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Phase composition of multilayer system TiN/CrN deposited by DC magnetron sputtering

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TiN/CrN multilayer coating system is a hard, wear resistant material which is widely used for cutting and forming tools and other components operating in an abrasive wear environment. This study offers a combined method of surface modification of tool steel including electron beam treatment (EBT), plasma nitriding (PN) and TiN/CrN multilayer deposition by DC (direct current) magnetron sputtering.

The phase composition and distribution, chemical composition and microstructure of the layers were investigated by X-ray diffraction (XRD); Scanning Electron Microscopy (SEM) and Dispersive X-ray Spectroscopy (EDX), respectively.

In this study was demonstrated the possibility of formation of multilayer coating of TiN/CrN on the substrate from tool steels.

Keywords: multilayer system TiN/CrN, magnetron sputtering, XRD.

INTRODUCTION

During the last decades many authors have worked on the development of methods and techniques for producing nanostructured and wear resistant coatings applicable in different fields of the modern industry [1–4].

Many investigations are concentrated on the improvement of the mechanical characteristics of tool steels and it has been shown that the deposition of nitride based coatings (e.g. TiN, VN, WN, CrN, etc.) is applicable for these purposes [5–8]. The TiN layer combine high hardness and low friction coefficient which is able to increase the lifetime of exploitation of different cutting and forming tools. The properties of other coatings have been also investigated as in the case of CrN the excellent mechanical and tribological properties and chemical and thermal stability of oxidation (700 °C) with application in different industrial branches was demonstrated [9].

Multilayer coatings for wear resistant applications, such as TiN/CrN, TiN/VN, TiN/NbN etc. are also subject of investigations in the modern material science [10–13]. Such multilayer coatings consist of alternately nanocoating with thickness from 7 to 100 nm. The effect of the deposition of large number of layers is related to additional strengthening and improving of the adhesion of the coating to the base material [14, 15]. It should be noted that multilayer nanostructured coatings are widely used for improving of the operational properties of different tools working in abrasive environments, as well as their hardness, wear resistance and resistance to corrosion. Due to the very low resistance to corrosion of TiN films (550 °C) it is widely combined with another nitridic layer (CrN, VN, NbN etc.) forming multilayer coating. In dependence of the conditions of the deposition, the hardness of the multilayer TiN/CrN coating varies from 18 to 41 GPa [16, 17].

There exist several technologies for obtaining of the discussed above coatings. The most common methods are chemical vapor deposition (CVD) which is applicable of the formation of thin and ultra-thin films widely used in the nanotechnologies. Another technique for developing of thin layers and coatings is physical vapor deposition (PVD) which includes arc deposition, electron-beam evaporation, radio-frequency and direct current magnetron sputtering [18–22].

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During the last years the so called "combined methods" which includes a combination of two or more techniques is of great interest. The formation of CrN deposits by combination of plasma nitriding (PN) and PVD methods and application of resulted coatings were proposed and discussed [23].

The application of the combination of plasma nitriding and magnetron sputtered CrN layer on AISI 4140 steel is discussed [24]. The XRD investigations, conducted after PN process show the presence α-Fe and γ-Fe_4N phases. After the PVD process, a single phase with CrN structure has been registered. The authors have reported a significant increment, of the hardness after PN – 12.1 GPa, after PN+CrN – 21 GPa as the hardness of the base material is 10.2 GPa.

The process of high thermal oxidation of multilayer TiN/CrN coatings has been investigated [25]. It has been found that after the thermal treatment at 500 °C for 300 min the adhesion of the coating with the substrate is greatly improved. At this kind of treatments no changes of the hardness have been observed.

Other authors have found that the crystallographic parameters of the deposited TiN/CrN coatings significantly affect the mechanical and exploitation properties. They strongly depend on the phase composition and grain size [26, 27].

The aim of this study is to investigate the phase composition of the magnetron sputtered TiN and TiN/CrN coatings deposited on tool steel as the base material was preliminary treated by scanning electron beam followed by plasma nitriding.

EXPERIMENTAL

The experiments were conducted on samples of W320 (0.31 wt% C; 0.30 wt% Si; 0.35 wt% Mn; 2.9 wt% Cr; 2,8 wt% Mo; 0.5 wt% V) hot-work tool steel that were heat-treated in advance. The size of the substrates was 20×20×4 mm. In this work we combining three technologies for surface modification of hot work tool steel: electron-beam treatment (EBT) + plasma nitriding (PN) + direct current (DC) magnetron sputtering (MS). The TiN layer and multilayer TiN/CrN coating are deposited by magnetron sputtering.

