

# Application of nuclear techniques for characterization of materials surfaces: own investigations examples

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**Abstract.** Different methods and techniques for material characterization are often used as a standard procedure for the determination of material properties. Nuclear techniques provide new and more detailed information about the investigated materials. The main goal of the carried out experiments was to improve surface properties including wear, corrosion and high temperature oxidation resistance. Modification processes were carried out using high intensity pulsed plasma beams – HIPPB ( $10^6$ – $10^8$  W·cm<sup>-2</sup>) generated in a rod plasma injector (RPI). In most solid materials such treatment leads to a fast transient melting of the surface layer of the substrate followed by rapid crystallization. Heating and cooling processes are of non-equilibrium type. Initial and modified materials were characterized using different investigation methods including nuclear techniques. Results of the used nuclear techniques such as nuclear reaction analysis (NRA), Rutherford backscattered spectroscopy (RBS) and conversion electron Mössbauer spectroscopy (CEMS) are presented in the paper.

**Key words:** conversion electron Mössbauer spectroscopy (CEMS) • nuclear reaction analysis (NRA) • nuclear techniques • Rutherford backscattered spectroscopy (RBS) • surface characterization • surface modification

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## Introduction

Surface engineering, especially surface modification is used for improving surface properties of different technical materials. It allows us also to design new advanced materials with properties tailored to specific requirements. Modification of technical material surfaces is applied for changing their surface properties. The concentration of different elements (introduced or present in an initial material), structure of the material (as a result of different kinds of plastic working and heat treatments) or both can be changed [3]. One of the methods used for surface modification is the remelting technique with laser, electron, plasma or ion beams applications. Knowledge of material properties including their elemental composition, phase composition and structure is of fundamental importance in respect of: (i) material future potential application, (ii) possibility of modification, it means improvement, of existing materials, (iii) possibility of production process changes. Different methods and techniques for material characterization are used for the determination of material properties. Nuclear techniques provide new and more detailed information about the investigated materials. Short description of the applied three nuclear techniques used in our investigation team is presented below.

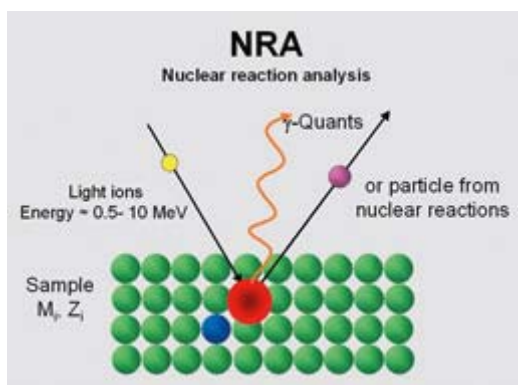


Fig. 1. Scheme of nuclear reaction analysis (NRA).

### Nuclear reaction analysis (NRA)

Nuclear reaction analysis (NRA) is a nuclear method applied in material science to obtain concentration vs. depth distributions for certain target elements present in a thin solid film. Once irradiated with selected projectile – nuclei at a defined kinetic energy in these target elements can undergo a nuclear reaction under resonance conditions for sharply defined resonance energy. The result of reaction is usually a nucleus in an excited state which immediately decays, emitting ionizing radiation. The scheme of NRA technique is presented in Fig. 1. To contribute to the nuclear reaction the projectile nuclei have to slow down in the sample to reach the resonance energy. Thus, each initial kinetic energy corresponds to a depth in the sample where the reaction occurs (the higher the energy, the deeper the reaction). Examples of nuclear reaction where only one particle is emitted are listed in Table 1 [16].

To obtain depth information about concentration of elements the initial kinetic energy of the projectile nucleus (which has to exceed the resonance energy) and its stopping power (energy loss per distance travelled) in the sample has to be known. NRA allows to quantify individual light isotope concentration and also to determine depth profile with nanometre resolution. It has been used, for example, to measure total nitrogen concentrations in hardened steels [7, 8]. NRA is particularly useful to determine very low amount of nitrogen in steels using nuclear reactions induced by different projectiles on the nitrogen isotopes ( $^{14}\text{N}$ ; 99.635% and  $^{15}\text{N}$ ; 0.365%). The main nuclear reactions for the determination of nitrogen concentration in steels are presented in Table 2 [16].

### Rutherford backscattering spectrometry (RBS)

Rutherford backscattering spectrometry (RBS) is an analytical technique used in material science. RBS is an ac-

Table 2. Examples of nuclear reactions used to determine nitrogen concentration in the investigations of steels

Short description	Full description
$^{15}\text{N}(p,\alpha)^{12}\text{C}$	$^{15}_7\text{N} + ^1_1\text{p} \rightarrow ^4_2\alpha + ^{12}_6\text{C}$
$^{14}\text{N}(\alpha,\gamma)^{18}\text{F}$	$^{14}_7\text{N} + ^4_2\alpha \rightarrow ^{18}_9\text{F} + \gamma$
$^{14}\text{N}(p,\gamma)^{15}\text{O}$	$^{14}_7\text{N} + ^1_1\text{p} \rightarrow ^{15}_8\text{O} + \gamma$
$^{14}\text{N}(d,\alpha)^{12}\text{C}$	$^{14}_7\text{N} + ^2_1\text{d} \rightarrow ^4_2\alpha + ^{12}_6\text{C}$

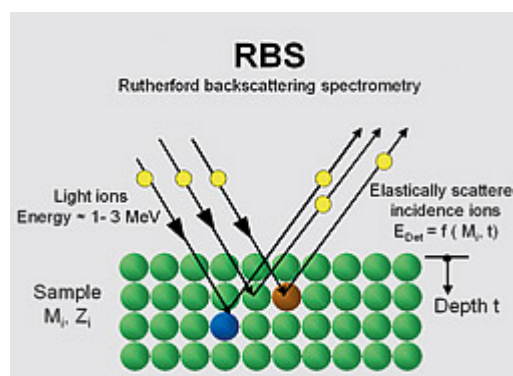


Fig. 2. Scheme of Rutherford backscattering spectrometry (RBS).

