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Changes of stainless steels surface morphology as a result of interaction with intense pulsed plasma beams containing ions of rare earth elements

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Abstract. Among different methods used in surface engineering such as CVD, PVD, ion implantation etc., the techniques using high intensity ion or plasma beams are relatively new ones. The results reported thus far show that the treatment of steel surface with high intensity plasma pulses can lead to changes of its morphology and mechanical properties. Stainless steels have very good corrosion resistance, but they have low hardness and poor tribological properties. The intense pulsed plasma beams were used for modification of alloyed steels especially austenitic (1.4301 and 1.4401) and ferritic (1.4016) stainless steels with various content of alloying elements. Samples were irradiated with 2, 5 or 10 short (μs scale) intense (density of energy was about 5 J/cm^2) pulses. Heating and cooling processes were of non-equilibrium type. In all samples the near surface layer of the thickness in μm range was melted and simultaneously doped with cerium and lanthanum. The aim of this work was to investigate the changes of stainless steel surface morphology after melting, rare earth elements (REE) addition and rapid solidification after interaction with intense pulsed plasma beams. The surface morphology was analyzed using a scanning electron microscopy (SEM) technique. Changes of surface roughness were determined by profilometric measurements. The efficiency of REE addition process was also determined.

Key words: intense plasma pulses • stainless steel • surface modification • REE addition

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Introduction

Stainless steels are used in numerous industrial applications, mainly due to their excellent corrosion resistance. However, in many cases their low hardness and poor tribological properties impose strong limitations. On the other hand, there are many examples that require the use of electrolyte corrosion and high temperature corrosion resistant materials, which at the same time exhibit good wear resistance. Examples of such applications include liquid flow sensors, temperature, pressure and humidity sensors for aggressive environments, interconnectors for solid oxide fuel cells (SOFC) etc. In all these cases stainless steels are frequently used.

The beneficial effect of active elements with high oxygen affinity, such as yttrium, cerium, lanthanum and other rare earth elements (REE) on high temperature oxidation resistance and corrosion resistance against aggressive media has already been studied, e.g. [1, 2]. In addition, these elements added to the bulk alloys or to their surfaces dramatically improve the oxide scale adherence [4]. On the other hand, it is known from our recent study that the surface modification process using intense plasma pulsed leads to improvement of the tribological properties of unalloyed steels [5–7].

Pulsed-plasma treatment – a procedure developed at the Soltan Institute for Nuclear Studies (SINS) Świerk, Poland, consists in treating a solid with plasma pulses of

