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SELECTED PROPERTIES OF DIFFUSION BORONIZED LAYER MODIFIED WITH COPPER

Summary

The paper presents the results of studies on microstructure, microhardness, fracture toughness, cohesion and wear resistance of copper modified boronized layers. Borocopperizing process consisted in simultaneous introduction of metallic copper and amorphous boron by diffusion. Borocopperized layers, similarly to boronized layers have a single-zone structure. It was observed that diffusion borocopperizing had a positive effect on microhardness, brittleness, cohesion and wear resistance.
***Key words**: boronizing, borocopperizing, microstructure, microhardness, fracture toughness, cohesion, wear resistance*

WYBRANE WŁAŚCIWOŚCI WARTSYW BOROWANEJ DYFUZYJNIE MODYFIKOWANEJ MIEDZIĄ

Streszczenie

W pracy przedstawiono wyniki mikrostruktury, mikrotwardości, odporności na kruche pękanie, kohezji i odporności na zużycie przez tarcie warstw borowanych modyfikowanych miedzią. Proces boromiedziowania polegał na dyfuzyjnym wprowadzeniu miedzi metalicznej i boru amorficznego. Otrzymane warstwy miały podobnie jak warstwy borowane budowę jednostrefową. Stwierdzono korzystny wpływ boromiedziowania dyfuzyjnego na mikrotwardość, kruchość, kohezję oraz odporność na zużycie przez tarcie.
***Słowa kluczowe**: borowanie, boromiedziowanie, mikrostruktura, mikrotwardość, odporność na kruche pękanie, kohezja, odporność na zużycie przez tarcie*

1. Introduction

There are many different materials treatments processes aimed at modifying the surface layer [1, 6, 8, 19, 25, 26] such as boriding processes [15, 19]. The main objective of surface modification is to improve properties such as microharndess [2, 3, 6, 13-23], wear resistance [3, 15, 17, 19], brittleness [7, 9, 11, 16, 21, 22, 23], and good cohesion between the layer and the substrate [24, 26]. The current trend in the materials development involves complex combinations of the known processes, aiming to obtain improved properties in the new layers. One method of surface layer modification is diffusion boronizing, which improves properties such as microhardness, wear resistance and corrosion resistance. Diffusion boronizing is one of heat treatment processes involving the saturation of the surface steel layer with boron, a result of which a needle-like structure composed of iron borides FeB and Fe_2B with microhardness up to 2000 HV is obtained. The advantage of such layers is increased microhardness and wear resistance, heat resistance up to 800°C, corrosion resistance, among others in many acid and alkaline solutions. Boronized layers despite the many advantages have also some disadvantages, such as the brittleness of the subsurface zone (FeB), which may be manifested by spalling and flaking from the substrate, and a high microhardness gradient between the layer and the substrate [15, 19]. Subsurface brittleness can be reduced by formation of a single-phase boride layer, which is composed of only iron borides Fe_2B [15], or by modifying with elements which are introduced by various methods [2-5, 10, 12-14, 17, 18] among others laser modification [4, 5, 15]. Currently, the research of many authors focuses on to the modification of the surface layer, which aims to reduce brittleness without degrading other properties.

Yu. A. Balandin [2] produced boronized and borocopperized layers in boronized and borocopperized processes in the fluidized bed. The author concluded that the microhardness gradient from the surface to the substrate for borocopperized layer was milder than for boronized layer and the borocopperized layers have higher wear resistance compared to boronized steel.

What is interesting Przybyłowicz et al. [18] found that regardless of the type of processes (boriding, borosulphurizing, borocopperizing, boronickelizing) and their parameters two-phase layers of iron borides are obtained with varying thicknesses and microhardness profiles. They conducted a boriding process on 45H steel with pastes with added modifiers S, Cu, Ni. Research has shown that the introduction of modifiers such as S and Cu causes a reduction in boronized layer thickness. The authors found that the addition of Cu and S reduces the hardness of the layer, and that the boronickelized layer has a hardness similar to the boronized layer. Furthermore, tribological test results showed that the addition of S and Cu to boron paste increases wear resistance in comparison to boronized layer. The authors didn't find significant difference in wear resistance of boronized layer modified with nickel.