celerator bound technique for quantitative composition analysis of thin layers or near surface regions of solids. Rutherford backscattering can be described as an elastic collision between a high kinetic energy particle from the incident beam – the projectile and a stationary particle located in the sample – the target. Elastic in this context means that no energy is either lost or gained during the collision. The scheme of RBS technique is presented in Fig. 2 [6]. The energy distribution of backscattered ions contains information on the depth dependence of the elemental composition in a depth range of typical  $1 \mu\text{m}$  below the surface. A well collimated beam of monoenergetic ions is directed to the sample. Usually, light ions as H, He or Li with energies ranging from 1 to 3 MeV are used. The ions penetrate into the material and lose their kinetic energy, at the beginning mainly in collisions with electrons until they come to rest in a depth of several micrometers. Backscattered ions can leave the sample and reach a particle spectrometer, where their energy is analysed. RBS measurement gives immediately information about the energy of ions scattered. The stopping cross-sections for light ions in any matter are available with low uncertainty. Thus, the depth dependent energy deficit allows calculating a depth scale for each scattering atomic mass. The obtainable depth resolution mainly depends on the energy resolution of the spectrometer.

Several codes exist to assist in the analysis of RBS spectra, for example: RUMP, RBX, GISA, NDF and SIMNRA. The RBS method is a part of nuclear micro-

Table 1. Examples of nuclear reactions with the emission of one particle

Proton reactions	Deuteron reactions	$^3\text{He}$ reactions	$\alpha$ particle reactions
$^7\text{Li}(p,\alpha)^4\text{He}$	$^9\text{Be}(d,\alpha)^7\text{Li}$	$^6\text{Li}(^3\text{He},p)^8\text{Be}$	$^{10}\text{B}(\alpha,p)^{13}\text{C}$
$^{11}\text{B}(p,\alpha)^8\text{Be}$	$^{13}\text{C}(d,p)^{14}\text{C}$	$^9\text{Be}(^3\text{He},\alpha)^8\text{Be}$	$^{19}\text{F}(\alpha,p)^{22}\text{Ne}$
$^{18}\text{O}(p,\alpha)^{15}\text{N}$	$^{14}\text{N}(d,p)^{15}\text{N}$	$^{11}\text{B}(^3\text{He},d)^{12}\text{C}$	$^{31}\text{P}(\alpha,p)^{34}\text{S}$
	$^{14}\text{N}(d,\alpha)^{12}\text{C}$	$^{12}\text{C}(^3\text{He},p)^{14}\text{N}$	

analysis used for the examination of surface layers of materials in terms of elemental composition, concentrations and depth profiles of individual chemical elements and, in consequence, also to estimate the thickness at a micrometer level. The RBS method can also be used to determine the degree of crystallographic perfection of single crystals and the depth distribution of defects in crystal structure [2]. The results may be easily transformed into absolute units and usually do not depend on the physicochemical properties of the studied material [2].

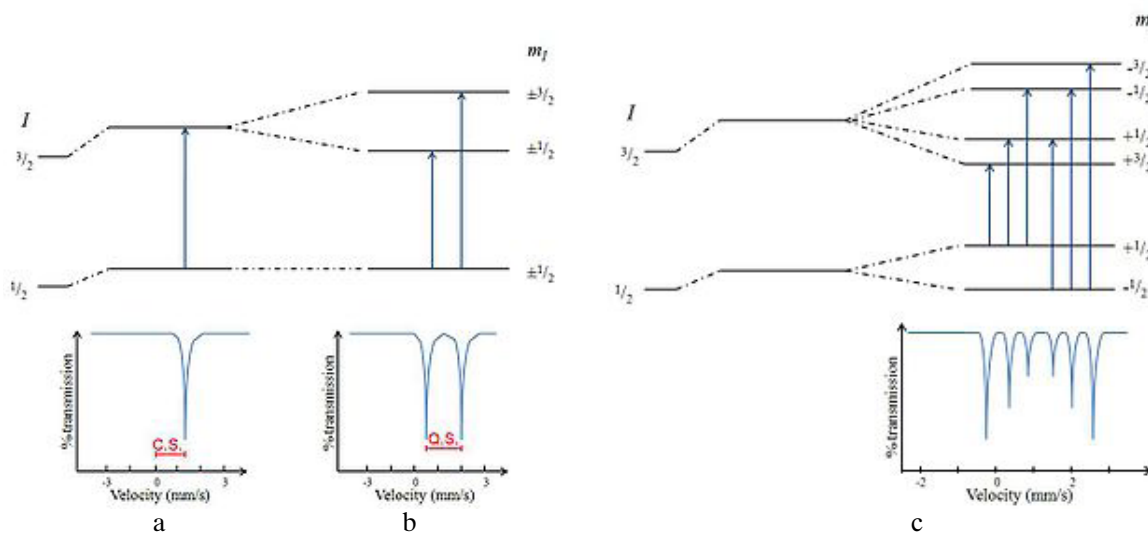
NRA and RBS investigation methods are non-destructive contrary to other methods used for elemental depth profiles determination. Cleaving of the sample or producing the cross-section of the surface layer is destructive. Investigation using the SEM + EDS method with line scan profile or elemental mapping provides limited information about the investigated layer composition. After ion etching in secondary ion mass spectroscopy (SIMS), glow discharge mass spectrometry (GDMS) or glow discharge optical emission spectrometry (GDOES) the craters are created on the surfaces of investigated samples.

