

# Modification of Structure and Tribological Properties of the Surface Layer of Metal-Ceramic Composite under Electron Irradiation in the Plasmas of Inert Gases

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**Abstract.** Metal-ceramic composites are the main materials for high-load parts in tribomechanical systems. Modern approaches to extend the operation life of tribomechanical systems are based on increasing the strength and tribological properties of the surface layer having 100 to 200 microns in depth. The essential improvement of the properties occurs when high dispersed structure is formed in the surface layer using high-energy processing. As a result of the dispersed structure formation the more uniform distribution of elastic stresses takes place under mechanical or thermal action, the energy of stress concentrators emergence significantly increases and the probability of internal defects formation reduces. The promising method to form the dispersed structure in the surface layer is pulse electron irradiation in the plasmas of inert gases combining electron irradiation and ion bombardment in one process. The present work reports upon the effect of pulse electron irradiation in plasmas of different inert gases with different atomic mass and ionization energy on the structure and tribological properties of the surface layer of TiC/(Ni-Cr) metal-ceramic composite with the volume ratio of the component being 50:50. It is experimentally shown that high-dispersed heterophase structure with a fraction of nanosized particles is formed during the irradiation. Electron microscopy study reveals that refining of the initial coarse TiC particles occurs via their dissolution in the molten metal binder followed by the precipitation of secondary fine particles in the interparticle layers of the binder. The depth of modified layer and the fraction of nanosized particles increase when the atomic number of the plasma gas increases and ionization energy decreases. The wear resistance of metal-ceramic composite improves in accordance to the formation of nanocrystalline structure in the surface layer.

## 1. Introduction

The metal-ceramic alloys on the base of refractory and hard chemical compounds (carbides, nitrides, carbonitrides, oxides) and metallic binder are promising composite materials exhibiting high mechanical and tribotechnical properties such as strength, hardness, crack- and wear resistance, fracture energy, thermal stability [1,2]. So they are applied as functional materials in the critical components of high-load tribomechanical systems including working parts of cutting tools.



Effectiveness and operational life of metal-ceramic parts under high-speed friction and abrasive action on their surface at high temperatures in aggressive environment are determined by a complex of tribological and strength characteristics of surface layers with the thickness of up to 100  $\mu\text{m}$ . One of efficient methods of improving the performance characteristics of the surface layers of metal-ceramic composites is modification of their structure and phase composition by the methods of high-energy treatment including high frequency current heating or plasma, laser, ion and electron irradiation. The given methods of surface treatment are aimed at creating structure with a significant volume fraction of grains or phases less than 100 nm in size. The effect of the nanostructured state of the surface layer on the properties of the material is due to the more uniform distribution of elastic stresses in the surface layer as compared to coarse-grained counterpart when it is subjected to external mechanical or thermal action [3-6]. As a result the energy of stress concentrators emergence in the surface layer significantly increases and the probability of internal defects formation reduces.

The unique opportunities for structure modification of the surface layers of metallic materials are provided by the method of pulse electron irradiation [7, 8] because electron beam has a number of advantages when it is used as a treatment tool. It includes (i) the high degree of electric energy transformation into the energy of electron beam (over 90 %); (ii) low coefficient of the electron beam reflection from the irradiated surface (less than 10 %); (iii) significant cross-section area of the electron beam on the surface of the irradiating material (over 10  $\text{cm}^2$ ); (iv) high electron-beam power density (over 10<sup>6</sup>  $\text{W}/\text{cm}^2$ ); (v) comparatively large depth of electron penetration into the irradiated material (several dozens of micron); (vi) high beam current pulse repetition rate ( $\sim 10\text{ s}^{-1}$ ). Within the millisecond range of pulse duration the mentioned above properties of the electron beam allow achieving ultrahigh heating rates (up to 10<sup>9</sup>  $\text{K}/\text{s}$ ) to heat the surface layer to the prescribed temperature with further cooling due to the heat removal to the bulk material at a rate of up to 10<sup>6</sup>  $\text{K}/\text{s}$  creating the thermokinetic conditions for formation of non-equilibrium structure including refining grain or phase size down to nanosize [9]. To obtain nanostructured state in the surface layers of composite materials containing particles of hard chemical compounds it is promising to combine pulse electron irradiation with surface layer bombardment by inert gas ions [10].

