

## Long-range effect of ion implantation of Raex and Hardox steels

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**Abstract.** Ion implantation involves introduction of ionized atoms of any element (nitrogen) to metals thanks to the high kinetic energy that they acquired in the electric field. The distribution of nitrogen ions implanted at  $E = 65$  keV energy and  $D = 1 \cdot 10^{17}$  N<sup>+</sup>/cm<sup>2</sup> fluence in the steel sample and vacancies produced by them was calculated using the SRIM program. This result was confirmed by RBS measurements. The initial maximum range of the implanted nitrogen ions is  $\sim 0.17$   $\mu\text{m}$ . This value is relatively small compared to the influence of nitriding on the thickness surface layer of modified steel piston rings. Measurements of the friction coefficient during the pin-on-disc tribological test were performed under dry friction conditions. The friction coefficient of the implanted sample increased to values characteristic of an unimplanted sample after ca. 1500 measurement cycles. The depth of wear trace is ca. 2.4  $\mu\text{m}$ . This implies that the thickness of the layer modified by the implantation process is  $\sim 2.4$   $\mu\text{m}$  and exceeds the initial range of the implanted ions by an order of magnitude. This effect, referred to as a long-range implantation effect, is caused by migration of vacancies and nitrogen atoms into the sample. This phenomenon makes ion implantation a legitimate process of modification of the surface layer in order to enhance the tribological properties of critical components of internal combustion engines such as steel piston rings.

### 1. Introduction

A rapid development of automotive technology requires designers to use modern materials. They must have high strength and low specific weight in order to reduce the overall weight of the vehicle. The materials used to construct the most loaded components such as the components of internal combustion engines are often subjected to various treatments to enhance their mechanical properties [1]. There is a widespread application of various coatings, for example nitriding or chrome-plated piston rings. Another example is the doping with other materials, for example by welding as is the case with the surfacing of stellite valve face and valve seat [1].

One of the known methods for material modification in terms of tribological, mechanical and chemical properties is ion implantation. It is a physical process which comprises implanting atoms of one element into the structure of another material. In the absence of specific requirements for the implantable element and the workpiece, it is possible to implant atoms of any element in any structure of the material [6].



Ion implantation is performed in a device called ion implanter. Atoms of an element are ionized and then accelerated along the electric field to reach the high-speed power from tens to hundreds of keV and to impact the surface of the workpiece, thereby permanently digging into its structure. This process is performed under vacuum and at relatively low temperatures ( $<200^{\circ}\text{C}$ ), so that heat causes no changes to the material structure. Another feature of ion implantation is that it does not affect the changes in external dimensions of the workpiece, so it can be applied as the final step in the production of components.

The influence of ion implantation on the mechanical, tribological [9] and chemical properties of the material is well known. There are a lot of works on the impact of the implantation process with respect to enhancing properties of different materials, such as [4] and [5]. Nitrogen atoms are most often used for implantation. In addition, carbon, titanium, boron and phosphorus are used, too. The use of ion implantation of nitrogen results in higher micro-hardness, lower friction coefficient, reduced tribological wear and higher corrosion resistance of materials [7].

In spite of so many advantages of ion implantation, the process is not often used in the engineering industry due to the fact that the atoms implanted into the element during implantation penetrate the structure of the material to a depth of  $\sim 0.2\mu\text{m}$ . However, when analysing the results of studies on the effect of implantation on the properties of materials, one can often encounter information that the impact of implanted ions is visible at much greater depths than the depth resulting from the implantation process [10]. This effect is called the long-range effect and it extends the life of the implanted element as a result of ion implantation. There is no definitive cause of the long-range effect. It is believed that this effect occurs due to migration of atoms implanted into the material during the friction process, as found during the tribological test reported in [3].

