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Nitrogen-like depth profiles of the selected noble gases and lubricant elements in WC-Co tools used in wood-based material machining

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Abstract: *Nitrogen-like depth profiles of the selected noble gases and lubricant elements in WC-Co material the tools used in wood-based material machining*. An attempt of the modelling of nitrogen-like depth profiles of ions for three noble gases and four lubricant elements. Modelling was executed in four stages. The similar profiles were obtained for the ion energy in the range from 13.7 to 125 keV. The difference in the obtained profile parameter values, such as the projected range and the range straggling, was less than 1%.

Keywords: ion implantation, depth profiles, modelling, WC-Co tools, wood machining

INTRODUCTION

The cemented tungsten carbides, named also WC-Co composites, are most popular tool materials used in the wood-based material machining, in the furniture industry and wood-based panels industry, due to many attractive properties such as strength, hardness, fracture toughness, refractoriness, stiffness, resistance to compressive deformation and wear resistance at room temperature as well as at higher temperatures up to 400°C (Ramasamy and Ratnasingam 2010, Wilkowski et al. 2021).

Unfortunately, the tools life made of this material is still insufficient, especially during of the particleboard machining. The ion implantation method can be used to improve this tool life. It is the relatively cheap and a good process for the modification of the tools, because the modified region is not an additional layer, hence no adhesion problem occurs (no delamination) and a change of dimensions and of the surface finish of the implanted material is negligible (Barlak et al. 2016, Barlak et al. 2017).

A several mechanisms for strengthening of WC-Co are described in the literature on the subject of the papers (Konyashin et al. 2014, Yeo and Kim 2015, Pittari III et al. 2021, Jing et al. 2022). We observed a few these mechanisms in our previous works (Wilkowski et al. 2021, Wilkowski et al. 2022). There were e.g. interstitial nitrogen, strengthening nitrides, lubricant carbon as a results of WC decomposition and self-regenerates reducing friction amorphous carbon layer, formed on the ion implanted tool surfaces, during the wood-based material machining (Wilkowski and Barlak 2022).

In the next steps we plan to check the influence of chemically inert elements, such as noble gases and lubricant elements on the tool life of WC-Co tools. The starting point will be the implantation of nitrogen ions with an energy of 50 keV and a dose of 5e17 cm^{-2}. These parameters gave the best results in our studies so far.

In the first case, ions of helium, neon, argon and reference nitrogen will be used to the modification of WC-Co tools. Such an approach will make it possible to compare the effect of reactive and inert gas, with the similar atomic mass (nitrogen vs. neon) on the modified material, a potential microstructure strengthening mechanisms, etc. Additionally, the influence of atomic mass on the material properties will be possible to the observation, for three inert gases (helium, neon and argon).

In the second case, we plan to check the influence of lubricant elements as above. There are no papers in the literature on the issue of self-lubrication of WC-Co. Only a few publications present the results of self-lubrication of WC ceramics in systems with other phases, e.g. (Du et al. 2006, Tian et al. 2021, Liu et al. 2021, Savchenko et al. 2022).

The ion implanted carbon was used to the form the solid film lubrication on Al_2O_3 ceramic (Jun et al. 1998). The significant change of the friction coefficient was observed for the fluences of 2.5e17 cm^{-2} and more.

In the papers (Akhadejdamrong et al. 2003, Aizawa et al. 2004) the results of the self-lubrication of nitride ceramic coating by the chlorine ion implantation were presented. The investigated friction coefficient decrease more than 80% for the fluence of 1e17 cm^2.

The positive effect of boron was presented in publication (Barnes et al. 2004). It is interesting that the source of boron were the machined wood boards.

Boron has a lubricating properties also in the combination with nitrogen and after the formation of BN phase. The authors of paper (Zhu et al. 2002) investigated the influence of ion implantation on the wear resistance of TiAlN coatings. The friction coefficient decrease about 35% for the fluence of 1e18 cm^2 and about 20% for 5e17 cm^2.

The authors of the paper (Duan et al. 2020) mention the excellent lubricating properties of the sulphur-tungsten compound WS_2 and its using for more than six decades.