The aim of the present work was studying the influence of pulse electron irradiation in the inert gas plasmas with varying values of ionization energy and atomic mass upon the microstructure and the tribological properties of the surface layer of metal-ceramic alloy.

## 2. Material and methods

Metal-ceramic alloy TiC/(Ni-Cr) with the volume ratio of 50:50 between the ceramic and the metallic components was used as a studied material. The samples of the alloy were irradiated with electron beam in Ar, Kr or Xe plasmas (Fig. 1). The energy of electrons was 25 KeV, pulse duration was 100, 150 and 200  $\mu\text{s}$ , pulse energy density was 40 and 60  $\text{J}/\text{cm}^2$  and pulse rate was 10  $\text{s}^{-1}$ .

The microstructure of the surface and cross-section of the surface layers was studied by SEM using Carl Zeiss Supra 55 Sapphire at accelerating voltage of 20 kV. TEM studies were carried out using JEM-2100 microscope at accelerating voltage of 200 kV. Thin foils in the cross-section of the surface layer were obtained by ion thinning using EM-09100IS ion slicer.

The wear resistance of the irradiated samples was studied using CSEM pin-on-disc tribometer. The load on the diamond cone was 5 N, the total number of sample rotations was 2500. The cross-section profile of the groove from diamond counterbody cutting the surface of the samples with numerical determination of the cutting depth were obtained u 3D profilometer "MICRO MEASURE 3D station".

## 3. Results and their discussion

TiC particles in the metal-ceramic composite in the as-received state are approximately equiaxed. Their size distribution is presented in Fig. 2. The average and maximum particles size is  $4.0 \pm 2.5$  and 12.6  $\mu\text{m}$ , respectively.

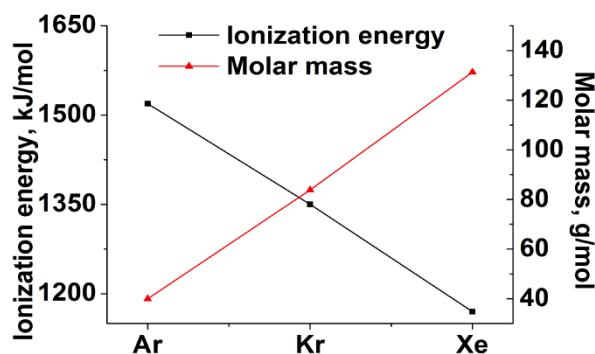


Figure 1. Values of ionization energy and atomic masses of the plasma gases

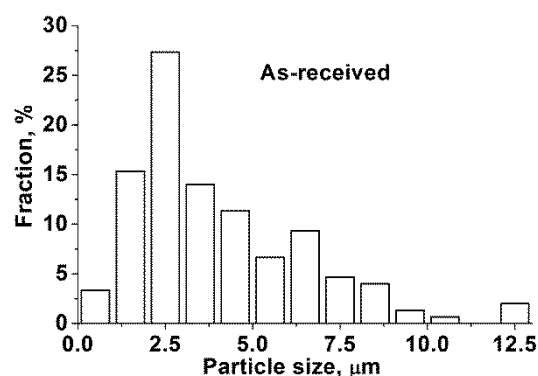


Figure 2. Size distribution of titanium carbide particle in the as-received composite