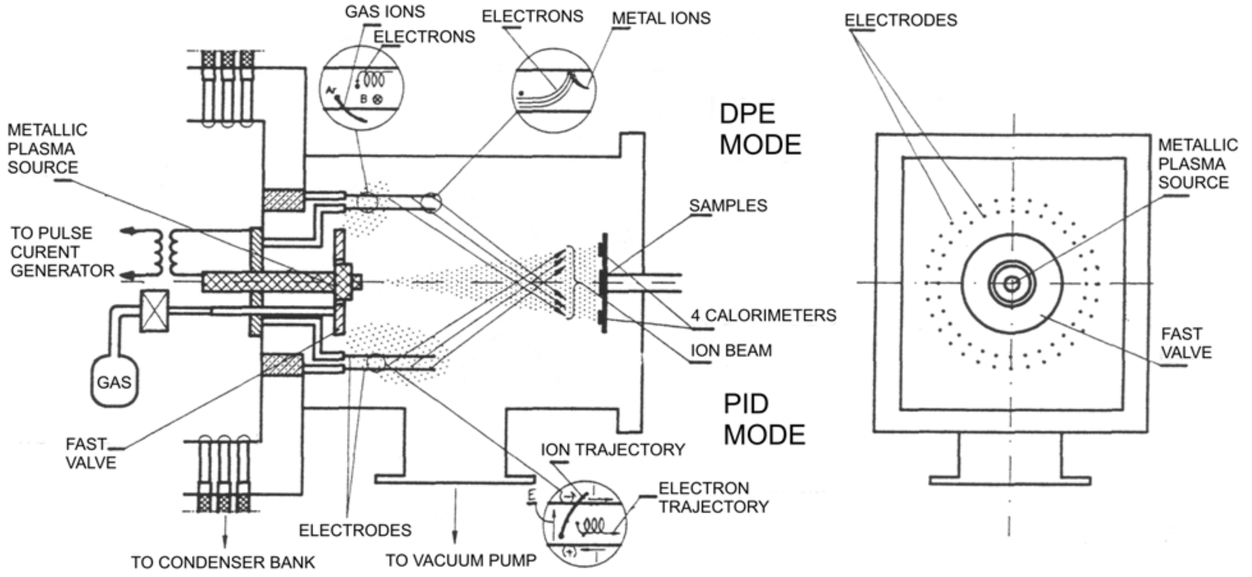

Fig. 1. A scheme of used RPI, called IBIS.

duration of about 1 μs and energy density in the range 1–10 J/cm^2. In most solids such treatment leads to a fast transient melting of the surface layer of the substrate followed by rapid crystallization. The rate of melt-solid boundary movement during crystallization may reach values of the order of several m/s which means that a 1 μm thick molten surface layer crystallizes in much less than 1 μs. At the SINS, plasma pulses are generated in a rod plasma injector (RPI), device originally developed for nuclear fusion studies and described in detail in [3, 8] (Fig. 1). The plasma contains ions of the working gas, but, under suitable conditions, it may carry a significant portion of metal ions originating from the discharge electrode corrosion.

Plasma pulses are formed at a low-pressure, high-current plasma discharge initiated between two concentric cylindrical sets of rods allowing for a free passage of particles through the electrode region (Fig. 2). A fast electromagnetic valve introduces a portion of the working gas into the interelectrode region. After some delay τ_D (150–250 μs) from the moment of valve opening, a voltage from the charge condenser bank is applied to the electrodes. Depending on the value of τ_D, two modes of operation are possible. In the first one, referred to as pulse implantation doping (PID), τ_D is sufficiently long to allow the injected working gas to fill the whole interelectrode space. Under such conditions, a short intense pulse is generated containing exclusively the ions of the working gas. In the second mode, referred to as deposition by pulsed erosion (DPE), delay τ_D is relatively short and the working gas expanding from the valve does not reach the electrode ends. Under such conditions, arc-evaporation of the electrode material occurs, and as a result, plasma becomes enriched with ions of the electrode material. The amount of metal ions may be as high as 10^{17}/cm^2. This allows one to make extremely well adhering coatings of variety of metals on any kind of the solid substrate.

The second feature of the approach consists in a very high cooling rate and, as a consequence – a very high crystallization rate. As a consequence, the crystallized structure is highly dispersed. One can also argue that fast crystallization gives rise to homogenization of the composition and consequently, reduced ability for galvanic cells to appear and hence – increased corrosion resistance.

