

Morphology and Chemical Composition of Silicon Carbide Surface in Interaction with Titanium Alloy under Micro-Scratching Conditions

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Abstract. The article describes features of the wear site morphology formation during micro-scratching of a titanium alloy by a silicon carbide crystal in comparison with a corundum crystal. The initial shape of the crystal top and the rate of micro-scratching were assumed to be constant. No lubricating or cooling process media were used. External factors: micro-scratch depth and cutting path length. The chemical composition of wear sites was studied using micro-x-ray spectral analysis. The content of chemical elements in the surface layer of silicon carbide and adhered metal was studied at separate points and by area scanning. The accelerating voltage of the excitation electrons was changed in the range from 5 to 20 kV. The concentration of chemical elements on the surface of the wear site was determined immediately after micro-scratching and after removing the adhered metal by etching. The regularities of changes in the concentration of chemical elements depending on the accelerating voltage of the excitation electrons were determined.

1 Introduction

Titanium alloys are among the most common structural metals used in aviation and space technology, rocket science, medicine, and other industries [1, 2]. Titanium-based alloys are used to produce the most critical parts, the surface quality of which is formed during the final processing operations [3-5]. Therefore, the study of the titanium alloy grinding process is relevant to the current issues of modern mechanical engineering.

In the periodic table of chemical elements, titanium is located in the IVB subgroup of the 5th period. The state of the valence electrons of an isolated atom corresponds to the d^2s^2 configuration. In the condensed state, possible variants of electronic rearrangement are $d \rightarrow p$ -, $s \rightarrow d$ -, $s \rightarrow p$ -transitions. Transitions of $d \rightarrow p$ type for elements of IVB subgroup are not energetically favorable, since the result is a configuration of d^1 which is less stable than d^2 .

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Due to the instability of the atom electronic configurations, titanium is one of the most adhesively active metals [6-9]. Therefore, one of the reasons for the low resistance of the abrasive tool when grinding titanium alloys is the metal adhering to the top of the abrasive material [10-12].

In this regard, the purpose of this paper was to study the morphology and chemical composition of the silicon carbide surface during micro-scratching of a titanium alloy.

2 Research Methods

Micro-scratching of the titanium alloy was performed with specially prepared silicon carbide indenters. The top of the silicon carbide crystal was sharpened as a cone with an angle at the top of 110 degrees. The radius of vertex rounding is 25-30 microns. The indenter was fixed in a steel disk. Titanium alloy VT-00 was used as the processed material. Before micro-scratching, the metal surface was treated with a wheel of cubic boron nitride on a ceramic bundle to a roughness of Ra 0.15 microns. Micro-scratching was performed on a precision profile Smart-B1224III CHEVALIER grinding machine with numerical control. The micro-cutting speed is 35 m/s.

The state of the relief and chemical composition in the surface nanolayers were studied using a FEI Versa 3D LoVac scanning two-beam electron microscope. The device performs a comprehensive study of the object with an amplification of up to 500,000 times. Chemical analysis of the surface of the silicon carbide wear site was determined by local micro-x-ray spectral analysis.

Before the study, the wear site was cleaned of possible contamination in an Elmasonic S40H ultrasonic bath. The samples were immersed for 30 minutes in a 95 % solution of ethyl alcohol at an ultrasonic vibration frequency of 30 kHz.

The morphology and chemical composition of the wear sites were studied immediately after micro-scratching of the titanium alloy and after removing the metal adhered to the crystal top. Etching was performed in a solution of hydrofluoric acid.

3 Research Results

In Fig. 1a, the direction of the main movement of the silicon carbide crystal top is from left to right, in Fig. 1b – from top to bottom at an angle of about 45°. The average depth of micro-scratches is 5-8 microns. There is a large amount of adhered metal on the front and side surfaces of the grain top. On the first indenter, a relatively flat site in the form of a rectangle is shown by arrow 1 (see Fig. 1a). Its size is 24x29 microns (Fig. 1c), which is about 3 % of the nominal size.

With a double increase in the depth of micro-scratching, the destruction of the wear site occurs faster. As a result of intensive chipping of the wear site micro volumes, the grain top gets cleaned from the adhered metal (Fig. 1d).