Electron irradiation of the metal-ceramic alloy in the inert gas plasmas radically changes the microstructure of the surface layer. The character of the obtained microstructures depends on the type of the used inert gas. Irradiation in argon plasma forms a two-phase structure on the surface of the alloy consisting of titanium carbide particles partly dissolved in the molten metal binder (Fig. 3a, shown with the arrows), areas where carbide particles dissolved in the molten binder (the areas in Fig.3a delineated by the black line), and areas with nanosized particles of secondary carbide in the binder (the area in Fig.3a delineated by the white line). When krypton plasma gas is used the refining of initial TiC particles down to 100 nm and less occurs forming a polycrystalline structure with dendrite-like framework in every crystal. One can see the remains of initial carbide particles in the center of each grain (Fig. 3b, shown by the arrows). Irradiation in xenon plasma also refines the initial carbide particles down to nanosize forming a surface polycrystalline structure consisting of nanosized metal-ceramic grains (in Fig. 3c the arrows show the remaining parts of the initial TiC particles in the metal-ceramic grains).

Investigation of the structure of the surface layers of the composite subjected to pulse electron irradiation in inert gas plasmas showed similarity in structure heterogeneity but revealed the influence of the plasma gas on the quantitative parameters of their structure. SEM images of the cross-sections of the surface layers show that they consist of a set of sublayers with characteristic microstructures at various depths. The depth of electron irradiation influence upon the structure of the composite increases as electron irradiation in argon plasma changes to that in krypton plasma and then to xenon one (Fig. 4).

Let us consider the surface layer irradiated in xenon plasma as an example (Fig. 4c). The mentioned set of sublayers looks as follows: the top sublayer which borders closely to the surface is characterized by columnar titanium carbide crystals oriented perpendicular to the irradiated surface of the sample (Fig. 4c, sublayer 1). The size of the crystals is  $1.2 \pm 0.73$  and  $0.39 \pm 0.205$   $\mu\text{m}$  for the longitudinal and transverse directions, respectively. Under this layer there is a thicker sublayer with oriented columnar structure (sublayer 2 in Fig. 4c). The next sublayer has a structure of dendrite type. It is a transition sublayer to the initial structure of the metal-ceramic composite (sublayer 3 in Fig. 4c).