The ion implantation of noble gases is relatively simple. The situation is worse during the implantation of boron, carbon, which can contaminate the vacuum chamber or chemically aggressive elements such as chlorine and sulphur. Additionally, nitrogen is needed to the formation of BN phase, during the ion implantation of boron (boron can be implanted after ion implantation of nitrogen), and tungsten is needed to the formation of WS_2 phase, during ion implantation of sulphur (the source of tungsten can be WC phase, decomposed during ion implantation).

Apart from the chemical affinity of implanted ions, the physical position of their depth profiles is very important, especially due to the difference in atomic masses. Therefore, it was decided to check a possibility of generation of the similar or identical depth profiles for nitrogen and selected noble gases and lubricant elements.

The first part of the modeling results, concerning noble gases is the subject of the HZDR Project No 23003338-ST, realized at IBC at the Helmholtz-Zentrum Dresden-Rossendorf e.V. in Dresden, Germany.

The second part of the modeling results, concerning the lubricant elements is planned as a subject of other grant proposal.

MATERIALS AND METHODS

The Stopping and Range of Ions in Matter (SRIM-2013.00), freeware type code, based on Monte Carlo method, was used for modelling (SRIM, Barlak et al. 2019a, Barlak et al. 2019b, Barlak et al. 2019c). The depth profile shape of all ions implanted to W-C-Co material, projected range R_p, range straggling ΔR_p and maximum of SRIM units, as an equivalent of the peak volume dopant concentrations ($SRIM_{max}$ instead N_{max}), kurtosis and skewness were modelled using this code. The detailed description of these parameters was included in our previous paper (Barlak et al. 2023).

The modelling was performed for 100 000 implanted ions in the each case. The angle of the ion incidence was defined as 0° (perpendicular to the implanted surface). The simulations were performed for room temperature implantation.

The modelling did not account for the phenomenon of substrate sputtering by the implanted ions, substrate damages and the chemical reactions between the implanted ions and the substrate components.

The theoretical values of the sputtering yield *Y*, defined as an average number of atoms sputtered (ejected) from the implanted substrate per incident ion, were calculated with the use of the quick ion implantation calculator SUSPRE, from the energy deposited in the surface region of the material using the Sigmund formula (SUSPRE).

W-C-Co implanted substrate material (modelling codes treat the sample as a set of atoms that do not form chemical compounds), including (at.%): 47.4% W, 47.4% C and 5.2% Co, i.e. in wt.%: 90.86% W, 5.94% C and 3.2% Co, with the density of 15.2 g/cm^3 was adopted as the substrate material to the modelling. This value of the density was declared by the supplier of the e.g. KCR08 type indexable knives (Ceratizit, Austria), commonly used in the furniture industry and presented at Fig. 1.

Nitrogen, three noble gases, i.e. helium, neon and argon and four lubricant elements, i.e. boron, carbon, sulphur and chlorine were used in the modelling processes, as implanted elements.

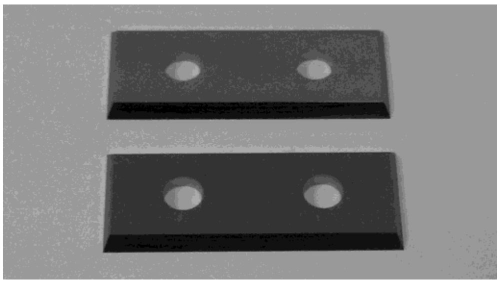

Figure 1. WC-Co composite indexable knives

The modelling processes was performed in four stages.

In the first stage, the depth profiles of all implanted elements were modelled for the ion energy range from 10 to 150 keV, due to the large difference in atomic masses of implanted elements. The proposed values are possible to obtain in many exploited implanters.

In the second stage, the values of the main peak parameters were determined and presented in acceleration voltage/ion energy-dependent graphs. Additionally, the calculated sputtering yield parameters were presented on the same graphs.

In the third stage, the values of the main peak parameters obtained for noble gases and the lubricant elements were compared with the same parameters obtained for nitrogen implanted with the ion energy of 50 keV. The proper values were determined from the prepared graphs. The projected range R_p, range straggling ΔR_p were the key parameters for this determination. The values of $SRIM_{max}$ was less important, due to the possible correction, using the right value of the fluence of implanted ions. The values of the kurtosis and the skewness had the least importance in these considerations. Additionally, the percent difference values of all parameters with regard to the same ones, obtained for nitrogen, were calculated.

