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Properties of Borided Cemented Carbides with Various Binders

Vojtěch Průcha[1,a*], David Bricín[2,b]

[1,2]University of West Bohemia, Univerzitní 8, 301 00 Plzeň, Czech Republic

[a]vprucha@kmm.zcu.cz, [b]bricda@kmm.zcu.cz

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Abstract. This paper explores the thermochemical treatment of cemented carbides (CC), specifically the boriding process. Six different types of CCs with different size of tungsten carbide (TC) grains were chosen as experimental materials. They contained binders of different chemical compositions. In five CCs, the binders were pure metals: cobalt (four of them) and nickel (one of them). In the six one, the binder was a complex Ni-Co-Cr-based alloy. Samples of the different types of CCs were prepared by grinding and polishing and then half of them underwent boriding process. The experiment aimed to find how boriding affects the final properties of CCs and their structure. Microstructural changes in the materials were examined using X-ray diffraction and optical and electron microscopy. Changes in mechanical properties and wear resistance were evaluated using hardness testing and the Ball on Disk test. The experimental results, for example, shown that CC with nickel binder had lowest wear resistance from all tested sorts of CC.

1 Introduction

Boriding is a thermochemical treatment method by which the surface of the workpiece is enriched with boron. In steel workpieces, a diffusion layer of Fe_2B or FeB-Fe_2B, which is 20 - 250 µm in thickness, is produced. This layer provides abrasion resistance and resistance to heat stress. Boriding is therefore primarily used for parts under abrasion loading. These include extrusion screws, drive chains and mandrels for glass production [1].

Boriding of WC-Co cemented carbides is a less-known field of application. It mainly involves cutting tools and is performed in two variants. In the first one, it produces a diffusion interlayer. This interlayer is intended to improve the adhesion of overlaying CVD diamond layers and to prevent reactions between the binder and the top layer. The reason is that the cobalt binder would react with carbon in the diamond layer, producing graphite and other undesirable carbon phases. These phases disrupt nucleation of the diamond layer, impairing its adhesion to the WC-Co substrate and reducing its mechanical properties [2, 3]. In the second variant, boriding becomes the final surface treatment of cutting tools. The tools can be used for machining those materials, in which the surface responds to cutting operations by hardening caused by martensitic transformation. Titanium and its alloys are among these materials. Boriding of WC-Co produces complex tungsten and cobalt-based borides. These phases possess high hardness and improve abrasion resistance of WC-Co in the machining process [4, 5].

The above overview shows that boriding is mainly used for cutting tool materials. A majority of them are composed of fine tungsten carbide grains and cobalt binder. However, this combination is not suitable for some applications, such as for cutting wood. In this case it is preferable to use cemented carbides with nickel binder or complex binders. It is because these binders, despite their less effective wetting of tungsten carbide grains during sintering, possess better corrosion resistance to acids in wood [6-9].

Therefore, this paper discusses boriding of cemented carbides which, apart from cobalt, contain other binders and are made of tungsten carbide powder with grains of various sizes. The goal of this experiment was to find differences between the resulting boride layers in terms of their thickness, hardness, phase composition and tribological properties. The findings were contrasted with values found for cemented carbides which lacked this type of layer.

2 Experimental Parameters

2.1 Materials and Heat Treatment

The experimental materials comprised six types of cemented carbides (CC). They were supplied by Ceratizit s.r.o. They contained binders of different chemical compositions and different sizes of WC grains, see Table 1.

Table 1: Cemented carbides used for the experiment. Chemical composition of the samples was measured by EDX on an area of 250×250 µm. The mean size of tungsten carbide grains was found by evaluation of micrographs.

Cemented carbide	Binder type	Binder amount [wt. %]	Grain size [µm]
C	Co	7.9±0.13	0.6±0.3
E	Ni-Co-Cr	11.7±0.06	4.7±3.0
M	Co	4.1±0.24	1.7±1.1
T	Co	8.3±0.12	0.4±0.1
U	Ni	8.4±0.07	0.8±0.8
X	Co	13.5±0.22	6.9±4.3

Before the experiment, uniform surfaces were prepared on all the samples by stepwise grinding and polishing. It was performed using Struers Tegramin 20 metallographic grinder. The surface preparation procedure is summarized below in Table 2. Afterwards, some samples were set aside for boriding.