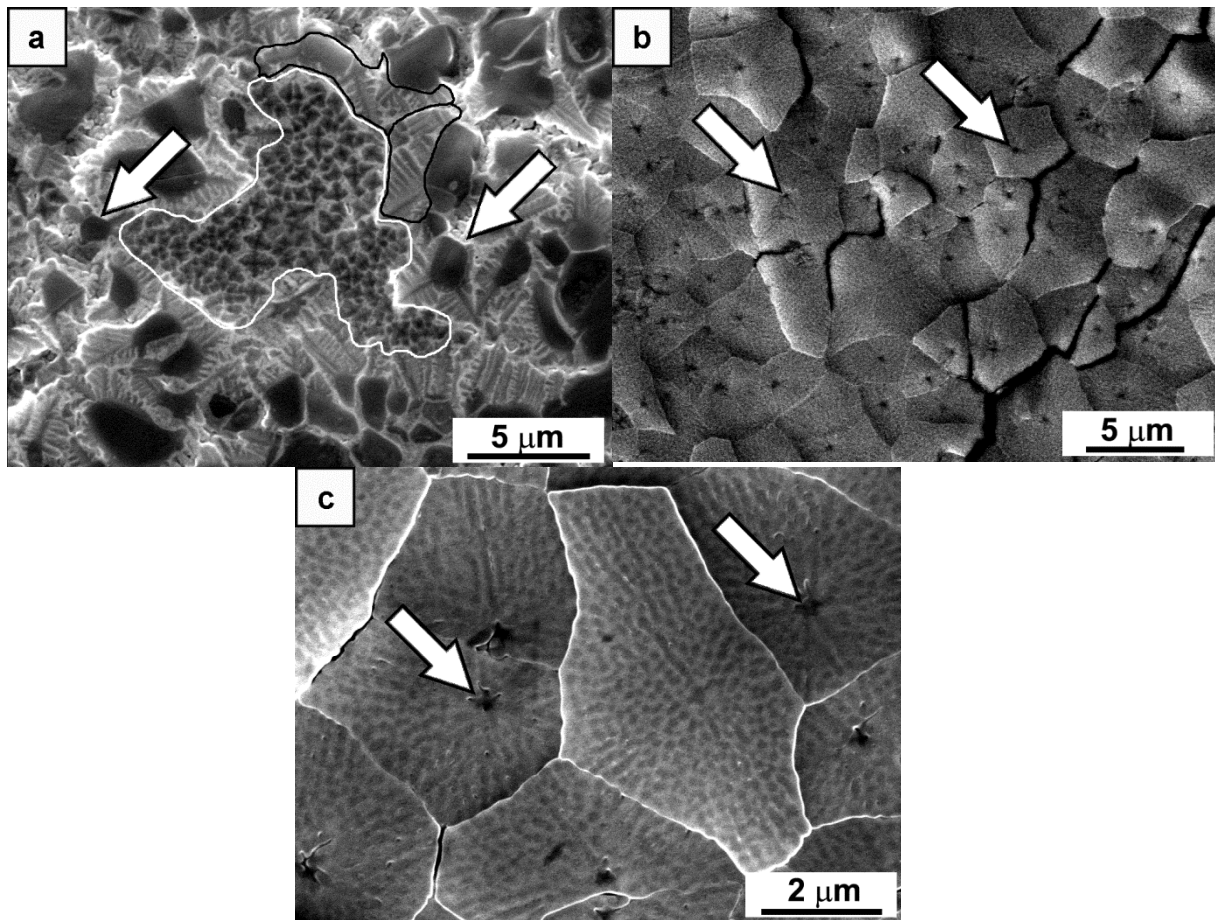


Figure 3. SEM images of the structure of the composite surface after pulse electron irradiation in the plasmas of argon (a), krypton (b) and xenon (c) ( $40 \text{ J/cm}^2$ ,  $150 \text{ } \mu\text{s}$ , 15 pulses)

Size reduction of titanium carbide particles is a distinctive feature of the structure of the surface layers of the composite after electron irradiation in the plasmas of inert gases. The degree of reduction depends on the type of plasma gas. Titanium carbide particles of micron size remain in the top sublayer 1 with columnar submicron sized structure after the irradiation in argon plasma (Fig. 4a). Micron sized carbide particles are found only in the next sublayer 2 with oriented columnar structure (Fig. 4b) after irradiation in krypton plasma. There are practically no micron sized carbide particles the modified surface layer after irradiation in xenon plasma (Fig. 4c).

