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# Reserach of the mechanic-tribological characteristics of $Ti_3SiC_2$/TiC coatings after annealing

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This article investigates the influence of thermal annealing on microhardness and wear resistance of the surface of steel U9/Y9 protected by a composite coating $Ti_3SiC_2$/TiC obtained by detonation sputtering. Thermal annealing was performed in the range of temperatures 700-900 ° C during 1 hour. Following annealing the formation of $TiO_2$ and an increase in the phase content of $Ti_3SiC_2$ are observed. Higher microhardness was obtained in coatings subjected to annealing at 800 ° C, which can be explained by an increase in the content of carbonized titanium. As the annealing temperature rises further, the thickness of the oxide layer increases, leading to a decrease in the microhardness for the coatings annealed at 900 ° C. According to the results of tribological tests, formation of the oxide increases wear resistance of $Ti_3SiC_2$/TiC composite surface coatings.

**Keywords:** steel U9, titanium carbosilicide, heat treatment, microhardness, wear resistance.

## Introduction

Currently, there is widespread use for the restoration of worn surfaces of a variety of products are found to be based on titanium carbocylicide. The $Ti_3SiC_2$ systems have good performance under abrasive wear, corrosion and elevated temperatures, as well as relatively low cost [1, 2]. In addition, titanium carbosilicide as an unique composite material includes properties of titanium carbide and titanium silicide. Moreover, the popularity of usage of titanium carbosilicide in the industry has increased significantly. Titanium carbosilicide, titanium carbide and titanium silicide those substances are ternary compounds that correspond to the formula Mn $^{+1}$ AXn, where M is a transition metal, A is an element of IIIA or IVA groups, X is carbon or nitrogen, $n = 1, 2$ or 3 (they are also called MAX compounds). A unique distinctive feature of these materials is the layered structure of their crystal lattice - the regular arrangement of the layers of atoms M and A elements (hence the name "nanolaminates"), which have a lower binding energy between them. There are many works devoted to the study of hardness and wear resistance of $Ti_3SiC_2$ coatings [3, 4]; however, only a few of these coatings were obtained by the method of detonation sputtering. At the same time, various properties of coatings obtained by the method of detonation spraying and other methods are noted; by this, it is of interest to study the tribological properties of the $Ti_3SiC_2$ detonation coating.

The main goal of this work is to study the influence of the heat treatment on microhardness and wear resistance of $Ti_3SiC_2$/TiC coatings obtained by detonation spraying on the surface of tool steel U9/Y9.

## Experimental procedure

Detonation coatings were obtained on a computerized detonation spraying complex of a new generation of CCDS2000 (Computer Controlled Detonation Spraying) [5-7], in which detonation is realized inside the barrel in an explosive mixture formed as a result of flow-through supply of gas components through a specialized mixing device. A schematic of a CCDS2000 facility is presented in (Figure 1) [8, 9].

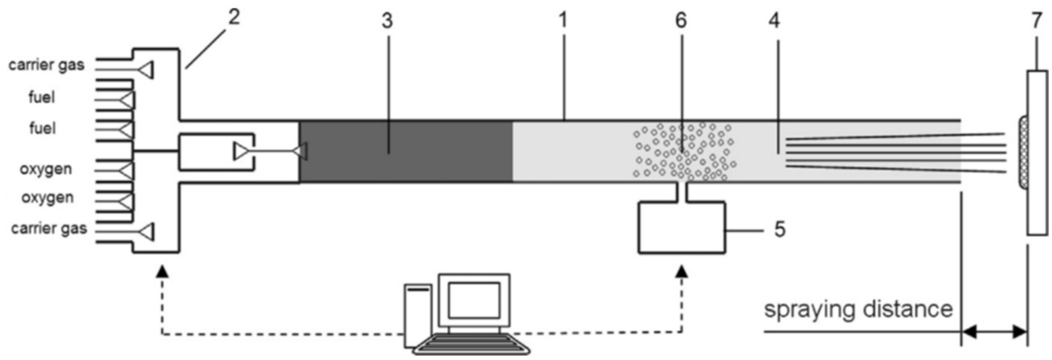



Figure 1. A schematic of a CCDS2000 facility [8]. 1 – gun barrel, 2 – computer-controlled precision gas distribution system, 3 – explosive charge, 4 – carrier gas, 5 – computer-controlled powder feeder, 6 – cloud of injected powder, 7 – substrate.