### Conversion electron Mössbauer spectroscopy (CEMS)

Conversion electron Mössbauer spectroscopy (CEMS) is a spectroscopic technique based on the Mössbauer effect. Mössbauer found that a significant fraction of emission and absorption events is recoil-free. It means gamma rays emitted by one nucleus can be resonantly absorbed by a sample containing nuclei of the same isotope, and this absorption can be measured. To bring the two nuclei into resonance it is necessary to change the energy of gamma ray slightly, and in practice this is always done using the Doppler effect [5]. Mössbauer spectroscopy probes small changes in the energy levels of an atomic nucleus in response to its environment. Typically, three types of nuclear interaction may be observed: (i) isomer shift – also known as chemical shift –  $\delta$  is a relative measure describing a shift in the resonance energy of a nucleus due to the transition of electrons within its  $\sigma$  orbital, (ii) quadrupole splitting

(QS) reflects the interaction between the nuclear energy levels and surrounding electric field gradient (EFG) and (iii) magnetic splitting – also known as the Zeeman effect – is a result of the interaction between the nucleus and surrounding magnetic field. Figure 3 presents these nuclear interactions and corresponding Mössbauer spectra. The three Mössbauer parameters: isomer shift, quadrupole splitting, and hyperfine splitting can be used to identify a particular compound by comparing it to known spectra. A large database, including most of the published Mössbauer parameters available in the literature, is maintained by the Mössbauer Effect Data Centre. Mössbauer spectroscopy is limited by the need for a suitable gamma-ray source. Usually, this consists of a radioactive parent that decays to the desired isotope. For example, the source for  $^{57}\text{Fe}$  consists of  $^{57}\text{Co}$ , which decays by electron capture to an excited state of  $^{57}\text{Fe}$ , then subsequently decays to a ground state emitting the desired gamma rays. Mössbauer spectroscopy is unique in its sensitivity and it has been especially useful in the investigations of phase transformations, oxidation state changes, elemental concentration changes and the magnetic environment of the sample [5, 9].

Modification of the near surface layer of unalloyed steels with intense argon and nitrogen plasma pulses were investigated. When stainless steel is exposed to nitrogen at elevated temperature different nitride phases are formed according to the Fe-N phase diagram and depending on the conditions of the process. Among these phases an expanded austenite attracts attention of the authors. The expanded austenite is an interstitial solution of nitrogen or carbon in iron, denoted by  $\gamma\text{N}$  or  $\gamma\text{C}$ , respectively due to the presence of nitrogen expanded austenite in stainless steel, good corrosion resistance is maintained while the wear resistance is increased. It is stated in [9] that this phase can only be formed if Fe, Cr and Ni components are available in a system. This may be the case in the stationary processing but not when melting and rapid solidification process is applied. It has been shown that  $\gamma\text{N}$  phase can be formed in unalloyed steels if the material is treated with high intensity nitrogen plasma pulses which melt the near surface layer of steel [10, 12].



**Fig. 3.** Chemical (isomer) shift (a), quadrupole splitting (b) and magnetic splitting (c) of the nuclear energy levels and the corresponding Mössbauer spectra.

Alloying the near surface layer of stainless steel with rare earth elements (REE) using high intensity pulsed plasma beams (HIPPB) were also investigated. Austenitic stainless steels are used in numerous industrial applications, mainly due to their excellent corrosion resistance in different environments. Thus, they received increased attention in nuclear and petrochemical industry, pulp and paper chemistry, food and chemical processing and biomedical industry. However, poor tribological and mechanical properties of austenitic stainless steels in terms of abrasion resistance limited their applications in engineering fields. Improvement of the wear resistance of austenitic stainless steels without loss of corrosion resistance can be achieved using different surface treatment, for example: re-solidification techniques or enrichment surface layer in reactive elements. High oxygen affinity elements such as Y, Ce, La, Er and other rare earth elements (REE) added to steels in small amounts can improve their resistance for electrochemical corrosion, high temperature oxidation and wear [1, 4, 14].

The main goal of this work is to present how chosen nuclear techniques applied for investigations of materials can improve our knowledge on structure and properties of the materials. Results obtained from the investigation of two types of modified steels are presented in this work.

## Experimental

Investigations of steels near surface layer modification were carried out at the Institute of Nuclear Chemistry and Technology (Warsaw, Poland) and at The Andrzej Soltan Institute for Nuclear Studies (Świerk/Otwock, Poland). Modification processes were performed using high intensity pulsed plasma beams – HIPPB ( $10^6$ – $10^8$  W·cm<sup>-2</sup>) generated in a rod plasma injector (RPI). The scheme of the used plasma generator is shown in Fig. 4 and the facility is described in details in [17]. The plasma pulses are generated as a result of a low-pressure, high-current discharge between two concentric sets of electrodes. The RPI may be operated in two modes: (i) pulse implantation doping (PID) when the plasma contains practically exclusively ions of the working gas and (ii) deposition by pulsed erosion (DPE) when the beam contains also ions/atoms eroded from the ends

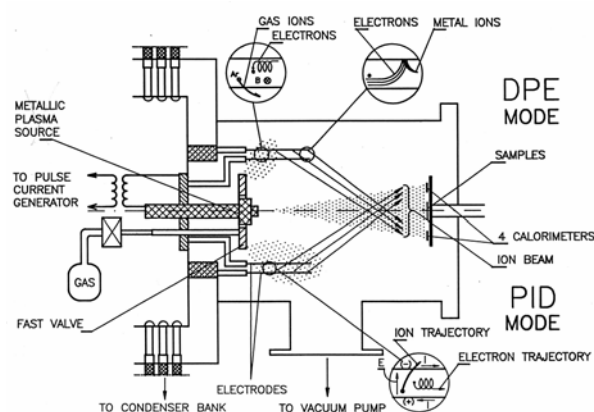


Fig. 4. Scheme of the rod plasma injector (RPI).