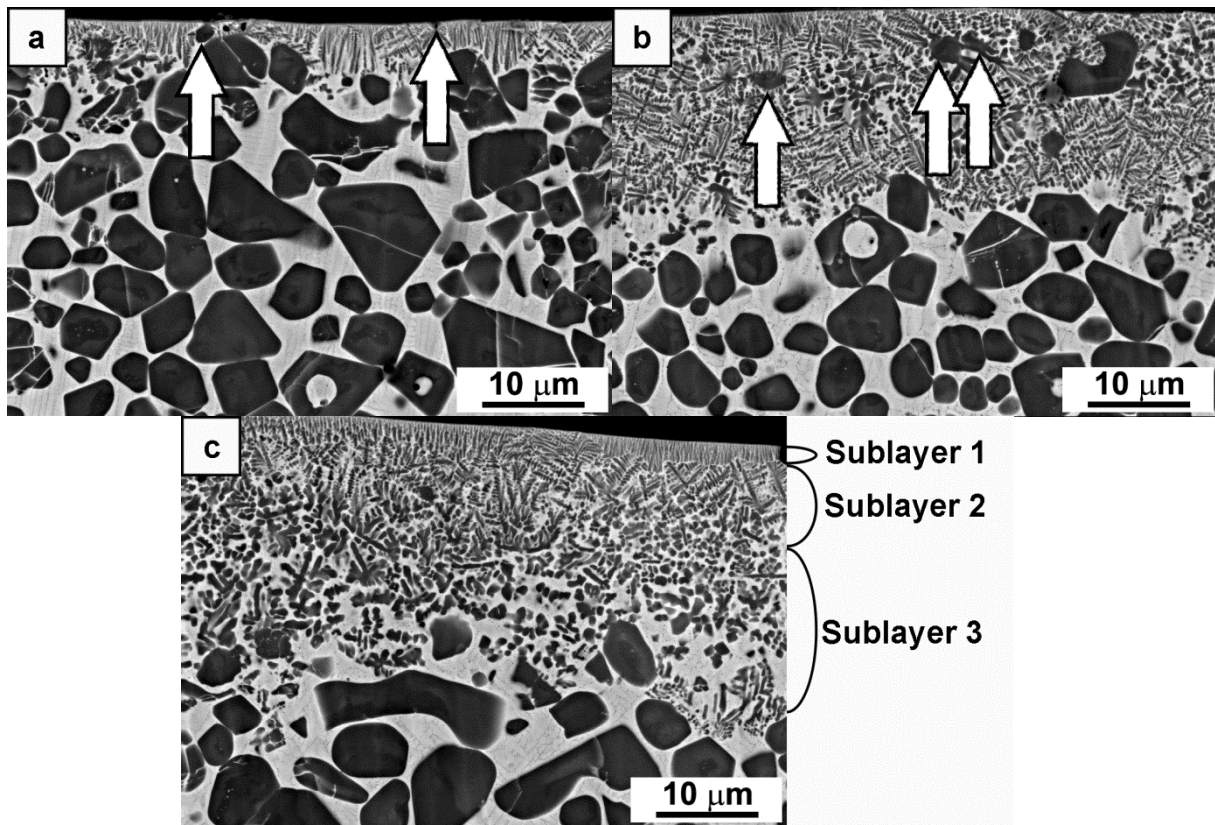


Figure 4. SEM images of the structure of the modified surface layer of the composite (cross-section) after pulse electron irradiation in the plasmas of argon (a), krypton (b) and xenon (c) ( $40 \text{ J/cm}^2$ ,  $150 \text{ μs}$ , 15 pulses). The coarse micron-sized titanium carbide particles are indicated by the arrows

The refining mechanism of carbide particles in the surface layer under the electron irradiation of the composite is illustrated in Fig. 5. The nanosized particles of titanium carbide are formed as precipitates from the supersaturated solid solution of carbon and titanium in the molten metallic binder right on the surface of initial coarse particle. The secondary carbide nanoparticles are oriented in the surface layer due to the temperature gradient occurrence during and just after irradiation. As a result a columnar and dendrite structures appeared in the top and lower sublayers, respectively.