At an average depth of 5-8 microns, the duration of the process was increased by 2 times. The diameter of the area as a result of a more intensive wear exceeded 500 microns (Fig. 1e). Reduction in the depth of micro-scratching, operating time, or options for scratch application did not change the wear mechanism: in all cases, titanium adheres to the top of the indenter, and micro-volumes of the crystal are dislodged and chipped.

When a titanium alloy is micro-scratched under such conditions by a corundum crystal, a flat wear site is formed on the back surface (Fig. 1e). The chemical composition on the visible part of the crystal 2 surface was determined in Spot 1 and Spot 2 (Fig. 2A) at accelerating voltages $U=5$ and $U=20$ kV. Micro-x-ray analysis revealed the presence of five elements: carbon, silicon, titanium, nitrogen, and oxygen (Fig. 2b-2d). The content of each

of the elements in the two analyzed microspots Spot 1 and Spot 2, taking into account the confidence interval for arithmetic mean values at $U=5$ kV, can be considered the same.

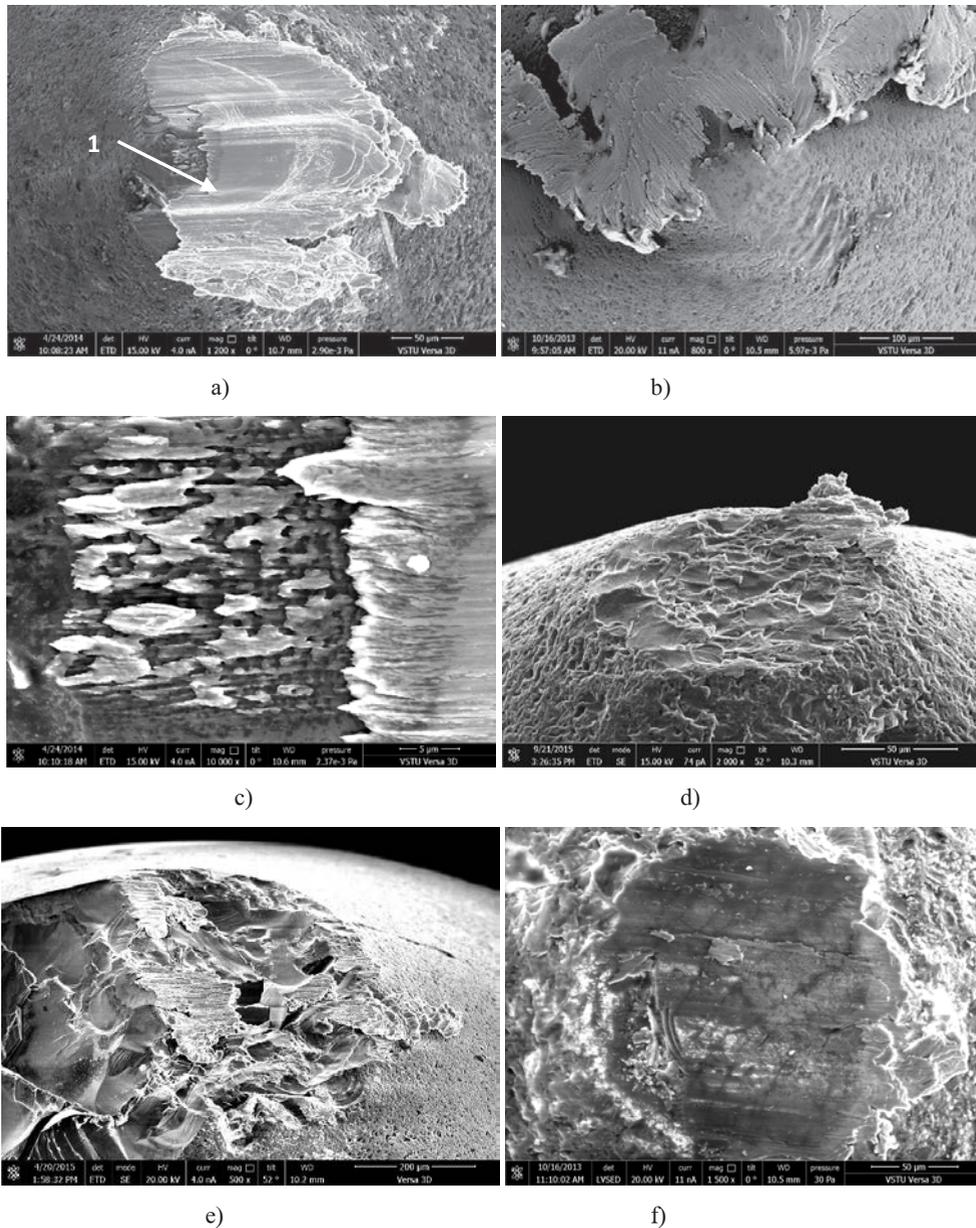


Fig. 1. Condition of the silicon carbide (a-e) and corundum (f) wear site after micro-scratching of titanium