In the fourth stage, additional depth profiles were modelled for the determined values of ion energies of noble gases and the lubricant elements. The obtained profiles were comparised with the profile of 50 keV nitrogen. The corrections of the high of the modelled peaks were introduced. Finally, the main parameters of the ion implantation processes were proposed.

The sputtering yield values were omitted at these stages of the modelling for the simplicity

RESULTS AND DISCUSSION

Fig. 2 shows the results obtained in the first stage of the modelling, i.e. the modelled profiles of the implantation of singly ionized ions of nitrogen, three noble gases, i.e. helium, neon and argon and four lubricant elements, i.e. boron, carbon, sulphur and chlorine to W-C-Co material, for an ion energy range from 10 to 150 keV, with the step of 10 keV. Additionally, He^+ profile for 13.7 keV, Ne^+ profile for 63 keV, Ar^+ profile for 125 keV, B^+ profile for 36 keV, C^+ profile for 42 keV, S^+ profile for 108 keV and Cl^+ profile for 123 keV were added. All above mentioned profiles and the reference profile of Ar of 50 keV were marked with a bolded lines. These additional profiles were described in the details at the end of this chapter.

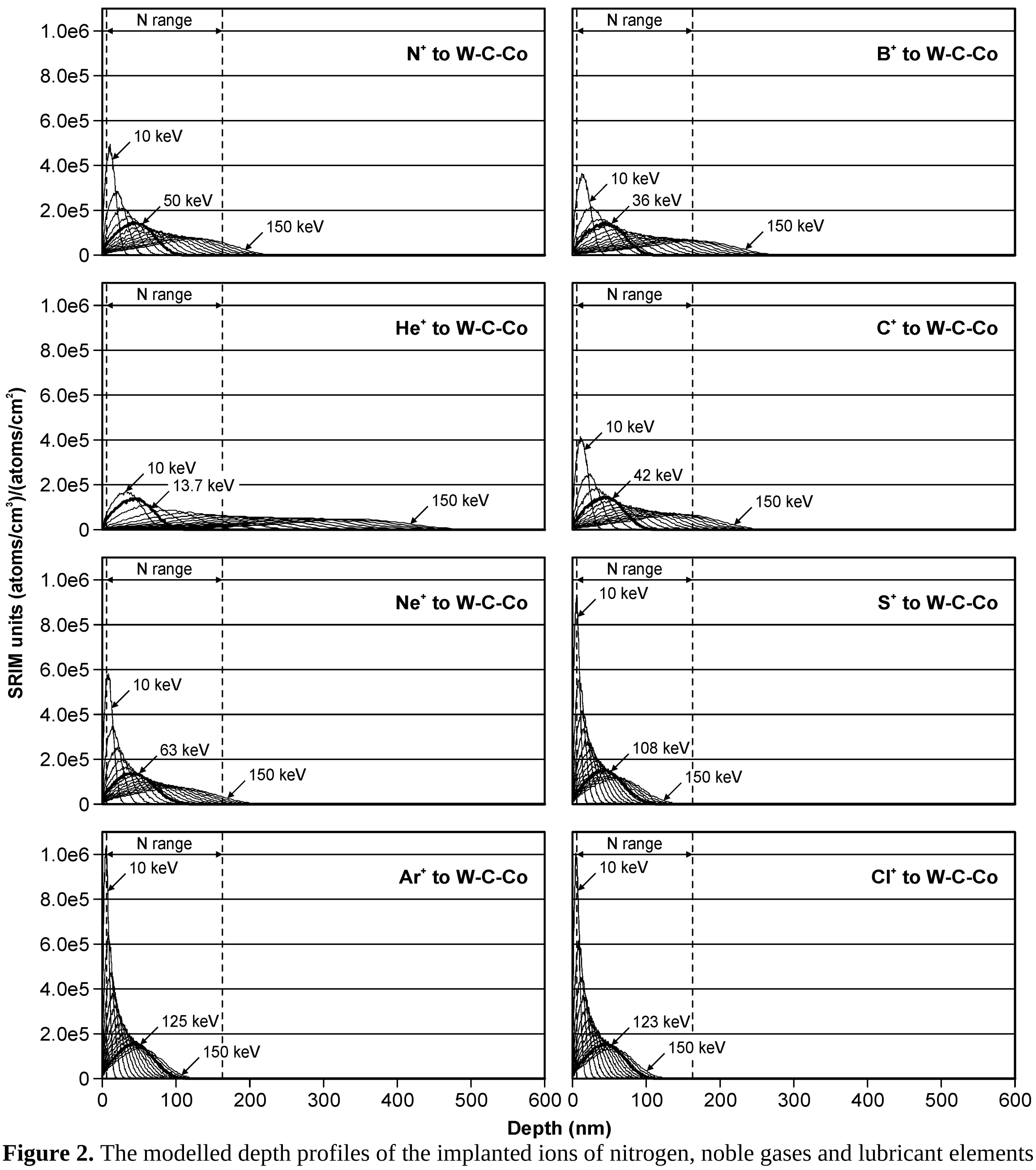

Figure 2. The modelled depth profiles of the implanted ions of nitrogen, noble gases and lubricant elements

Only few selected profiles (first, last and reference/additional profiles for each element) have been labelled, for the better clarity in the figures. It should be noted, that the adopted scales on the abscissa axis and the ordinate axis are the same for all modelled cases for easier comparison of the profile position. It is seen, that the profiles become lower and wider with the ion energy increasing. Moreover, the height and the width of the profiles strongly depends on the mass of the implanted ions. The depth profiles are lower and wider for light elements, like helium with an atomic mass of 4.0026 u, and higher and narrower for the elements with the higher atomic mass, like sulphur (32.065 u), chlorine (35.453 u) and argon (39.948 u). The profiles for nitrogen and neon are similar, due to similar atomic mass, i.e. 14.0067 u and 20.1797 u, respectively.

