THE INFLUENCE OF BORIDING ON THE PROPERTIES OF CEMENTED CARBIDES

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Abstract

Sintered carbide boriding is used either to form interlayers to increase the adhesion of deposited diamond layers to them by chemical vapor deposition (CVD) or to form layers on machine tools, which are then used without further processing in machining. To this end, it is necessary to ensure that the layer formed has the desired properties, i.e. adhesion to the substrate of the sintered carbide (SC), phase composition and integrity. The article deals with the properties of different types of SC after the boriding process. The aim of the experiment was to verify the adhesion of the formed layers to the SC substrate, their resistance to dynamic stress and the changes in corrosion resistance in a chemically active environment of a 3.5% aqueous solution of sodium chloride. The adhesion-cohesive behaviour of the SC substrate and the formed layer was evaluated by the Mercedes test. The dynamic load rating was evaluated using impact testing. The change in corrosion resistance of SC was measured as the change in corrosion resistance and corrosion rate using a potentiostat. These experiments were supplemented by metallographic analysis after the boriding process, both on the surface of the samples and on a metallographic section, where the hardness depth profile was also measured. The metallographic analysis revealed changes in the SC surface layer after boriding. The boride layers formed were in most cases with low adhesion to the SC substrate. In addition, due to the boriding process, SC resistance to dynamic stress and corrosion resistance to the selected corrosion environment was reduced.

Keywords: *Cemented carbide, boriding process, corrosive resistance, adhesive-cohesive behaviour*

1. INTRODUCTION

Sintered carbides are an important technical material used in the machining of non-ferrous metal, steel alloys or wood composite *(Sarin, 2014; Upadhyaya, 1998).* When machining non-ferrous metals, SC is often deposited with a thin diamond layer, which is created by CVD methods and aims to significantly increase the tool life in the cutting process *(Campos et al., 2015; Almeida et al., 2011)*. The adhesion and integrity of this layer to the SC substrate tends to be affected by the carbon reactions that diffuse from the formed thin layer to the SC substrate. Carbon reacts with cobalt to form a graphitic phase that worsens the deposition of a diamond thin film on the SC substrate *(Campos et al., 2015; Johnston, Baker and Catledge, 2016)*. In order to prevent the binder from reacting with the carbon from the deposited thin layer, so-called interlayers are formed between it and the substrate SC, which prevents the carbon from diffusing into the SC substrate. These include, for example, boron-based layers. The second alternative is to etch the surface of the SC substrate using various techniques which remove cobalt from the surface layer. The adhesion of the subsequently applied thin layer to the SC substrate is then largely dependent on the etching depth *(Haubner and Kalss, 2010).*

Boron reacts with the SC substrate to form various structural phases. Depending on the selected method and methodology of chemical-thermal treatment, it is possible to find borides of the CoB, Co_2B, CoWB or CoW_2B_2 types in the surface layer. The phase composition of the diffusion layer formed and its thickness then greatly affect the toughness of the SC substrate surface, its brittle fracture behaviour, and hardness. These properties then greatly affect the service life of the deposited thin diamond layers *(Zakhariev, 2011; Johnston and Catledge, 2016; Tang, Wang and Lu, 2000; Dearnley, Schellewald and Dahm, 2005; Dash and Nayak, 2016)*.

Most of the published scientific studies deal with the evaluation of the adhesive behaviour of diamond layers formed on the diffuse interlayer of borides in SC used in machining *(Dearnley, Schellewald and Dahm, 2005; Márquez-Herrera et al., 2016)*. The aim of this article is to present the behaviour of the diffuse layer of borides on different types of SC. Individual grades differ in the type and volume of the binder, as well as the tungsten carbide grain size. The article follows the experimental programme presented in the previous study (*Průcha, 2020)*, which was focused on the evaluation of the phase composition of the created diffusion layers and the evaluation of the mechanical and tribological properties of sintered carbides, which are also applied in areas other than machining of iron alloys and non-ferrous metals. This study focuses on the evaluation of the adhesive-cohesive behaviour of the substrate and the diffusion layer, its dynamic resistance, i.e. resistance to cyclic stress and corrosion resistance. All of these properties greatly affect the applicability of boride sintered carbides, either in the thin film forming process or in their direct application in the cutting process without deposition processes. The Mercedes-test was used to evaluate the adhesive-cohesive behaviour of the diffusion layer formed. Impact testing was used to determine the substrate resistance to dynamic stress. The change of the corrosion resistance depending on the selected environment and the corrosion rate was determined based on the potentiostat measurement. The above analyses were supplemented by metallographic analysis of the surface and cross-section of the SC after boriding and measuring the depth profile of hardness.