Table 2: Surface preparation procedure for CC samples.

Process	Wheel type	Lubricant	Duration [min]
Grinding	MD-piano 220	Water	2
	MD-piano 500		2
	MD-piano 1200		2
	MD-piano 2000		2
Polishing	MD-Dac	DiaPro- MOL B3 suspension	5
	MD-Chem	OP-U suspension	0.5

No inert atmosphere was used in the boriding process which took place in Durborit powder in a box furnace. However, access of oxygen to samples' surfaces was reduced by enclosing the samples and the powder in a hermetically-sealed steel container. The cover of the container was sealed with fire-clay. The treatment temperature and time were 900°C and 240 minutes.

2.2 Characterization Methods

The treated specimens were examined using several separate steps. The first of them was metallographic analysis. It was performed using CarlZeiss Observer.Z1m optical microscope and PHILIPS XL30ESEM scanning electron microscope which was used for WC grain size measuring and it also offers the EDX analysis which was used for chemical composition evaluation of the samples before boriding. Microstructures of the samples were revealed by etching with Murakami's reagent. The etching procedure followed ASTM B657 – 18 [10]. Micrographs were analysed using Axio-Vision software. Measurement of mechanical and tribological properties was the next step in the analysis of the treated specimens. Their tribological properties were assessed using the ball-on-disk method, in which the sample is worn primarily by abrasion and adhesion. The wear volume was determined in accordance with ASTM- G99 [11]. Wear rate was expressed as the wear coefficient:

$$W = \frac{V}{L \cdot s} \tag{1}$$

Where:
V… wear volume
L… normal load Fn
s… total test distance

Changes in mechanical properties were assessed by hardness measurement using Vickers scale and 30 kgf load. Hardness values were input into calculations of changes of fracture toughness in the specimens. The calculation followed the Shetty procedure, equation 1 below [6, 12].

$$K_{IC} = 0{,}150449 \cdot \left(\frac{HV(30)}{\sum L}\right)^{\frac{1}{2}} \tag{2}$$

The phase composition of boride layers was measured using Bragg-Brentano method in the PANalytical X´Pert PRO X-ray diffractometer with $Cu_{K\alpha}$ radiation.

3 Results and Discussion

3.1 Metallographic and X-ray Diffraction Analysis

The goal of the metallographic analysis was to determine the thickness of the diffusion layer produced by the thermochemical treatment. Fig. 1 below shows the differences between the layers in various CCs. The graph in Fig. 2 shows the calculated thicknesses of the layers.