According to the chemical formula of silicon carbide (SiC), the atomic concentrations of silicon and carbon must be the same. According to experimental data (Fig. 2b), the atomic concentration of carbon is almost 70% higher, which indicates an excess amount of carbon.

The silicon carbide surface contains about 3 Atomic % titanium, 1.5 Atomic % nitrogen, and 1.1 Atomic % oxygen.

With a four-fold increase in the activation energy U to 20 kV, the atomic concentration of carbon decreases by an average of 18%, and the concentration of silicon increases by almost 40%. Taking into account the confidence intervals for the average values, the difference in the atomic concentrations of silicon and carbon in this case can be considered insignificant, which corresponds to the chemical formula of silicon carbide (SiC). The oxygen concentration is reduced by almost an order of magnitude, and the average concentrations in Spot 1 and Spot 2 are close to 0.1 Atomic %. The average concentration of nitrogen atoms for $U=20$ kV decreased by 4-5 times. The confidence interval for the average concentration exceeds 50%, which indicates low confidence in determining the average nitrogen concentrations.

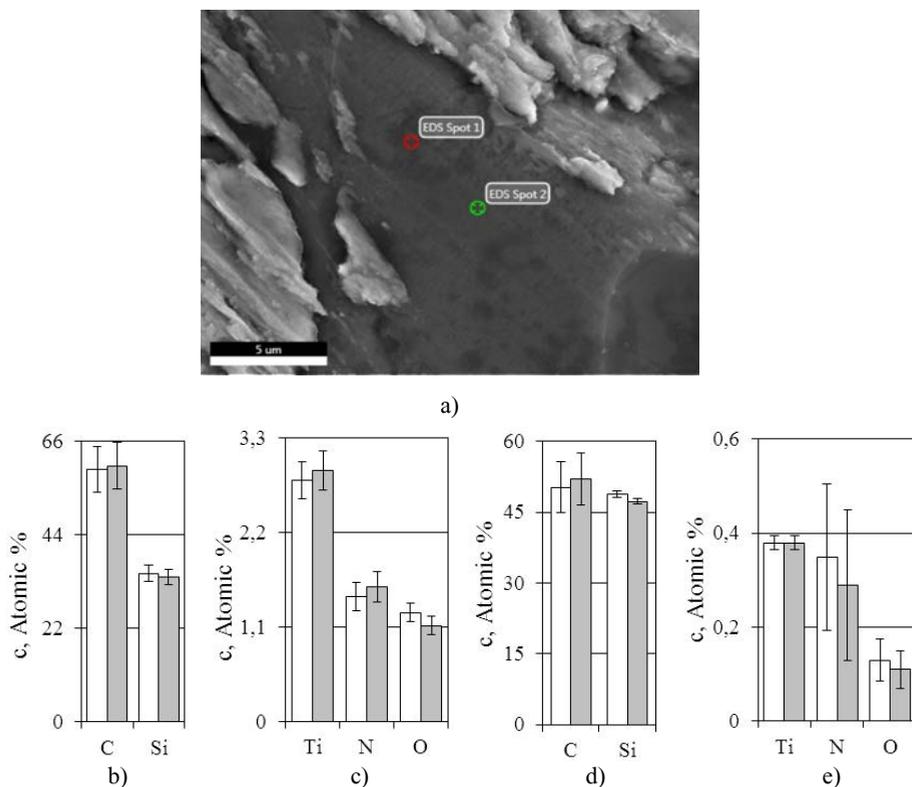


Fig. 2. Crystal 2 surface and chemical composition diagrams of the selected spots at accelerating voltages of 5 kV (b, c) and 20 kV (d, e): □ – Spot 1; ■ – Spot 2