As a object of research was selected instrumental carbon steel grade U9/Y9, the surface of which was previously subjected to sandblasting. The chemical composition of the powder: Ti - 74 wt.%; SiC - 20 wt.%; C - 6.0 wt.%. Thermal annealing of coated samples was carried out in a laboratory tubular electric resistance furnace of the SUOL-0.4.4/12-M2-U4.2 type in a vacuum of 10-2 Pa at temperatures of 700 ° C, 800 ° C and 900 ° C for 1 h, with subsequent cooling. The temperature was measured and regulated by a precision temperature regulator VRT-2, using two thermocouples of the type of CCI 1378. The microhardness of the samples was measured by the method of indentation of the diamond indenter on the device PMT-3 in accordance with GOST 9450-76, with a load of 200 g and an exposure under load of 10 s. The phase composition of the samples was studied by X-ray diffraction analysis on the X'PertPro diffractometer using CuK $\alpha$ radiation. The study of the surface microstructure was carried out on a scanning electron microscope Vega3 Tescan. Tribological sliding friction tests were carried out on a tribometer THT-S-BE-0000 using the standard "ball-disk" technique (international standards ASTM G 133-95 and ASTM G 99) [10, 11]. As a counterbody, a VK ball with a diameter of 3 mm was used. The parameters of the studies were the same for the studied samples: the path length was 31 m, the load 10 N, speed 5 cm/s, at room temperature. The wear tracks were studied by using the contactless 3D profilometer of MICROMEASURE 3D station.

## Results and Discussion

On the bases of the analysis of literature sources [1, 12-14] and preliminary studies, it was suggested that if detonation sputtering of the Ti-C-Si system was carried out, a multi-layer coating containing phases such as titanium carbides, silicides and carbosilicides is possible. During subsequent heat treatment - regulation of its phase composition. Thermal annealing of the coated samples was carried out in a laboratory tubular electric furnace at temperatures of 700 ° C, 800 ° C, and 900 ° C for 1 h, followed by cooling.

Figure 2 shows a plot of microhardness versus annealing temperature. It can be seen that the microhardness of the initial coating is 700 $HV_{0.2}$. After annealing, there is an increase in microhardness: at $T$=700 ° C, the microhardness is 1150 $HV_{0.2}$, at $T$=800 ° C, the microhardness is 1400 $HV_{0.2}$, and at $T$=900 ° C, the microhardness is 850 $HV_{0.2}$. With the aim of identifying the reasons for the change of the microhardness, we have conducted X-ray phase analysis of the coatings before and after annealing.

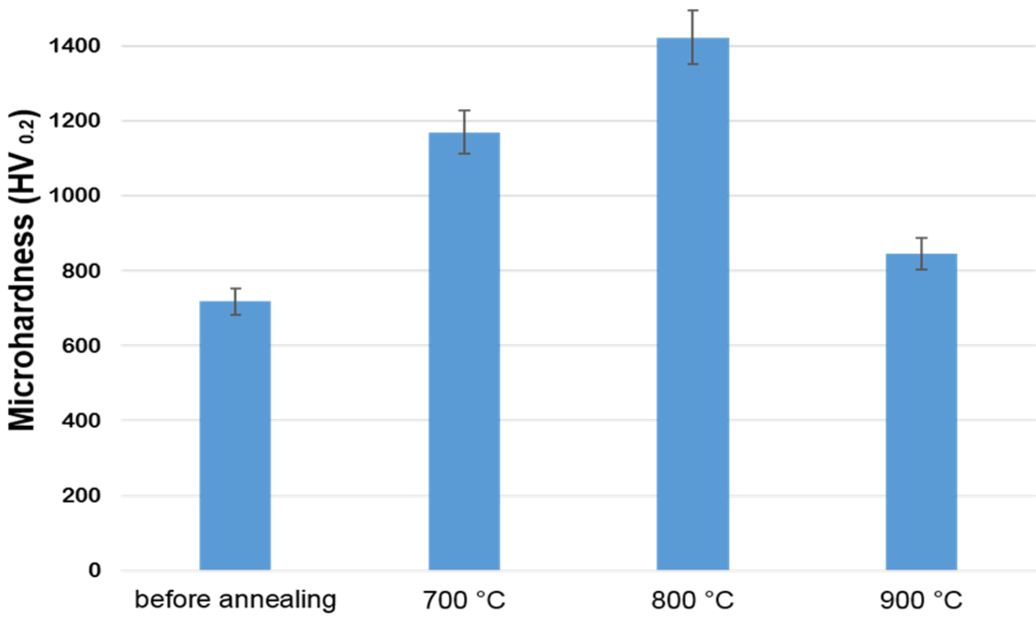



Figure 2. The effect of annealing temperature on microhardness of coating based on $Ti_3SiC_2$/TiC.