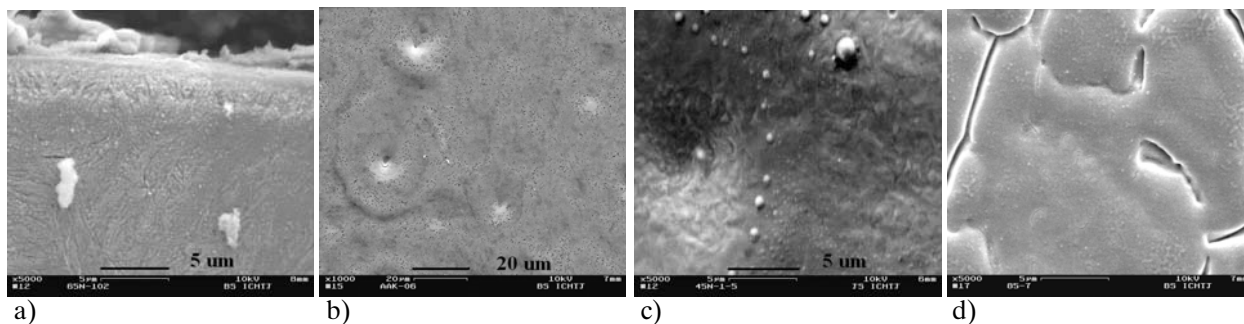
of the electrodes. When high intensity, short duration ion or plasma pulses hit a solid, they can modify the structure of its near-surface region. They can induce various processes such as: crystalline defects annealing, drive-in of the dopant predeposited on the surface, mixing of the predeposited films with substrate material, formation of new stable or/and metastable phases and grain refinement. In the case of surface layer melting is followed by rapid solidification with a cooling rate in the range of  $10^7$ – $10^{10}$  K·s<sup>-1</sup>, and usually significant changes occur in the substrate structure and surface morphology. Heating and cooling processes were of non-equilibrium type. The near surface layer of the thickness in  $\mu$ m range was melted and simultaneously doped with reactive elements.

Unalloyed steels with different carbon concentration (in wt.%): Armco iron – 0.018, 1C25 – 0.38, 1C45 – 0.52, 1C65 – 0.65 and C90U – 0.93 heat treated by standard procedures were used for investigations. The samples were irradiated in PID mode with argon or nitrogen plasma pulses at an energy density of about 5 J·cm<sup>-2</sup> and at duration on a microsecond scale.

Austenitic stainless steel AISI 316L, hot rolled, with the main elements concentration (in wt.%) Cr – 16.29, Ni – 11.47, Mo – 2.03, Mn – 1.27, Fe balance was used as substrate for the investigations and mischmetal with a composition (in wt.%): Ce – 65.3, La – 34.0 and balance of Fe, Mg, Pr was used as a REE source. The samples were irradiated with 3 pulses with an energy density of 3 J·cm<sup>-2</sup>, in DPE mode with titanium rods coated with mischmetal tips as electrodes and nitrogen as the working gas.

Initial and modified materials were characterized by:

- scanning electron microscopy (SEM) with DSM 942 (Zeiss, Germany) for surface morphology observations and cross-section investigations;
- nuclear reaction analysis (NRA) with the reaction:  $^{14}\text{N}(d,\alpha)^{12}\text{C}$  for determination of the retained nitrogen dose. The deuterons with energy of 1300 keV were produced from a van de Graaf accelerator and the light products of the nuclear reaction were detected. Measurements were carried out with absorber according to geometry proposed by Tesmer [16]. The simulation program SIMNRA was used to determine the depth profile of nitrogen concentration;
- Rutherford backscattered spectroscopy (RBS) measurements to determine the elemental composition. The spectra were recorded using 1.7 MeV He<sup>+</sup> ion beam at normal incidence to the sample. The back scattered particles were detected at an angle of 170° using a Si(Li) detector of 15 keV energy resolution. The RBS spectra were analyzed using SIMNRA program;
- dispersive X-ray spectrometry – EDX with Quantax 400 (Bruker, Germany) to determine elemental concentrations;
- grazing incidence X-ray diffraction analysis (GXR) at  $\omega = 1^\circ$  and  $2^\circ$  using CuK $\alpha$  radiation with ARL X'TRA (Applied Research Laboratories, Switzerland) for phase identification and determination of the austenite lattice parameters;
- conversion electron Mössbauer spectroscopy (CEMS) for  $^{57}\text{Fe}$  nuclei to identify and quan-



**Fig. 5.** SEM images of steels modified with HIPPB: a – cross-section of base material and modified layer at 1C65 nitrogen; b – modified surface – Armco argon; c – drops at the modified surface – 1C45 nitrogen; d – surface of AISI 316L enriched with REE up to 2.1 at.%.

tify phases in modified samples to about 100 nm depth.

## Results and discussion

Microscopic observation of surface morphology was the first investigation step of samples. It confirmed that modification process was realized (Fig. 5). The cross-sections of modified materials allow us to determine the thickness of modified layers as about  $1.42 \pm 0.15 \mu\text{m}$ . Figure 5a presents an example of cross-section of 1C65 modified with nitrogen. The martensitic structure of the basic material and the modified surface layer with a thickness of  $1.36 \mu\text{m}$  can be clearly seen. Craters (Fig. 5b) and post melting morphological details (Fig. 5c) were observed on the modified surfaces of unalloyed steels. Grain boundaries present at the surface of the initial AISI 316L steel almost disappeared and features of the mixed deposit-substrate material form can be seen (Fig. 5d). These results are typical of melted and rapid solidified material and were described in details in [15, 18].