For a more detailed study of the chemical composition of the silicon carbide contact surface, the fragment shown in Fig. 3a was isolated on the crystal surface. The concentration of chemical elements was determined by scanning the area. The chemical composition was measured in three areas: Area 1 is selected on a relatively clean silicon carbide surface, Area 2 is selected next to the tip, and Area 3 is selected directly on the tip. The dimensions of the first rectangle (Area 1) are 2.4×1.7 microns, of the second one (Area 2) – 1.8×1.6 microns, and of the third one (Area 3) – 1.7×1.8 microns. The scanning spacing on all surfaces is 50 nm.

The main chemical elements in Area 1 and Area 2 are carbon, silicon, and titanium. Taking into account the confidence interval, the carbon content in Area 1 and Area 2 can be considered the same (Fig. 3c). There is less atomic silicon in Area 2, but almost 2 times more titanium (Fig. 3d). In the tip, the main chemical element is titanium – about 66 Atomic %. The carbon content in adhering titanium, compared to the silicon carbide

surface, is reduced by more than two times and is about 26 Atomic %. Traces of silicon, about 0.3 Atomic%, were also found in the tip.

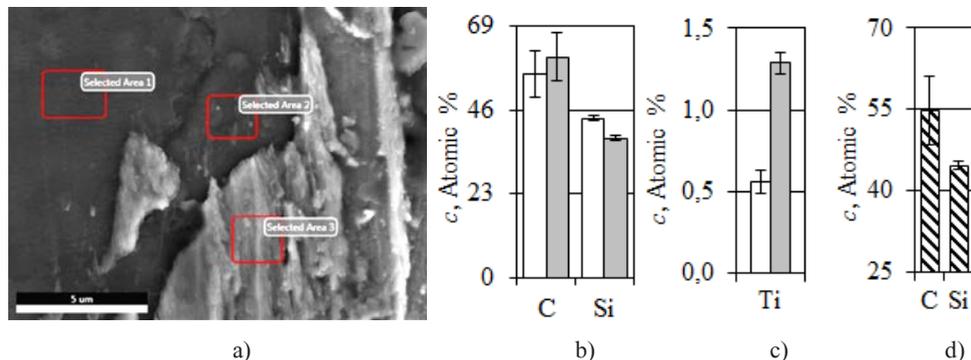


Fig. 3. Scanning areas on the silicon carbide surface (a), and diagrams of chemical elements (b-d) □ – Area 1; ▨ – Area 2; ▩ – Area 3

In the initial titanium alloy VT1-00, the silicon content does not exceed 0.08 Atomic %. The presence of silicon in adhering titanium is explained by the possible transfer from silicon carbide.

An increased carbon content was found in titanium tips at the wear site in micro-scratching with corundum [13] and in nanolayers of titanium alloy when grinding with a wheel of silicon carbide without the use of lubricating and cooling process media [14, 15].

Therefore, the transfer of metal from the air should be considered the main reason for the increase in carbon content.

After etching the metal adhered to the indenter tops (see Fig. 1a, b), the nominal diameter of the silicon carbide wear site, taking into account the material chips, was about 165-170 microns.

The state of the surface of the second indenter after removing the adhered metal is shown in Fig. 4a. At the second indenter, a layer of crystal 1 with a width of about 100 microns and a length of more than 300 microns chipped off from the back of the wear site.

The silicon carbide wear site is almost completely destroyed, leaving only three fragments shown by arrows (Fig. 4b). It is obvious that these fragments were supports on which the adhered metal was held. Metal may also be mechanically stuck in the surface micro-roughness.

After etching the metal and wiping the wear site, the part of the crystal top present in Fig. 1b was removed. Figure 4c shows the same surface tilted by 50° relative to the horizontal, which gives an idea of the three-dimensional image of the wear site.

Micro-x-ray-spectral analysis was performed at individual points of the surface 2 (Fig. 5a) and by area scanning (Fig. 5b).

The content of titanium in the studied micro-objects (points), taking into account the confidence interval for arithmetic mean values, can be considered the same (Fig. 5c). The same is true for the carbon concentration (Fig. 5d).