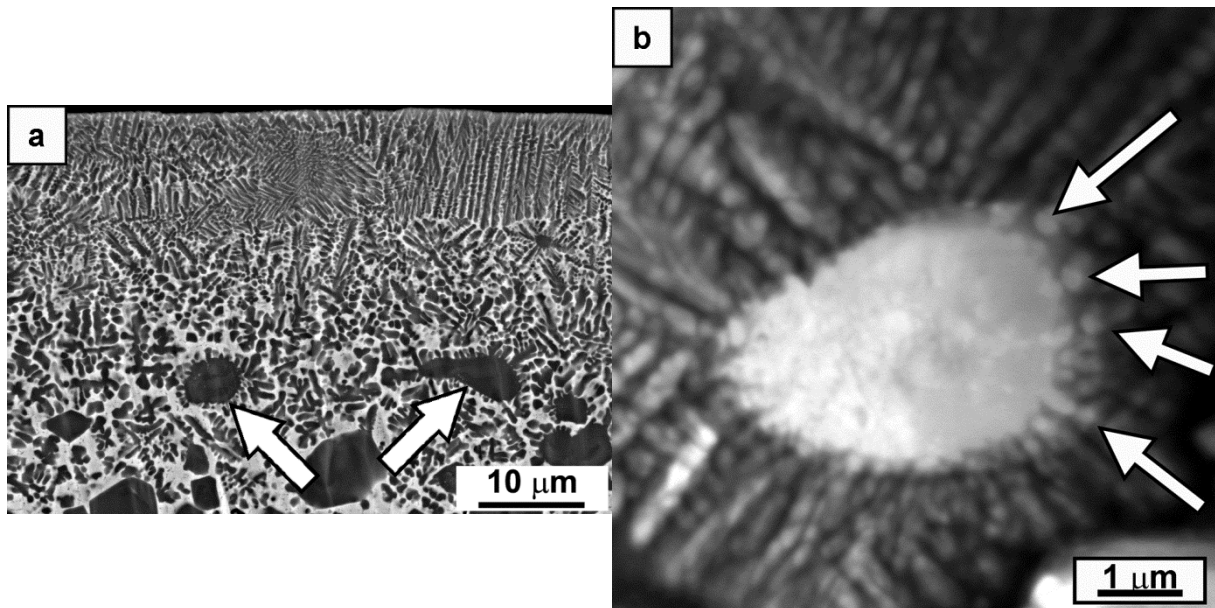


Figure 5. SEM (a) and TEM (b) images of the structure of the modified surface layer of the composite (cross-section) after pulse electron irradiation demonstrating formation of nanoparticles of secondary carbide nearby the surface of the initial coarse titanium carbide particles (indicated by the arrows). Krypton plasma, 60 J/cm<sup>2</sup>, 150 μs, 15 pulses (a) and xenon plasma, 60 J/cm<sup>2</sup>, 100 μs, 15 pulses (b)

Structural investigation suggests that reduction of the ionization energy of the used inert gas (and simultaneous increase of its atomic mass) increases amount of the entered energy into the surface layer of the composite increasing the depth and the temperature gradient in it. As a result, the depth of the modified surface layer increases and the size distribution of titanium carbide particles in the top, middle and bottom sublayers changes when passing from irradiation in argon plasma to irradiation in krypton plasma and then to that in xenon plasma (Figs. 6, 7). It is evident from Fig. 7 that titanium carbide particles become coarser as the distance from the surface grows. The coarsening is least demonstrated when the composite is irradiated in xenon plasma.

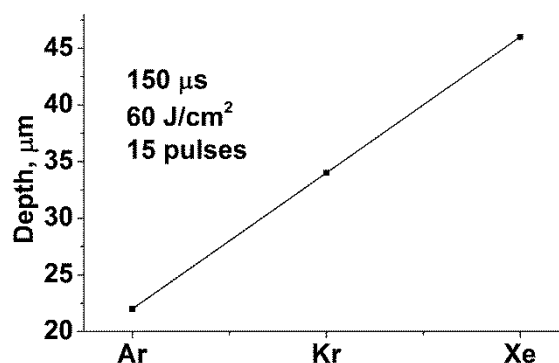


Figure 6. Dependence of the depth of modified surface layer on the type of plasma gas