The schematic diagram of electron beam treatment with scanning electron beam is presented on Figure 1. The electron beam, formed in an electron optical system (EOS), is scanned over the surface of the sample treated by means of electromagnetic lenses. The interaction between the electron beam and the surface of the treated specimen results in transformation of the kinetic energy to heat. After the achievement of the structural transformation temperature of the steels the sample is cooled down in a controlled way in order to reduce the residual stresses and the oxidation.

Table 1. Sequence of experiments

Sample	Treatment	Size
1	EBH + PN+ TiN	20×20×4 mm
2	EBH + PN + TiN/CrN	20×20×4 mm

The electron beam treatment with scanning electron beam was performed on Leybold Heraus (EWS 300/15–60) at the following technological parameters: accelerated voltage – U = 55 kV, electron beam current – I = 40 mA, speed of the specimen movement – V = 4 cm/s, frequency of the electron beam – f = 1 kHz, diameter of the electron beam – d = 0.1 mm.

The plasma nitriding surface treatment was conducted on "ION 500" at 600 °C for 8–24 h, in a gas mixture of 70% N_2 + 30% H_2. After the nitriding process, the samples were cooled down at a high vacuum state in order to minimize the residual stresses and the oxidation.

The TiN and TiN/CrN coatings were deposited by direct current (DC) magnetron sputtering (MS). The diameter of the sputtered targets was 100 mm as the purity of Ti and Cr one was 99.8%. The process took place in Ar-N_2 atmosphere at working pressure of 1.2×10^{-1} Pa. The deposition time for TiN with thickness 2 μm is 120 minutes, 60 minutes for TiN with thickness 1 μm and 40 minutes for CrN with thickness 1 μm. In order to minimize the residual

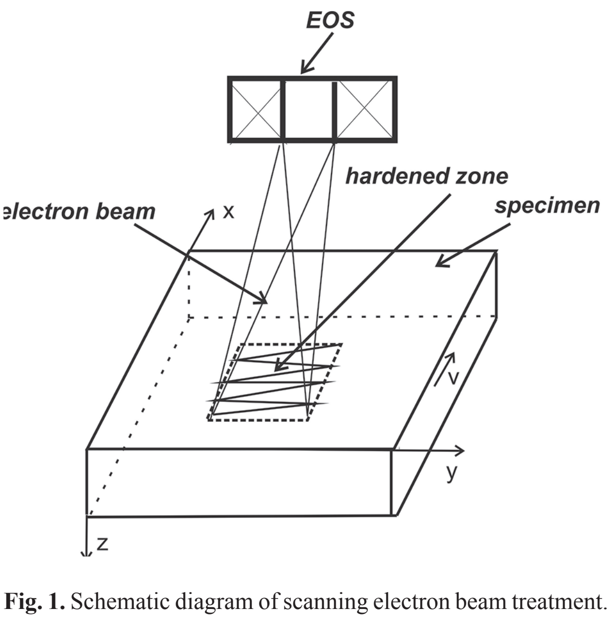

Fig. 1. Schematic diagram of scanning electron beam treatment.

stresses and the oxidation the samples with deposited coating were retrieved from the vacuum chamber after the achievement of room temperature.

X-ray diffraction experiments were performed on a URD6 Seiferd & Co diffractometer with Cu Kα radiation. The XRD patterns were recorded within the range from 30° to 80° at 2θ scale with a step 0.1°. The measurements were performed in symmetric (Bragg–Brentano) mode.

The microstructure of the obtained layers was investigated by Scanning Electron Microscopy (SEM EVO MA10 Carl Zeiss equipped with EDX detector – Quantax 200, Bruker), as secondary electrons have been used. The accelerated voltage was 20 kV.