2. MATERIALS AND METHODS

2.1. Experimental material

Six different types of cemented carbides were selected for the experimental programme. The cemented carbides differed in the proportion of the binder (β-phase), chemical composition and the WC grain size (α-phase), see Table 1. Before heat treatment, the surface condition of the samples was made uniform by grinding and polishing. After the surface preparation of the samples, their chemical-thermal treatment was carried out by boriding.

Designation of the sample	Chemical composition	Binder content (wt. %.)	WC grain size (μm)
C	WC-Co	7.9±0.13	0.6±0.3
E	WC-(Ni-Co-Cr)	11.7±0.06	4.7±3.0
M	WC-Co	4.1±0.24	1.7±1.1
T	WC-Co	8.3±0.12	0.4±0.1
U	WC--Ni	8.4±0.07	0.8±0.8
X	WC-Co	13.5±0.22	6.9±4.3

Table 1. Types of SC used for the experiment. The chemical composition of the samples was determined by the EDX method on an area of 250 x 250 μm. The average grain size of tungsten carbide was determined by evaluating metallographic images obtained by SEM microscopy (Průcha, 2020)

2.2. Methods of experiments

The experimental material was processed in a Durborit boride powder backfill in a chamber furnace without introducing an inert atmosphere. The rate of temperature increase to the process temperature of 900°C was 15°C / min. The hold at this temperature was then 240 minutes. After this time, the samples were cooled continuously in the furnace, followed by an evaluation of their properties.

The first analysis was the metallographic analysis of samples. This was done using a PHILIPS XL30 ESEM scanning electron microscope, first on the surface of the samples and then on a metallographic cross section, in SE and BSE mode.

Before the transverse metallographic cross section was done, the adhesion-cohesive behaviour of the SC substrate with the boride surface layer formed was analysed. This was done using the Mercedes test. The test consists in injecting a conical diamond indentor into the surface of the prepared sample. In this case, a load force of 18.750 N was chosen. The resulting damage can be divided into six different classes, see Figure 1 below.

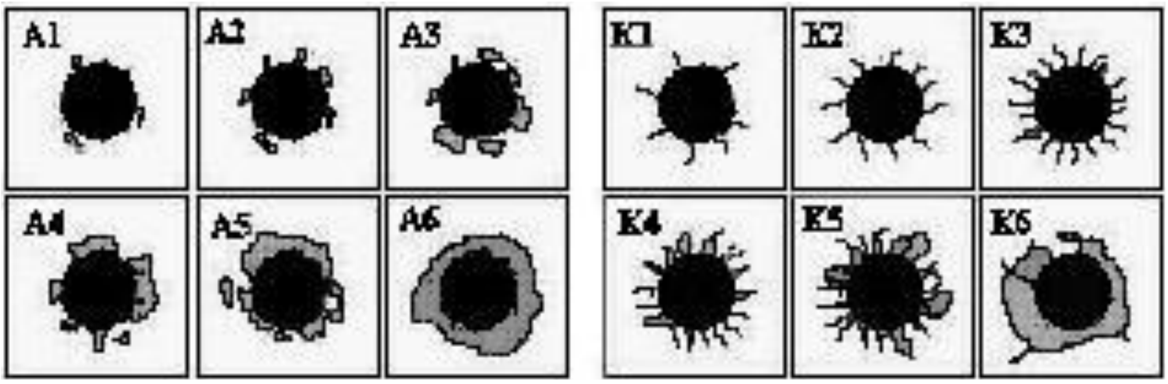

Fig. 1. Overview of violations that may occur after the Mercedes test. The table is divided into adhesive (A1-A6) and cohesive (K1-K6) thin-film failure *(Sosnová, 2007).*

An impact test was performed after analysis of the adhesion-cohesive behaviour of the SC substrate. The aim of this test was to assess how the formed layer affects the dynamic load rating of the SC substrate. The method consisted of cyclic impact loading of the surface of the analysed sample by striking with a 20 mm diameter ball indentor. The frequency of indentor strikes was 3 Hz, with an impact load of 1200 daN. The impact count was set at 20,000 cycles. The indentor strikes created impact craters on the sample surface. By measuring them, it was then possible to determine the change in the resistance of the SC substrate to its dynamic stress after boriding and to compare it with the original state.

In addition to the above, the change in corrosion resistance and corrosion rate of the samples after their chemical-thermal treatment was checked and again compared with the original state. These changes were measured using the SP150 potentiostat. The scanning range of the measurement was set to ± 2.5 V, the scan rate was 0.1 s / point, the environment was a 3.5% aqueous NaCl solution with a pH = 7.3.