Since the application of ion implantation seems to result in a much longer service life than initially expected, this process appears suitable for producing machine parts. This paper presents the long-range effect of ion implantation on the tribological properties of Hardox 450 and Raex 400 steels. These steels are similar to the steel used for piston rings in an internal combustion engine, so they are used to investigate the suitability of using ion implantation in the construction of vehicle engines.

## 2. Material and methods

To study the long-range effect of ion implantation on the tribological properties of the material, we performed tests on Raex 400 and Hardox 450 steels. They have been selected due to the fact that their physical properties are very similar to those of the steel used in the production of piston rings for internal combustion engines. The mechanical properties of the selected steels and those of the steel used for producing rings [8] are given in Table 1, while Table 2 shows the chemical composition of the tested steels.

**Table 1.** Properties of the tested steels.

	Hardness (HRC)	Tensile strength (MPa)	Young modulus (GPa)	Density (g/cm <sup>3</sup> )
MS 064	48-54	1125-1325	210	7.80
Hardox 450	48	1400	210	7.85
Raex 400	41	1250	210	7.85

**Table 2.** Chemical composition of the tested steels.

	C, %	Si, %	Mn, %	P, %	S, %	Cr, %	Ni, %	Mo, %	B, %
Hardox 450	0.26	0.70	1.60	0.025	0.010	1.40	1.50	0.60	0.005
Raex 400	0.20	0.70	1.70	0.030	0.015	1.50	0.40	0.50	0.004

Test samples were made of a steel sheet metal. They were cut by a high pressure water jet in order to avoid structural changes induced by high temperature typical of waste machining methods. The samples had the shape of discs with a diameter  $\phi = 25$  mm. The sample surface was polished to  $Ra = 0.01$ . The samples were implanted using nitrogen ions. The implantation process was run with the power  $E = 65$  keV, and the dose of implanted ions was set to  $D = 1 \cdot 10^{17} \text{ N}^+/\text{cm}^2$ .

After that, the samples were subjected to tribological tests on a pin-on-disc stand using the Nano Tribometer (NTR2) manufactured by Anton Paar. As counter sample, we used a ball with a diameter 0.5 mm made of WC (tungsten carbide). A load of 0.5 N was applied to the ball. As a result, we could determine variations in the friction coefficient for individual samples under dry friction conditions.

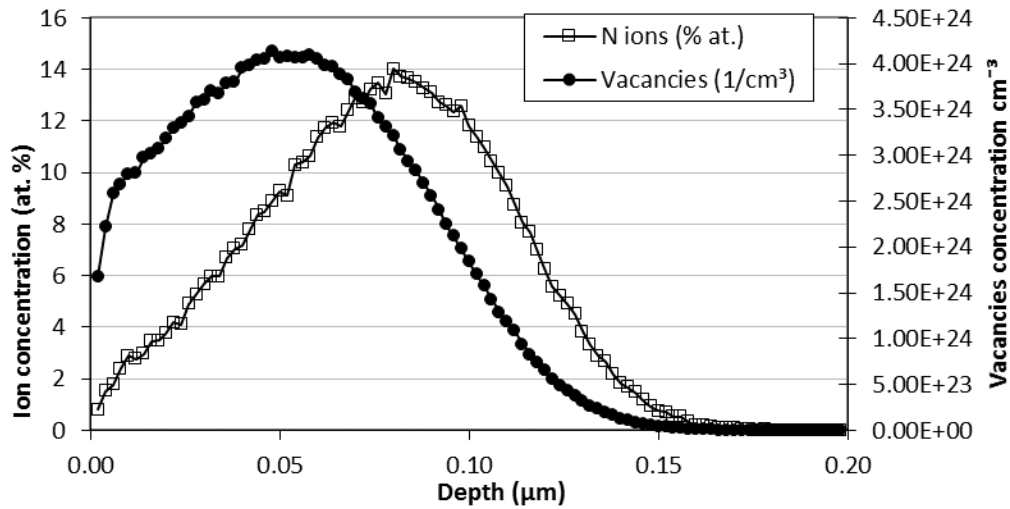
Next, the wear trace was measured using the Taylor Hobson Form Talysurf 50mm Intra profile measurement gauge. The measurements provided profilograms enabling determination of the mean wear and the depth of wear trace. The wear was defined as the mean surface of the cross section of contact between the sample and the counter-sample.