Nowacki [10] investigated reactionary sintering of mixture of iron with copper and boron powders at a concentration of 5-15% copper and 9% boron. He found that the structure and properties of the cermets vary depending on chemical composition of the powder mixture and sintering parameters. The best cermets were obtained at weight concentration of 9% boron and 5-10% Cu and they consisted of two phases: hard grain iron boride - copper - $(FeCu)_2B$ (1700 HV0.1) as a reinforcement and relatively softer and more ductile eutectic mixture of FeCu - $(FeCu)_2B$ ($\alpha+\beta$) (300-400 HV0.1) with a small addition of iron as the matrix. The resulting reactionary sintered cermet had high hardness and wear resistance.

On the basis of the literature it can be concluded that the modifying elements such as copper improve the properties of the boronized layers. They make it possible to obtain a smooth transition of hardness from the surface to the substrate; they also increased wear resistance.

2. Research methodology

The aim of the study was to evaluate the impact of modifications of copper boronized layers by studying changes in microstructure, microhardness profiles, fracture toughness, cohesion and wear resistance. Borocopperizing consisted of simultaneous introduction of metallic copper and amorphous boron by diffusion. To the boronizing mixture a powder of 2% and 4% metallic copper was added. The material investigated was C45steel and its chemical composition is given in Table 1. The ring-shaped specimens were used for the study, and they had the following dimensions: external diameter 20 mm, internal diameter 12 mm and height 12 mm.

Table 1. Chemical composition of C45 steel [wt %]
Tab. 1. Skład chemiczny stali C45 [%wag.]

C	Mn	Si	P	S
0.42	0.72	0.19	0.008	0.03

Diffusion boronizing was performed at 950°C for 4h using gas-contact method. The boronizing mixture used in the process contained: amorphous boron, KBF_4 as activator and carbon black as filler. Diffusion borocopperizing was performed at 950°C for 4h and boronizing mixture used in the process contained: amorphous boron, metallic copper in the amount of 2% and 4%, KBF_4, and carbon black. After boronizing and borocopperizing the specimens were hardened in water from 850°C to room temperature and then tempered at 150°C for 1h.

Microstructure observations were performed using an optical microscope Metaval Carl Zeiss Jena with a camera 2300 3.0 MP and Live Motic Images Plus 2.0 Resolution software. The samples were first polished by using abrasive papers of different granularities, and, finally with Al_2O_3. Specimens were etched in 2% HNO_3 solution.

To determine microhardness profiles a ZWICK 3212 B Vickers hardness tester was used with indentation load of 100 G (HV0,1). Vickers hardness measurements were made using a Vickers/Brinell GPM 308/258 hardness tester. The studies were carried out according to standard PN-EN ISO 6507–1 [28].

Fracture toughness study was conducted with the Palmqvist method. This method consisted of Vickers hardness indentation performed with a load of 147 N, 196 N, 294N, followed by diagonal measurements of indentations and the lengths of cracks coming out of corners of indentations (Fig.). As a measure of susceptibility to sudden fracture of diffusion boronized and boronickelized layers a critical stress intensity factor Kc was assumed, expressed by the formula [11, 24]:

$$\mathbf{Kc = AP/c^{3/2}\ [MPa \cdot m^{1/2}]}$$

where:
P – load [N],
c – radial crack length measured from the center of indentation [m],
A – a constant,
$A = 0.028\ (E/H)^{1/2}$
E – Young's modulus of iron boride Fe_2B [12, 23],
$E\ Fe_2B = 2.9 \cdot 10^5$ [MPa],
H – hardness [MPa].

The value A is the residual-indentation coefficient which depends on hardness-to-modulus ratio (H/E) of the borided layer. The constant A is $0.028\ (E/H)^{1/2}$ where E and H are the Young's modulus and hardness of boride layer, respectively. P is the applied load and the value of E for Fe_2B is approximately $2.9 \cdot 10^5$ MPa for fracture toughness calculations, and c is the sum of half diagonal length of Vickers indentation and crack length generated at the corners of the indentation.

Adhesion tests of surface layers were conducted in accordance with the standard VDI 3198 [24, 30]. This method consisted of comparing Rockwell indentations [29] with scale standards appearing in Figure 1. A standard Rockwell tester as a destructive quality test for examined layers was employed in this study and damage to the layers was compared to the adhesion strength quality maps HF1-HF6 (Fig. 1). In general, the adhesion strength quality HF1-HF4 defined acceptable failure, whereas HF5 and HF6 represented unacceptable failure [24, 28]. Rockwell hardness test was performed on PRL type hardness tester 610A.

