The Influence of Heat Treatment on Mechanical and Corrosion Properties of High-Chromium White Cast Irons Modified by Titanium and Boron

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Abstract: *The effect of individual additions of Ti and B into high chromium white cast irons (HCWCIs) on the structure, corrosion and selected mechanical properties was investigated. Two different heat treatments were applied, high-temperature treatment at 960 ^{o}C/1h, and subcritical treatment at 550 ^{o}C/4 h. The microstructure was investigated by OM and SEM; compositions of matrix and carbides were analyzed by EDS. Mechanical behavior of HCWCIs was analyzed by measuring hardness, toughness, abrasive/wear resistance and resistance to repeated impacts. Corrosion behavior was evaluated electrochemically, by linear and Tafel polarization methods in 0,1M NaCl solution. The properties of the modified HCWCIs were compared with the properties of the base unmodified HCWCI alloy (ASTM A532-IIE).*

Keywords*: HCWCI, GRINDING BALLS, TITANIUM, BORON, CORROSION, IMPACT, WEAR RESISTANCE*

1. Introduction

High Chromium White Cast Irons (HCWCIs) are iron-based alloys containing 11-30 wt% Cr and 1.8-3.6 wt% C, often additionally alloyed with Mo, Mg, Cu and Ni [1]. HCWCI has been proven to be an effective material for applications in aggressive environments where abrasion and erosion resistances are required. The high wear resistance of HCCI is attributed to the combination of hard primary and/or eutectic carbides of M_7C_3 (M: Fe, Cr and other strong carbide formers) and relatively ductile ferrous matrix [2]. The properties of these irons are influenced by the type, hardness, morphology, distribution, volume fraction and orientation of eutectic carbides, as well as the matrix microstructure, which supports the carbide phase [3, 4]. Different structures of the matrix can be achieved by alloying element and applying specific heat treatments. Pearlite, martensite and austenite are among the typical microconstituents in the matrix [2]. Most researchers have focused on either strengthening the matrix by destabilizing it or improving wear resistance with alloy additions [1, 5]. The addition of small amounts of carbide-forming elements (Ti, B, V, W,..) that bind carbon in the form of carbides, different from cementite, with higher hardness and a much more favorable morphology and reduce the carbon content in the matrix, enable the improvement of both impact toughness and resistance to abrasion wear [4]. Different critical and subcritical heat treatments also alter the initial casting microstructure of HCCIs and lead to varying degrees of secondary carbide precipitation [1, 6, 7]. HCWI alloys with B addition have been investigated and found to increase the wear resistance [8-15]. Boron influences the microstructure of HCWI alloys in three ways: B is a C substitute element and effectively increases the C equivalent of the alloy, resulting in a higher volume fraction of carbides, most of the B is distributed in the carbides, forming complex carboborides such as $M_3(C,B)$ and $M_7(C,B)_3$, instead of M_3C and M_7C_3; higher B content promotes the formation of M_2B and M_3B boride phases which have a much higher hardness and fracture toughness compared to carbide phases of M_7C_3; B addition decreases the solubility of carbon in γ-Fe which increases carbide nucleation sites during solidification resulting in carbide refinement [8]. The addition of Ti gives the strongest driving force for carbide formation, indicating that TiC carbide is expected to precipitate preferentially from the melt, even in rapid cooling conditions [16]. Titanium addition influences the microstructure of HCWI in these ways: Ti addition alters the solidification sequence by forming TiC; by TiC forming Ti addition depletes the carbon concentration in the melt which leads to a decrease in the volume fraction of M_7C_3 carbide [16];

For this study, four sets of HCWCI grinding balls with dimensions of ø60 mm were cast, with the addition of 0.36% and 2.37% by weight Ti and the addition of 0.021% and 0.071% by weight B. Additionally, one set of "base alloy" grinding balls (chemical composition defined by ASTM A532-IIE) was cast and tested under the same conditions, with the aim of comparing the properties of novel cast balls with the properties of standard alloys.