The difference between the elements under consideration is that with an increase in the activation energy of the excitation electrons, the concentration of titanium decreases, while the concentration of carbon remains almost unchanged.

The silicon concentration in the micro-objects under consideration is the same only at U=5 kV (Fig. 5e).

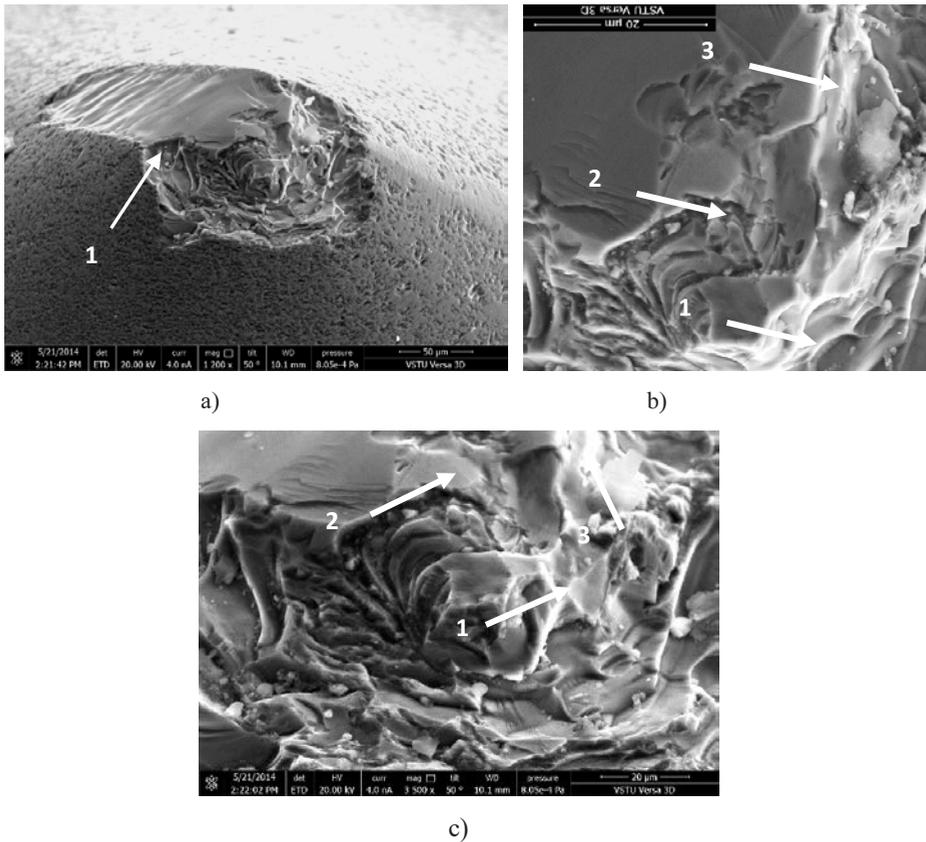


Fig. 4. Silicon carbide crystal surface after micro-scratching of titanium and removal of adhered metal

As the activation energy increases, the difference between the arithmetic mean atomic concentrations of silicon in Spot 1, Spot 2, and Spot 3 should be considered significant, which indicates that the silicon content in the studied surface is not uniform. As U increases, the silicon concentration increases, too.

When scanning the surface (see Fig. 5b), the growth of U also leads to a decrease in the concentration of titanium (Fig. 5f), which is consistent with the data in Fig. 5c. The carbon concentration does not change when scanning the surface with the increasing U (Fig. 5g). For silicon, there is a clear pattern of growth of the content with the increasing U (Fig. 5h).

The values of chemical element concentrations at the points were averaged. The confidence interval for arithmetic mean values was determined based on the condition that there were no significant differences in variances.

Comparison of the arithmetic mean concentrations obtained by measuring at individual points and by scanning the surface showed that, taking into account the confidence intervals, there is no significant difference between them.

This allows us to consider the samples under consideration as belonging to the same general entirety.

Since the sample of values during surface scanning is significantly larger than at points, the statistical parameters obtained during surface scanning should be considered more reliable.

Using these data and data obtained by measuring the surface of silicon carbide immediately after micro-scratching, graphical dependences of changes in the atomic concentrations of elements on the accelerating voltage are constructed (Fig. 6).

