

The wettability of nitrogen and argon implanted WC-Co indexable knives used for wood-based material machining

MAREK BARLAK¹, JACEK WILKOWSKI², ZBIGNIEW WERNER¹,
PIOTR PODZIEWSKI²

¹ Plasma/Ion Beam Technology Division, Material Physics Department, National Centre for Nuclear Research Świerk, 7 Andrzeja Sołtana St., 05-400 Otwock, Poland

² Department of Mechanical Processing of Wood, Institute of Wood Sciences and Furniture, Warsaw University of Life Sciences, 159 Nowoursynowska St., 02-776 Warsaw, Poland

Abstract: *The wettability of nitrogen and argon implanted WC-Co indexable knives used for wood-based material machining.* An attempt was made to examine the effect of the depth profiles of the implanted ions on the wettability of ion implanted WC-Co tools used for wood-based material machining. The tests were carried for two types of the tool surfaces, i.e. initial and polished, two commonly used gases, i.e. nitrogen and argon, and for the values of the parameters, possible to control in the case of classic ion implanters. Four depth profiles were modelled for two different values of the acceleration voltage, two for each implanted element. The modelling parameters were selected so that the two modelled depth profiles for both implanted elements were similar. The wettability tests were carried using a computer-supported test stand. The obtained results did not confirm the hypothesis about the relationship between the wettability and the position and the shape of the depth profiles.

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

INTRODUCTION

Ion implantation is a low temperature method of the modification of near-surface regions of different materials. This method is used in material engineering processes to change the physical and chemical properties of the near-surface regions of the modified materials, using a different kinds of the electrically accelerated ions. The most popular and easiest to use are ions of the gases, mainly nitrogen. Argon is also often used. Other noble gases, oxygen or methane, can also be used (Piekoszewski et al. 2004, Werner et al. 2007), but they are more expensive. The ions of the different metals can also be used, but this requires the more complicated ion sources, e.g. MEVVA (Metal Vapor Vacuum Arc) type (Brown and Washburn 1987).

Another important issue is the problem of mass separation of the ion beam. A separating magnets, used for mass separation of the ion beam in order to obtain a homogenous beam in terms of constant e/m ratio, generate an additional high cost of the devices and are often not used. Whereas, the ion beam generated by an ion implanter without mass separation contains several kinds of ions with different degrees of ionization. Additionally, the percentage shares of individual ion types are also different, which makes it more difficult to properly model the parameters and significantly limits their use (Barlak et al. 2019c).

The modified region is not an additional layer, hence no adhesion problem occurs (no delamination), and the change of dimensions and of the surface finish of the implanted material is negligible. More information about this method can be found in our previous publications (Barlak et al. 2016, Barlak et al. 2017, Wilkowski et al. 2019).

Ion implantation used as a modification method of WC-Co tools for wood-based material machining can produce spectacular results. The observed tool durability usually increases by two times or more (Barlak et al. 2019a, Wilkowski et al. 2021, Wilkowski et al.

2022). Moreover, the variability of the tools, modified in this way decreases, which is advantageous from the viewpoint of their use in automated systems.

Wettability is a parameter, often used in description of the surface state of the modified materials (Barlak et al. 2009, Betlej et al. 2022). Therefore, it was decided to check a dependence of the wettability on the position of the depth profiles of the implanted elements.

MATERIALS AND METHODS

Commercially available WC-Co composite indexable KCR08 type knives with dimensions of $29.5 \times 12 \times 1.5 \text{ mm}^3$, produced by Ceratizit Company (Reutte, Austria), commonly used in the furniture industry (presented in the upper right corner of Fig. 2), were used for the investigations. The surface opposite to the rake surface was polished manually for the half of the investigated tools, using Struers MD-Dac™ type polishing cloths (Polishing Cloths) and Struers DiaPro Allegro/Largo 9 type water based diamond suspension with diamond diameter of $9 \text{ }\mu\text{m}$ (Diapro). Prior to the investigation, they were washed in high purity acetone under ultrasonic agitation for 15 min. at room temperature.

The roughness and other surface parameters were measured using Hommel-Tester T 2000 profilometer (Hommelwerke, Villingen-Schwenningen, Germany), for six places at the measured surface, in section length of 1 mm each.