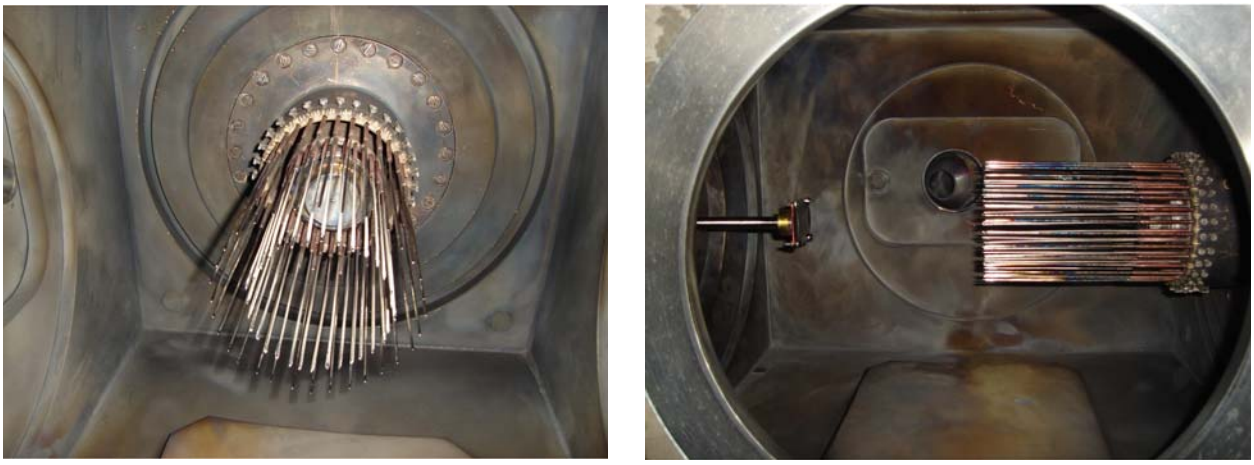

Fig. 2. An interior of IBIS chamber with: two concentric cylindrical sets of electrodes (left) and electrodes and the sample place (right).

Table 1. Elemental composition of stainless steels used in experiments

Steel	Composition (wt.%)										
	C	Cr	Ni	Mo	N	V	Cu	Si	Mn	P	S
430	0.041	**16.190**	**0.09**	**0.020**	0.040	\	0.021	0.287	0.374	0.024	0.005
304	0.038	**18.160**	**8.08**	**0.260**	0.059	0.09	0.470	0.370	1.280	0.032	0.002
316	0.022	**16.758**	**10.25**	**2.098**	0.044	\	\	0.363	1.232	0.026	0.002

Table 2. Parameters of the DPE mode of RPI

HV (kV)	29–31.5
Energy density (J/cm^2)	5.0
Delay time τ_D (μs)	150–180
Pulse duration (μs)	0.1–0.5
Working gas	nitrogen
Number of pulses	2, 5 and 10
64 Inner and outer electrodes (250 mm length, 2 mm diameter)	Ce-La tiped unalloyed steel rods

The aim of this work was to investigate the changes of stainless steel surface morphology after melting, rare earth elements (REE) addition and rapid solidification as a result of interaction with intense pulsed plasma beams.

Experiment

Three kinds of steels were used as the substrates: 1.4301 (AISI 304), 1.4401 (AISI 316) and 1.4016 (AISI 430) with the elemental composition presented in Table 1. AISI 304 and AISI 316 samples of size 20 × 20 × 1 mm were cut out from hot rolled and AISI 430 from cold rolled sheets. The main tool used for their modification was the rod plasma injector type (RPI) called IBIS. The electrodes of plasma pulse generator were formed of reactive elements. The electrode tips of 40 mm in length and 2 mm diameter were machined from the chunk of mischmetal containing Ce 64.7 wt.%, La 33.7 wt.%, and below 0.5 wt.% of Pr, Fe and Mg. During machining special precautions were taken due to the high flammability of this material. In of our experiments the DPE mode of RPI was used with parameters presented in Table 2.

The modified surfaces of the samples were characterized using: scanning electron microscopy technique with SEM DSM 942 (Zeiss, Germany) for surface morphology observations and profilometer measurements using a LV-50 device (Hommelwerke, Germany) for the determination of roughness changes. Additionally, the EDS elemental analysis using a microanalysis system (Bruker, Germany), were carried out for the determination of efficiency of REE addition process determination.

Results and discussion

Results of morphology observations are presented in Fig. 3. At the surfaces of initial 304 and 316 steels, the grains in different sizes are visible as a result of production process. Grains are distributed evenly, no special direction can be distinguished. The parallel scratches resulted by cold rolling can be seen at the initial 430 steel surface.

After pulse modifications, the changes of surface morphology were observed for all applied processes. The initial grains and scratches disappeared and different morphological details were observed. After modification with 2 intense pulses, the surfaces were smoothed. The “waves” were observed for all steels. After modification with 5 intense pulses, the cracks in the modified layer were observed. The surface of 430 steel was most cracked, the layer delamination was clearly seen. The surface of 304 steel was cracked, too, but without visible delamination. There were more clearly seen “waves” at the 316 steel surface as compared with results after 2 pulses modification. The bubbles among “waves” were visible at the surface. Modification with 10 intense pulses led to form cracked modified layers of all investigated steels. The surfaces of 430 and 304 were also delaminated. There were “waves”, closed and opened bubbles and droplets at the modified 316 steel surface.