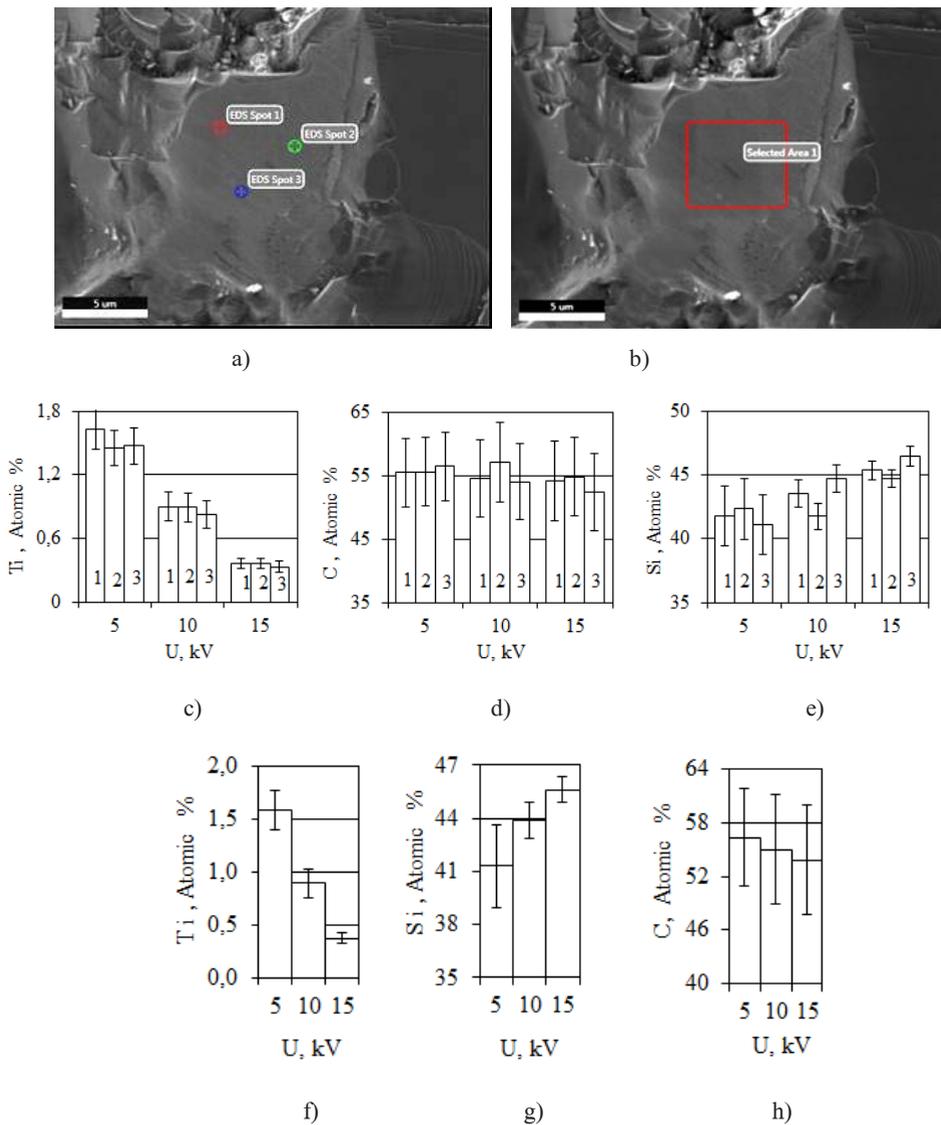


Fig. 5. The crystal surface after the removal of the adhered metal with the selected objects of analysis (a, b) and the concentration of chemical elements in Spot (c-e) and Area (f-h)

With an increase in the activation energy of the excitation electrons by a factor of 3, the atomic concentration of carbon changes insignificantly, both on the surface of silicon carbide after micro-scratching, and after removing titanium by etching in a solution of hydrofluoric acid. There is no significant difference in the content of atomic carbon in the surface of silicon carbide before and after etching.