The ion implantation processes were preceded by the modelling, using the Stopping and Range of Ions in Matter (SRIM-2013.00), using Monte Carlo method (SRIM, Barlak et al. 2019b, Barlak et al. 2019c, Barlak et al. 2019d).

The modelling concerned the determination of the depth profiles of the implanted elements and the values of the projected range R_p , range straggling ΔR_p and peak volume dopant concentrations N_{max} , calculated from the values of the maximum of SRIM units $SRIM_{max}$. "SRIM units" in $(\text{atoms}/\text{cm}^3)/(\text{atoms}/\text{cm}^2)$ 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 is a kind of equivalent of the peak volume dopant concentration, used for the profiles multiplied by the fluence of the implanted ions.

The modelling was performed for 100 000 implanted ions in each case. The angle of the ion incidence was set 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, therefore the theoretical values of the sputtering yield Y , defined as an average number of atoms sputtered (ejected) from the implanted substrate per an incident ion, were calculated with the use 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 material (modelling codes treat the sample as a set of atoms that do not form chemical compounds) including in 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 $15.2 \text{ g}/\text{cm}^3$ was adopted as the substrate material for the modelling. The density was declared by the supplier of the investigated knives (Ceratizit, Reutte, Austria).

The depth profile shape, the peak volume dopant concentration, the projected range and the range straggling are basic parameters, that may affect the wettability. Therefore, it was decided to check a possibility of generation of the similar or identical depth profiles for two popular gases, used in laboratories and in industry, i.e. chemically active nitrogen and inert argon. Due to the almost 3-fold difference in the atomic weight of these elements, which is: 14.0067 u for nitrogen and 39.948 u for argon, the technological tests had to be supported by modelling.

In the case of direct implantation, i.e. without mass separation, nitrogen is delivered as two kinds of ions, i.e. $N_2^+ + N^+$, in $\sim 1:1$ ratio, so there are two elementary charges per three atoms. In the case of N_2^+ molecule implanted e.g. with the acceleration voltage of 65 kV, each atom carries the energy of 32.5 keV, according to the law of energy conservation (Barlak et al. 2019a). Therefore, the depth profile of nitrogen will be the sum of two profiles for both types of nitrogen implanted ions. For the same situation for a heavier argon, it is necessary to apply the sum of two profiles, obtained for two different values of the acceleration voltage, i.e. for some value of the acceleration voltage and for a half of this value. This procedure was described in detail in our previous paper (Barlak et al. 2023). For simplicity, it is assumed that the argon beam contains one type of ion, i.e. Ar^+ (multiple ionisation is ignored).

Due to single ionisation of the modelled ions, the values of the ion kinetic energy are numerically identical with the values of the accelerating voltage, i.e. 25 kV and 25 keV. The modelling was performed for the following energies of the implanted ions: 12.5, 25, 32.5 and 65 keV for both implanted elements. Finally, the depth profiles and the main peak parameter values were determined for the following ion energies: 12.5 keV, 25 keV, 25 + 12.5 keV (total), 32.5 keV, 65 keV and 65 + 32.5 keV (total), for both implanted elements. Such conditions permit to obtain similar depth profiles for two different types of the implanted elements. All the above selected accelerating voltage values are possible to achieve, using typical implanters. The total fluence adopted in the modelling was $3e17 \text{ cm}^{-2}$ for nitrogen and 2.72 cm^{-2} for argon. The sputtering values were skipped for simplicity, at this stage of modelling.

The ion implantation processes were performed using, semi-industrial implanter of gaseous ions, with non-mass separated ion beam, operated by the National Centre for Nuclear Research Świerk (Otwock, Poland), described in detail elsewhere (Betlej et al. 2022).

Four sets of the WC-Co indexable knives, each including two initial and two polished knives, were implanted in the modelled conditions, at the room temperature.

The base pressure in the vacuum chamber was at a level of about $8e-4 \text{ Pa}$ ($8e-6 \text{ mbar}$). Nitrogen and argon of 5N purity were used as the source of the implanted gaseous ions. The implanted fluence was at a level of $3e17 \text{ cm}^{-2}$. The acceleration voltages are presented in Table 1. At double implantation, the higher values of the acceleration voltage were used first in order to minimize physical-chemical changes in the surface layers of the modified material at the first stage of ion implantation. The beam current was at a level of 150 and 300 μA (Table 1) for the cross-sectional area of the ion beam of about 30 cm^2 . The beam current density was at a level of about 5 and 10 $\mu\text{A}/\text{cm}^2$.