For the Raex 400 steel sample, the number of cycles (revolutions) was determined based on the value of friction coefficient. The threshold friction coefficient characteristic of the unimplanted sample was set. After reaching this value by the implanted sample, the test was stopped and the average cross-sectional area and the depth of wear track were measured. The same number of cycles was performed for both samples of Hardox 450.

### 3. Results and discussion

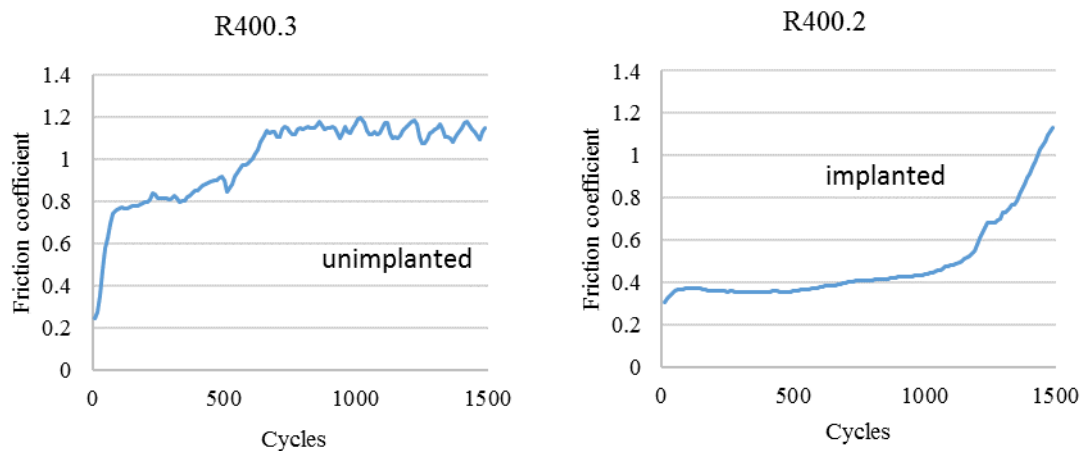
For the purpose of preliminary determination of ion-implantation, a numerical simulation was performed. The distribution of implanted ions and point defects (gaps) at various depths can be calculated with the use of numerical programs. SRIM is the most commonly used program for this type of calculations [11]. Usually, numerical results correspond well with experimental findings obtained with e.g. RBS or SIMS methods.

Figure 1 shows the calculated distribution of nitrogen ions implanted at energy  $E = 65$  keV and fluence  $D = 1 \cdot 10^{17} \text{ N}^+/\text{cm}^2$  into a Raex 400 sample and the vacancies generated by them. It is clear that the calculated range of the implanted nitrogen ions does not exceed  $0.17 \text{ }\mu\text{m}$ , and the maximum concentration of gaps is located at a depth of ca.  $0.05 \text{ }\mu\text{m}$ .