The metallographic cross-section was used to measure the depth profile of the hardness from the sample surface to a depth of 50 µm. The aim of this measurement was to verify the effect of boriding on the change in the hardness of the SC. The hardness curve was measured using a DuraScan semi-automatic hardness tester, using the Vickers HV0.05 hardness measurement method.

3. RESULTS AND DISCUSSION

3.1. Metallographic analysis

The structure of the formed layer was studied both from the surface of the samples and then on a cross-sectional metallographic cut, see Fig. 2. In order to increase the contrast between the borided layer and the SC substrate, cuts were etched using Murakami etching.

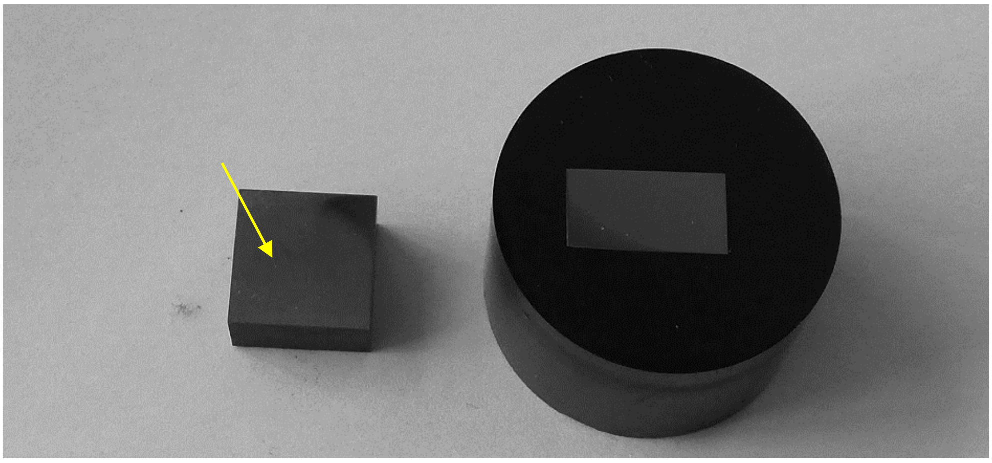

Fig. 2. On the left is the sample before embedding - showing the area that was analysed. On the right is the cross-sectional metallographic cut.

From Fig. 3 below, it is evident that a layer with a sharp transition between it and the substrate of the SC has formed on the sample surface; see samples M, T and U where boron diffuses to the depth of the substrate of the SC. In the case of coarse-grained grades of SC, i.e. X and E, this diffusion layer was not as pronounced. For samples U and E, the presence of a layer above the substrate SC was noted. A comparison of the above images, samples U and E, shows that this layer has a different integrity. For sample E, it was formed by separate islands, while for sample U, it formed over its entire area during the SC boriding process. Analysis of the chemical composition of this layer in sample U revealed that this layer was rich in nickel, see Fig. 4 below.