RESULTS AND DISCUSSION

X-ray diffraction investigation of phase composition has been performed in Bragg-Brentano (B-B) mode. Fig. 2a and 2b represent XRD patterns of the samples with deposited TiN and TiN/CrN coatings. All diffractions maximums are indexed as both patterns demonstrate relatively low background. Phase identification was carried out with ICDD Database file PDF #38-1420 for TiN and PDF#11-0065 for CrN crystal phase. Fig. 2a shows presence face-centered cubic (fcc) TiN phase with space group Fm-3m (225) and reflections, corresponding to (111), (200), (220), (311) and (222) crystallographic planes. Fig. 2b represents XRD pattern of EBT+PN+TiN/CrN, where diffraction maximums of TiN and CrN (fcc and space group Fm$\bar{3}$m (225)) phases are identified. No peaks corresponding to Ti_2N, Cr_2N etc. are observed indicating that the coatings are made of single phase polycrystalline layers. The application of the preliminary treatments (electron-beam treatment (EBT) and plasma nitriding (PN)) on the sample of tool steel and technological parameters on the deposition of coatings it is possible to form TiN and TiN / CrN coatings which is of the greatest interest from practical point of view.

In the case of monolayer TiN coating, the calculated by the obtained diffraction lines parameter a is 4.254 (±0.003) Å. This result is in agreement with those from the ICDD database where the value of the lattice parameter of TiN is 4.241 Å. In many studies describing the formation of TiN coatings, the reported deviation of the calculated lattice parameter is much greater than in our case [28]. Therefore, the application of the discussed above technological conditions leads to formation of nanostructured coatings with small amount of residual stresses, microstrains, etc., because the obtained values for the lattice parameters of both phases are very similar to that applied in ICDD Database.

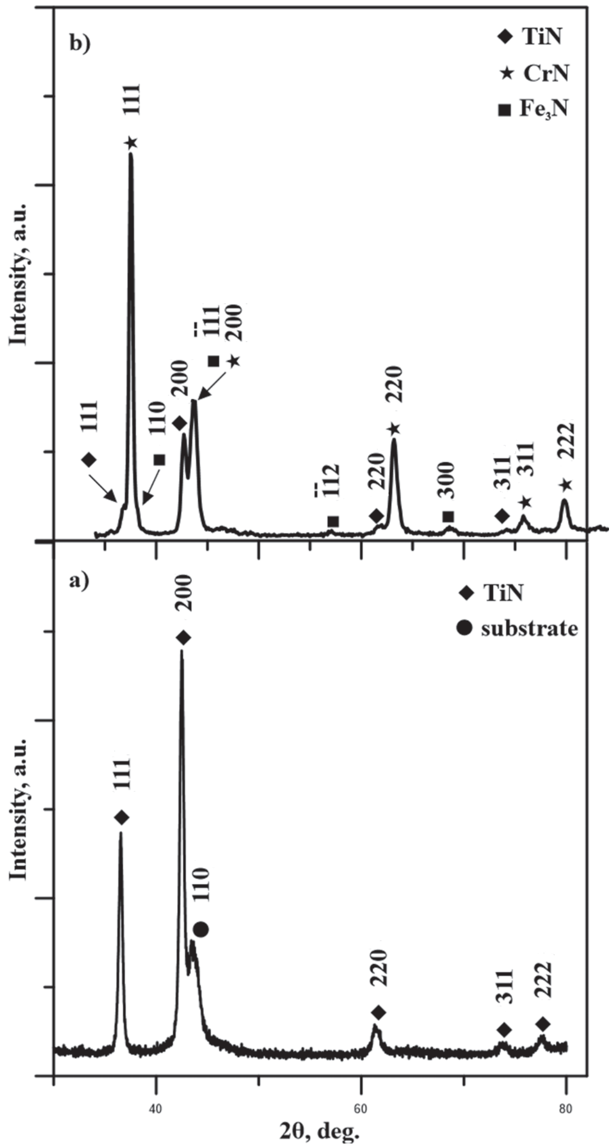

Fig. 2. XRD pattern of the samples with deposited TiN (a) and TiN/CrN (b) coatings.