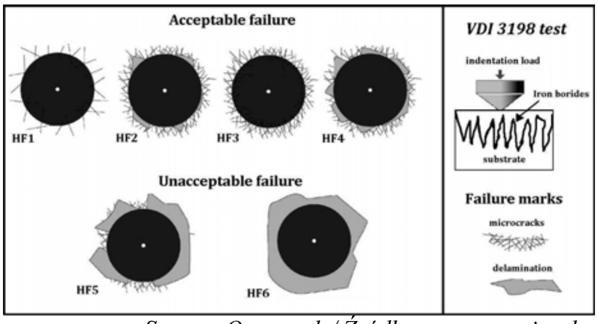

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Fig. 1. Scale of models to test cohesion [24, 30]
Rys. 1. Skala wzorców do badania kohezji [24, 30]

Wear resistance tests were carried out with tribometer MBT-01 type Amsler [27]. A ring as specimen and sintered carbide plate S20S as counterspecimen were used to examine wear resistance. Wear resistance tests were carried out under the load F = 147 N and at specimen rotation speed of n = 250 rev/min, in dry friction conditions. Wear resistance was evaluated by specimen mass loss (Δm [mg]) per friction surface (S [cm^2]) in a time unit (t [h]). Wear intensity coefficient (Iw) was determined from the equation: $Iw = \Delta m/(S \cdot t)$ [mg / ($cm^2 \cdot h$)].

Corrosion resistance of laser modified layers was studied in a 5% solution of NaCl at temperature 22°C on the surface of 50 mm^2. The studies were performed on a potentiostat-galvanostat ATLAS 0531 EU & IA ATLAS SOLLICH. Auxiliary electrode was a platinum electrode, and the reference electrode was a calomel electrode. The test procedure and recording of the results were performed using AtlasCorr and AtlasLab computer programs. The polarization of the samples was carried out in the direction of the anode in the range of potentials from -1.5 to 1.5 V. The study was conducted at a rate of change in potential of 0.5 mV/min. Based on the analysis of current curves potentiodynamic corrosion and corrosion potential were determined.

3. Results and discussion

Microstructure of boronized layer after hardening and tempering of 150°C is shown in Figure 2. This layer had a needle-like structure and was closely related to a martensite substrate. It was composed of iron borides FeB and Fe_2B. The thickness of the produced boronized layers was about 100 µm.

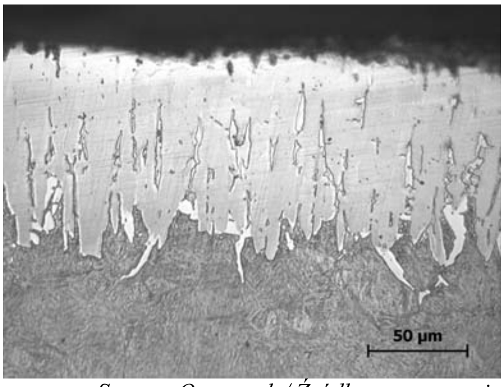

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Fig. 2. Microstructure of boronized layer

Rys. 2. Mikrostruktura warstwy borowanej

Microstructure after diffusion borocopperizing is shown in Figures 3a and 3b. Borocopperized layers consist of a single zone, looking like iron borides. The thickness of borocopperized layers ranged approximately 100 µm.