The samples in the sample holders were clamped onto a stainless steel plate to reduce the intensity of heat generation. The holder temperature was measured continuously during the ion implantation processes. The maximum values of the measured temperature for all cases are presented in Table 1.

Table 1. The values of the beam current and the maximum measured temperature

Implanted ion	Acceleration voltage (kV)	Beam current (μA)	Maximum measured temperature ($^\circ\text{C}$)
N	25	300	139
	65		240
Ar	25+12.5	150*	53
	65+32.5	300	178

Note: *high load of the power supply was observed for the beam current of 300 μA

The static contact angle measurements, using sessile drop method, were provided for six spots on each un-implanted and implanted (initial, i.e. as supplied by the manufacturer and polished) knife, at room temperature, using a tester, supported by Surfaceware 9 code

(SURFACEWARE). This program automatically determines the base of the drop, its outline and two tangents and generates an analysis report, which includes among others the values of: average contact angle, left and right contact angle values, drop volume, wetting energy, work of adhesion.

The example code screenshot is presented in Fig. 1. A drop of the deionized water is shown in the lower part of photo and a fragment of the tube of the dispenser is visible in the upper part.

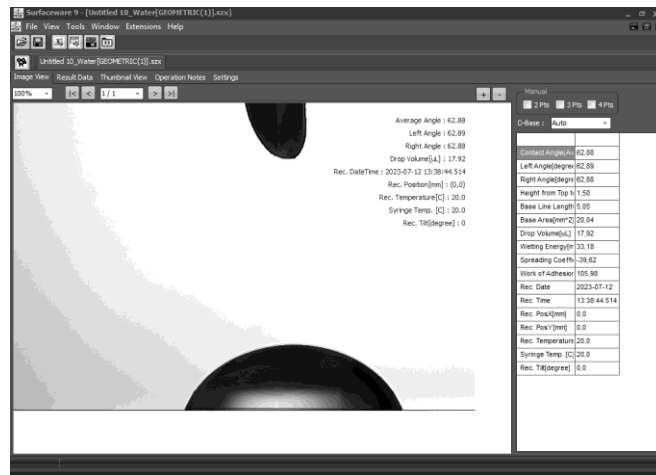


Figure 1. The example screenshot of Surfaceware 9 code

RESULTS AND DISCUSSION

Fig. 2 shows the average values of the roughness of the initial and the polished surface, opposite to the rake surface of WC-Co knives, presented in the upper right corner. The standard deviation bars were added. It is seen, that the value of R_a parameter was more than 10-fold smaller for the polished surfaces. Additionally, the standard deviation values decreases from about $0.006 \mu\text{m}$ to practically zero.

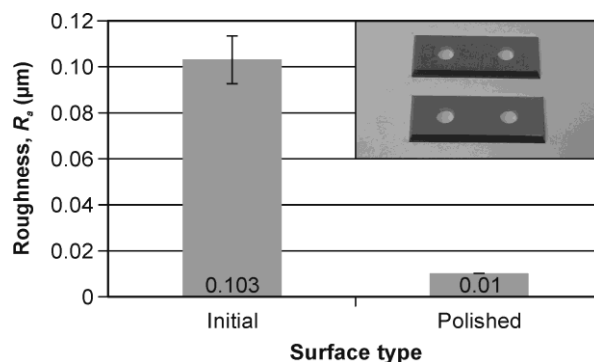


Figure 2. The values of the roughness and the standard deviation of initial and polished WC-Co knives

Fig. 3 presents the modelling results of the depth profiles of nitrogen and argon ions implanted to W-C-Co material, for all modelled cases.