2. Experimental procedure

The chemical composition of tested alloys is listed in Table 1. The melting process of HCWC irons, individually alloyed with titanium (0,36 wt%, and 2,37 wt%) and boron (0,021 wt%, and 0,071 wt%), was carried out in an induction furnace. Grinding balls with 60mm of diameter were cast into gray cast iron water cooled permanent molds with alloyed-steel inserts (a cluster of eight balls). The casting temperature was 1470 ^{o}C - 1490 ^{o}C and the mold temperature was 130 ^{o}C - 140 ^{o}C. After casting, the grinding balls were kept 3 minutes in the mold and further cooled in ambient air. Two different heat treatments were applied: heating to the destabilization temperature of 960 ^{o}C, holding at this temperature for 1 h, then cooling in air; subcritical thermal treatment - heating to a temperature of 550 ^{o}C, holding at this temperature for 4 h, then cooling in air. The samples were tested in the as-cast and both heat treated tempers. The microstructure was investigated by optical microscopy and SEM, and compositions of matrix and carbides were analyzed by EDS.

Table 1. Chemical composition of tested HCWCI alloys, wt%

Element,	Base alloy[1] wt%	Alloy 1 (add. Ti)	Alloy 2 (add. Ti)	Alloy 3 (add. B)	Alloy 4 (add. B)
C	2,91	2,93	2,72	2,64	3,28
Si	0,83	0,97	1,81	1,28	0,96
Mn	0,79	0,79	0,93	0,80	0,71
P	0,029	0,024	0,018	0,047	0,031
S	0,016	0,015	0,014	0,013	0,012
Cr	17,83	17,96	14,53	14,28	17,92
Mo	1,15	1,15	1,16	1,08	1,02
Cu	0,84	0,89	1,51	0,92	0,97
Ni	0,11	0,11	0,12	0,10	0,13
Al	0,051				
B	<0,002	<0,002	<0,002	**0,021**	**0,071**
Ti	0,021	**0,360**	**2,370**	0,109	0,038
V	0,041	0,060	0,130	0,072	0,060
Nb		0,008	0,022	0,056	0,180
W	<0,001	<0,001	0,102	<0,001	<0,001
Cr/C	6,13	6,13	5,34	5,41	5,46

[1] high chromium cast white iron, chemical composition ASTM A532-IIE

Mechanical behavior of HCWCIs was analyzed by measuring Rockwell hardness, toughness (Charpy V notch pendulum impact test), wear resistance and resistance to repeated impacts. The dry sand/rubber wheel method, defined by the ASTM G65 standard, was used to test abrasion resistance. The resistance to repeated impacts is tested by simulating ball impacts during rotary milling (repeated or cyclic impacts). In this test, grinding balls are dropped from a height of 3.5 m and hit another grinding balls located in the bent section of the tube of the device. There are usually 18 grinding balls in the bent section of the tube, while another four are located in the transport system, so the test is carried out with a total of 22 grinding balls. Corrosion behavior was evaluated by linear and

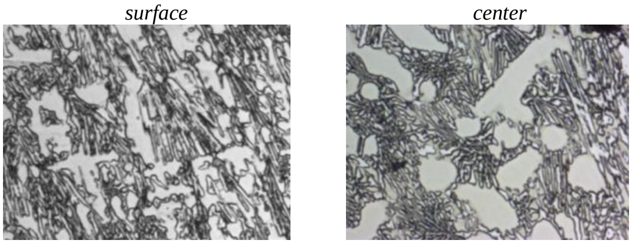
Tafel polarization electrochemical methods in 0,1 M NaCl solution. Electrochemical measurements were carried out in a conventional three-electrode glass cell, composed of a specimen as a working electrode (HCWCIs samples), graphite counter electrode and Ag/AgCl,KCl electrode as a reference electrode. The working surfaces of these electrodes were 1 cm^2. Before each measurement, a sample was ground with a series of SiC abrasive papers and then polished. The properties of the novel modified HCWCIs in the as-cast and heat-treated tempers were compared with the properties of the base unmodified HCWCI (ASTM A532-IIE).