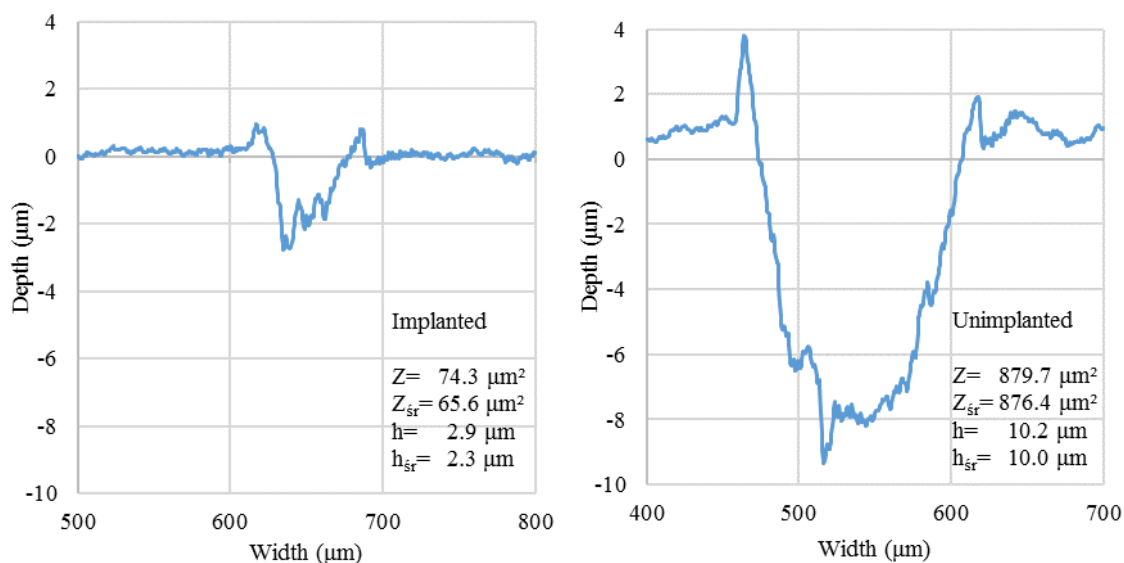
**Figure 1.** Calculated distribution of nitrogen ions implanted at energy  $E = 65$  keV and fluence  $D = 1 \cdot 10^{17}$  N+/cm<sup>2</sup> into Raex steel and the generated vacancies.

The results of friction coefficient for the Raex 400 sample are shown in Figure 2. The implantation of nitrogen leads to a significant reduction in the coefficient of friction.



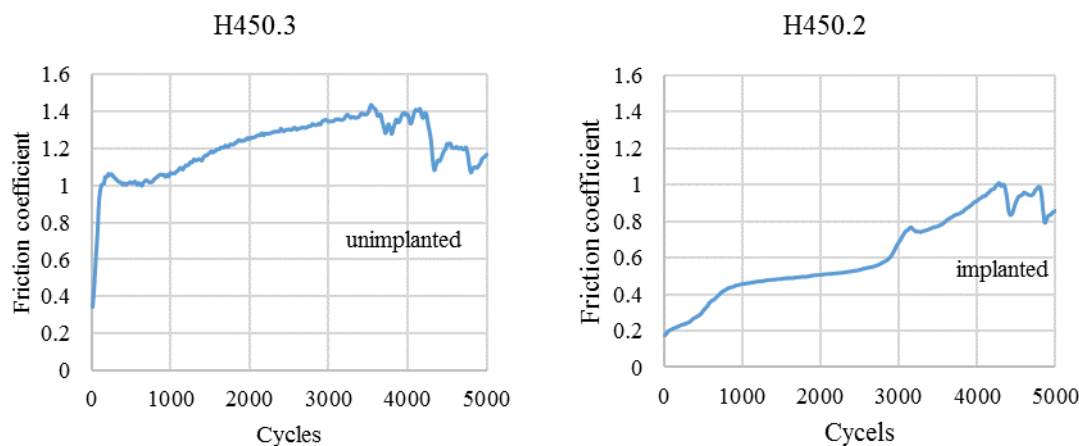
**Figure 2.** Friction coefficient of Raex 400 sample before and after implantation of nitrogen ions.

This means that the thickness of the modified layer in the implantation depth can be determined from the track produced during the test when the friction coefficient is lower than that of the unimplanted sample. The testing of the samples implanted was stopped when the value of the friction coefficient reached the value characteristic of the unimplanted sample, that is  $\mu = 1.15$ . The cross section of the track is measured using a profilometer (Figure 3).