The useful energy range of the implanted nitrogen, defined from R_p - 0.5ΔR_p for 10 keV to R_p + 0.5ΔR_p for 150 keV, was marked as “N range”. This proposed range can be used for the determination of the useful energy range of other presented elements, in the connection with nitrogen.

The presented “SRIM units” in (atoms/cm^3)/(atoms/cm^2) are a special units of plot ordinate used in SRIM code results. With these units, by multiplying by the ion fluence (in atoms/cm^2), the ordinate values convert directly into a density distribution with the unit of atoms/cm^3. The maximum of SRIM units ($SRIM_{max}$) is a kind of equivalent of the peak volume dopant concentration (N_{max}), used for the profiles multiplied by the fluence of the implanted ions. The use of SRIM units allows for more flexible modelling, without introduce of the values of the fluences of the implanted ions.

The modelling results of the acceleration voltage/ion energy-dependent change of the maximum of SRIM units, sputtering yield, projected range, range straggling, kurtosis and skewness, obtained in the second stage, are presented in Fig. 3 (for nitrogen), Fig. 4 (for noble gases) and Fig. 5 (for lubricant elements). Additionally, the trend lines, the equations and the values of the coefficient of determination R^2, determined using Microsoft Excel 2010 spreadsheet, are presented in all figures. The determined equations can be potentially use to the values calculation of the peak parameters for the data not included in the modelling, e.g. in the next stage of these considerations. They were used in the next stage of the described considerations.

Due to single ionisation of the ions, the values of the ion kinetic energy are numerically identical with the values of the accelerating voltage, e.g. 50 kV and 50 keV.