The silicon concentration increases with the increasing U from 5 to 15 kV: after micro-scratching – by 25 %; after etching-by 10 %. After etching, the silicon content in the nanolayers of the silicon carbide surface is significantly higher. For example, at U=5 kV, the silicon concentration after etching is 20% higher, while at U=15 kV it is only 4 % higher. Thus, with the increasing U, the difference in the silicon concentration in the silicon carbide surface decreases.

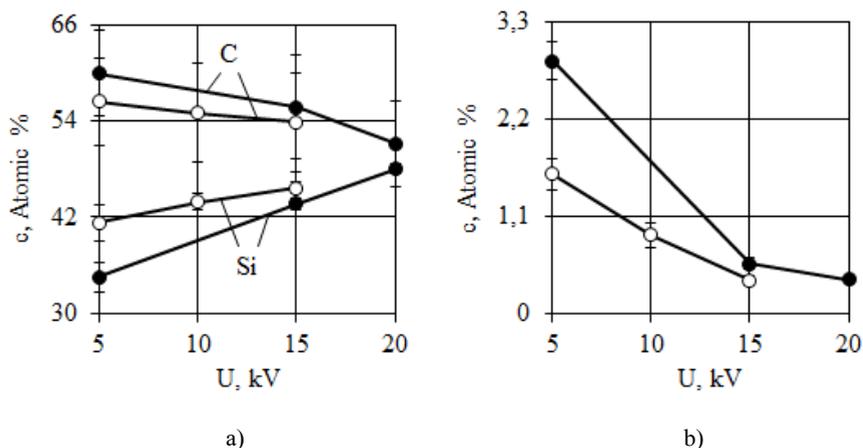


Fig. 6. Dependence of the concentration of chemical elements c on the accelerating voltage of excitation electrons U : ● – after micro – scratching; ○ - after titanium removal

It is also necessary to take into account the depth factor of the x-ray characteristic radiation generation zone. With an increase in the accelerating voltage, the electron energy and the depth of its penetration into the surface layer of the material under study increases, as does the depth and volume of the x-ray characteristic radiation generation zone.

Calculations have shown that at $U=5$ kV, the depth of the x-ray characteristic radiation generation zone $K\alpha$ for carbon and silicon should not exceed 324 and 270 nm, respectively. Only L-level electrons are excited in titanium atoms. The maximum depth of x-ray characteristic radiation generation $TiL\alpha$ is within the same range. As U increases three times to 15 kV, the maximum depth of the atomic generation zone increases 6-7 times and reaches 2,000 nm.

Analysis of the visually clean silicon carbide surface at $U=5$ kV (see Fig. 2 and 3) showed that a material layer about 300 nm deep can contain almost 3 Atomic % titanium. If we assume that the transfer of titanium occurred as a result of diffusion or chemical interaction with silicon carbide, the depth of the modified layer should not exceed tens of nanometers. In other words, the content of titanium in the near-surface layer is noticeably higher than in the volume of x-ray characteristic radiation generation. After etching, the titanium concentration decreases by a factor of 1.8 from 2.9 to 1.6 Atomic %.

As U increases, the concentration of titanium decreases, since the same amount of titanium concentrated in the near-surface layer is now averaged over a much larger volume. At $U=15$ kV, the titanium concentration on the non-etched and etched surfaces was 0.56 and 0.36 Atomic %, respectively.

4 Conclusions

As a result of micro-x-ray analysis of the silicon carbide surface after micro-scratching of titanium, it was found that titanium is present in the silicon carbide nanolayers, which is not removed by etching in a solution of hydrofluoric acid. In titanium, which is adhere to the silicon carbide surface, an increase in the silicon content is observed.

At an accelerating excitation electron voltage $U=5$ kV, micro-x-ray spectral analysis of visually clean areas of the silicon carbide surface after micro-scratching of titanium showed the presence of C, Si, Ti, O, and N atoms. The ratio between Si and C atoms in silicon carbide indicates the presence of excess carbon. After etching of the titanium, the excess carbon content is reduced.

As U increases from 5 to 20 kV, the concentration of carbon decreases, and that of silicon increases. At U=20 kV, taking into account the confidence interval for the arithmetic mean values of the concentrations of silicon and carbon atoms differ insignificantly. The concentration of titanium atoms determined by the method of micro-x-ray spectral analysis, is reduced on the silicon carbide surface after macro-scratching and after etching of titanium with the increasing accelerating voltage of the electron excitation, which indicates the concentration of titanium atoms in the wear site surface nanolayers.

