K. Delijić[1], M. Filipović[2], V. Manojlović[2]
[1] Univerza v Črni Gori, Črna Gora / University of Montenegro, Montenegro,
[2] Univerza v Beogradu, Srbija / University of Belgrade, Serbia

Korozijsko vedenje krogel za mletje iz belega litega železa z visoko vsebnostjo kroma, izdelanih s cepivom Al5Ti1B

Corrosion Behavior of High-Chromium White Cast Iron Grinding Balls Produced with Al5Ti1B Inoculant

Povzetek

Korozijsko vedenje krogel za mletje iz zlitine belega litega železa z visokim deležem kroma (HCWCI), izdelanih z udrobnjevalcem Al5Ti1B (masni delež 0,5–2,0 wt.%), smo ocenili z elektrokemijskimi metodami, ki jim je sledila analiza mikrostrukture in merjenje trdote. Kot inokulant smo uporabili predzlitino Al5Ti1B, ki ima dvojno vlogo: je sredstvo za razplinjanje in sredstvo za modifikacijo, saj poleg aluminija vsebuje tudi karbidotvorne elemente, tj. titan in bor. Korozijske preskuse smo opravili v 0,1 M NaCl in v sladki vodi. Vzorce smo preskusili v litem stanju. Zlitina HCWCI, modificirana z 0,5 wt.% Al5Ti1B, je zagotovila optimalno kombinacijo preskušenih lastnosti.

Ključne besede: belo lito železo z visoko vsebnostjo kroma, krogle za mletje, cepiva Al5Ti1B, korozija

Summary

Corrosion behavior of high-chromium white cast iron (HCWCI) alloys for grinding balls produced with the addition of Al5Ti1B grain refiner (0,5 - 2,0 wt.%), were evaluated by electrochemical methods, followed by microstructure analysis and hardness measuring. An Al5Ti1B master alloy is used as an inoculant, having a double role: a degassing agent and a modification agent since in addition to aluminum, it contains carbide-forming elements, titanium and boron. Corrosion tests were performed in 0,1 M NaCl and fresh water. The samples were tested in the as-cast conditions. The HCWCI alloy modified by 0,5 wt.% of Al5Ti1B, showed the optimal combination of tested properties.

Keywords: high-chromium white cast iron, grinding balls, Al5Ti1B inoculants, corrosion

1 Uvod

Belo lito železo z visoko vsebnostjo kroma (HCWCI) je odličen obrabni material in predstavlja tretjo generacijo te vrste materialov z ugodnim razmerjem med obrabo zaradi abrazije in žilavostjo [1, 2, 3]. Dobra odpornost proti obrabi je predvsem posledica prisotnosti velikega volumskega deleža zelo trdih evtektičnih

1 Introduction

High-chromium white cast irons (HCWCIs) represent excellent wearable materials, as a third generation of this type of material, with a favorable ratio of abrasion wear and toughness [1, 2, 3]. Good wear resistance is a consequence primarily of the presence of high-volume fraction of very hard eutectic carbides in a strong supporting matrix in their karbidov v močni podporni matrici v njihovi mikrostrukturi [4, 5, 6, 7]. Obstaja veliko člankov in modelov, povezanih z razmerjem med obrabo in mikrostrukturnimi lastnostmi belega litega železa z visoko vsebnostjo kroma [12]. Vendar so obrabni elementi HCWCI pogosto izpostavljeni delu v korozivnem okolju, informacije o vedenju HCWCI v korozivnih okoljih pa so v dostopni literaturi razmeroma omejene [12]. Obstajajo eksperimentalni dokazi, da je belo železo z visoko vsebnostjo kroma z dobrimi mehanskimi lastnostmi manj odporno proti koroziji in da te zlitine v korozivnih pogojih postanejo manj odporne proti obrabi [13]. Korozijska odpornost zlitin HCWCI je odvisna od kemijske sestave železove matrice in koncentracije prostega Cr v matrici, ki povečuje korozijsko odpornost zlitin HCWCI, ter od razmerij Cr/C in Cr_{M7C3}/Cr_{matrix} [12, 13, 14, 15]. Dodajanje drugih legirnih elementov, kot so Si, Mo, Ni, Cu, V, Ti itd., prav tako vpliva na korozijsko vedenje.

Namen tega prispevka je predstaviti nekatere rezultate in razmisleke o vplivu inokulacije HCWCI z Al5Ti1B (od 0,5 wt.% do 2,0 wt.%) na mikrostrukturo in korozijske lastnosti zlitin HCWCI. V primeru železz visoko vsebnostjo kroma ima predzlitina Al5Ti1B dvojno vlogo: je sredstvo za razplinjanje in sredstvo za tvorbo/modifikacijo karbidov, saj poleg aluminija vsebuje tudi karbidotvorne elemente, tj. titan in bor.