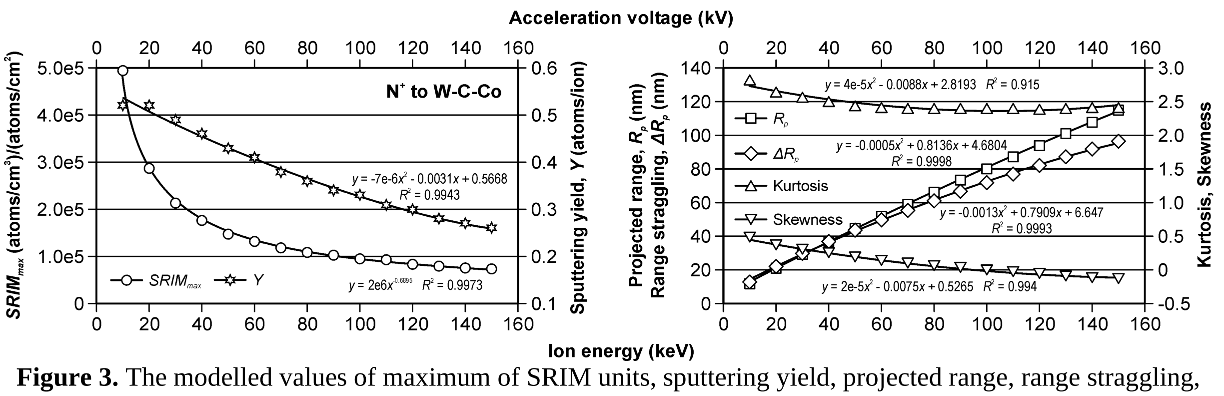

Figure 3. The modelled values of maximum of SRIM units, sputtering yield, projected range, range straggling, kurtosis and skewness for N^+ ions implantation to W-C-Co substrate

The acceleration voltage/ion energy-dependent curves for maximum of SRIM units have a exponential character for all implanted ions. The curves for all other parameters can be described by a 2nd degree polynomial trend lines.

The values of the determination factor are the highest for the proposed trend lines.