**Figure 3.** Profilogram of a track left by the ball on Raex 400 sample in a 1500-cycle test.

As shown in Figure 2, the value of the friction coefficient of the implanted sample is equal to the values of the friction coefficient of the unimplanted sample after ca. 1500 cycles. The depth of the wear track is approx.  $2.3 \mu\text{m}$ . This indicates that the thickness of the layer modified during the implantation of the Raex 400 sample is ca.  $2.3 \mu\text{m}$  and it exceeds the initial range of the implanted ions by an order of magnitude. This effect is known as the long-range implantation. A similar effect of implantation of nitrogen ions with an energy of 65 keV and a fluence of  $1 \cdot 10^{17} \text{ N}^+/\text{cm}^2$  leading to reduction in the friction coefficient was observed for the Hardox 450 sample (Figure 4).

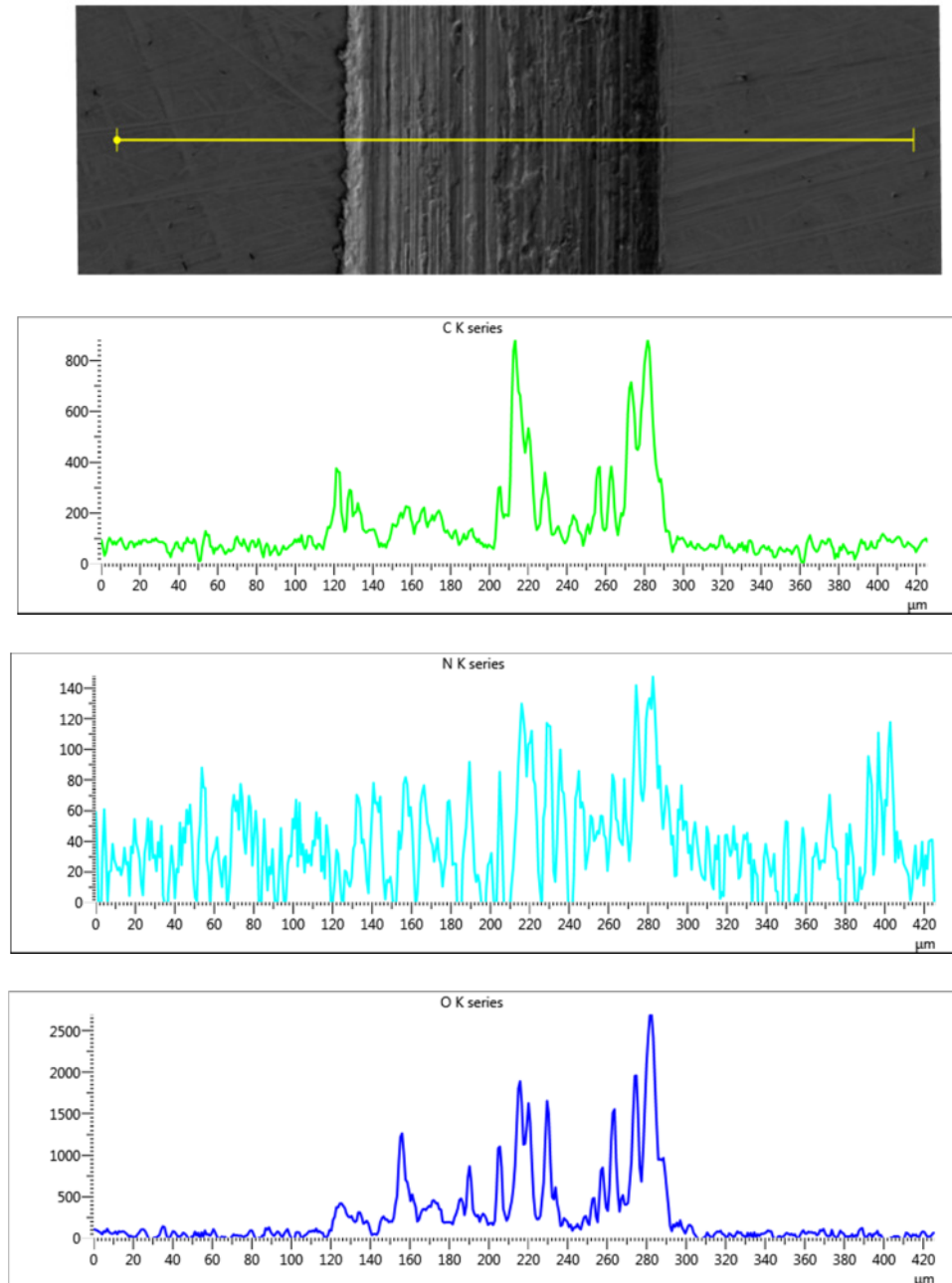