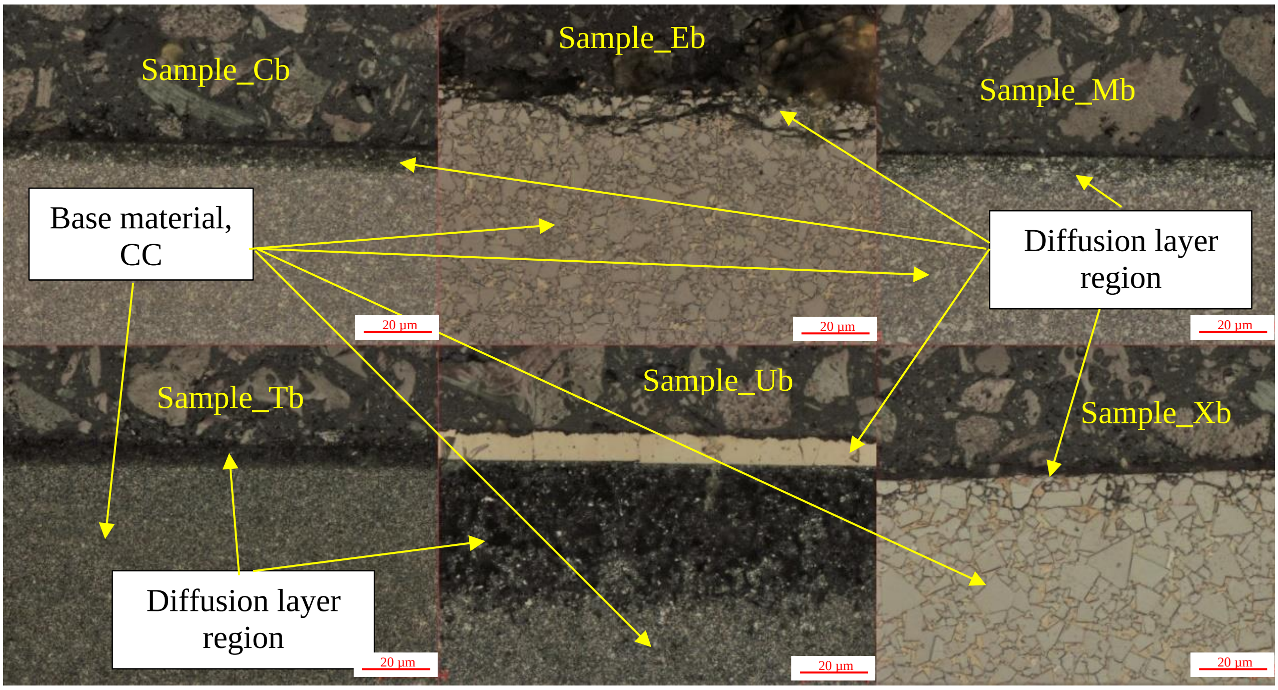


Fig. 1. Transverse metallographic sections through borided CC samples. The subscript (b) indicates borided samples.

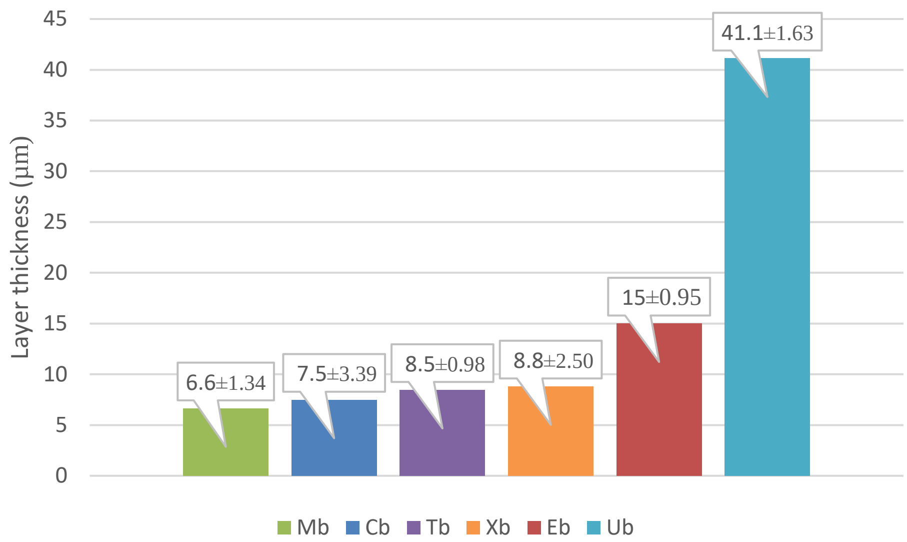


Fig. 2. Thickness of the diffusion layer in the different CCs. The thickness of the diffusion layer was measured on the transverse metallographic section, see Fig. 1.

Fig. 1 and 2 above show that the thickest borided layers were found in samples of the U-type CC with nickel binder. In this type of cemented carbide, the diffusion layer consisted of two regions: the diffusion region with a gradual transition into the CC base material, and the region above it. There is a sharp interface between them, as seen in Fig. 1. It was found by EDX analysis that the layer with the sharp interface was nickel-based. It probably consisted of Ni_2B, Ni_3B borides or its amorphous based on Ni-B. In the CCs with Co binder, the layer only comprised the diffusion region. There were no appreciable differences between the thickness of the layer across all samples. The average thickness was about 6-8 micrometre. The graph in Fig. 2 shows the effects of WC grain size on the thickness of the diffusion boride layer. The finer was the WC grain, the greater was the thickness of the layer. It proved impossible to determine the thickness of the diffusion layer by metallographic analysis in coarse-grained CCs. This was due to the partial or even complete failure of the surface in samples with the diffusion layer, as seen in Fig. 1.