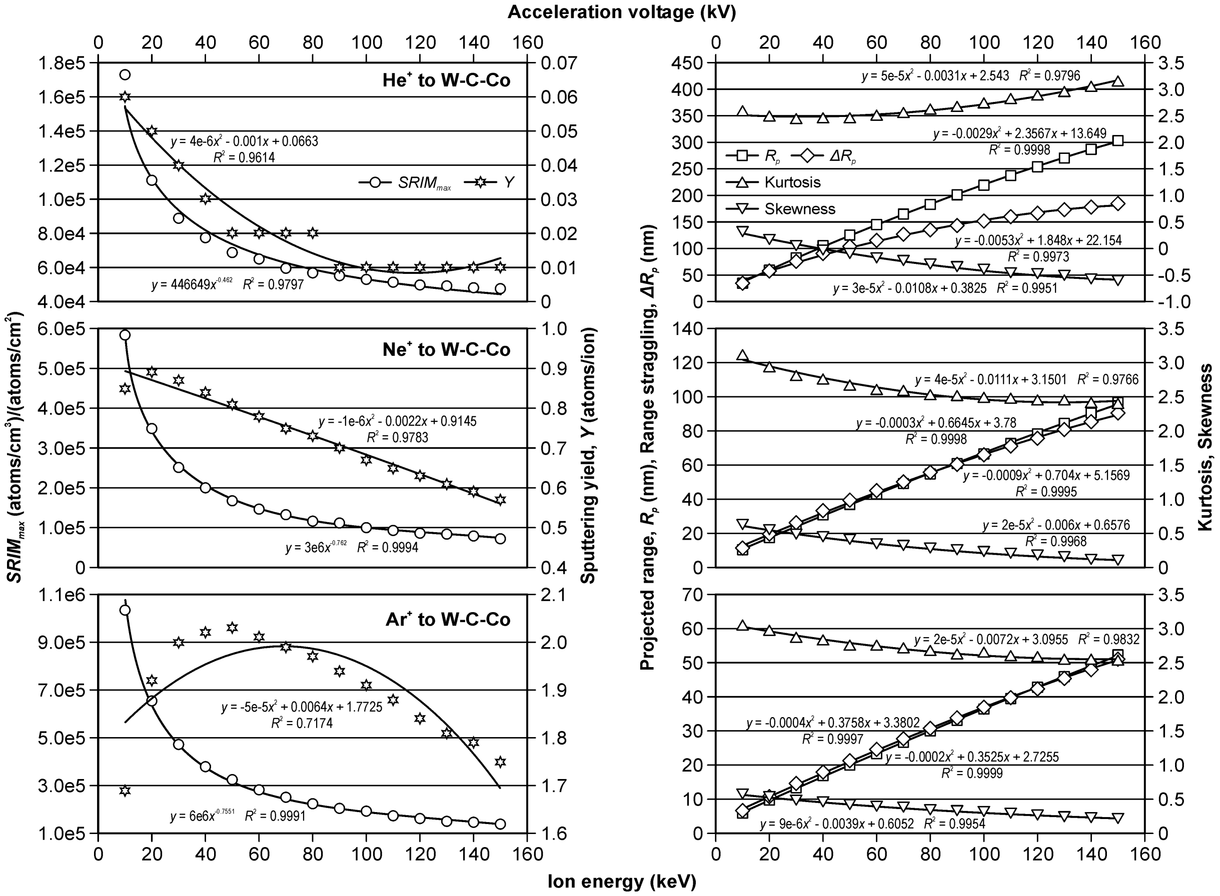

Figure 4. The modelled values of maximum of SRIM units, sputtering yield, projected range, range straggling, kurtosis and skewness for the He^+, Ne^+ and Ar^+ ions implantation to W-C-Co substrate

It is seen, for example that the values of the maximum of SRIM units, obtained for the ion energy of 10 keV, are more than 2.8-fold higher for helium implantation and about 2-fold lower for chlorine implantation, i.e. for two extreme cases, in comparison to the nitrogen one. It is different for the values of the projected range and the range straggling.

In this case, the values of both parameters are about 3-fold higher for helium and about 2-fold lower for chlorine, for the conditions like previously.

The values of the kurtosis and the skewness are at the similar level for discussed elements. It should be noted that the skewness for He, B, C and N profiles changes its character, from the positively skewed distribution to negatively skewed distribution for the highest values of the energy of the implanted ions.

Unfortunately, the sputtering yield is maximum about 4-fold higher for argon ions and about 8-fold lower for helium ions, in the comparison to nitrogen.