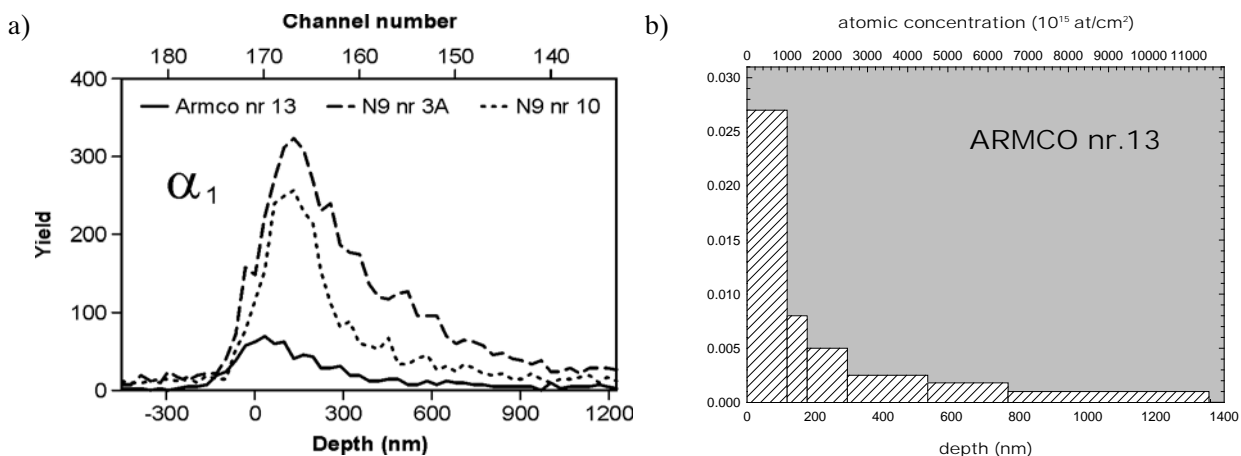
### Unalloyed steels

Nuclear reaction analysis (NRA) with the nuclear reaction  $^{14}\text{N}(d,\alpha)^{12}\text{C}$  allowed us to determine the nitrogen content in the modified samples of unalloyed steels. The

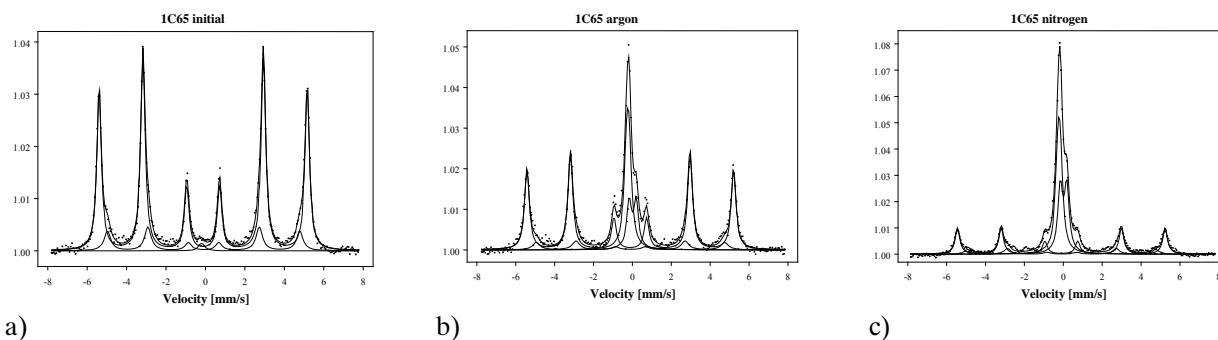
retained nitrogen dose was in the range of  $(1.0\text{--}1.4) \times 10^{17} \text{cm}^{-2}$ . The average value was  $1.2 \times 10^{17} \text{cm}^{-2}$ , with a standard deviation (SD)  $\sigma = 2.0 \times 10^{16} \text{cm}^{-2}$ .

Depth profiles of nitrogen concentration in the modified materials were also determined. The fragments of NRA spectra – the  $\alpha_1$  peak – for three samples with different nitrogen dose are presented in Fig. 6a. It can be seen that maxima of  $\alpha_1$  peaks exist under the surface and decrease towards the core of the modified samples. Presented examples show that these maxima were located at a depth of 25 nm for Armco with a nitrogen dose of  $1.62 \times 10^{17} \text{cm}^{-2}$  and 125 nm for C90U steel samples with nitrogen doses of  $2.78 \times 10^{17} \text{cm}^{-2}$  and  $5.63 \times 10^{17} \text{cm}^{-2}$ . The depth profile of nitrogen concentration in the Armco modified with nitrogen sample up to  $1.24 \times 10^{17} \text{cm}^{-2}$  is presented in Fig. 6b. It is clearly seen that the maximum of nitrogen concentration was present near the surface. Nitrogen concentration decreased quickly toward the core. Similar nitrogen concentration profiles were obtained in all cases of unalloyed steels modified with intense nitrogen plasma pulses [11].

The phase composition of HIPPB modified unalloyed steels was determined using GXRd with angles up to  $\omega = 2^\circ$ . In the sample irradiated with argon, the bcc Fe and fcc  $\gamma$ -Fe were detected. In the sample irradiated with nitrogen, the bcc Fe ( $\alpha$  phases), fcc  $\gamma$ -Fe and fcc  $\gamma$ -Fe with enlarged lattice parameter – expanded austenite were found. The difference between normal fcc  $\gamma$ -Fe lattice parameter and that of expanded austenite was estimated from the peak (111) shift as 0.83% of



**Fig. 6.** Depth profile of nitrogen concentration in steels: a – examples of fragments of NRA spectra,  $\alpha_1$  peak for samples Armco  $1.62 \times 10^{17} \text{cm}^{-2}$ , C90U (N9/3A)  $2.78 \times 10^{17} \text{cm}^{-2}$  and C90U (N9/10)  $5.63 \times 10^{17} \text{cm}^{-2}$ ; b – profile of nitrogen for modified Armco sample up to  $1.24 \times 10^{17} \text{cm}^{-2}$ .