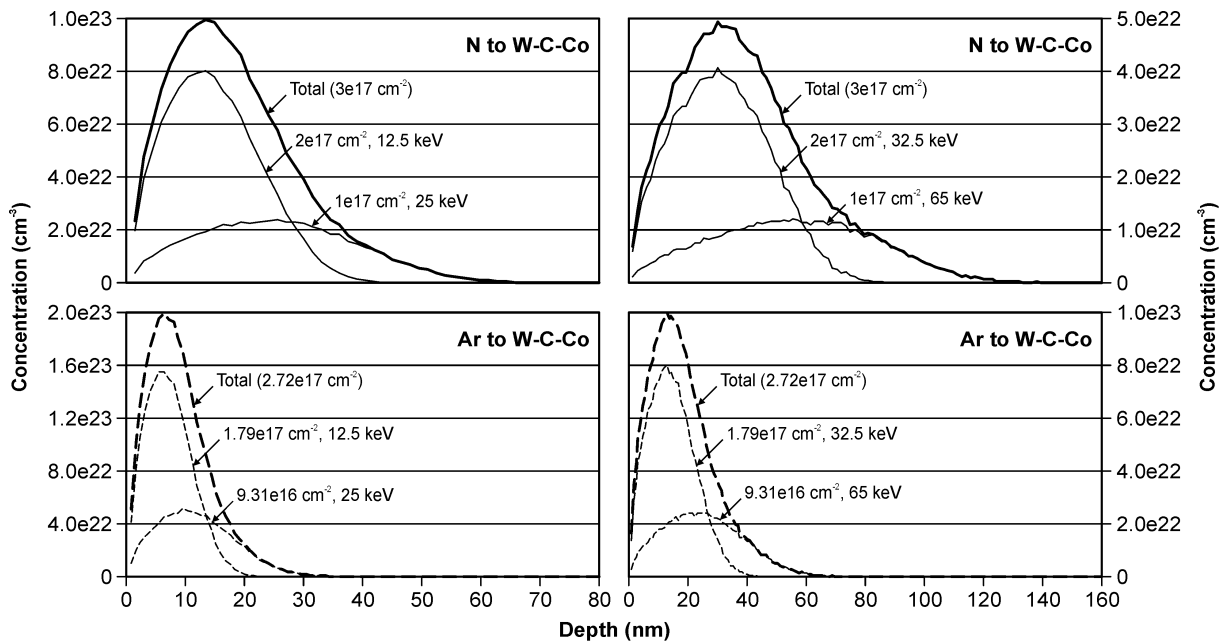


Figure 3. The modelled depth profiles of the implanted ions of nitrogen and argon for the selected values of the acceleration voltage

The upper graphs show nitrogen profiles for the fluence of $3 \times 10^{17} \text{ cm}^{-2}$ and the acceleration voltage of 25 kV (left) and 65 kV (right). The thin lines mark profiles that are components of the thick lines marked “total” profiles, and they result from the previously mentioned non-homogeneity of the nitrogen ion beam.

The middle graphs present the profiles obtained for argon ions, implanted with two values of the acceleration voltage (25 + 12.5 kV left and 65 + 32.5 kV right). They assume single ionisation of this element. The adopted fluence of the implanted argon ions is smaller about 10% than for nitrogen, to obtain similar values of the peak volume dopant concentration N_{max} .

The lower graphs show a comparison of the total profiles obtained for both elements and both conditions of the acceleration voltage.

It should be noted, that in the both cases of implanted ion, the adopted scale on the abscissa axis and the scale on the ordinate axis differ by a factor of two for the acceleration voltage of 65 kV with respect to that of 25 kV.

Fig. 4 presents the set of all total depth profiles in the same scales, for a better visualization. It is seen, that the profiles for 25 kV nitrogen and 65 + 32.5 kV argon are similar.

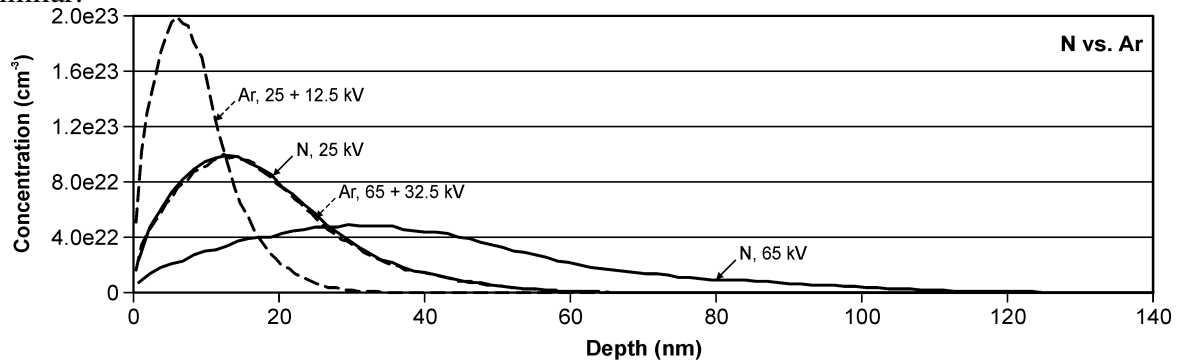


Figure 4. The total depth profiles for all modelled case.