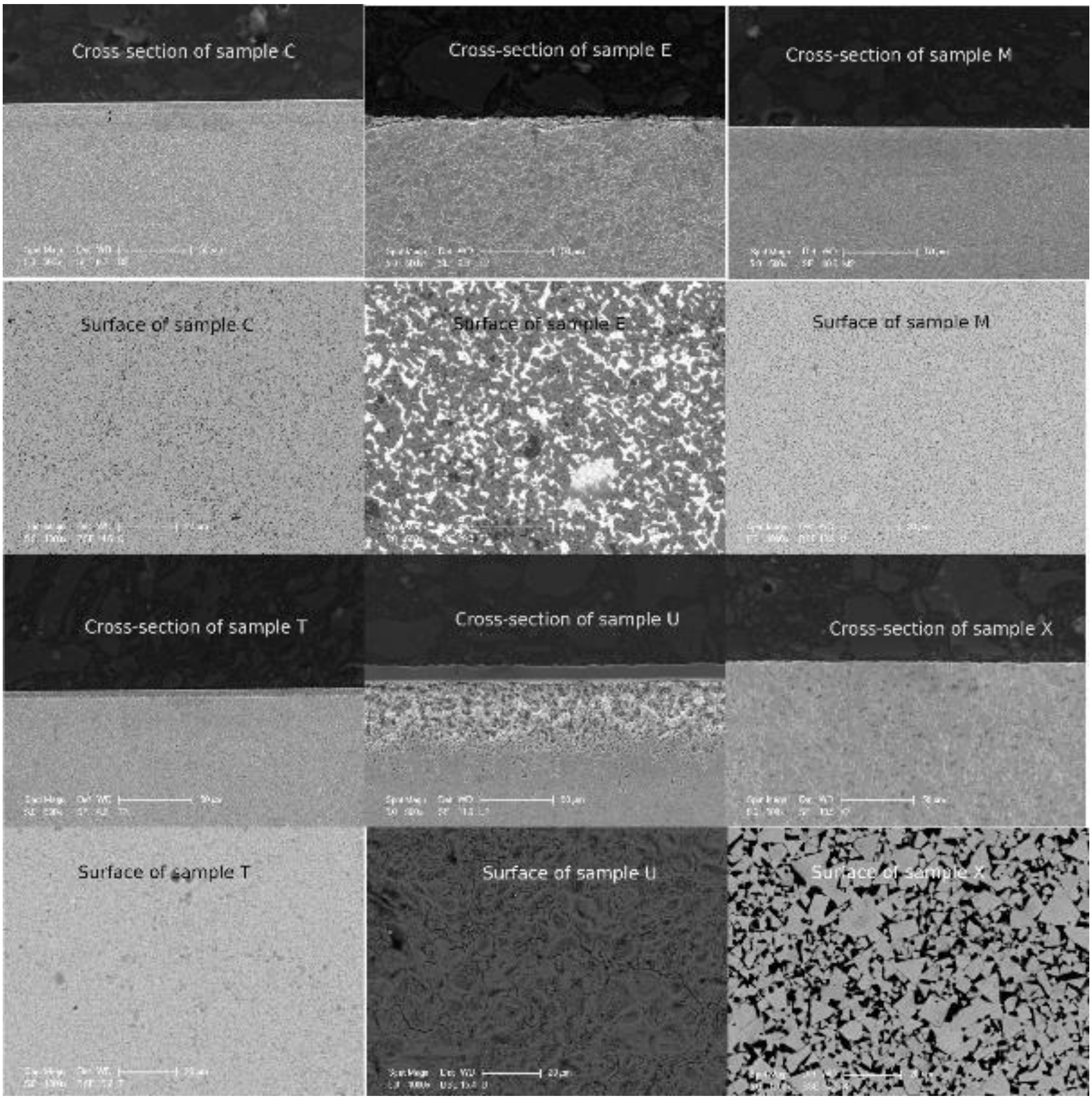

Fig. 3. Metallographic images of SC after boriding.

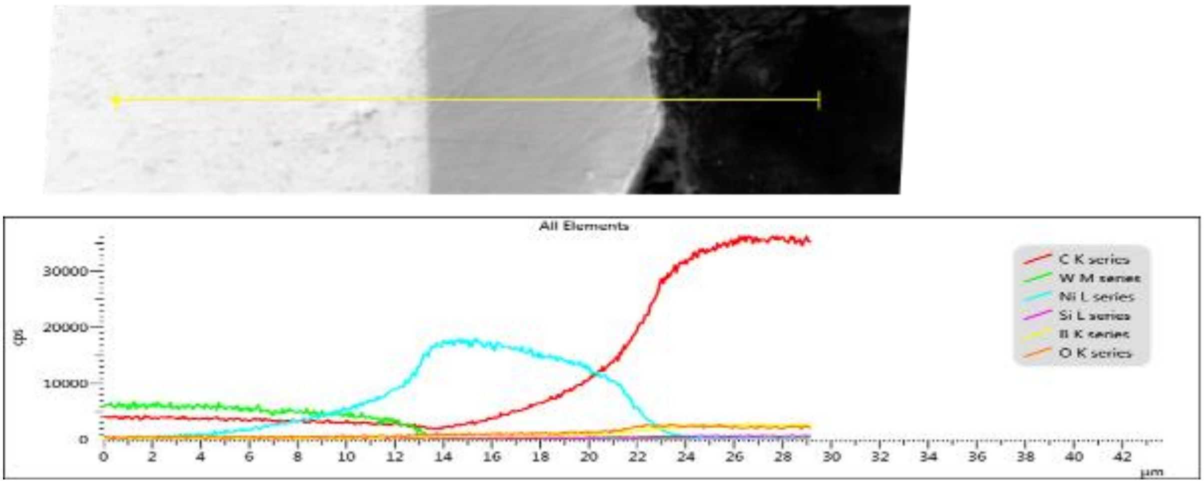

Fig. 4. The chemical composition of sample U. The chemical composition was collected from the substrate SC, through the region of the diffusion layer with a higher content of Ni to the area of the embedding compound with a high content of C.

The presence of a high proportion of nickel in the diffusion layer formed suggests that this layer had a higher toughness than the underlying SC substrate. The diffusion of nickel into the surface layer essentially relaxed the positions in the crystal lattice of the substrate SC below. Carbon diffusion and graphite formation at WC grain boundaries could then occur in these areas due to diffuse phenomena. The depth of the diffusion layer affected in this way could be determined by etching of the SC structure due to its more intense destruction by Murakami etching than the SC substrate and nickel-rich surface layer.