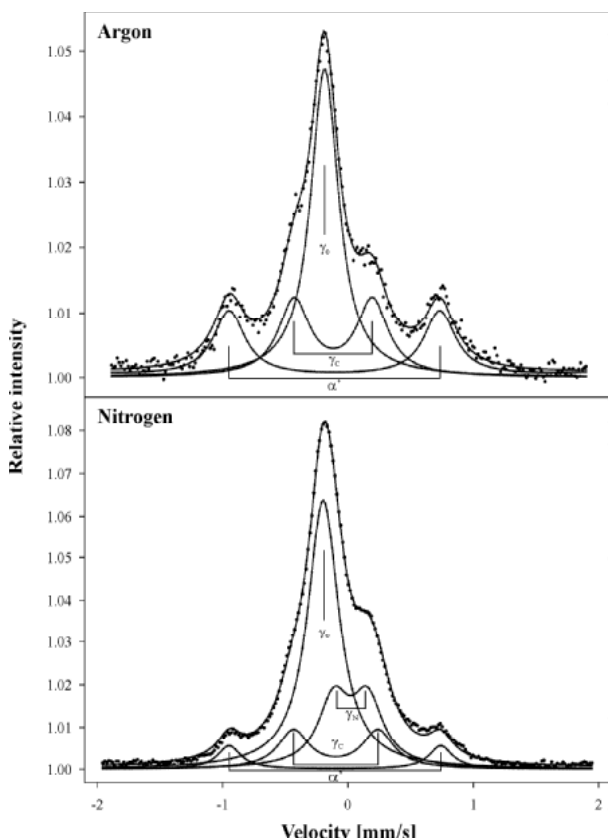


**Fig. 7.** CEMS spectra of 1C65 steel surfaces: a – initial and modified with intense plasma pulses; b – argon; c – nitrogen.

the austenite lattice parameter [9]. Unfortunately, at such a small content of C and N it was impossible to resolve  $\gamma$  into  $\gamma_0$ ,  $\gamma_N$  and  $\gamma_C$ .

Conversion electron Mössbauer spectroscopy was applied for more detailed phase analysis in unalloyed steels modified with HIPPB. As an example, the set of CEMS spectra obtained for 1C65 steel is presented in Fig. 7. The spectra of initial samples show six peaks characteristic of the Zeeman pattern (Fig. 7a). After pulse irradiation, the complex paramagnetic patterns occur in the central part of the spectra (Figs. 7b and 7c). In the case of modification of the steel samples with argon, the peaks in the central part of the spectrum appear. No changes are observed in the CEMS spectrum for Armco. In the case of nitrogen modification, the substantial changes in the central part of CEMS spectra are observed for all samples including Armco. The analysis of the central peaks intensities shows clearly

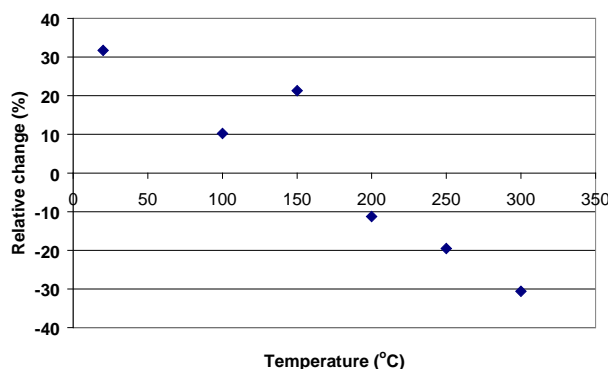
the differences in austenitization efficiency between argon and nitrogen modification processes. The computer fitting based on the literature data allowed us to identify without doubts the following phases:  $\alpha$ -Fe,  $\gamma_0$  (austenite with no interstitial nearest neighbours at Fe atoms),  $\gamma_C$  and  $\gamma_N$ , i.e. carbon and nitrogen expanded austenite, respectively and nitrides of  $F_{3-x}N$  type. In steels irradiated with argon, the phases  $\alpha$ -Fe,  $\gamma$ -Fe and  $\gamma_C$  – carbon expanded austenite were found. In iron and steels irradiated with nitrogen the phases,  $\alpha$ -Fe,  $\gamma$ -Fe,  $\gamma_N$  – nitrogen expanded austenite,  $\gamma_C$  (except Armco) and  $\varepsilon$ -Fe<sub>3</sub>N were found. The fit of the spectra obtained for steel 1C65 modified with intense pulsed plasma beam of argon and nitrogen are shown together with the CEMS data in Fig. 8 [11]. The obtained results proved the presence of nitrogen expanded austenite in unalloyed steels although the samples do not contain Cr and Ni, which is in contradiction with the statement in [9].