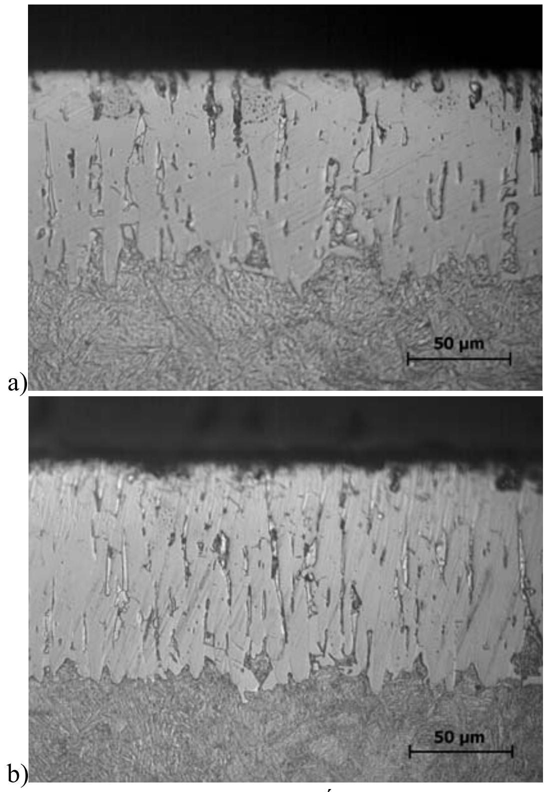

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Fig. 3. Microstructure of borocopperized layer; a) 2% Cu; b) 4% Cu

Rys. 3. Mikrostruktura warstwy boromiedziowanej; a) 2% Cu; b) 4% Cu

Microhardness of boronized layers was about 1800–1600 HV0,1. With increasing distance from the surface, microhardness of boronized layer gradually decreases towards the substrate (Fig. 4). Microhardness of borocopperized layers showed a milder microhardness gradient from the surface to the substrate compared to boronized layer. Borocopperized layers had a microhardness of approximately 1600-1200 HV0.1 (Fig. 4). After the diffusion borocopperizing process, the layers are characterized by a microhardness similar to that of iron boride Fe_2B.

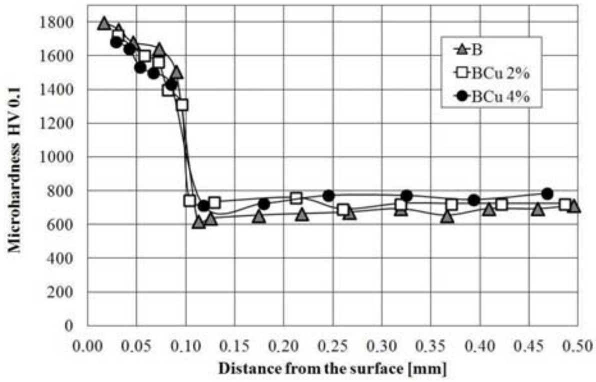

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Fig. 4. Microhardness profiles of borocopperized and boronized layers

Rys. 4. Profile mikrotwardości warstw boromiedziowanych i borowanej dyfuzyjnie

Figures 5 and 6 show examples of Vickers indentations with cracks after studies of fracture toughness with the Palmqvist method.

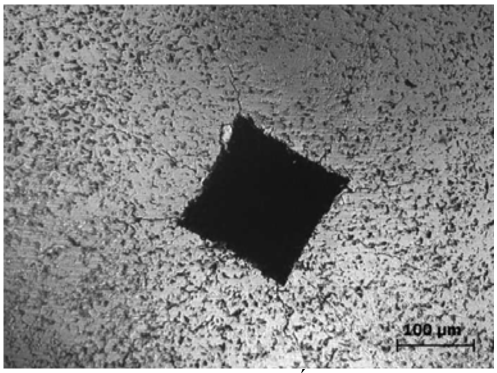

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Fig. 5. Vickers indentation with cracks on steel after boronizing; P = 196 N

Rys. 5. Odcisk Vickersa z pęknięciami na stali po borowaniu; P = 196 N

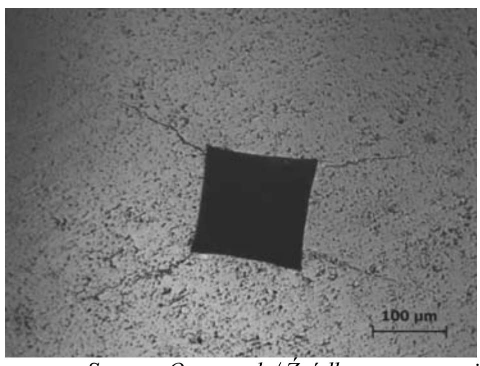

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Fig. 5. Vickers indentation with cracks on steel after borocopperizing (4%Cu); P = 196 N

Rys. 5. Odcisk Vickersa z pęknięciami na stali po boromiedziowaniu (4%Cu); P = 196 N