The higher toughness of the surface layer in sample U was confirmed by the analysis of the microhardness HV0.05. This analysis also showed that despite a faint diffusion layer crated on the coarse sorts E and X, there was a change in the hardness of their surface layers, see Fig. 5.

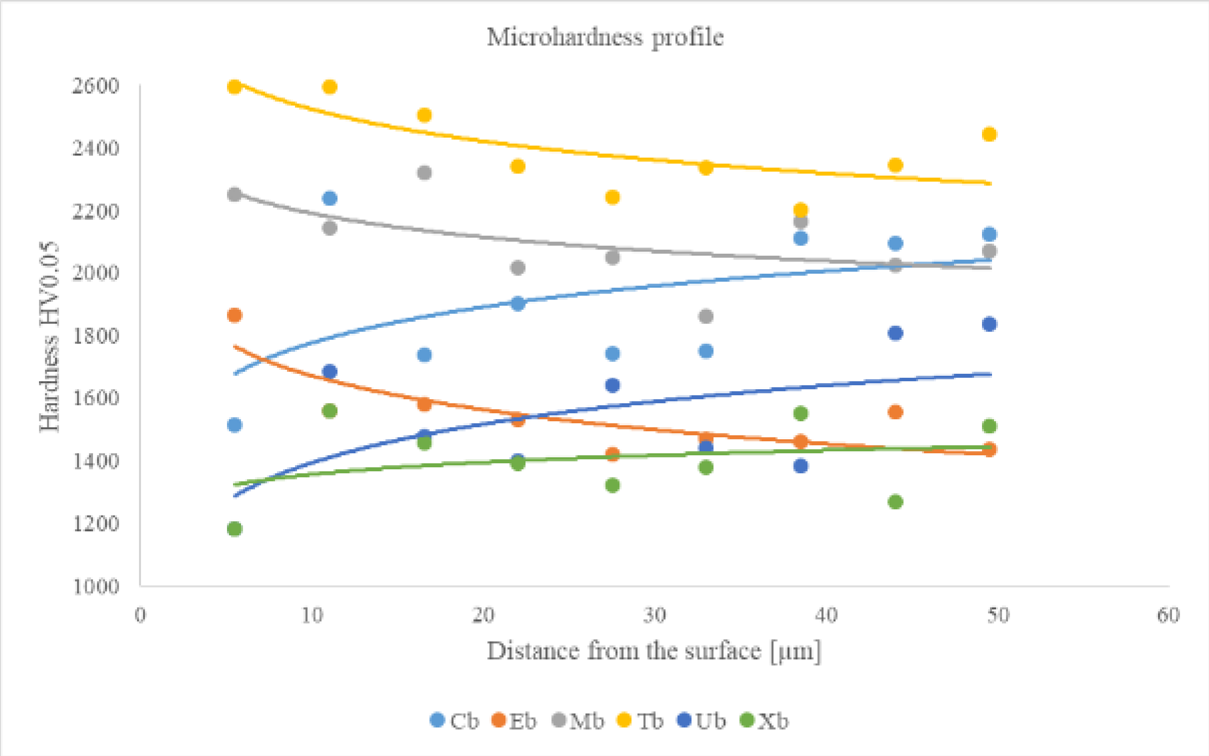

Fig. 5. Progress in the hardness HV0.05. Microhardness was measured from the sample surface to a distance of 50 µm. The distance between the indentations was 5.5 µm. The letter b next to the SC group mark indicates samples after the boriding process.

The results above show that for samples C, U, and X, the hardness in the surface layer of the substrate SC was reduced due to the boriding process. For sample U, this was associated with the formation of a nickel-rich surface layer. In the case of samples X and C, this is in turn was associated with the brittleness of the surface layer of the SC substrate after boriding. This brittleness was manifested by the cracking of the SC material around the indentation formed and its larger size, as opposed to indentations further away from the surface, see Fig. 6.