Details of observed morphologies show that the quality of obtained layers was not satisfactory. Cracks and crevices are the result of shrink of material during rapid cooling and they were observed at the modified surface (Fig. 4a). Delaminating of the layer from the base material can be due to a poor adhesion/binding of the modified layer to the substrate (Fig. 4b). The closed and open bubbles and droplets were observed at the modified surfaces (Fig. 4c). Holes and cavities were the places of bubble nucleation initiated by boiling which takes place in the molten layer. All these observed features and morphological objects are characteristic of remelting techniques applied in surface modification [9]. In conditions of our present experiments, such kinds of objects could be expected as well.

The steel modifications were carried out with the same process parameters. Analysis of the obtained SEM images show that the morphology of modified surface was connected with the different elemental composition of the investigated steels. Applied modifications lead probably to different phases and structures formation. Structural investigations are still carried out and for now our researches are not finished.

Surface functional parameters depend on the shape and depth of roughness. These parameters can be for example: wear resistance, suitability for a static or variable load transfer, corrosion resistance and fatigue strength. Surface modification of chosen steels with intense plasma pulses led to change of the shape of their initial morphology as was described above. Initial materials had different roughness characterized by the R_a parameter: 0.01 and 0.05 for 430 steel and both 304 and 316, respectively. The value of R_a parameter increases after pulse treatment independently of its initial value, but does not exceed the value of 0.3 μm (Fig. 5). It can be seen that R_a reached its maximum after modification of 2 (steel 304) or 5 (steel 430 and steel 316) pulses.