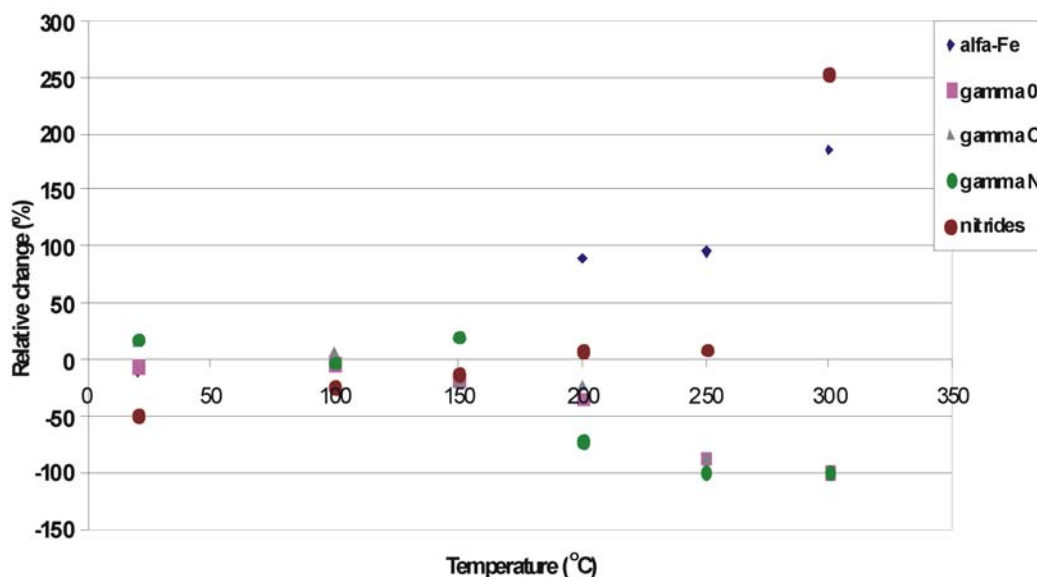
**Fig. 8.** CEMS data with fitted phases for steel 1C65 modified with intense pulsed plasma beam with argon and nitrogen, respectively.

Knowledge about the stability of the phases, particularly of the expanded austenite phase is very important from the practical point of view. Unalloyed steel 1C45 with the nitrogen retained dose of  $1.2 \cdot 10^{17}$  N/cm<sup>2</sup> were investigated. The annealing experimental processes of the modified unalloyed steels were carried out at a temperature between 100 to 300°C with a step of 50°C for one hour in inert gas – argon.

Relative changes of the determined parameters were defined as:  $(AM-IM)/IM \times 100\%$  where AM and IM are the values of investigated parameter for the annealed and initial material, respectively. Relative changes of the relative surface nitrogen concentration obtained from NRA are presented in Fig. 9. The surface nitrogen concentration starts to decrease from 150°C. The main reason for that could be the release of the interstitial nitrogen atoms from the  $\gamma_N$  – nitrogen



**Fig. 9.** Changes of the surface nitrogen concentration as a result of the annealing of the modified samples of 1C45 steel.



**Fig. 10.** Changes of the identified phases' content as a result of annealing of HIPPB modified unalloyed steel 1C45.

expanded austenite lattice at elevated temperatures and their diffusion into the surface and the bulk of the samples [13].

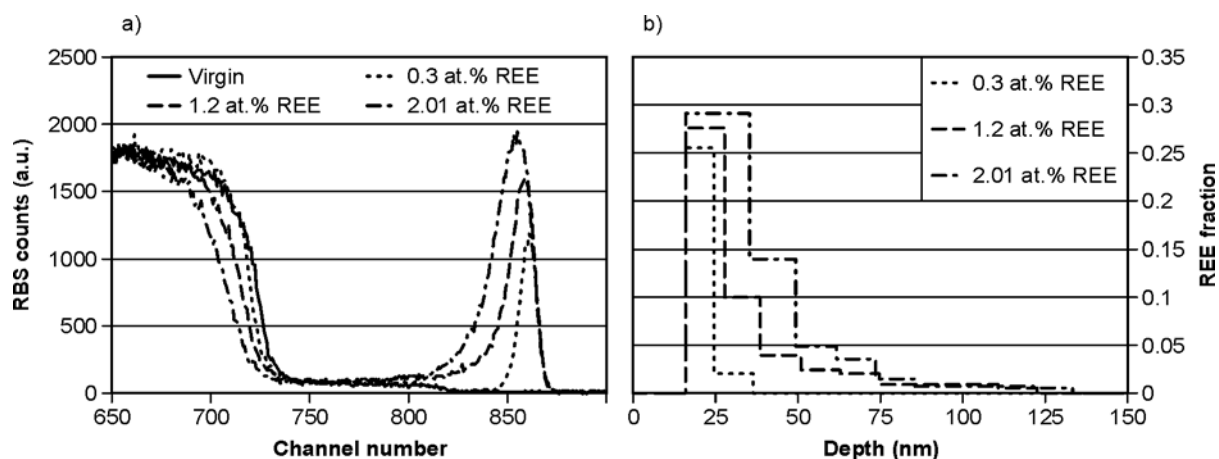
Relative changes of identified phases' content obtained from CEMS are presented in Fig. 10. The transformation process of the phases started at an annealing temperature of 150°C. The content of all austenities ( $\gamma_0$ ,  $\gamma_C$  and  $\gamma_N$ ) decreases with temperature, while the content of  $\alpha$ -Fe phases and content of nitrides increased. The decrease of the austenitic phases' content above 150°C has a rapid character. The content of  $\alpha$ -Fe phases increases at the expense of austenitic phases' decomposition. For the same reason we observed also the increase of nitrides content. Released interstitial nitrogen atoms become available for the nitrogen phases formation [13]. The temperature of 150°C is the limit for the practical applications of modified surface layer of unalloyed steels with nitrogen HIPPB.

#### Alloyed steel AISI 316L

Atomic concentrations of REE (Ce+La) incorporated into specimens measured by EDX were found in the

range of 0.3–2.8 at.%. The ratio of Ce/La concentrations was the same as in the used mischmetal.

