should be pointed that much lower interpenetration of components is intrinsic for multilayer coatings, where the layers of transition-metal nitrides alternate with layers of SiN_x, which is caused by the mutual insolubility of these two phases [2, 5, 6]. A high thermal stability of the multilayer structure is possible due to this fact. In addition, the presence of a large number of interfaces between layers inhibits the formation of a columnar structure of the coating [5, 7], which in turn prevents the formation of the continuous pores. The mentioned factors allow one to consider these multilayer coatings as promising materials operating under high-temperature corrosion conditions.

As it was revealed in our previous studies, the oxidation stability of ZrN/SiN_x coatings strongly depends on the thickness' ratio of individual layers [3]. In this work, the stability of CrN/SiN_x coatings with different ratio of monolayers thicknesses upon annealing in air is investigated. The comparison with ZrN/SiN_x coatings has also carried out.

Experimental details

Multilayered CrN/SiN_x films were grown by reactive magnetron sputter-deposition in a high vacuum chamber (base pressure < 10^{-5} Pa) equipped with three confocal targets configuration and a cryogenic pump (max. 500 l/s). Films were deposited on Si substrates at 450 °C. A constant bias voltage of −60 V was applied to the substrate during deposition. CrN/SiN_x multilayers with CrN and SiN_x layer thickness varying from 2 to 5 nm were synthesized. Monolithic CrN and

SiN_x films were also deposited as the reference films. The total film thickness was ~300 nm.

Water-cooled, 7.62-cm-diameter Cr (99.95% purity) and Si_3N_4 (99.99% purity) targets, located at 18 cm from the substrate holder, were used under $Ar+N_2$ plasma discharges at constant power mode. The Cr target was operated in magnetically unbalanced configuration using a DC power supply, while a RF power supply was used for the Si_3N_4 target in balanced mode. The total working pressure was 0.21 Pa.

X-ray Diffraction (XRD) analysis was employed for structural identification using a D8 Bruker AXS X-ray diffractometer operating in Bragg-Brentano configuration and equipped with CuK_α wavelength (0.15418 nm) and LynxEye detector.

The films were annealed at ambient air at different sequential temperatures from 400 °C up to 950 °C. The oxidation process was investigated using in situ XRD experiments. The samples were placed on a resistive heating stage implemented on the Bruker D8 diffractometer, consisting in an AlN sample holder and a hemispheric graphite dome. Total scan time during isothermal annealing was 40-60 min.

The elemental composition of films in their as-deposited and air-annealed states was determined using elemental probe microanalysis. A wavelength dispersive spectrometer (WDS) unit from Oxford Instruments attached to a JEOL 7001 TTLS scanning electron microscope (SEM) operated at 10 kV and 10 nA was used for the quantification with a precision better than 1 at.%. The same microscope was used for obtaining top-view SEM micrographs of the films after air annealing at 950 °C.

Results and discussion

As described in the previous section, the CrN/SiN_x films were formed with different CrN to SiN_x layer thickness ratios. The elemental composition of the individual layers in multilayered systems corresponds to composition of CrN and SiN_x monolithic reference films: 54.6 at.% Cr and 45.4 at.% N for CrN film, 43.3 at.% Si and 56.7 at.% N for SiN_x film.

The elemental composition of individual layers in the multilayer systems corresponds to the composition of CrN and Si_3N_4 mononitride films.

The results of the X-ray analysis of CrN mononitride films in comparison with CrN/SiN_x multilayer films during annealing in air in the temperature range of 400-950°C are given in Fig. 1. The CrN films starts to oxidize at 700°C and the peak corresponding to the CrN phase disappears at 860°C (Fig. 1a). In this case, peaks corresponding to the t-Cr_2O_3 oxide arise.

Analysis of the resistance to oxidation of CrN monolithic reference coating upon annealing in air in the temperature range of 400-950°C (Fig. 1b-d) indicates their significantly higher stability as compared to CrN/SiN_x multilayer coatings. At the CrN-SiN_x layer thickness ratios of 5 nm/5 nm and 2nm/5 nm, the oxide phase is not detected using X-ray analysis (Figs. 1c-d), and the peak of the CrN phase almost retains its intensity up to a temperature of 950°C (Fig. 1b-c). The structure of the CrN/SiN_x multilayer film with an individual layer thickness ratio of 2nm/5 nm remains X-ray amorphous at all temperatures of annealing (Fig. 1d).