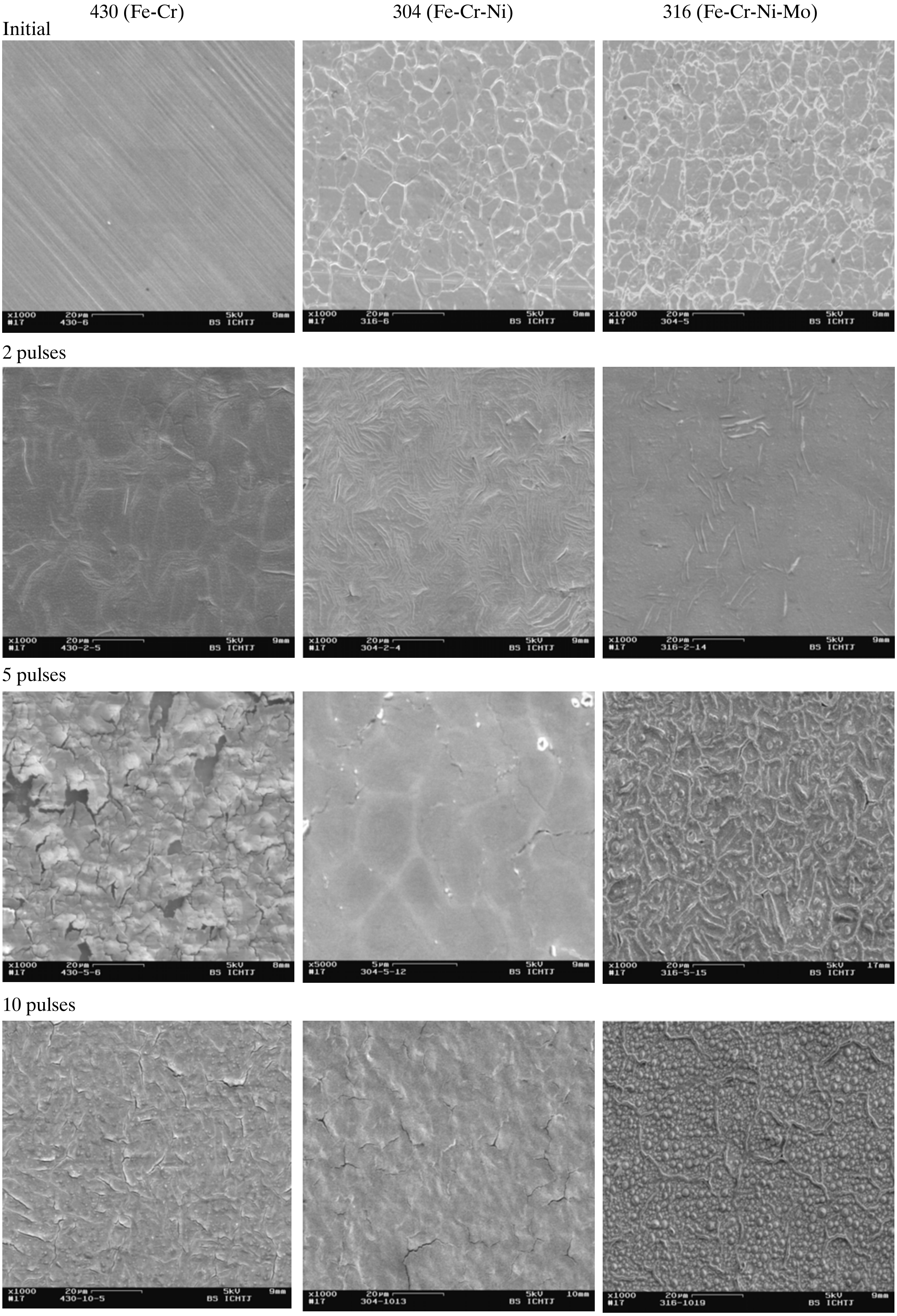

Fig. 3. The surface morphology of initial and modified steels.

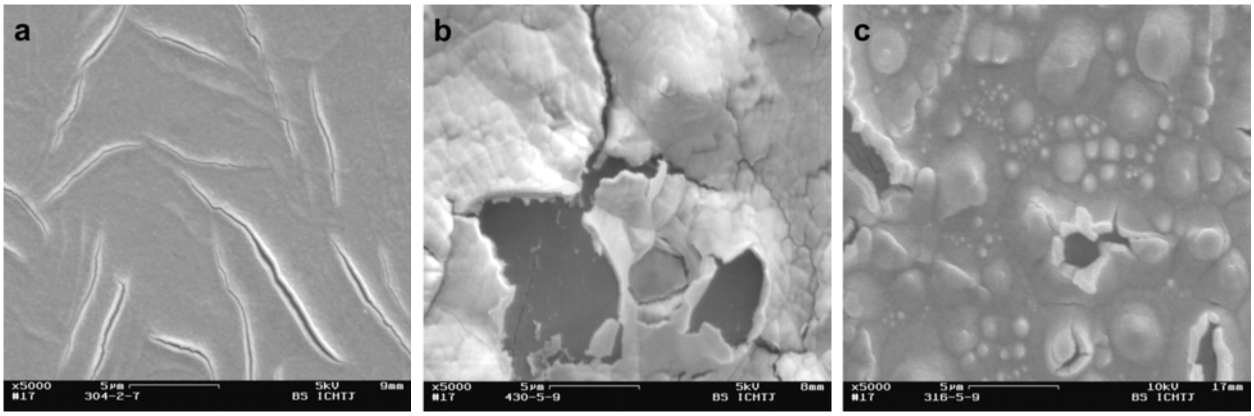

Fig. 4. Examples of different morphologies of modified steel: a – modified layers with cracks (steel 304, 2 pulses); b – cracked modified layers with delamination (steel 430, 5 pulses); c – droplets, closed and opened bubbles (steel 316, 5 pulses).

After 10 pulses, the R_a parameter decreased, but its steel was higher as compared with the initial material. The changes of morphology of pulse treated steels usually are unwanted. However, when their other properties are improved the morphological flows in many cases should not limit practical application of the treatment described above.