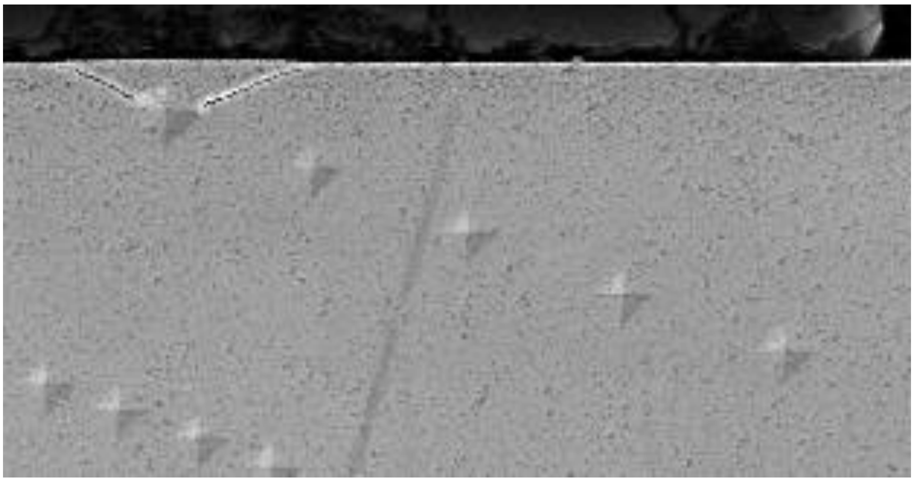

Fig. 6. Recorded cracks around the indentation of the type C sample.

In contrast, samples E, M and T increased the hardness in the surface layer of the SC substrate. The different behaviour of the analysed SC grades is connected with their differences both in the chemical composition of the binder and its volume and also with the size and distribution of WC grains. Due to these differences, different types of borides were formed in the surface structure of the analysed samples. Previously published results (*Průcha, 2020)*, show that the presence of CoB borides in the surface layer was observed in samples C and X. The presence of complex boride CoWB was reported for other sorts of SC with the cobalt binder. It follows that the presence of CoB borides reduces the hardness of the surface layer of the SC substrate and thus affects its further behaviour.

3.2. Adhesive properties and dynamic load capacity of samples

The analysis of adhesion-cohesive behaviour by Mercedes testing showed further differences in the behaviour of different types of SC after boriding, see Fig. 7 below.

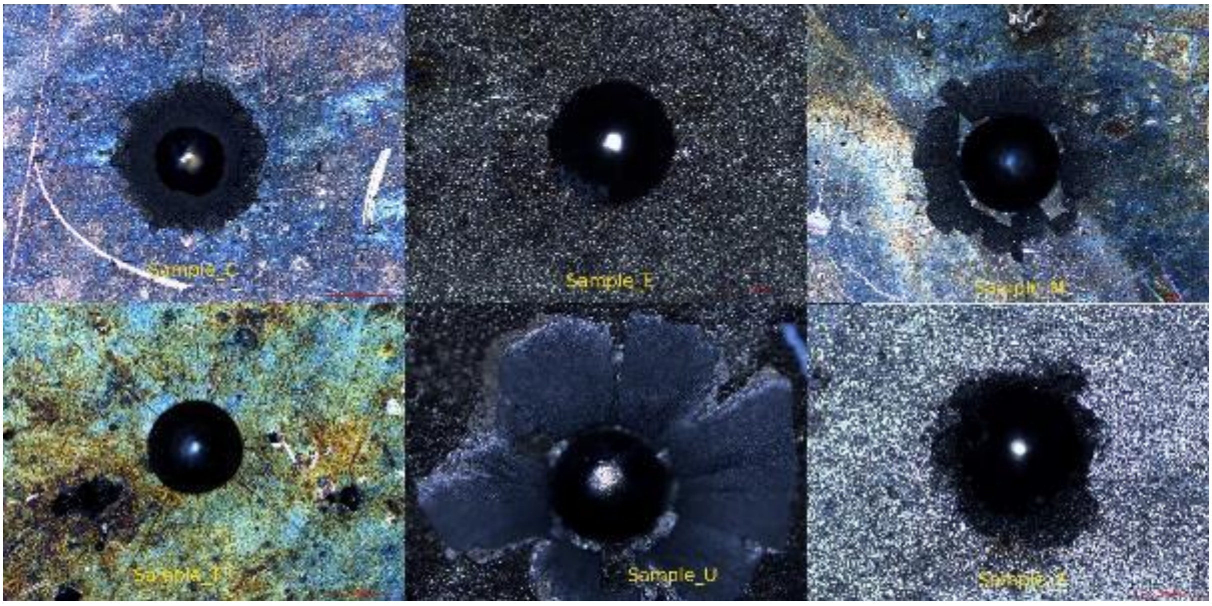

Fig. 7. Differences in adhesion-cohesive behaviour of analysed SC species after boriding. The analysis was performed using the Mercedes test (18.750N).

The above results show that the most significant adhesive failure occurred in samples C, M and U. In contrast, samples T and E showed the lowest susceptibility to adhesive failure. This is associated with the phase composition of the diffusion layer SC and the original microstructure of the substrate SC. Low adhesion of the diffusion layer was further associated with a sharp transition between it and the substrate SC, see Fig. 3. In addition to adhesive-cohesive behaviour, its resistance to cyclic dynamic stress is important for the further application of the borided substrate SC. This resistance was measured on the samples prior to the boriding process and after it. The results of this analysis are shown below, in Figure 8.