3. Results

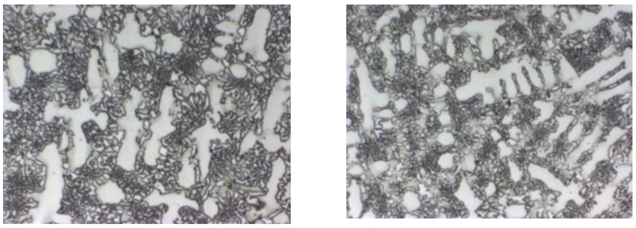
Microstructures of investigated as-cast grinding balls, at the surface and in central zones of the cross-sections, are presented in Fig. 1. Titanium influences the formation of a fine-grained and more homogeneous structure in the cross-section of the tested as-cast grinding balls, Fig. 1.b.c. The difference in the size of the surface-center phases exists, but much less pronounced in Ti-modified HCWCIs than in the base ASTM A532-IIE alloy. Also, the volume fraction of primary austenite dendrites is higher, and the amount of eutectic and M_7C_3 carbides is lower if compared to the base alloy, noting that with increasing Ti content this difference is greater, Figure 1.b-c. The presence of TiC carbide particles is observed, with the volume fraction of TiC being significantly higher in HCWCI alloys containing higher amount of titanium, Figure 2. The influence of boron on the microstructure is also very obvious - boron-modified HCWCI alloys have a significantly finer structure compared to the base and titanium-modified alloys, Figure 1.d-e. Boron also affects the transformation of austenite during cooling after crystallization, and the degree of transformation of austenite into martensite is higher than in Ti-modified HCWCs. With increasing of boron content in the HCWCIs, the volume fraction of martensite increases, Figure 3. Subcritical heat treatment of HCWCIs is generally used to eliminate retained austenite. Subcritical heat treatment of Ti-modified HCWCIs resulted in almost complete transformation of the eutectic austenite into martensite. In addition, martensite is present in a wider surface zone of primary austenite dendrites along the boundary with the eutectic M_7C_3 carbide. Subcritical heat treatment causes significant changes in the microstructure of HCWCI alloy containing 0.021%B. The degree of martensitic transformation of eutectic and primary austenite is high, with the note that a certain level of austenite to pearlite transformation can also be observed. The microstructure of the metal-matrix of the HCWCI alloys after high-temperature treatment at 960 ^{o}C/1h is typical for this type of material and this heat treatment regime. It consists mainly of precipitated secondary carbides and martensite, with a very small volume fraction of retained austenite. In this type of alloy, fine and almost globular particles of secondary carbide of the $M_{23}C_6$ type (zone axis [100]), with a size of less than 1 μm, precipitate at the destabilization temperature.

Mechanical properties

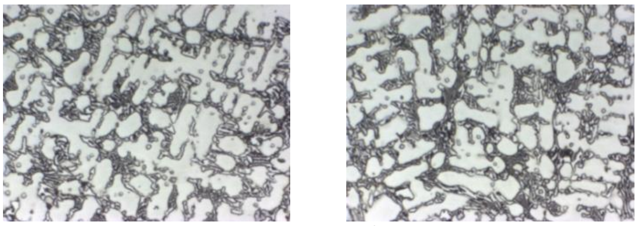
The measured Rockwell hardness values, as the average measured values for the cross-section of the balls are reported in Table 2. The results obtained from the hardness measurements of the samples are relatively close among the different alloys in the same tempers. The differences in hardness of the grinding balls are a consequence of the different volume fraction of the carbide phases as well as the volume fraction of austenite, or martensite in the structure. Subcritical heat treatment increases the hardness of all tested alloys. The highest increase in hardness (about 7%) is indicated for the alloy modified with 0.021 wt% boron. The tested grinding balls have the highest hardness after high-temperature heat treatment. The highest hardness increase after this heat treatment, (≈ 26%), in relation to the as-cast temper, is indicated for the Ti-modified HCWCI alloy modified with 2.37 wt% Ti. The highest hardness (63.3 HRC) is measured on grinding balls made of the HCWCI alloy modified with the addition of 0.071 wt% boron.