In addition to metallographic examination, X-ray diffraction analysis of phase composition was performed, as shown in Figure 3 below. This analysis was carried out on the surface of the borided samples.

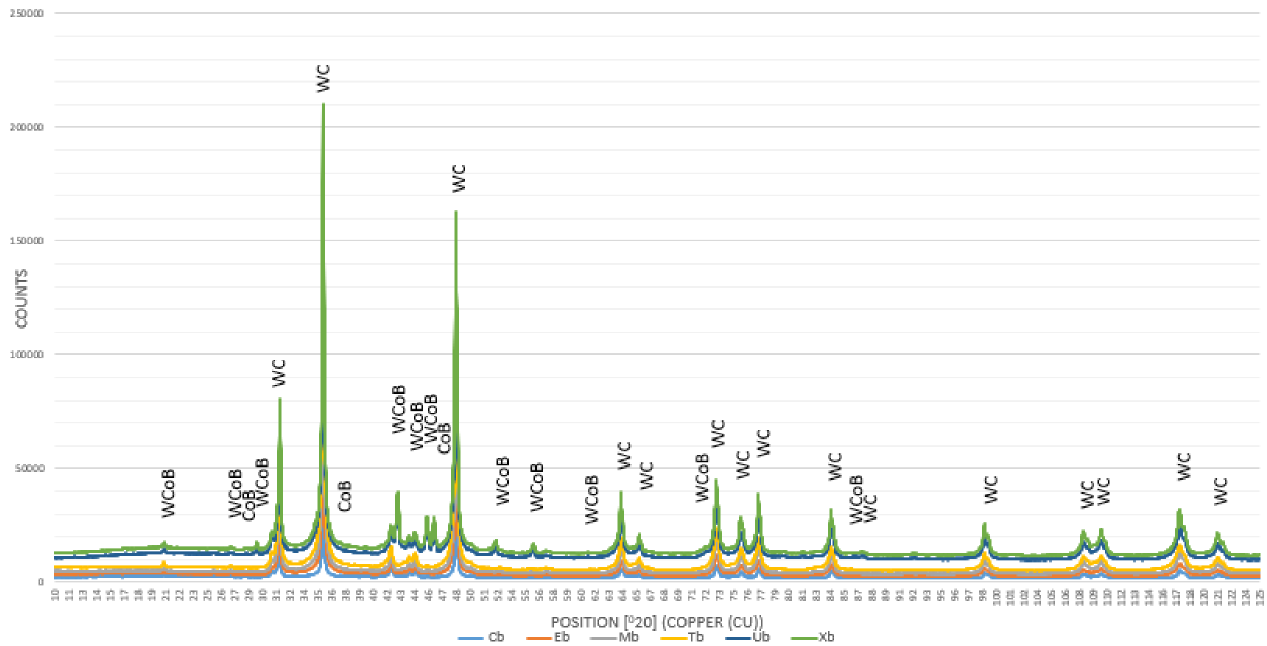


Fig. 3. Phase composition of diffusion layers.

The graph in Fig. 3 above shows that the diffusion layers in most samples with the cobalt binder consisted of the CoWB phase. In addition, CoB boride was found in samples C and X. In the sample that contained nickel binder (type U), the diffusion layer on top of the substrate surface was probably amorphous contain B-Ni-W based phase. It was reflected in low signal intensity during measurement when was used a low angle of signal collection. This fact is seen for thin amorphous layers.

The phase composition of the diffusion layer predetermines the possible applications of the thermochemically-treated CC. The presence of the complex boride CoWB improves the wear resistance of the surface [13]. It is because this boride has higher hardness than other borides, such as CoB, Co_2B or Ni_2B, Ni_3B [13, 14]. Hence, the CoWB diffusion layer can be applied as the surface finish for cutting tools. On the other hand, the last-named cobalt and nickel borides also enhance fracture toughness of the surface layer of cemented carbide. The presence of graphite in the sub-surface layer of the CC with nickel binder might have a positive impact on the sliding properties of the substrate. However, it is a brittle phase which substantially compromises mechanical strength of cemented carbide, as does the large amount of the carbide phase.