Table 2 shows the peak parameters and the sputtering yield values for all profiles presented in Fig. 4. Additionally, the percent difference between the parameters of the similar profiles are shown in bold.

It can be seen, that the difference is less than 1% for the significant parameters, like the peak volume dopant concentration, the projected range and the range straggling.

Table 2. The modelled values of the peak volume dopant concentration, projected range, range straggling, kurtosis, skewness and sputtering yield and the values of the percent difference in their values for both similar profiles of the implanted elements

Parameter	Peak volume dopant concentration, N_{max} (cm ⁻³)	Projected range, R_p (nm)	Range straggling, ΔR_p (nm)	Kurtosis	Skewness	Sputtering yield, Y (atoms/ion)
Argon (25 + 12.5 kV)	1.99e23	8.5	10.6	4.1701	0.9934	1.59
Nitrogen (25 kV)	9.93e22	17.8	22	3.8995	0.9376	0.47
Argon (65 + 32.5 kV)	9.99e22	17.9	22.2	4.0518	0.9778	1.83
Nitrogen (65 kV)	4.94e22	39.4	46.4	3.4495	0.7953	0.44
Difference N/Ar (%)	-0.57	-0.56	-0.91	-3.91	-4.29	-289.36
Difference Ar/N (%)	0.57	0.56	0.90	3.76	4.11	74.32

The average measurements results of the contact angle, the calculated results of the relative index (the contact angle values obtained for implanted surfaces compared to the values for un-implanted surfaces) and the coefficients of variation (the indicator, combining average wettability and variability in the wettability) are presented in Fig. 5. The bars for the similar depth profiles, i.e. for the cases of 25 kV nitrogen and 65 + 32.5 kV argon, are outlined in the all graphs, for better visualization.

It is seen, that the average contact angle values are in the range from 42.98° to 50.61° for the initial surface and in the range from 45.65° to 58.74° for the polished one.

All values of the contact angle are smaller for the implanted surfaces (for the same surface preparation), both for initial and polished indexable knives. The difference in the comparison to the un-implanted surface is from 1.55° to 7.63° for the initial surface and from 6.1° to 13.09° for the polished. These changes are statistically insignificant, due to the absolute value of standard deviation range of 0.33-4.39° for the initial surface and 2.56-5.45° for the polished.

All contact angle values after polishing are higher than the initial ones, except for one case (Ar 25 + 12.5 kV). The contact angles are very similar for the similar depth profiles of nitrogen and argon.

The values of the relative index are in the range 0.85-0.97 for the initial surface and 0.78-0.9 for polished ones. The results obtained for the depth similar profiles are similar. Higher difference is observed for the extreme cases/profiles, i.e. for 25 + 12.5 kV argon and 65 kV nitrogen.

The coefficient of variation is at a similar level of 0.14-15 for six out of ten cases. This parameter is practically the same for the extreme cases/profiles and very different (the difference at the level of 40% or more) for the similar depth profiles.