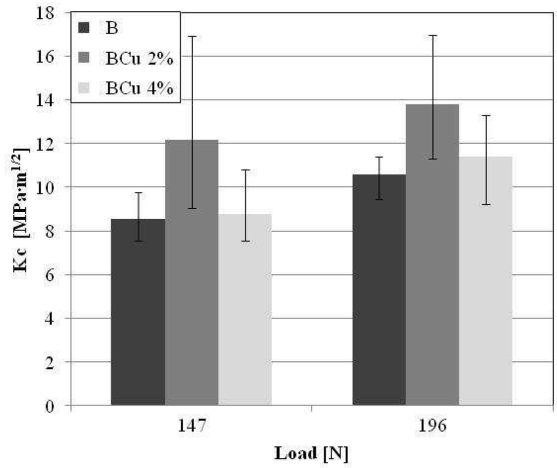

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Fig. 6. Fracture toughness for boronized and borocopperized layers

Rys. 6. Odporność na kruche pękanie dla warstw borowanej i boromiedziowanej

Figure 6 shows a graph of the fracture toughness of the load. The addition of copper improves the fracture toughness of boronized layers. Figures 7-9 show the results of the study surface cohesion of the boronized and borocopperized layers. In each case analyzed, surface layers are formed on a scale of acceptable failures based on VDI standard 3198. Figure 7 shows an image of the surface of diffusion boronized layer with Rockwell indentation, from which micro-cracks radiate, and layer adhesion conforms to the standard in terms of HF1 and HF2 (Fig. 1). Figures 8 and 9 show the resulting indentation on steel after borocopperizing process, which can be classified as standard HF1 and HF2, the failures which are also acceptable. It can be seen that the addition of copper affects the increase in the amount of cracks.

The studies of both cohesion of borocopperized layer with a content of 2% copper (Fig. 8) as well as borocopperized layer with a content of 4% copper (Fig. 9) show good adhesion to the substrate. The layers do not have a delamination and spalling.

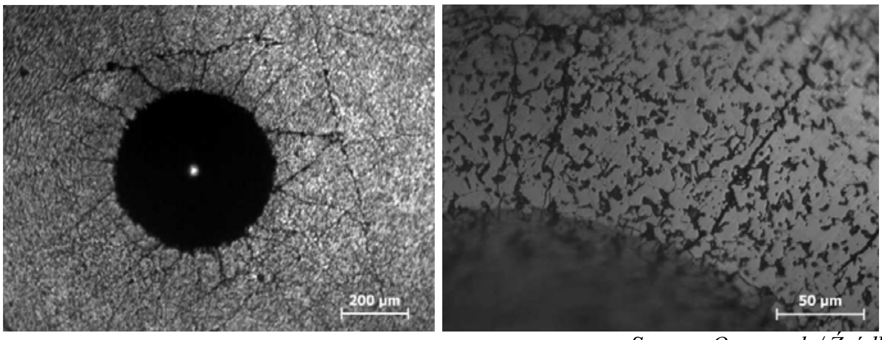

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Fig. 7. Rockwell indentation image made on C45 steel after boronizing

Rys. 7. Odcisk Rockwella na stali C45 po borowaniu

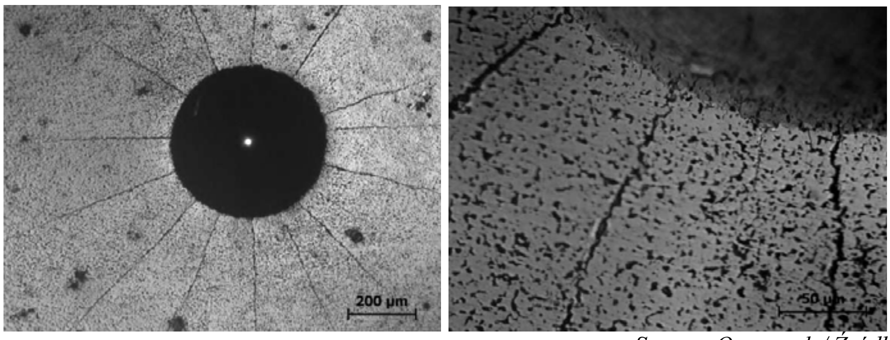

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Fig. 8. Rockwell indentation image made on C45 steel after borocopperizing (2% Cu)