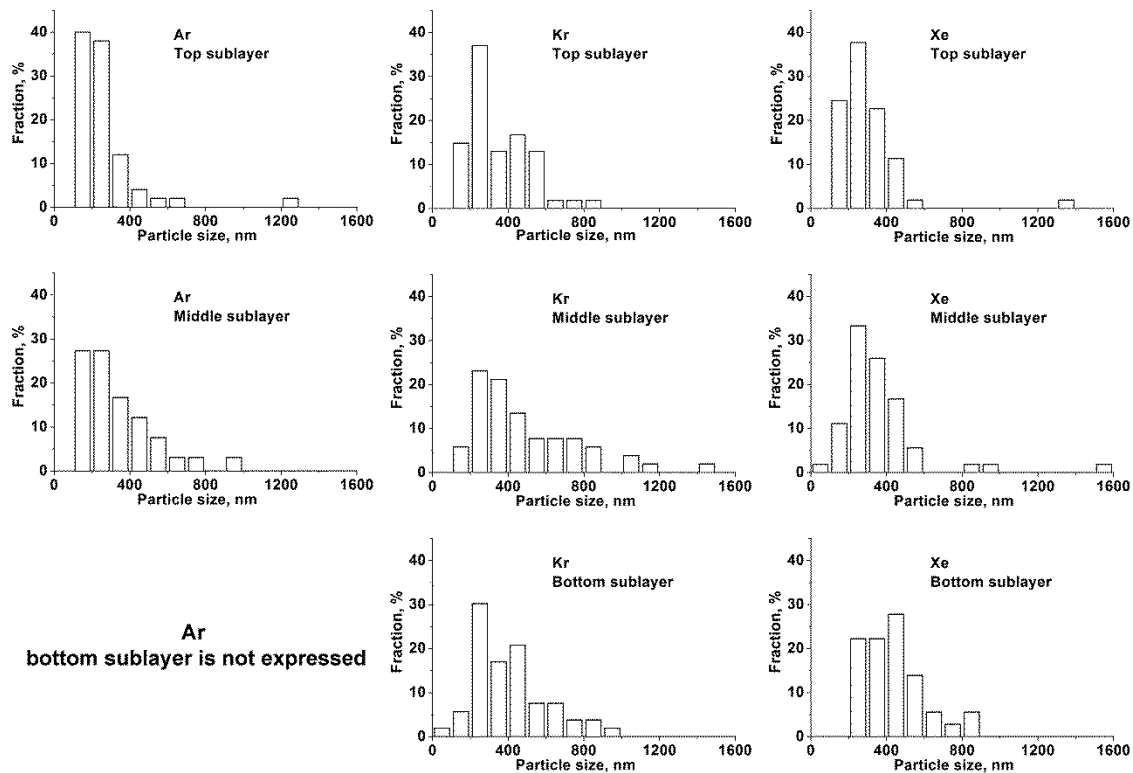


Figure 7. Size distribution of carbide particles in the top, middle and bottom sublayers of the modified surface layer after irradiation in the plasmas of argon, krypton and xenon ( $40 \text{ J/cm}^2$ ,  $150 \mu\text{s}$ , 15 pulses)

Fig. 8 shows the dependence of the groove depth cut with a diamond cone on the surface of irradiated composite samples. One can conclude that modification of the structure of the surface layer of the composite as a result of electron irradiation in the plasmas of inert gases increases its wear resistance for the all used gases. Wear resistance increases when passing from irradiation in argon plasma to irradiation in krypton plasma and then to irradiation in xenon plasma.

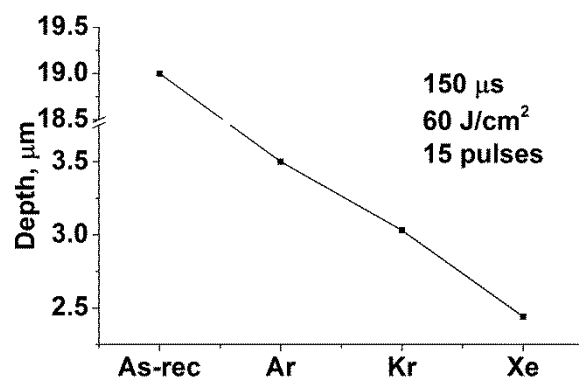


Figure 8. Dependence of the groove depth cut with a diamond cone on the surface of the irradiated composite on the type of plasma gas

#### 4. Conclusion

Nanostructured heterophase structure is formed in the surface layer of metal-ceramic TiC/(Ni-Cr) alloy as a result of pulse electron irradiation in the plasmas of inert gases with different atomic mass and ionization energy. As the inert gas atomic mass increases together with the decrease of ionization energy the depth of the modified surface layer grows and fraction of submicron sized particles in the surface layer increases. The wear resistance of metal-ceramic composite improves in accordance to the formation of nanocrystalline structure in the surface layer.

#### Acknowledgements

This work was supported by the Program for Basic Scientific Research at the State Academies of Sciences for 2013–2020 (Project No. 23.2.2). Access to the experimental equipment in the “Nanotech” Common Use Center (ISPMS SBRAS) is acknowledged.

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