Elemental analysis of the CrN mononitride film and CrN/SiN_x multilayer films after annealing in air is given in Table 1.

Table. 1. Results of the oxygen content analysis for CrN, Si_3N_4 mononitride coatings as well as for CrN/SiN_x multilayered coatings after air annealing in the the temperature range of 400–950 °C.

Coating	Oxygen content, at. %
CrN	62.7
Si_3N_4	28.0
CrN/SiN_x (5 nm/2 nm)	23.5
CrN/SiN_x (5 nm/5 nm)	17.6
CrN/SiN_x (2 nm/5 nm)	19.1

Quite lower oxygen content in the CrN/SiN_x multilayer films exposed to annealing in air should be noted (Table 1).

In contrast to the CrN mononitride film, which was oxidized completely, the oxygen

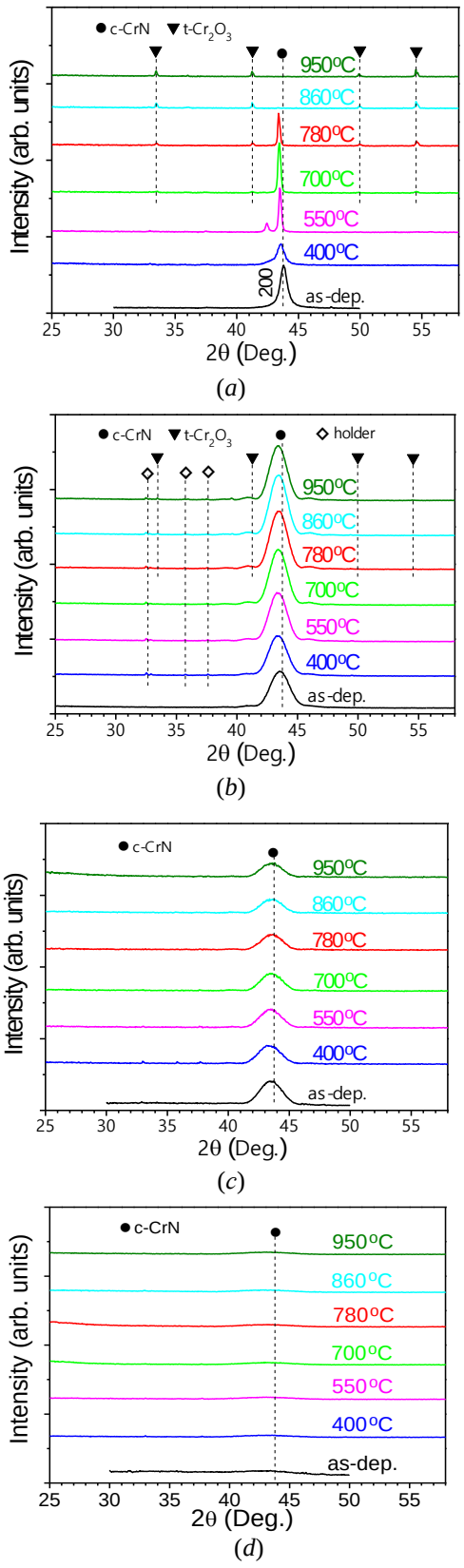


Fig. 1. Evolution of XRD patterns under air annealing for CrN reference coating (*a*); and CrN/SiN_x multilayered coatings with different thicknesses ratio of CrN and SiN_x elementary layers: (*b*) 5 nm/2 nm; (*c*) 5 nm/5 nm; (*d*) 2 nm/5 nm

content in the CrN/SiN_x multilayer films after annealing is 17-24 at %. It should be noted that, in contrast to the ZrN/SiN_x system, the oxidation rate does not change significantly upon varying the thickness-ratio values in the case of CrN/SiN_x films with CrN-SiN_x individual layer thickness ratios of 5 nm/2 nm, 5 nm/5 nm, and 2 nm/5 nm. This represents a clear difference between the CrN/SiN_x system and the ZrN/SiN_x system, in which the predominance of the SiN_x layer thickness to that of ZrN is a factor, which increases the resistance of the coating to high-temperature oxidation [3].