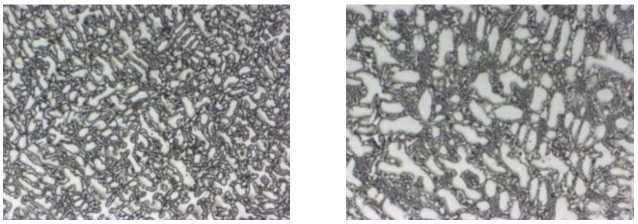
(a) Base alloy, ASTM A532-IIE



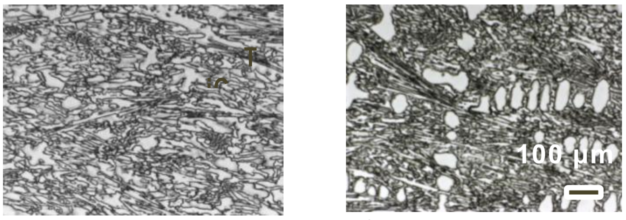
(b) Alloy 1, (addition of 0,36 wt% Ti)



(c) Alloy 2, (addition of 2,37wt% Ti)

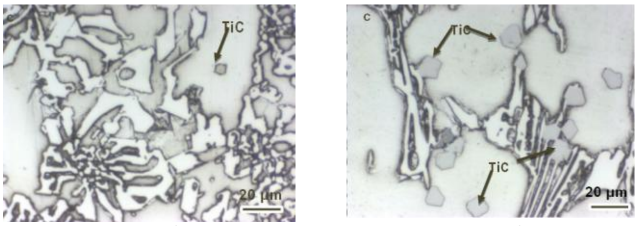


(d) Alloy 3 (addition of 0,021 wt% B



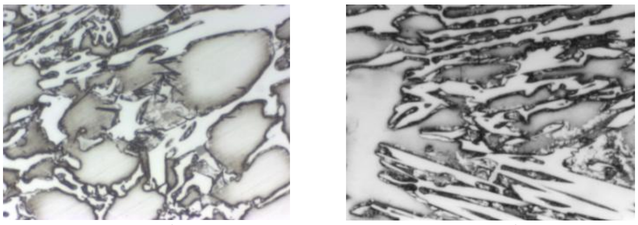
(e) Alloy 4 (addition of 0,071 wt% B

Fig. 1. Optical micrographs of as-cast grinding balls structure (surface and center of grinding ball



Alloy 1, (addition of 0,36 wt% Ti) Alloy 2, (addition of 2,37wt% Ti)

Fig. 2. Optical micrographs of as-cast grinding balls structure (center)modified by Ti adition



Alloy 3, (addition of 0,021 wt% B) Alloy 4, (addition of 0,071wt% B)

Fig. 3. Optical micrographs of as-cast grinding balls structure (center)modified by B addition

Table 2. The influence of heat treatments (subcritical and high-temperature) on hardness of HCWCIs, modified with Ti (0,36 and 2,37 wt%) and B (0,021 and 0,071wt%).

Type of alloy	Rockwell hardness, HRC		
	As-cast	Subcritical heat treatment	High-temp. treatment
Base alloy*	52,5	54,4	60,2
Alloy 1 (0,36 wt% Ti)	53,8	55,1	62,1
Alloy 2 (2,37 wt% Ti)	46,8	48,4	59,2
Alloy 3 (0,021 wt% B)	51,8	55,5	61,4
Alloy 4 (0,071 wt% B)	53,4	55,1	63,3

Impact toughness tests were performed on an instrumented Charpy pendulum 150/300 J (V notch pendulum impact test), according to Standard EN ISO 14556. The influence of modification of tested HCWCIs by addition of Ti and B on the impact toughness in the as-cast temper is presented in Figure 4.