Results of elemental analysis of the added REE to the modified layer allow us to state that the proportion of Ce/La added to the surface layer is the same as the ratio of content of these both REE in the initial mischmetal. The values are: 2.07; 2.03 and 1.96 for 2, 5 and 10 pulses with 5 J/cm^2 energy density, respectively and 1.92 in mischmetal. The amount of REE added to the modified steel surfaces increases with number of applied pulses (Fig. 6a). Points at the vertical axis show the Ce and La concentrations in mischmetal. Analysis of the efficiency of a single pulse shows an interesting rule, namely, the greater number of applied pulses – the lower efficiency of single pulse (Fig. 6b). This can be due to the following fact. Each pulse causes evaporation of part of the near surface material. At the beginning, say after one pulse, an amount of deposited REE is small, and a plume of evaporated atoms consists mostly of the initial substrate elements. After a larger number of pulses, the composition of the near surface layer become rich in REE, so the probability of their removal due to evaporation rises and a net amount of this deposited atoms decreases. Such an effect is analogous to that observed in ion implantation technique when an increase of the implanted dose of given ions results in the increase of the sputtering yield, so more atoms introduced into the substrate are sputtered away.

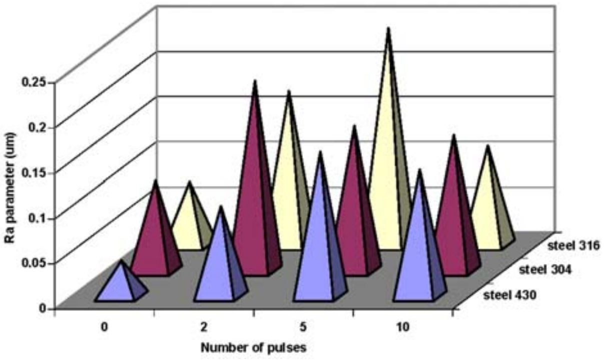

Fig. 5. Roughness (defined with R_a parameter) changes as a result of modification with intense plasma pulses.

In order to improve the quality of the surface morphology by reducing the presence of features described above, we plan to carry out further experiments at lower energy densities of pulses.

Conclusions

The irradiation of stainless steels with intense plasma pulses with energy density of 5 J/cm^2 containing REE ions and nitrogen as the working gas leads to the formation of modified their surface layer. Observed at

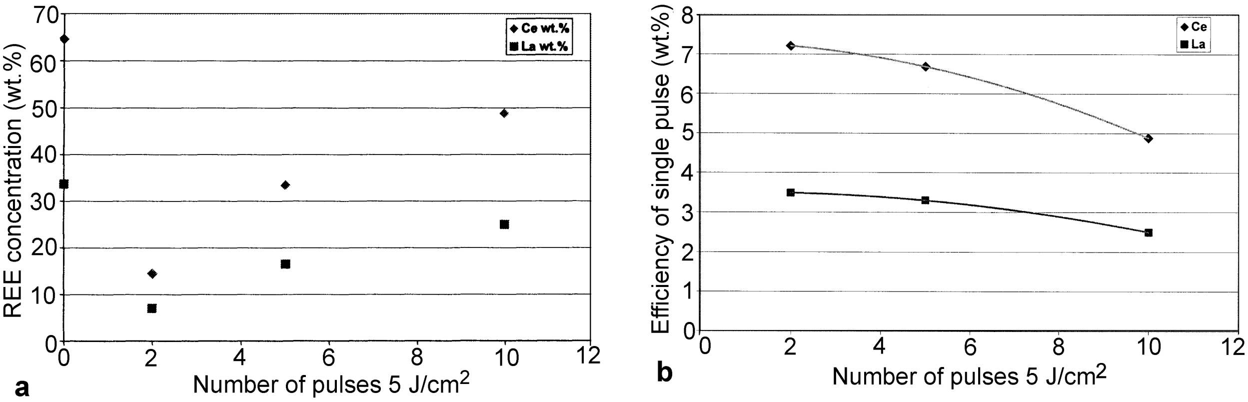

Fig. 6. REE addition in the DPE processes to the modified layer of steels: a – REE concentration; b – efficiency of a single 5 J/cm^2 pulse.

the modified surfaces cracks and other morphological features like droplets and bubbles are characteristic of remelting techniques based on the melting of near surface layer of the substrate.

The REE addition corresponds to the proportion of Ce/La in the tips of electrodes manufactured from initial mischmetal. Efficiencies of DPE process for REE incorporation as determined in the present work allows us to plan the conditions of further experiments aimed at an improvement of corrosion and wear resistance of stainless steel.

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