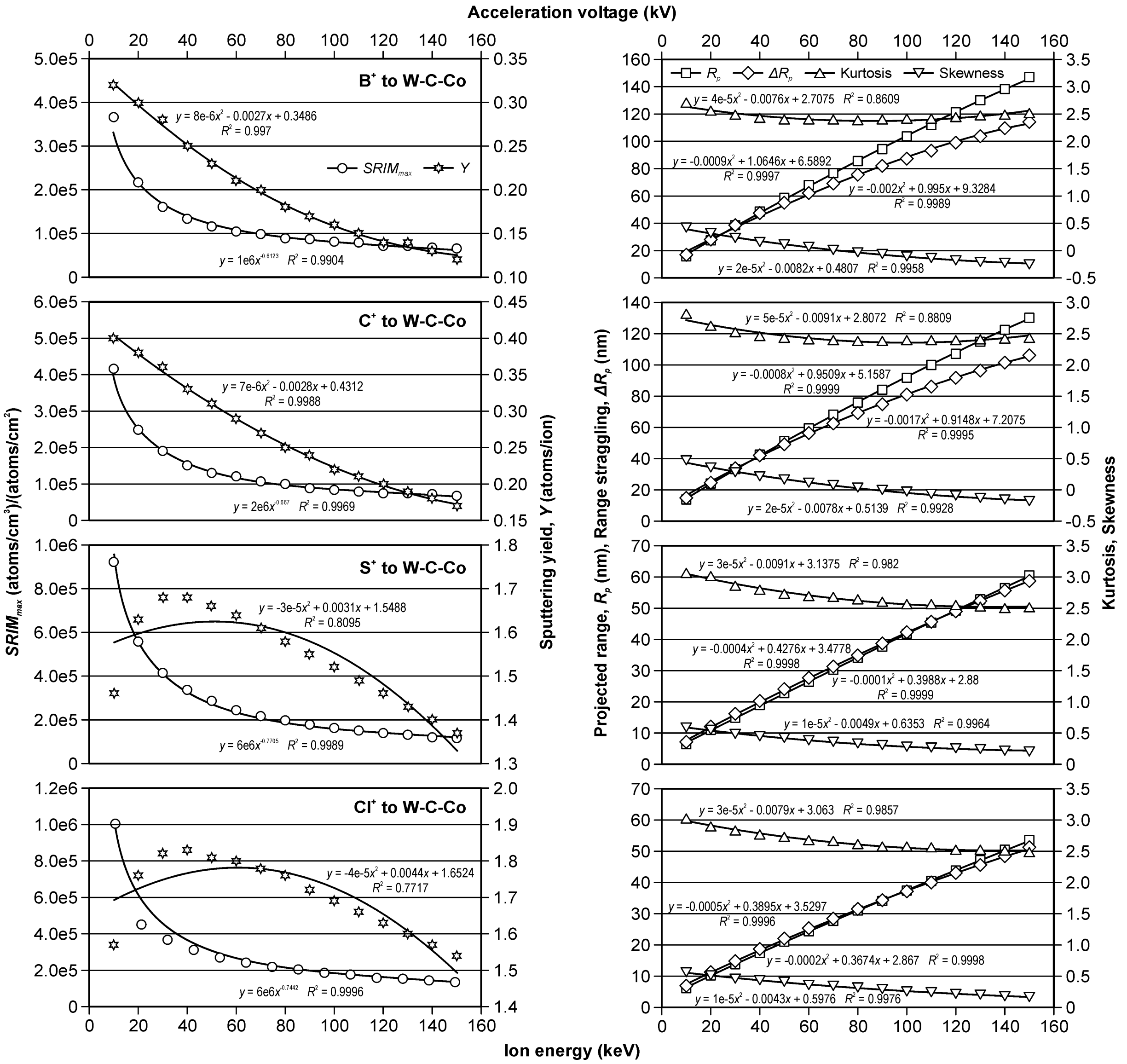

Figure 5. The modelled values of maximum of SRIM units, sputtering yield, projected range, range straggling, kurtosis and skewness for the B^+, C^+, S^+ and Cl^+ ions implantation to W-C-Co substrate

Table 1 presents the results of third stage of the modelling, i.e. the results of the determination values of the main peak parameters and the sputtering yield for nitrogen-like depth profiles of other elements. The modelled values of $SRIM_{max}$, kurtosis and skewness have been rounded to 2 decimal places. The percentage change in peak parameter values, relative to nitrogen, has been shown in the round brackets. Negative numbers mean a decrease in the values. Some "inconsistent" values are due to rounding of numbers, e.g. $SRIM_{max}$ values and Ne^+ are 1.4e5 (atoms/cm^3)/(atoms/cm^2) and -4.53% for He^+ and 1.4e5 (atoms/cm^3)/(atoms/cm^2) and -4.3% for Ne^+.

It is seen that, the difference of two main considered parameters, i.e. projected range and range straggling for nitrogen and all other elements is less than 1%, for each case. The difference of $SRIM_{max}$ is higher and requires the correction in the next stage. The difference of the kurtosis and skewness is less significant and may be neglected. The difference of the sputtering yield is more significant and should be taken into account in more advanced considerations.

Table 1. The modelled values of the maximum of SRIM units, projected range, range straggling, kurtosis, skewness, sputtering yield and their percentage change for nitrogen-like profiles of other elements

Ion	Acceleration voltage (kV) / Ion energy (keV)	Maximum of SRIM units, $SRIM_{max}$ (atoms/cm^3) / (atoms/cm^2)	Projected range, R_p (nm)	Range straggling, ΔR_p (nm)	Kurtosis	Skewness	Sputtering Yield, Y (atoms/ion)
N^+	50	1.46e5	44.5	43.8	2.44	0.19	0.43
He^+	13.7 (-72.6%)	1.4e5 (-4.53%)	44.4 (-0.22%)	44.2 (0.91%)	2.55 (4.67%)	0.26 (39.86%)	0.06 (-86.05%)
Ne^+	63 (26%)	1.4e5 (-4.3%)	44.6 (0.22%)	46 (5.02%)	2.61 (7.03%)	0.34 (77.88%)	0.77 (79.07%)
Ar^+	125 (150%)	1.63e5 (11.64%)	44.3 (-0.45%)	44 (0.46%)	2.58 (5.95%)	0.26 (39.7%)	1.83 (325.58%)
B^+	36 (-28%)	1.48e5 (1.11%)	44.7 (0.45%)	44 (0.46%)	2.46 (0.71%)	0.21 (8.66%)	0.26 (-39.53%)
C^+	42 (-16%)	1.46e5 (-0.37%)	44.4 (-0.22%)	43.6 (-0.46%)	2.46 (0.73%)	0.2 (5.54%)	0.32 (-25.58%)
S^+	108 (116%)	1.54e5 (5.21%)	44.5 (0%)	44.8 (2.28%)	2.59 (6.08%)	0.29 (50.58%)	1.5 (248.84%)
Cl^+	123 (146%)	1.61e5 (10.1%)	44.9 (0.9%)	43.8 (0%)	2.52 (3.2%)	0.21 (10.61%)	1.62 (276.74%)

The results of the fourth stage of the modelling are presented in Fig. 6 and partially in Table 2 (fluence correction factor). At this stage, only the graphs of depth profiles obtained for the determined parameters have been compiled and the fluence correction factor was determined based on the authors' subjective observations and using Microsoft Excel 2010 spreadsheet.