3.2 Mechanical and Tribological Characteristics

The aspects of cemented carbides which depend on phase composition of the diffusion layer include their mechanical properties and wear resistance as well as their potential applications. Changes observed in hardness and fracture toughness K_{IC} of the surfaces of borided CCs are shown in Figs. 4 and 5.

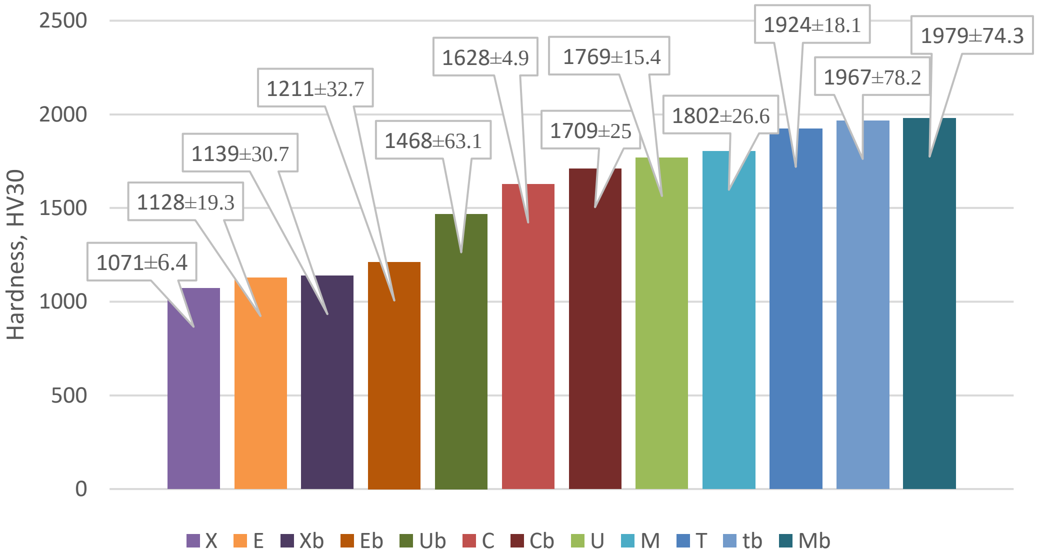


Fig. 4. The impact of boriding on the surface hardness of different types of cemented carbides. The subscript (b) indicates borided samples.

The graph in Fig. 4 above shows that boriding increased surface hardness in almost all CCs. The only exception were the samples with nickel binder which exhibited reduced hardness after boriding. It was probably associated with formation of the amorphous B-Ni-W diffusion layer on the interface with the substrate. The decline in surface hardness, however, was accompanied by an increase in fracture toughness of the surface layer, as indicated in Fig. 5. The hardness of the surface layer in all the CCs increased, on average, by approximately 100 points on the Vickers scale. In coarse-grained CCs, i.e. types E and X, fracture toughness dropped. It was probably associated with initiation of cracks at the interface between the diffusion layer and the substrate, as seen in Figure 1. The likely cause was the high stresses generated by the thermochemical treatment. By contrast, in fine-grained CCs the fracture toughness increased, as shown in Fig. 5 below.