Rys. 8. Odcisk Rockwella na stali C45 po boromiedziowaniu (2% Cu)

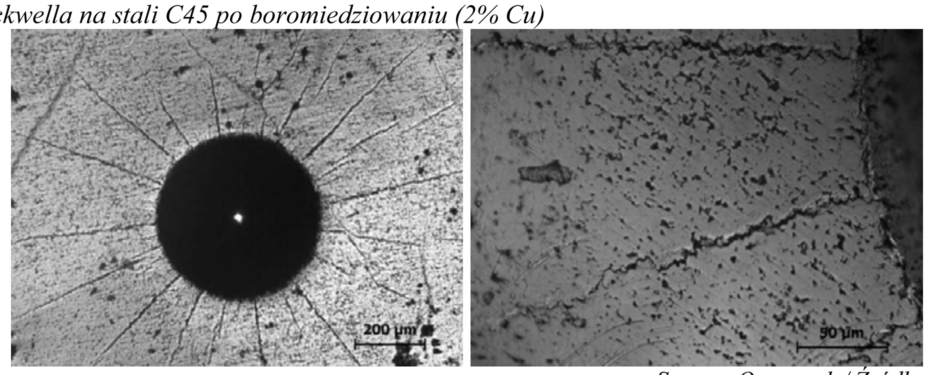

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Fig. 9. Rockwell indentation image made on C45 steel after borocopperizing (4% Cu)

Rys. 9. Odcisk Rockwella na stali C45 po boromiedziowaniu (4% Cu)

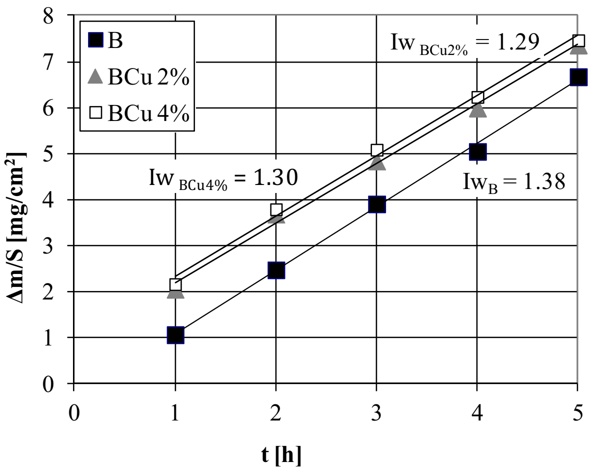

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Fig. 10. Wear resistance of boronized and borocopperized layers

Rys. 10. Odporność na zużycie przez tarcie warstw borowanej i boromiedziowanej

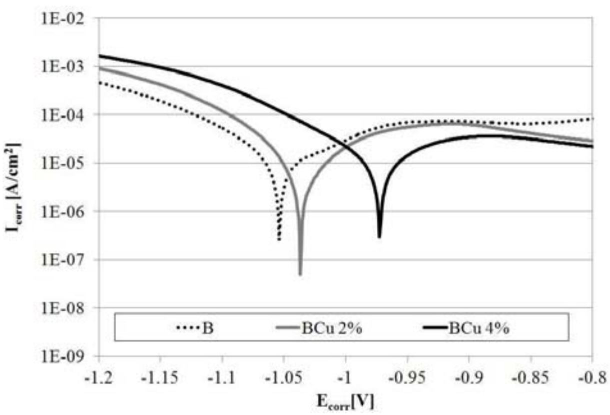

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Fig. 11. Corrosion resistance of boronized and borocopperized layers

Rys. 11. Odporność na korozję warstw borowanych i boromiedziowanych

Figure 10 shows the results of wear resistance studies of boronized and borocopperized layers with a 2% and 4% copper content. Borocopperized layers are characterized by lower wear intensity coefficient than boronized layers.

Figure 11 shows the results of corrosion resistance studies of boronized and borocopperiezed layers. It can be seen that the metallic copper increases corrosion resistance.

4. Conclusions

- After boronizing and borocopperizing processes, samples have a needle-like structure.
- Copper modified boronized layers have lower microhardness than boronized layers, and are characterized by gradual decrease of hardness from the surface to the substrate.
- Wear resistance, fracture toughness, cohesion and corrosion resistance of copper modified boronized layers is higher than in layers that were only boronized.

5. References

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