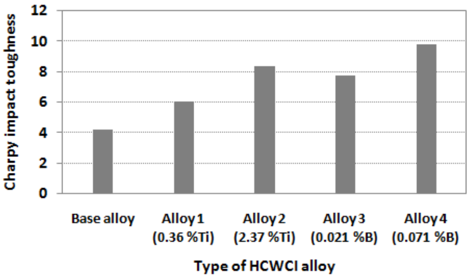


Figure 4. The influence of the individual addition of Ti and B on the Charpy V notch impact toughness of tested as-cast HCWCIs

The Charpy impact toughness of all modified HCWCI alloys is 45–133% higher than the impact energy of the reference base alloy. The highest total impact energy was measured for the alloy containing 0.071 wt% B. Impact toughness increases with increasing titanium content. The HCWCI alloy with 2.37 wt% Ti has approximately 40% higher total impact energy compared to the alloy with 0.36 wt% Ti, and 100% higher than the reference alloy. This is mainly due to the lower volume fraction of carbide in the structure, taking into account the fact that cracks propagate easily through the eutectic carbide phase. These alloys have an austenitic metal matrix microstructure. Similarly, impact toughness increases with increasing boron content. The HCWCI alloy modified with 0.071 wt% B has 25% higher total impact energy than the alloy with 0.021 wt% B, and 133% higher than the reference alloy.

The results of the abrasion resistance tests are presented in Figure 5. The dry sand/rubber wheel method ("Asian" device), defined by the ASTM G65 standard, was used. All tested HCWCIs modified with Ti or B additions show better resistance to abrasion wear, noting that higher Ti or B content also results in lower mass/volume losses. Furthermore, both applied heat treatments improve the abrasion wear resistance of all tested alloys. Subcritical heat treatment can reduce the mass/volume loss by 1.6 – 10%, and high-temperature treatment can reduce it by 15 – 27% compared to the as-cast temper.

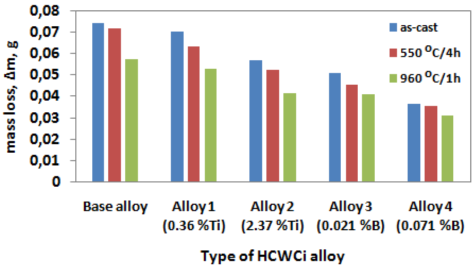


Figure 5. The influence of heat treatments and Ti or B addition on abrasion wear resistance of tested HCWCIs

The best resistance to abrasion wear is indicated for the HCWCI alloy modified with the addition of 0.071 wt% B. It is interesting to note that, for example, HCWCI alloy with 2.37 wt% Ti has a lower volume fraction of carbide phase in the structure and lower hardness, but has almost 26% higher wear resistance than the reference alloy in all tested tempers.

The results of testing the resistance to repeated impacts of grinding balls of three as-cast alloys (base alloy and alloys modified individually with 0.36 wt% Ti and 0.071 wt% B) are presented in Figure 6.

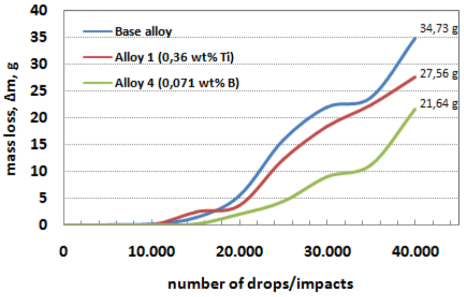


Figure 6. Resistance to repeated impacts of as-cast grinding balls

The weight loss of the tested grinding balls was insignificant up to 20,000 drops - it is less than 4 grams. After 20,000 drops, the beginning of flaking on the surface of some samples was noticed. With a further increase in the number of falls/impacts, the mass loss of the tested balls increases significantly, with a smaller weight loss measured for the modified alloys compared to the base alloy. The lowest mass loss after 40,000 drops was measured for the alloy with the addition of 0.071 wt% B, and compared to the base alloy it is 37% lower mass loss levels.