Rutherford backscattering spectroscopy method allowed us to investigate the REE concentration in the thin modified surface layer. RBS spectra obtained for three AISI 316L samples enriched up to different concentration of REE are presented in Fig. 11a. In the coarse interpretation of an RBS spectrum, the location of the front edge of the peak on the energy (channel number) scale permits identification of the chemical element, the location of the rear edge of the peak permits the determination of the thickness occupied by the element and the height of peak provides information about the concentration of elements. The main part of the spectra of initial and REE enriched material is similar. As Ce and La are neighbour elements in the lanthanide series, it was not possible to analyse them separately and the results are presented with respect to REE (Ce+La) concentrations. The peak at about 850 channel confirms the presence of REE in the system. Analysis of the shape of peaks – their height and width – shows a good correlation with the known REE concentration. Doses of REE incorporated into the AISI 316L steel were:  $1.99 \times 10^{16} \text{ cm}^{-2}$ ,  $4.85 \times 10^{16} \text{ cm}^{-2}$  and



**Fig. 11.** An example of (a) RBS spectrum of AISI 316L substrate enriched with REE up to (in at.%) 0.3; 1.4 and 2.01 (b) depth profiles of elements present in the modified material with REE up to (in at.%) 0.3; 1.4 and 2.01.

$7.61 \times 10^{16} \text{ cm}^{-2}$ . The depth profiles obtained for REE and the remaining elements present in the investigated material were obtained and are presented in Fig. 11b. It is clearly seen that the maximum of REE concentration was present near the modified surface. The REE concentration decreased quickly toward the core.

## Conclusions

Initial materials – unalloyed and alloyed steels and modified materials with HIPPB were characterized using different investigation methods including non-destructive nuclear techniques. Those methods can extend our knowledge on the structure of materials. Nuclear reaction analysis, Rutherford backscattered spectroscopy and conversion electron Mössbauer spectroscopy were used for materials characterization and each of them has enriched the data on modified surface properties and provided new important information without destruction of the investigated samples.

1. The NRA method allowed us to determine the remaining nitrogen concentration and its depth profiles in the HIPPB modified unalloyed steels.
2. On the basis of RBS measurements, the presence of investigated elements (here: REE Ce+La), their retain dose and depth profile were determined.
3. Expanded austenite was identified by CEMS and GXR, but only CEMS allowed us to identify if nitrogen or/and carbon expanded austenite was formed during the carried out modification.
4. Using the NRA and CEMS methods, the temperature limit for practical applications of surface layer of unalloyed steels modified with nitrogen HIPPB was determined.

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## References

1. Abreu CM, Cristobal MJ, Novoa XR, Pena G, Perez MC, Rodriguez RJ (2002) Modifications of the stainless steel passive film induced by cerium implantation. *Surf Coat Technol* 158/159:582–587
2. Barlak M (2010) High intensity plasma pulses in ceramic wettability improvement. The Andrzej Soltan Institute for Nuclear Studies, Otwock/Świerk
3. Burakowski T, Wierzchoń T (1999) Surface engineering of metals. Principles, equipment, technologies. CRC Press, Boca Raton
4. Cleugh D, Blawert C, Steinbach J, Ferkel H, Mordike BL, Bell T (2001) Effects of rare earth additions on nitriding of EN40B by plasma immersion ion implantation. *Surf Coat Technol* 142/144:392–396
5. Gawlik G (1996) Influence of implantation and heat treatment conditions on iron alloys structure. PhD thesis, Institute of Electronic Materials, Warsaw (in Polish)
6. Grötzschel R (2008) Rutherford backscattering spectrometry (RBS). SciTopics. Retrieved August 24, 2011, from [http://www.scitopics.com/Rutherford\\_Backscattering\\_Spectroscopy\\_RBS.html](http://www.scitopics.com/Rutherford_Backscattering_Spectroscopy_RBS.html)
7. Han M, Landry F, Lieb K-P, Schaaf P (1999) Analysis of laser-nitrided stainless steel via nuclear methods. *Appl Phys A* 69:Suppl:S795–S797
8. Illgner C, Schaaf P, Lieb K-P, Quetsch R, Schutte K, Bergman H-W (1997) Mechanism of laser nitriding in  $^{14}\text{N}$  and  $^{15}\text{N}$  atmospheres studied with RNRA. *Appl Surf Sci* 109/110:150–153
9. Menthe E, Rie KT, Schultze JW, Simson S (1995) Structure and properties of plasma-nitrided stainless steel. *Surf Coat Technol* 74/75:412–416
10. Piekoszewski J, Dąbrowski L, Sartowska B *et al.* (2007) Austenite formation of carbon and alloyed steels by intense argon and nitrogen plasma pulses: Role of carbon, chromium and nitrogen. *Vacuum* 81:1403–1407
11. Sartowska B (2007) Modification of the structure and properties of the surface layer of unalloyed steels using high intense nitrogen and argon plasma pulses. PhD thesis, Institute of Precision Mechanics, Warsaw (in Polish)
12. Sartowska B, Piekoszewski J, Waliś L *et al.* (2007) Structural and tribological properties of carbon steels modified by plasma pulses containing the inert and active ions. *Surf Coat Technol* 201:8295–8298
13. Sartowska B, Piekoszewski J, Waliś L *et al.* (2007) Thermal stability of the phases formed in the near surface layers of unalloyed steels by nitrogen pulsed plasma treatment. *Vacuum* 81:1188–1190
14. Sartowska B, Piekoszewski J, Waliś L *et al.* (2011) Improvement of tribological properties of stainless steel by alloying its surface layer with rare earth elements using high intensity pulsed plasma beams. *Surf Coat Technol* 205:S124–S127
15. Sartowska B, Piekoszewski J, Waliś L, Barlak M (2010) Surface morphology of unalloyed steels remelted with intense plasma pulses. *J Microscopy* 237:3:370–373
16. Tesmer JR, Nastasi M (eds) (1995) Handbook of modern ion beam materials analysis. MRS, Pittsburgh, Pennsylvania
17. Werner Z, Piekoszewski J, Szymczyk W (2001) Generation of high intensity pulsed ion and plasma beams for material processing. *Vacuum* 63:701–708
18. Yan S, Le XY, Zhao WJ, Xue JM, Wang YG (2005) A possible thermodynamic mechanism of craters formation on metal surfaces caused by intense pulsed ion beams. *Surf Coat Technol* 193:69–74