Figure 3 shows the XRD patterns of coating based on $Ti_3SiC_2$ before and after annealing. The results of X-ray phase analysis of coatings showed that the coating before annealing consists of phases TiC and $Ti_3SiC_2$.

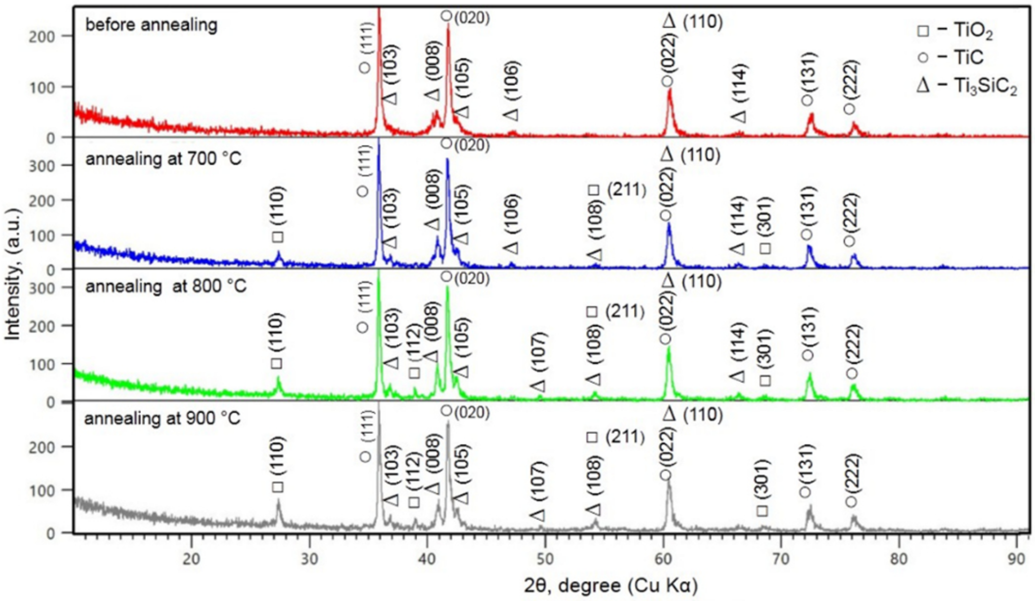
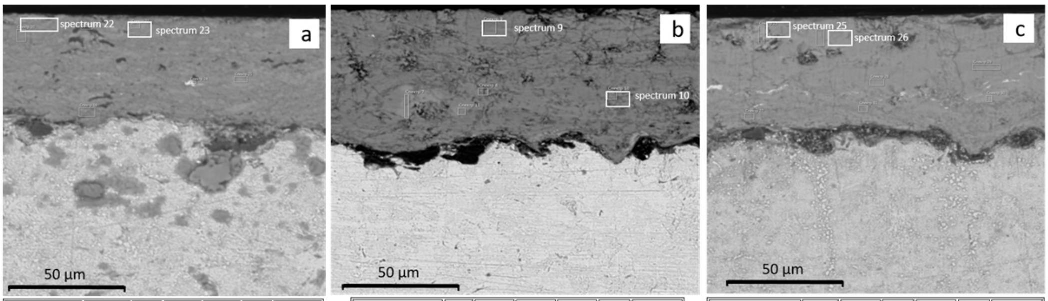



Figure 3. XRD patterns of coating based on $Ti_3SiC_2$ under different annealing temperature.




| Name | C | O | Si | Ti | Fe | Amount |
|---|---|---|---|---|---|---|
| Spectrum 22 | 11.29 | 9.75 | 13.56 | 64.89 | 0.51 | 100.00 |
| Spectrum 23 | 17.08 | 5.54 | 9.34 | 68.03 | - | 100.00 |

| Name | C | O | Si | Ti | Fe | Amount |
|---|---|---|---|---|---|---|
| Spectrum 9 | 7.85 | 13.65 | 5.29 | 72.28 | 0.92 | 7.85 |
| Spectrum 10 | 6.87 | - | 22.61 | 70.53 | - | 100.00 |

| Name | C | O | Si | Ti | Fe | Amount |
|---|---|---|---|---|---|---|
| Spectrum 25 | 6.48 | 22.09 | 3.67 | 66.56 | 1.21 | 100.00 |
| Spectrum 26 | 18.94 | 33.10 | 3.66 | 43.59 | 0.71 | 100.00 |

Figure 4. Cross section of coatings after thermal annealing: a) 700 ° C; b) 800 ° C; c) 900 ° C.