Corrosion properties

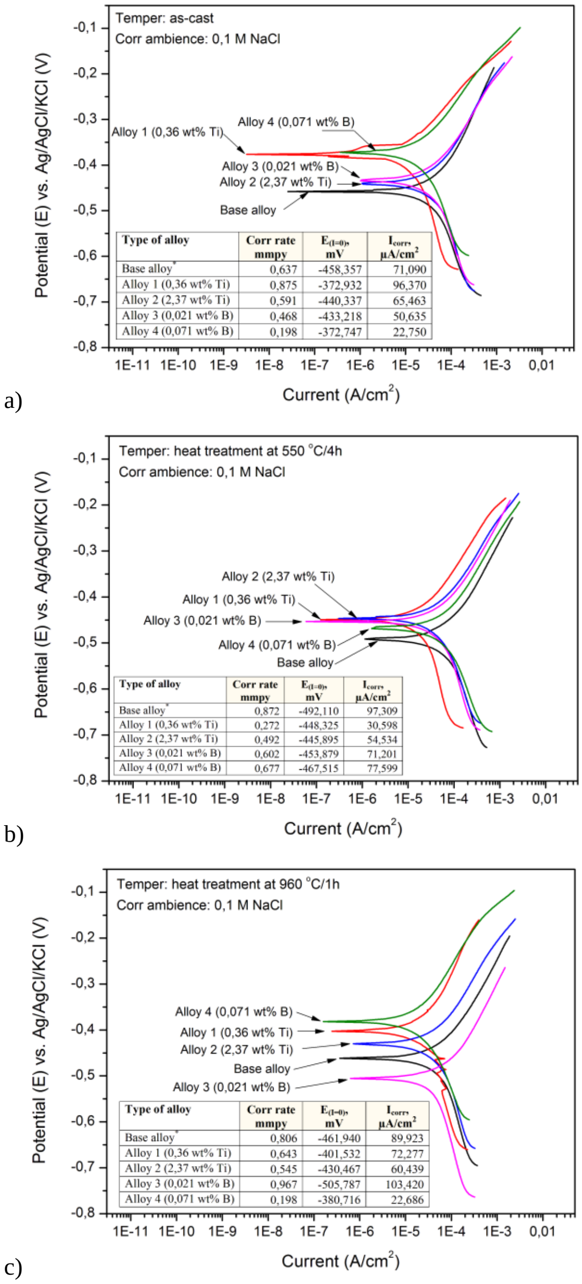
Two techniques have been used for testing of corrosion properties of grinding balls: linear polarization and Tafel extrapolation. The influence of subcritical and high temperature heat treatments on corrosion rates of tested HCWCI alloys in 0,1 M NaCl under linear polarization is presented in Table 3.

Table 3. The influence of subcritical and high temperature heat treatments on corrosion rates of tested HCWCI alloys in 0,1 M NaCl (linear polarization)

Type of alloy	Corrosion rate mmpy		
	As-cast	Subcritical heat treatment	High-temp. treatment
Base alloy	0,319	0,471	0,401
Alloy 1 (0,36 wt% Ti)	0,131	0,172	0,166
Alloy 2 (2,37 wt% Ti)	0,303	0,343	0,359
Alloy 3 (0,021 wt% B)	0,089	0,391	0,319
Alloy 4 (0,071 wt% B)	0,164	0,537	0,132

Modification of HCWCI alloys by individual additions of titanium or boron reduces corrosion rates, if compared to the corrosion rates of the base alloy, for all of three tempers: as-cast, subcritical and high temperature heat treatments. Both types of applied heat treatments cause a certain increase in the corrosion rates, when compared to their as-cast state, for all tested HCWCI alloys, under linear polarization.