Figures 2 shows the surface topography of the CrN mononitride films and CrN/SiN_x multilayer coatings annealed in the temperature range of 400-950°C. A high degree of damage upon annealing of the CrN mononitride coatings should be noted (Fig. 2a).

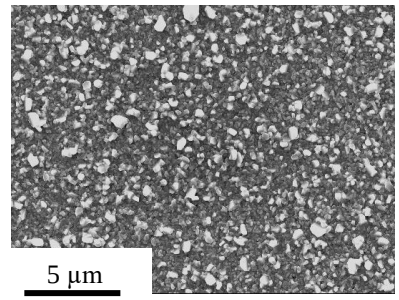
In the case of the CrN/SiN_x films, isolated sites of high-temperature corrosion arise at all thickness-ratio values (Fig. 2b-d). However, these sites usually do not transform into complexes, which results in the absence of delayering regions of the coating resulting in distortion of its integrity. Exception is the CrN/SiN_x (5 nm/2 nm) coating where the corrosion complexes can be detected (Fig. 2b).

It is interesting to compare the behavior of CrN/SiN_x coatings with the ZrN/SiN_x coatings. It was found that resistance of the ZrN/SiN_x films to oxidation increases with a decrease in the ZrN individual-layer thickness to that of SiN_x, as well as an increase in the number of layers in the film [3]. At the same time, it is clear that there is no such dependence on the CrN individual-layer thickness to that of SiN_x in the case of CrN/SiN_x coatings studied in the present work. However, it should be noted that oxidation stability in the last case is much higher.

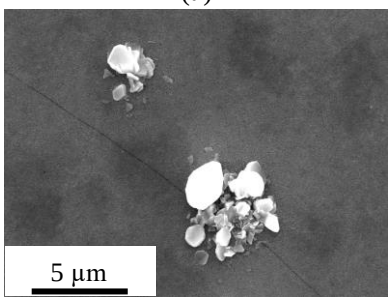
The CrN/SiN_x (5 nm/5 nm) coating is the most stable to oxidation at the high temperatures.

Conclusions

CrN/SiN_x multilayer coatings formed



(*a*)



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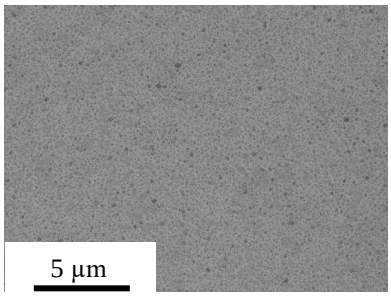

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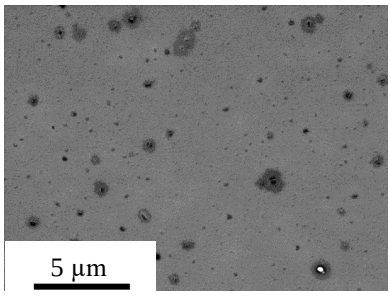

(*d*)

Fig. 2. Surface topography of the CrN reference coating (*a*); and CrN/SiN_x multilayered coatings with different thicknesses ratio of CrN and SiN_x elementary layers: (*b*) 5 nm/2 nm; (*c*) 5 nm/5 nm; (*d*) 2 nm/5 nm annealed in air up to the temperature of 950 °C

through magnetron sputtering represent alternating nanocrystalline layers of the CrN phase possessing (002) preferred orientation and amorphous layers of SiN_x. The lattice parameter of the metal nitride phase in the multilayer structures exceeds the lattice parameter corresponding to the CrN mononitride film, which indicates the presence of compressive stresses.

Analysis of the CrN/SiN_x multilayer films allows a conclusion regarding their higher resistance to high-temperature oxidation as compared to the CrN, Si_3N_4 mononitride films and ZrN/SiN_x multilayered films. In contrast to the ZrN/SiN_x films, the individual layer ratio is not a decisive factor in the case of the CrN/SiN_x films.

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