After annealing, the formation of $TiO_2$ phases and an increase in the intensity of the (103) and (108) reflections of the $Ti_3SiC_2$ phases are observed. After annealing at $T$ =900 ° C, a decrease in the intensity of the TiC line and an increase in the intensity of the $TiO_2$ line are observed, which indicates an increase in the thickness of the oxide layer. An increase in the microhardness after annealing is associated with an increase in the content of the $Ti_3SiC_2$ phases in the coatings. At the same time, after annealing at $T$ =900 ° C, the increase in microhardness is insignificant due to the increase in the thickness of the oxide layer. Thus, materials based on a $Ti_3SiC_2$/TiC compound with a nanolaminate structure combine the properties of ceramics and metals, are characterized by high values of elastic modulus (326 GPa) and shear (135 GPa), significant fracture toughness ($7 \div 12$ MPa $\cdot$ $m^{0.5}$), strength, crack resistance, heat resistance, chemical resistance and low density (4.52 g/$cm^3$) [1-4, 13].

Figure 4 presents the cross section of coatings after thermal annealing is shown. Coating thickness is 50 μm. The main factors affecting the pattern of the formation of detonation coatings are heating, melting (full or partial), deformation and spreading of particles over the surface. Moreover, oxide films and pores between particles must inevitably be present in the structure itself. With the help of EMF analysis, the elemental composition of coatings was determined, which confirms the formation of oxygen compounds after annealing. The increasing in the oxygen content in the surface layers of the coatings is observed under increasing in the annealing temperature to 900 ° C, as well as increase in the thickness of the oxide layer occurs. It is possible that the decrease in microhardness is associated with an increase in the thickness of the oxide layer.

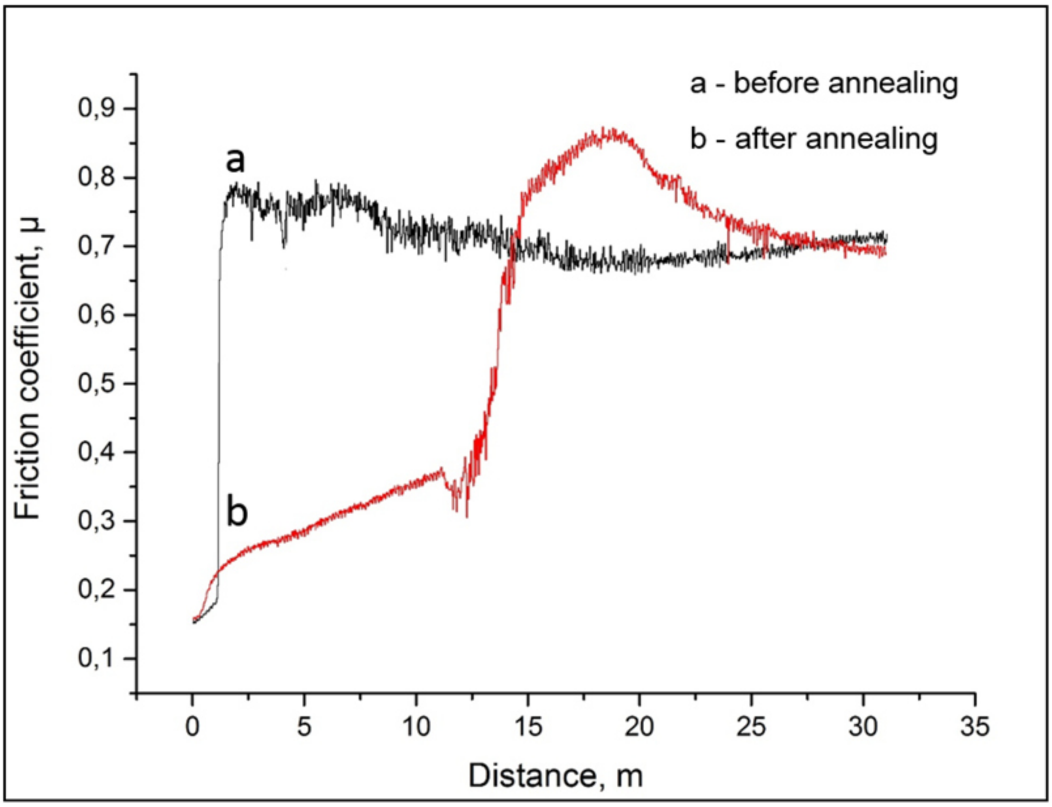



Figure 5. Results of tribological experiments of composite coatings $Ti_3SiC_2$/TiC before and after annealing at 800 ° C.