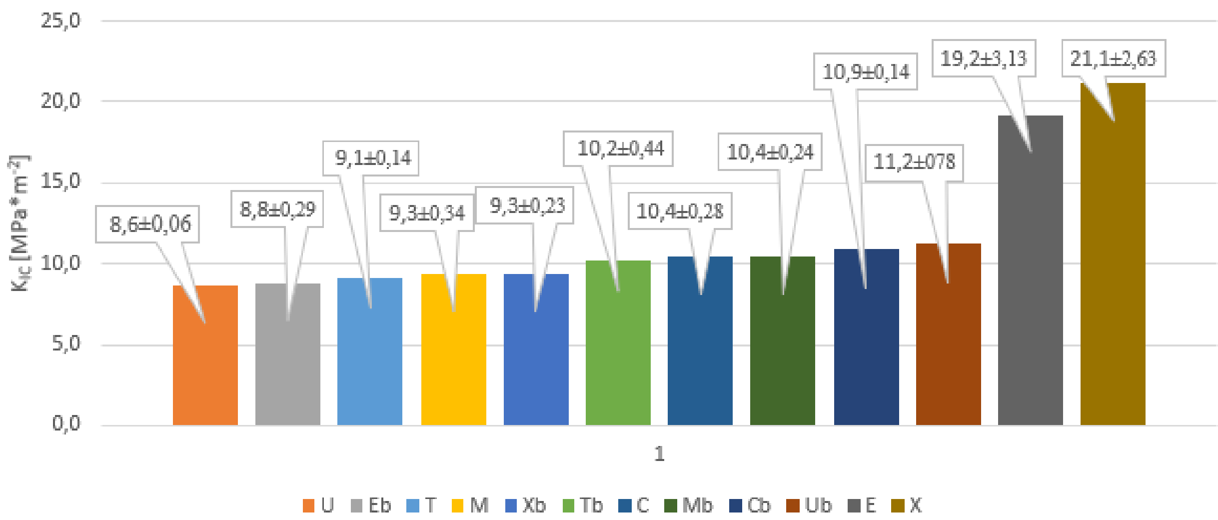


Fig. 5. The impact of boriding on the surface fracture toughness of different types of cemented carbides. The subscript (b) indicates borided samples.

The diffusion layer was found to control not only hardness and fracture toughness of the surface layer but also the resistance of the cemented carbide to wear, Fig. 6.

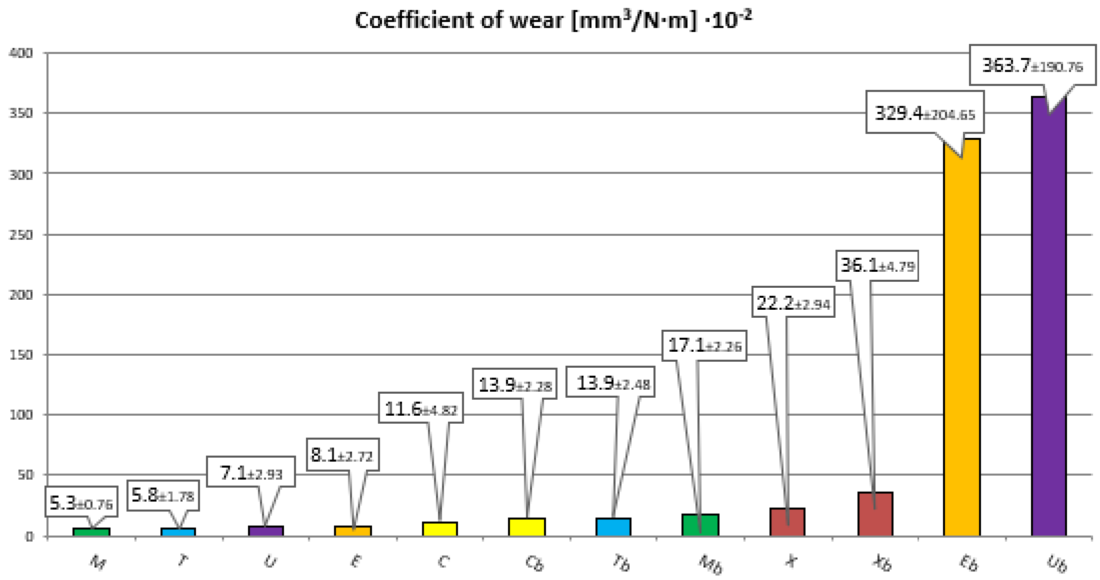
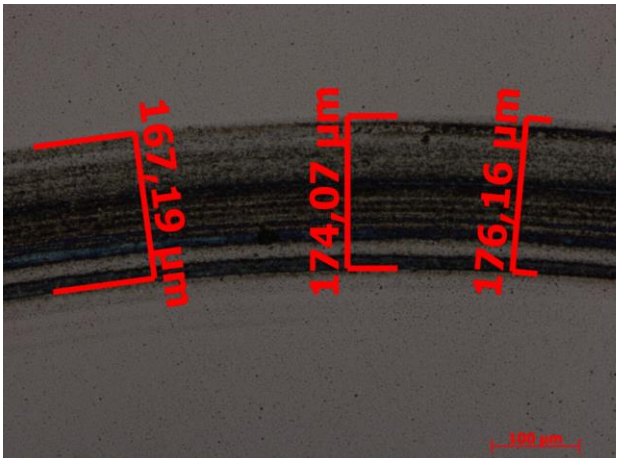


Fig. 6. Effect of boriding on the resistance of cemented carbide to contact loading. In this graph, contact loading is expressed in terms of the wear coefficient. The subscript (b) indicates borided samples.