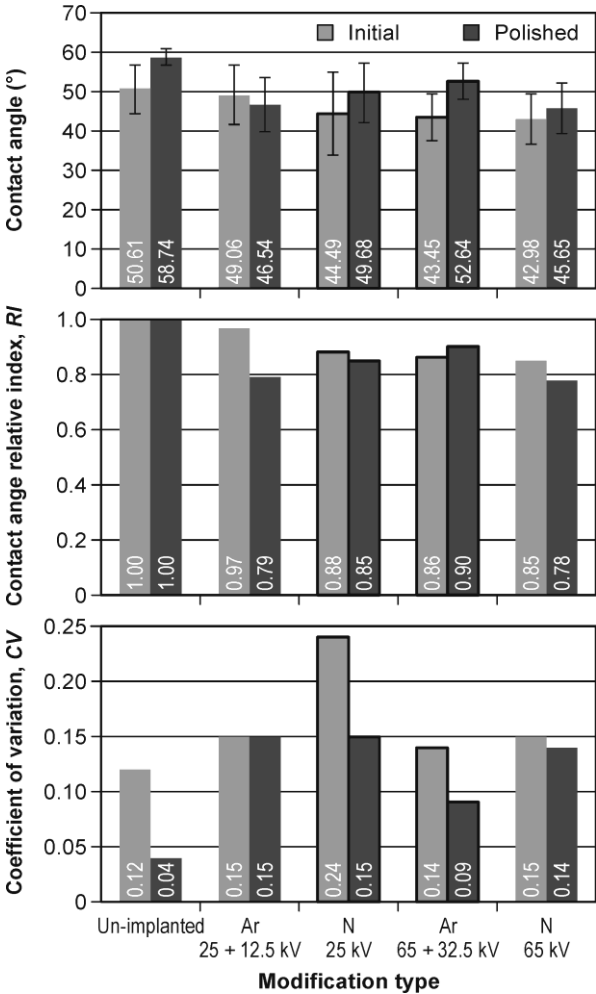


Figure 5. The values of the contact angle, the relative index and the coefficient of variation for un-implanted WC-Co knives and for the knives implanted with nitrogen and argon

CONCLUSIONS

Based on the presented results, it can be concluded, that the ion implantation causes a decrease in the contact angle, regardless of the surface roughness. The differences between the average values of the contact angle are not statistically significant due to the variability, but the decrease in the average values is obvious.

To get more definite conclusions, we suggest that the energy range of the implanted ions should be increased and/or further investigations should be carried out with a different set of elements.

In the next step, the calculated sputtering yield values should be also taken into account and the fluences of the implanted ions should be increased, up to reasonable values.

However, it is unlikely that a possible presence and amount of new chemical compounds formed as a result of nitrogen implantation into the WC-Co substrate may have a significant effect on the obtained results.

ACKNOWLEDGMENTS

The authors wish to thank Mr. J. Zagórski for the technical assistance during the ion implantation processes.

REFERENCES

1. BARLAK M., PIEKOSZEWSKI J., WERNER Z., STANISLAWSKI J., SKLADNIK-SADOWSKA E., BORKOWSKA K., MISKIEWICZ M., KOLITSCH A., GRÖTZSCHEL R., STAROSTA W., SARTOWSKA B., KIERZEK J., 2009: Wettability improvement of carbon ceramic materials by mono and multi energy plasma pulses, *Surface and Coatings Technology* 203, 2536-2540. DOI: 10.1016/j.surfcoat.2009.02.070
2. BARLAK M., WILKOWSKI J., SZYMANOWSKI K., CZARNIAK P., PODZIEWSKI P., WERNER Z., ZAGÓRSKI J., STASZKIEWICZ B., 2019a: Influence of the ion implantation of nitrogen and selected metals on the lifetime of WC-Co indexable knives during MDF machining, *Annals of Warsaw University of Life Science - SGGW, Forestry and Wood Technology* 108, 45-52. DOI: 10.5604/01.3001.0013.7680
3. BARLAK M., WILKOWSKI J., WERNER Z., 2019b: Modelling of the ion implantation modification of WC-Co indexable knives for wood machining, *Annals of Warsaw University of Life Science - SGGW, Forestry and Wood Technology* 106, 57-61. DOI: 10.5604/01.3001.0013.7737
4. BARLAK M., WILKOWSKI J., WERNER Z., 2019c: Modelling of nitrogen implantation processes into WC-Co indexable knives for wood-based material machining using ion implanters with or without direct ion beam, *Annals of Warsaw University of Life Science - SGGW, Forestry and Wood Technology* 108, 68-78. DOI: 10.5604/01.3001.0013.7684
5. BARLAK M., WILKOWSKI J., WERNER Z., 2019d: The selected problems of the modelling of the depth profiles of the elements implanted to the tools used in wood material machining, *Biuletyn Informacyjny OB-RPPD* 3-4, 118-134. DOI: 10.32086/biuletyn.2019.5
6. BARLAK M., WILKOWSKI J., WERNER Z., 2023: Modelling of the similar depth profiles of two different kinds of the ions, implanted to WC-Co tools, used in wood-based material machining, *Annals of Warsaw University of Life Science - SGGW, Forestry and Wood Technology*, in publish.
7. BETLEJ I., BARLAK M., WILKOWSKI J., WERNER Z., ZAGÓRSKI J., LIPSKA K., BORUSZEWSKI P., 2022: Wettability of the surface of bacterial cellulose film modified with the ion implantation, *Annals of Warsaw University of Life Science - SGGW, Forestry and Wood Technology* 118, 15-21. DOI: 10.5604/01.3001.0015.9369
8. BROWN I., WASHBURN J., 1987: The MEVVA ion source for high current metal ion implantation. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 21, 201-204: DOI: 10.1016/0168-583X(87)90826-3
9. Diapro. <https://www.struers.com/en/Products/Grinding-and-Polishing/Grinding-and-polishing-consumables/Diapro#>
10. PIEKOSZEWSKI J., OLESINSKA W., JAGIESLKI J., KALIŃSKI D., CHMIELEWSKI M., WERENR Z., BARLAK M., SZYMCZYK W., 2004: Ion implanted nanolayer in AlN for direct bonding with copper. *Solid State Phenomena* 99-100, 231-234. DOI: 10.4028/www.scientific.net/SSP.99-100.231
11. Polishing Cloths. <https://www.struers.com/en/Products/Grinding-and-Polishing/Grinding-and-polishing-consumables/Polishing-Cloths#>
12. SRIM. <http://www.srim.org/>
13. SURFACEWARE. <http://www.kromtek.com.my/products/seo-phoenix-smart-m-a-t-portable-contact-angle-analyzer/>