Tafel curves of the as-cast and heat treated HCWCI alloys are shown in Figure 7. The single addition of titanium or boron shifts the Tafel curves of modified HCWCIs towards less negative values, compared to the curves that characterize the behavior of the basic HCWCI alloy in 0.1 M NaCl. Modifying the composition/structure of HCWCIs by individual additions of titanium or boron reduces the corrosion rates of as-cast and heat treated grinding balls. The lowest corrosion rate in the as-cast state and after high-temperature heat treatment was measured for HCWCI alloy modified with the addition of 0.071 wt% B. Subcritical heat treatment reduces the corrosion rate, indicating that the alloy with the addition of 0.36 wt% Ti shows the lowest corrosion rates at this temper. The results of both electrochemical techniques indicate the less active corrosion of titanium or boron modified HCWCIs grinding balls in 0,1M NaCl solution if compared to base HCWCI alloy behavior.



Type of alloy	Corr rate mmpy	$E_{(I=0)}$, mV	I_{corr}, µA/cm^2
Base alloy*	0,637	-458,357	71,090
Alloy 1 (0,36 wt% Ti)	0,875	-372,932	96,370
Alloy 2 (2,37 wt% Ti)	0,591	-440,337	65,463
Alloy 3 (0,021 wt% B)	0,468	-433,218	50,635
Alloy 4 (0,071 wt% B)	0,198	-372,747	22,750

Type of alloy	Corr rate mmpy	$E_{(I=0)}$, mV	I_{corr}, µA/cm^2
Base alloy*	0,872	-492,110	97,309
Alloy 1 (0,36 wt% Ti)	0,272	-448,325	30,598
Alloy 2 (2,37 wt% Ti)	0,492	-445,895	54,534
Alloy 3 (0,021 wt% B)	0,602	-453,879	71,201
Alloy 4 (0,071 wt% B)	0,677	-467,515	77,599

Type of alloy	Corr rate mmpy	$E_{(I=0)}$, mV	I_{corr}, µA/cm^2
Base alloy*	0,806	-461,940	89,923
Alloy 1 (0,36 wt% Ti)	0,643	-401,532	72,277
Alloy 2 (2,37 wt% Ti)	0,545	-430,467	60,439
Alloy 3 (0,021 wt% B)	0,967	-505,787	103,420
Alloy 4 (0,071 wt% B)	0,198	-380,716	22,686

Figure 7. Tafel curves for tested HCWCI alloys modified by individual addition of Ti an B: (a) as-cast, (b) heat treated at 550 ^{o}C/4h and (c) heat treated at 960 ^{o}C/1h.

4. Conclusion

HCWCI alloys modified with the addition of Ti or B have a significantly finer structure if compared to the base unmodified alloy. Boron especially affects the transformation of austenite during cooling after crystallization, and the degree of transformation of austenite into martensite is higher than in titanium-modified HCWCs. Subcritical and high-temperature heat treatment increases the hardness of all tested alloys. The highest increase in hardness (≈ 7%) after subcritical treatment is indicated for the alloy modified with 0.021 wt% B. The highest increase in hardness after high-temperature treatment, (≈ 26%) compared to the as-cast temper, is indicated for the HCWCI modified with 2.37 wt% titanium. The Charpy impact toughness of all modified HCWCI alloys is 45–133% higher than the impact energy of the reference base alloy. The highest total impact energy was measured for the alloy containing 0.071 wt% B. HCWCIs modified with Ti or B show better resistance to abrasion wear, noting that higher Ti or B content also results in lower mass/volume losses. Both applied heat treatments improve the abrasion wear resistance of all tested alloys. Subcritical heat treatment can reduce the mass/volume loss by 1.6 – 10%, and high-temperature treatment can reduce it by 15 – 27% compared to the as-cast temper. The best resistance to abrasion wear is indicated for the HCWCI alloy modified with the addition of 0.071 wt% B. Modification of HCWCI alloys by individual additions of titanium or boron reduces corrosion rates, if compared to the corrosion rates of the base alloy, for all of three tempers: as-cast, subcritical and high temperature heat treatments. Both types of applied heat treatments cause a certain increase in the corrosion rates, when compared to their as-cast state.

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