In the case of multilayer TiN/CrN coating, the calculated lattice parameters are the following: a_{TiN} = 4.228 (±0.003) Å and a_{CrN} = 4.155 (±0.002) Å. It is clearly visible that for TiN it decreases while for CrN is closed to the theoretical one of 4.140 Å (PDF#11-0065). This means that the application of CrN layer on steel – TiN system is able to form additional residual stresses and microstrains in the TiN film but for the CrN coating it is monophasic with Cr-N stoichiometry. This problem has been investigated many times [29, 30, 31]. The possibility of formation of single phase structure of the deposited CrN coatings is able to reflect on significantly improved mechanical properties. Therefore, the application of the discussed above technology is able

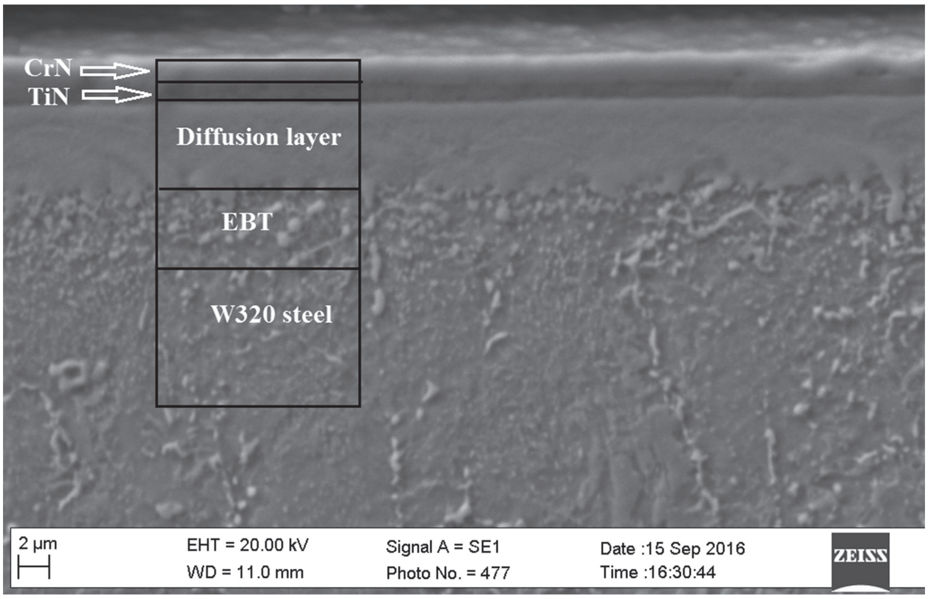

Fig. 3. Cross section SEM image of the sample with deposited TiN/CrN coatings.

to form single phase CrN coatings with improved exploitation properties.

A cross section SEM image of the sample with TiN/CrN coating is presented on Figure 3. The microstructure of the tool steel which acts as a substrate in the present particular case consists of equally-axes grains of ferrite. The grains become larger towards the core of the sample. The depth of the treated by electron-beam treatment zone is about 10–15 µm. Due to the plasma nitriding the diffusion layer with thickness of about 4–5 µm has been formed. The presence of the deposited TiN and CrN coatings is clearly visible as their thickness is about 1 µm for each layer.

CONCLUSIONS

DC magnetron sputtering system was used to deposit nanostructured TiN/CrN multilayer coatings on tool steel substrates. The control of the process parameters resulted in the deposition of a monolayer of TiN and multilayer TiN/CrN coatings with face-centered cubic structure. The obtained stoichiometry for the monolayer TiN coating is Ti-N, for the multilayer TiN/CrN it is Ti-N and Cr-N, which is of great interest from a practical point of view. The lattice parameters of TiN and CrN are similar with those from the ICDD database, which means that the amount of residual stresses and micro-strains is very low. The deposition of CrN coating on the preliminary deposited TiN layer is able to form monophasic CrN coating with the discussed above stoichiometry, which reflects on the improvement of the operational properties.

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ФАЗОВ СЪСТАВ НА МНОГОСЛОЙНО ПОКРИТИЕ TIN/CRN, ОТЛОЖЕНО ЧРЕЗ МАГНЕТРОННО РАЗПРАШВАНЕ

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(Резюме)

Многослойното покритие от TiN/CrN е твърд и устойчив на износване материал, който се използва широко за изработка на режещи и формоващи инструменти и други компоненти работещи в среда с абразивно износване. Това изследване предлага комбиниран метод за повърхностна модификация на инструментални стомани включващ електронно-лъчева обработка (ЕЛО), плазмено нитриране (ПН) и многослойно покритие от TiN/CrN отложено чрез магнетронно разпрашване.

Фазовият и химичния състав, както и микроструктурата на слоевете са изследване чрез рентгенова дифракция; сканираща електронна микроскопия (СЕМ) и енергийно дисперсионна рентгенова спектроскопия, съответно.

В това изследване е демонстрирана възможност за формиране на многослойно покритие от TiN/CrN върху подложка от инструментални стомани.