14. SUSPRE. <https://uknibc.co.uk/SUSPRE/>
15. WILKOWSKI J., BARLAK M., BÖTTGER R., WERNER Z., KONARSKI P., PISAREK M., WACHOWICZ J., VON BORANY J., AURIGA A., 2021: Effect of nitrogen ion implantation on the life time of WC-Co tools used in particleboard milling. *Wood Material Science and Engineering* 1-12. DOI: 10.1080/17480272.2021.1900391
16. WILKOWSKI J., BARLAK M., KWIDZIŃSKI Z., WILCZYŃSKI A., FILIPCZUK P., PĘDZIK M., DREWZYŃSKI M., ZAGÓRSKI J., STASZKIEWICZ B., ROGOZIŃSKI T., 2022: Influence of Ion Implantation on the Wear and Lifetime of Circular Saw Blades in Industrial Production of Wooden Door Frames. *Applied Sciences* 12, 10211. DOI: 10.3390/app122010211
17. WERNER Z., BARLAK M., GRĄDZKA-DAHLKE M., DIDUSZKO R., SZYMCZYK W., DĄBROWSKI J., PIEKOSZEWSKI J., BORKOWSKA K., 2007: The effect of ion implantation on the wear of C-Cr-Mo alloy. *Vacuum* 81 1191-1194. DOI: 10.1016/j.vacuum.2007.01.014

Streszczenie: *Zwilżalność implantowanych azotem i argonem narzędzi WC-Co, wykorzystywanych w obróbce materiałów drewnopochodnych.* Podjęto próbę sprawdzenia wpływu profili głębokości implantowanych jonów na zwilżalność implantowanych jonowo narzędzi WC-Co, stosowanych do obróbki materiałów drzewnych. Badania przeprowadzono dla dwóch rodzajów powierzchni narzędzi, tj. wyjściowej i polerowanej, dwóch powszechnie stosowanych gazów, tj. azotu i argonu oraz dla wartości parametrów możliwych do uzyskania w przypadku klasycznych implantatorów jonów. Zamodelowano cztery głębokościowe profile dla dwóch różnych wartości napięcia przyspieszającego, po dwa dla każdego implantowanego pierwiastka. Parametry modelowania dobrano tak, aby dwa modelowane profile głębokości dla obu implantowanych pierwiastków były podobne. Badania zwilżalności były prowadzone na wspomaganym komputerowo stanowisku testowym. Uzyskane wyniki nie potwierdzają hipotezy o zależności między zwilżalnością a położeniem i kształtem głębokościowych profili implantowanych pierwiastków.

Corresponding author:

Marek Barlak
7 Andrzeja Sołtana St.
05-400 Otwock, Poland
Marek.Barlak@ncbj.gov.pl
(22) 273 16 44