As seen in the image above, the diffusion layers reduced the resistance of the surface to this type of contact loading. The most severe wear was found in U samples which contained nickel binder. Here, interaction between boron and nickel produced a diffusion layer on the surface of the substrate. This layer was not solid. It wore off during the test by both abrasion and adhesion. Wear tracks in a specimen of the U-type cemented carbide are compared in Fig. 7. On the left, there is a portion of a wear track in specimen C prior to boriding; on the right there is a wear track after boriding.



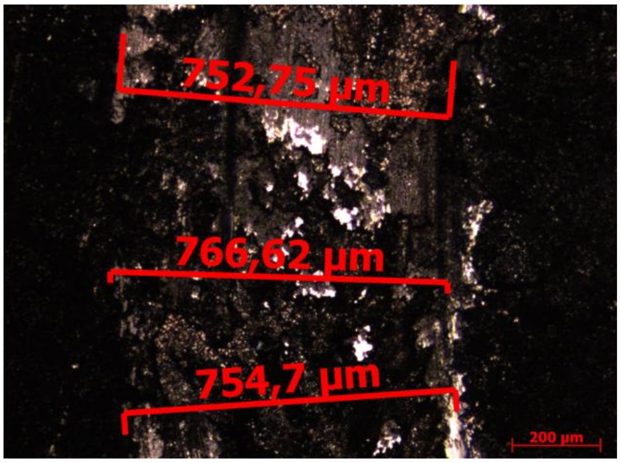


Fig. 7. On the left, there is a portion of a wear track in specimen C prior to boriding; on the right there is a wear track after boriding. In the first case, only abrasive wear was involved, whereas in the second case, abrasive wear was combined with appreciable adhesive wear.

In coarse-grained CCs of E and X types, wear resistance was found to decrease. As in the previous case, this was probably linked to the sub-surface cracks found in the samples, Fig. 1.

4 Conclusion

The aim of this experimental study was to verify the usability of boriding for various types of cemented carbides. The experiments led to the following conclusions:

- The chemical composition of the binder and the size of tungsten carbide grains affect the thickness of the diffusion layer of borides. The largest layer thickness was found in cemented carbides with nickel binder. In CCs with cobalt binder, grain size was found to affect the thickness of the diffusion layer. It was found that reducing the WC grain size increases the thickness of the diffusion layer of borides.
- Diffusion layer of borides had a favourable impact on the hardness of all CCs, except the one with nickel binder. In this type of cemented carbide, hardness decreased substantially. It was probably due to a tough nickel-based boride layer which had formed on the surface of the substrate.
- In coarse-grained CCs, the diffusion layer suffered delamination, causing a decline in fracture toughness K_{IC}. This was observed in type X and E cemented carbides. The same occurred in the cemented carbide with nickel binder. Here, the likely cause was diffusion of nickel into the boride layer on top of the substrate. This cemented carbide became brittle due to less nickel in the substrate and due to newly-formed graphite phase. As a result, its fracture toughness decreased. Fine-grained CCs with cobalt binder experienced a slight increase in fracture toughness in relation to the phase composition of the boride layer.
- In all the types of CCs, tribological testing demonstrated a reduction in their resistance to wear. The most severe wear was recorded in the CC with nickel binder. This finding is related to nickel diffusion in the surface of the substrate where it reacted with boron to form a amorphous diffusion layer. As discussed above, this fact along with the presence of graphite caused substrate embrittlement and significant wear.

The above results were found in samples which had been borided under conventional thermochemical treatment conditions. The next stage of this experimental investigation will focus on the effect of changes in parameters of boriding on the properties of boride layer in the types of CCs examined in this study. It will also explore the impact of heat treatment thermochemical treatment methods on the properties of other cemented carbides.

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