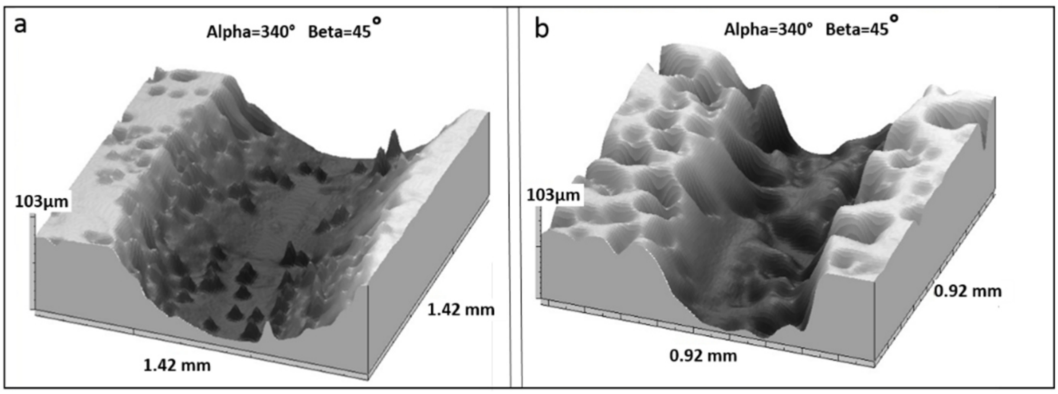



Figure 6. Track profiles of $Ti_3SiC_2$/TiC composite coatings: a) before annealing; b) after annealing at 800 ° C.

The results of tribological experiments of coatings showed that the temperature of thermal annealing and the structure of the coatings themselves have a significant impact on the value of the coefficient of friction of the surface of coatings and wear resistance. So, in the case of composite coatings $Ti_3SiC_2$/TiC before annealing, the friction coefficient is 0.65-0.70. After thermal impact at temperatures up to 800 ° C, the coefficient of friction at the initial stage of testing (up to 12.40 m) is 0.30-0.35 and there is a slight increase, in which the coefficient of friction monotonically increases from 0.35 to 0.70 as in the case before annealing (Figure 5). According to the result of X-ray phase analysis, an increase in the wear resistance of the near-surface layers of the $Ti_3SiC_2$/TiC composite material after 800 ° C is associated with the formation of $TiO_2$ and the presence of a large proportion of the hardening carbide phase TiC (Figure 3). In [15-18], it is stated that the oxide compound based on $TiO_2$ increases the wear resistance and strength of materials. It was established that during detonation spraying of $Ti_3SiC_2$ powders a coating with a higher microhardness and wear resistance is formed [19, 20].

With the help of profilometer was taken pictures of the wear track of the test samples before and after annealing (Figure 6). Assessing the wear resistance of the samples based on the geometrical parameters of the wear tracks it can be said that the depth of the sample after annealing is much smaller compared to the sample before annealing.

The wear rate under the influence of the tip is calculated based on the volume of the displaced material during the test, which was calculated by the following equation:

$$I = \frac{V}{F \times l}, \quad (1)$$

where: $I$ – wear rate, [$mm^3/N \cdot m$]; $l$ is the friction path, [m]; $F$ – nominal load, [N]; $V$ is the volume of the worn part, [$mm^3$]. As a result of the calculations, we obtained the data on the wear rate for the samples before and after annealing the composite coatings $Ti_3SiC_2$/TiC, which are given in Table 1.

Table 1.
Data on wear rate and wear volume of composite coatings $Ti_3SiC_2$/TiC.

| No. | Name of samples | Intensity of wear, $mm^3/N \cdot m$ | Wear volume, $\mu m^3$ |
|---|---|---|---|
| 1 | before annealing | 8450±1098 | 1763.6±229 |
| 2 | after annealing at 800°C | 1498±194 | 154.1±20 |

# Conclusion

It was found that the maximum microhardness of the $Ti_3SiC_2$/TiC composite material after annealing at a temperature of 800 ° C is due to an increase in the content of the $Ti_3SiC_2$ phase. It is possible that the decrease in microhardness at a temperature of 900 ° C and an increase in the wear resistance of the near-surface layers of the $Ti_3SiC_2$/TiC composite material is associated with the formation of $TiO_2$ after annealing.

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