The results show that after the boriding process, almost all specimens have reduced resistance to dynamic loading. The only exception was Sample X, which increased.

This is probably related to the different volume representation of the structural phase of the borides in the diffusion layer formed. This difference is probably associated with different binder proportions between tungsten carbide grains, i.e. different cobalt-free lengths. However, in order to better understand this issue, further experiments will be needed to test this idea.

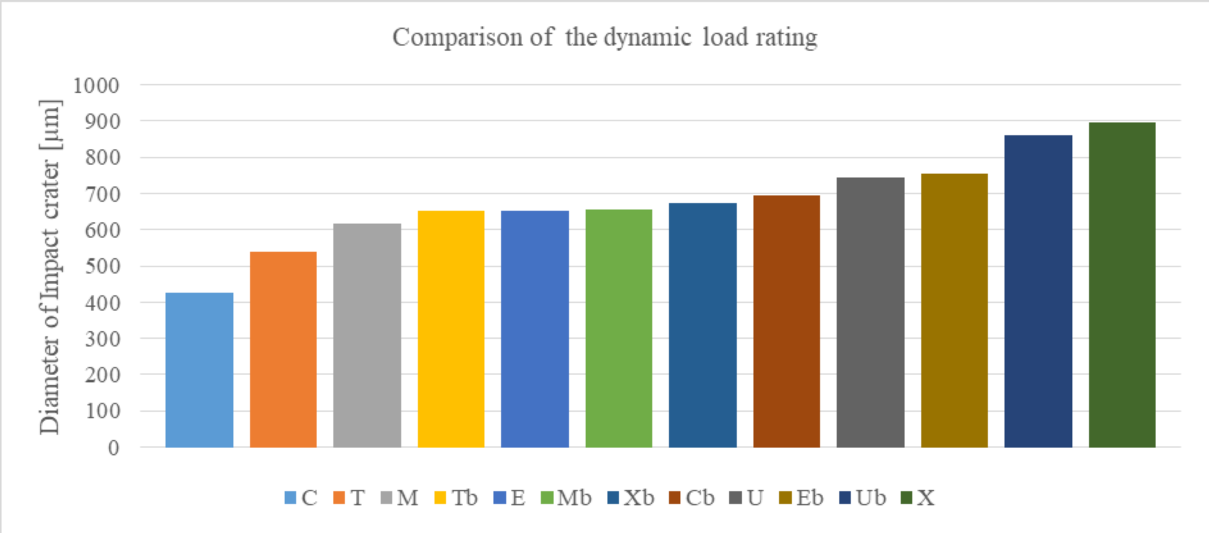

Fig. 8. Comparison of the impact crater sizes resulting from cyclic shock loading of the SC substrate before and after boriding. The samples with the smallest craters have the highest resistance to this type of load. The letter b next to the SC group mark indicates samples after the boriding process.

3.3. Corrosion analysis results

The aim of the last analysis was to assess how the formed diffusion layer affects the corrosion resistance of the SC substrate after the boriding process. A 3.5% aqueous NaCl solution was used as the corrosion medium. The polarization resistance and the corrosion rate at which SC degradation occurs was determined based on the evaluation of the polarization curves. The results of the analyses are summarized below, in Fig. 9. This image shows that the formed diffuse layer of borides has a lower corrosion resistance than the substrate SC without boriding and as a result there is a significant increase in the corrosion loss of the substrate of the SC. It is also evident that the cobalt binder grades of SC showed the highest corrosion resistance both before and after the boriding process. The lowest corrosion resistance was measured in the sample U with nickel binder, where it significantly decreased.