References

1. S. Gialanella, A. Malandrucolo, *Aerospace Alloys* (Topics in Mining, Metallurgy and Materials Engineering, Cham, Switzerland, 2020).
2. A. Khorev, *Fundamental and applied research in constructional titanium alloys and advanced lines of development thereof*, Titan, v. **1(35)**, pp. 29-32 (2012)
3. H. Garbacz, P. Wiciński, D. Kuczyńska, D. Kubacka, K. J. Kurzydłowski, *The effect of grain size on the surface properties of titanium grade 2 after different treatments*, Surface and Coatings Technology, v. **(335)**, pp. 13-24 (2018) DOI: 10.1016/j.surfcoat.2017.12.005
4. Z. Tao, S. Yaoyao, S. Laakso, S. Jinming, *Investigation of the Effect of Grinding Parameters on Surface Quality in Grinding of TC4 Titanium Alloy*, Procedia Manufacturing, v. **(11)**, pp. 2131-2138 (2017)
5. Z. Biao, D. Wenfeng, Z. Yi, S. Honghua, X. Jiuhua, *Effect of grain wear on material removal behaviour during grinding of Ti-6Al-4V titanium alloy with single aggregated cBN grain*, Ceramics International, v. **(45)**, pp.14842-14850 (2019) DOI: 10.1016/j.jallcom.2020.154882
6. V.A. Nosenko, *Interaction intensity criterion for machined and abrasive materials in grinding*, Problemy Mashinostraeniya i Nadezhnos'ti Mashin, v. **(5)**, pp. 85-91 (2001)
7. V.A. Nosenko, *On contact interaction intensity of d-transition metals with silicon carbide in grinding*, Problemy Mashinostraeniya i Nadezhnos'ti Mashin. v. **(5)**, pp. 78-84 (2002)
8. V.A. Nosenko, *Improvement of abrasive tools on vinyl resin binder*, Problemy Mashinostraeniya i Nadezhnos'ti Mashin, v. **(3)**, pp. 85-90 (2004)
9. V.A. Nosenko, *Contact interaction effect on abrasive tool wear in grinding*, Problemy Mashinostraeniya i Nadezhnos'ti Mashin, v. **(1)**, pp. 73-77 (2005)
10. V.A. Nosenko, A.V. Fetisov, V. Ye. Puzyrkova, *Morphology and chemical composition of silicon carbide surfaces interacting with iron, cobalt, and nickel in microscratching*, Solid State Phenomena, v. **(284)**, pp. 363-368 (2018) DOI: 10.4028/www.scientific.net/SSP.284.363
11. S.V. Nosenko, V.A. Nosenko, A.A. Koryazhkin, *The effect of the operating speed and wheel characteristics on the surface quality at creep-feed grinding titanium alloys*, Solid State Phenomena, v. **(284)**, pp. 369-374 (2018) DOI: 10.4028/www.scientific.net/SSP.284.369
12. V.A. Nosenko, *Unidirectional and opposing deep grinding of titanium alloy with periodic wheel adjustment*, Russian Engineering Research, v. **30(10)**, pp. 1016-1021 (2010) DOI: 10.3103/S1068798X10100114

13. V.A. Nosenko, A.V. Fetisov, S.P. Kuznetsov, V.E. Puzyrkova, *The morphology and chemical composition of titanium alloy with electro-corundum with grinding and microscratching*, Izvestia VSTU, v. **8(231)**, pp.31-37 (2019)
14. S.V. Nosenko, V.A. Nosenko, A.A. Krutikova, L.L. Kremenetskii, *Surface-layer composition of titanium alloy after dry grinding by a silicon-carbide wheel*, Russian Engineering Research, v. **35(7)**, pp. 554-557 (2015) DOI: 10.3103/S1068798X15070163
15. S.V. Nosenko, V.A. Nosenko, L.L. Kremenetskii, (2016) *Concentration gradients in the surface layer of titanium alloy ground by a silicon-carbide wheel*, Russian Engineering Research, v. **36(1)**, pp. 43-45 (2016) DOI: 10.3103/S1068798X16010160