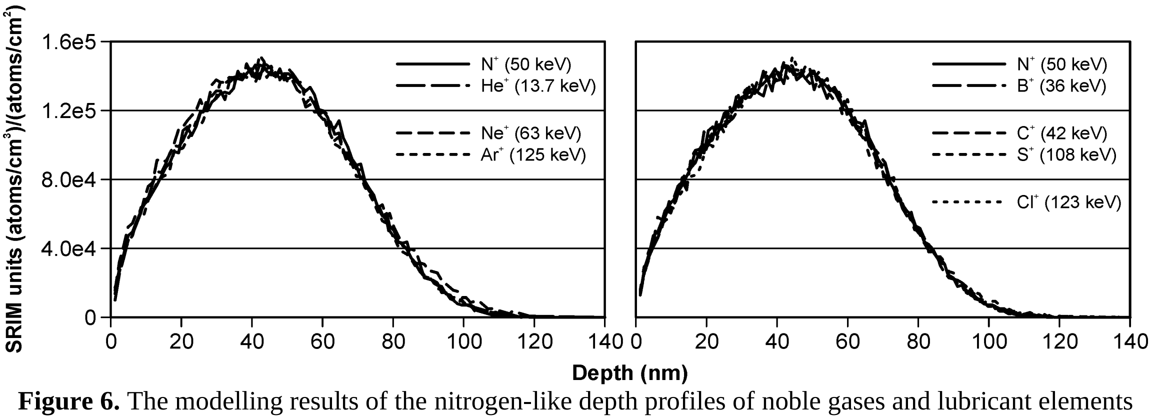

Figure 6. The modelling results of the nitrogen-like depth profiles of noble gases and lubricant elements implanted to W-C-Co material

Finally, the main parameters of the ion implantation processes, i.e. the values of the ion energy and the fluence related to nitrogen reference fluence of 5e17 cm^{-2} were presented in Table 2.

Table 2. The proposed values of the ion energy, fluence correction factor and implanted fluence, for noble gases and lubricant elements, to obtain nitrogen-like profiles with the implanted fluence of 5e17 cm^{-2}

Ions	Reference	Noble gases			Lubricant elements			
	N^+	He^+	Ne^+	Ar^+	B^+	C^+	S^+	Cl^+
Ion energy (keV)	50	13.7	63	125	36	42	108	123
Fluence correction factor	-	1.05	1.04	0.93	1	1	0.96	0.94
Fluence (cm^{-2})	5e17	5.25e17	5.2e17	4.65e17	5e17	5e17	4.8e17	4.7e17

CONCLUSIONS

Based on the results of the research, the following conclusions can be drawn:
- modelling of the nitrogen-like depth profiles for the implanted ions of selected noble gases and lubricant elements was successful,
- the differences for the obtained significant parameters, like the projected range and the range straggling were less than 1%,
- unfortunately, the necessary energy range of the implanted ions may be larger than the energy range of typical implanters,
- the sputtering yield values should be considered in the next step of the consideration, for a better projection of the real processes.

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Streszczenie: *Podobne do azotowych profile głębokości wybranych gazów szlachetnych i pierwiastków smarnych w narzędziach WC-Co stosowanych w obróbce materiałów drewnopochodnych*. Podjęto próbę modelowania podobnych do azotowych profili głębokości jonów dla trzech gazów szlachetnych i czterech pierwiastków smarnych. Modelowanie przeprowadzono w czterech etapach. Podobne profile uzyskano dla energii jonów w zakresie od 13,7 do 125 keV. Różnica w uzyskanych wartościach parametrów profilu, takich jak zasięg rzutowany oraz rozrzut zasięgu, była mniejsza niż 1%.

Słowa kluczowe: implantacja jonowa, profile głębokości, modelowanie, narzędzia WC-Co, obróbka drewna

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