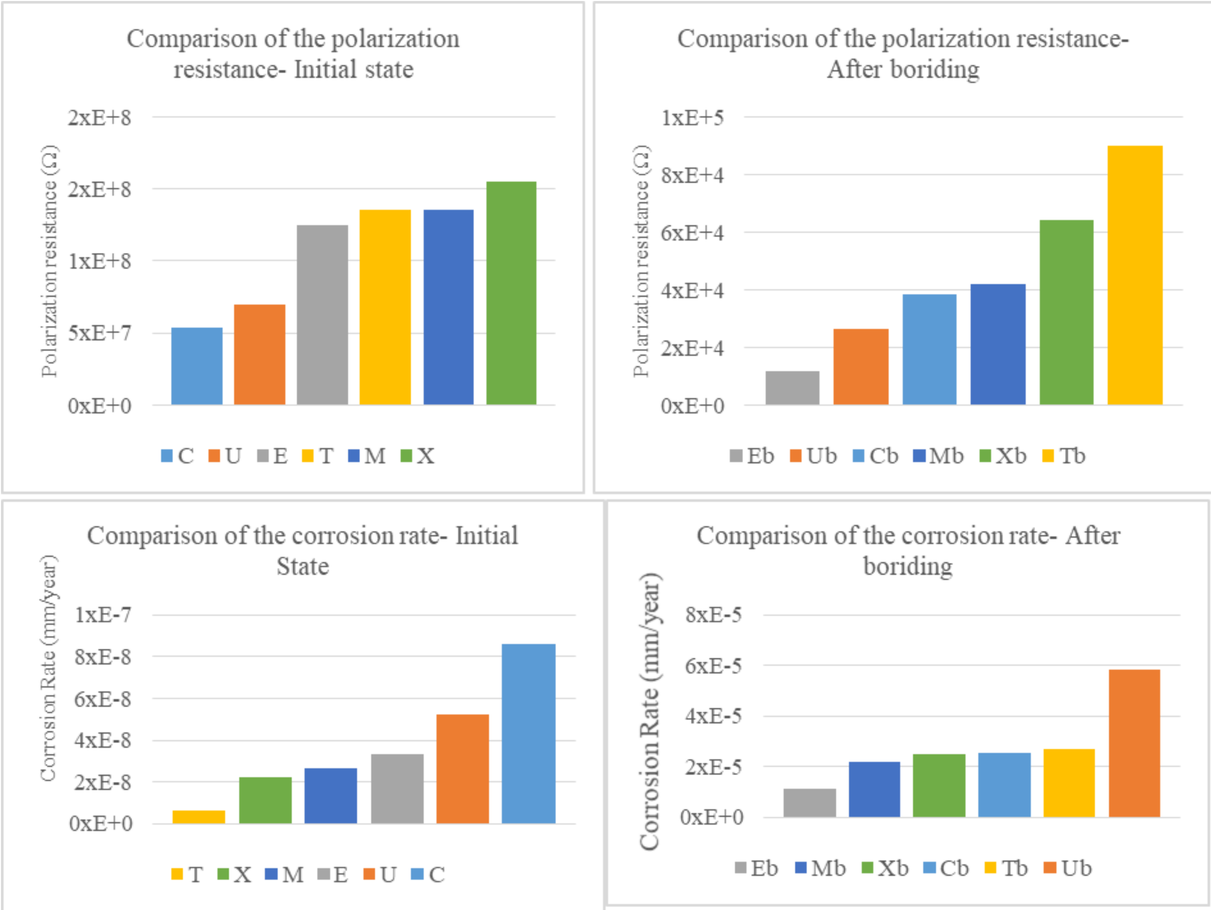

Fig. 9. Results of corrosion analysis of various SC grades before and after boriding. The top graphs show the change in polarization resistance. The bottom graphs show the difference in corrosion loss. The letter b next to the SC group mark indicates samples after the boriding process.

4. CONCLUSIONS

The aim of this research was to obtain new, additional information on the behaviour of various types of cemented carbides after the boriding process and thus to complement the information obtained in the previous experimental study. Based on the analyses performed, the following can be stated:

- The formed diffusion layer was separated from the SC substrate by a sharp boundary-transition, see Fig. 3. In most cases, diffusion processes occurred to the depth of the SC substrate volume. Samples with nickel binder (U) and SC grade with complex Co-Cr-Ni binder (E) also formed an amorphous layer above the surface of the SC substrate. This amorphous layer had different integrity. For samples of pure nickel binder (grade U), this layer formed over the entire surface of the samples. For samples with the complex binder (class E), this layer was formed locally.
- The resulting diffusion layer influenced the surface hardness of the SC substrate. For grades C, U and X, the surface hardness decreased, see Fig. 4. In the other samples, the surface hardness of the substrate SC increased. This was probably related to the phase composition of the formed diffusion layer of borides.
- The Mercedes test showed low adhesion of the formed layers to the SC substrate, especially in samples of type C, M, and U.
- Impact testing showed deterioration of dynamic load capacity after boriding in all SC grades except for X grades.

- In terms of corrosion resistance of SC, there was a significant decrease in corrosion resistance and an increase in the rate of corrosion loss in all analysed types of SC after the boriding process.

The above results indicate a deterioration in the properties of the SC after the boriding process, which substantially limits their applicability in processes technically important to them. These results summarize the first of a series of planned experiments with the process of boriding different SC grades. Future experimental studies will investigate the effect of changing the boundary conditions of the boriding process on the final quality of the formed diffusion layer on the substrate of various types of SC.

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