**Figure 4.** Friction coefficient of Hardox 450 steel, unimplanted and implanted with nitrogen ions at energy  $E = 65 \text{ keV}$  and fluence  $D = 1 \cdot 10^{17} \text{ N}^+/\text{cm}^2$ .

The reduction in the friction coefficient after nitrogen implantation in the Hardox 450 sample occurs within ca. 4000 measurement cycles. The depth of wear track is  $2.1 \mu\text{m}$ . In the case of the Hardox 450 sample, the thickness of the layer with tribological properties enhanced by an order of magnitude exceeds the range of the implanted nitrogen ions.

The long-range effect is caused by the migration of vacancies and nitrogen ions into the sample. The migration of vacancies deeper inside the sample is caused by the pressure generated by a high

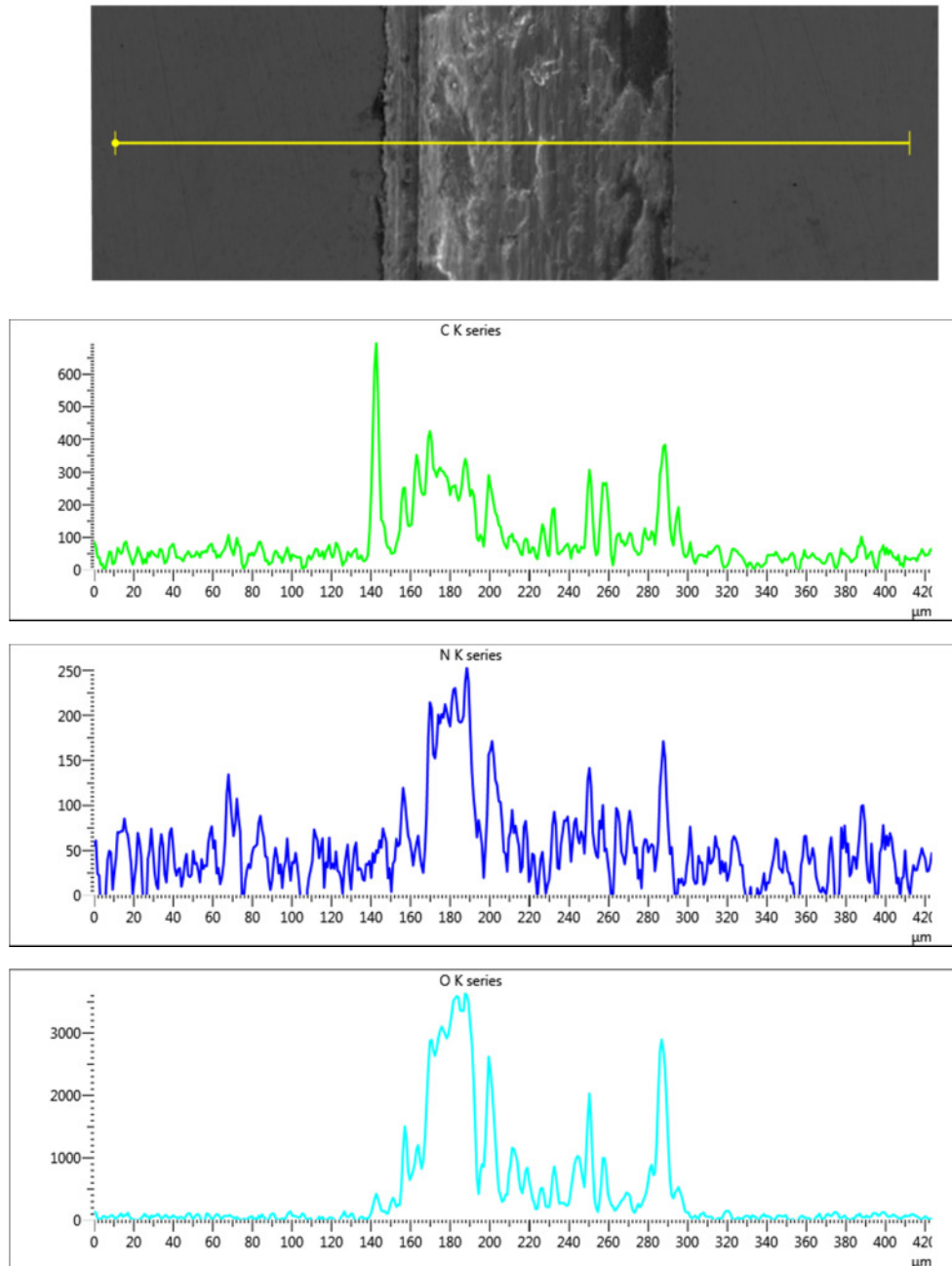
concentration thereof at a depth of ca. 0.05  $\mu\text{m}$ , which is only slightly lower than the maximum concentration of the implanted nitrogen ions. In turn, the migration of nitrogen atoms is caused by diffusion driven by the gradient of the chemical potential, which depends on the temperature, pressure, and concentration [6].



**Figure 5.** Microphotograph of a fragment of implanted Raex 400 sample and the scan line and distribution of carbon, nitrogen, and oxygen ions.

The distribution of oxygen, carbon, and nitrogen atoms on the sample surface and on the track bottom was examined by EDS method. As shown in Figures 5 and 6, the content of carbon and nitrogen on the track bottom introduced during the implantation process is greater than that on the sample surface. This

implies that the migration of nitrogen and carbon atoms into the sample facilitates radiation damage and an increase in the diffusion coefficient caused by a local temperature increase during the tribological test. The increased numbers of carbon atoms in the implanted sample requires a comment. The carbon originated from vacuum oil vapours deposits on the sample during implantation although the pressure in the collector chamber was  $p = 2 \cdot 10^{-6}$  Pa. The temperature of the sample during the implantation process did not exceed  $50^{\circ}\text{C}$  to prevent implantation heat effects, which could have contributed to deposition of oil vapours on the relatively cool sample.



**Figure 6.** Microphotograph of a fragment of implanted Hardox 450 sample and the scan line and distribution of carbon, nitrogen, and oxygen ions.

#### 4. Conclusions

The results have demonstrated that the long-range effect is caused by the movement of both the implanted nitrogen and dopant atoms in the vicinity of the friction zone. The study is the first to document the diffusion of carbon atoms. In addition, the increased content of oxygen in the bottom trace shows the dominant oxidizing wear of the Raex 400 and Hardox 450 samples after the implantation of nitrogen at an energy of 65 keV and a dose of  $1 \cdot 10^{17} \text{ N}^+/\text{cm}^2$ . The results of the friction coefficient have revealed that the effect of ion implantation is several times greater than assumed. With the ion implantation of nitrogen, it is possible to extend the life of the implanted part of the machine. The implantation can be used to enhance the mechanical properties and chemical combustion of vehicle engine components.

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