2 Materiali in metode

Kemijska sestava preskušenih zlitin HCWCI je navedena v Preglednici 1. Vzorci so bili izdelani z dodatkom Al5Ti1B (0,5–2,0 wt.%). Taljenje zlitin je potekalo v indukcijski peči, krogle za mletje s premerom 60 mm pa so bile ulite v vodno hlajene trajne forme.

microstructure [4, 5, 6, 7]. There are many articles and models related to the wear and microstructure properties relationship of HCWCIs [12]. However, wearable HCWCI elements are often exposed to work in a corrosive environment, and information on the behavior of HCWCIs in corrosive environments is relatively limited in the open literature [12]. There are experimental evidences that HCWCIs with high mechanical properties are less resistant to corrosion and these alloys become less resistant to wear under corrosive conditions [13]. The corrosion resistance of HCWCI alloys depends on the chemical composition of the ferrous matrix and the concentration of free Cr in the matrix, which increases the corrosion resistance of HCWCI alloys as well as on the Cr/C and Cr_{M7C3}/Cr_{matrix} ratios [12, 13, 14, 15]. The addition of other alloying elements, such as Si, Mo, Ni, Cu, V, Ti, etc., also affects the corrosion behavior.

This paper aims to present some results and considerations related to the influence of the inoculation of HCWCIs with Al5Ti1B (as 0,5 wt.% - 2,0 wt.%) on microstructure and corrosion properties of HCWCI alloys. In the case of high-chromium master master alloy would have a double role: a degassing agent and a carbide forming/modification agent, since in addition to aluminum, it also contains carbide-forming elements, titanium and boron.

2 Materials and Methods

The chemical composition of tested HCWCI alloys is listed in Table 1. The samples were produced by the addition of Al5Ti1B (0,5 - 2,0 wt.%). The melting of alloys was performed in induction furnace and grinding balls with 60 mm of diameter were cast in water-cooled permanent molds. The casting temperature was 1470 °C - 1490 °C

Preglednica 1. Kemijska sestava zlitin HCWCI, uporabljenih v poskusih, wt.%

Table 1. Chemical composition of HCWCI alloys used in experiments, wt.%

Zlitina / Alloy	C	Si	Mn	P	S	Cr,	Mo	Cu	Ni	Al	B	Ti	V
Osnovni / Base HCWCI	2,91	0,83	0,79	0,029	0,016	17,83	1,15	0,84	0,11	0,051	<0,002	0,021	0,041
HCWCI + 0,5 wt.% AlTiB	3,08	0,78	0,69	0,019	0,021	18,37	1,13	0,84	0,11	0,495	<0,002	0,046	0,043
HCWCI + 1,0 wt.% AlTiB	2,93	0,79	0,68	0,022	0,019	18,68	1,17	0,83	0,12	1,173	0,003	0,074	0,043
HCWCI + 2,0 wt.% AlTiB	2,90	0,79	0,78	0,029	0,015	15,53	1,24	0,76	0,09	2,271	0,021	0,16	0,043

Temperatura litja je bila 1470 °C–1490 °C, temperatura forme pa 130 °C–140 °C. Ulite krogle so bile v formi 3 minute, po odstranitvi iz form so se ohlajale na zraku. Litje in preskušanje »osnovne zlitine« HCWCI (kemijska sestava, določena s standardom ASTM A532-IIE) sta bila izvedena pod enakimi pogoji, in sicer da bi ju lahko primerjali z lastnostmi ulitih krogel, izdelanih s cepivom Al5Ti1B.

Vzorci so bili preskušeni v litem stanju. Mikrostrukturo vzorcev smo preiskali z optičnim in vrstičnim elektronskim mikroskopom. Korozijsko vedenje zlitin HCWCI smo analizirali s potenciostatom/galvanostatom Ametek Versa 3. Za analizo elektrokemičnih podatkov smo uporabili programsko opremo VersaStudio (različica 2.62.2.0). Pri korozijskih preskusih smo uporabili standardno celico, sestavljeno iz vzorca kot delovne elektrode, grafitne protielektrode in elektrode Ag/AgCl kot referenčne elektrode. Taflove polarizacijske preskuse smo izvedli z uporabo postopka, ki samodejno izbere podatke, ki ležijo znotraj Taflovega območja (±250 mV glede na korozijski potencial). Preskuse linearne polarizacije smo izvedli s postopkom, ki samodejno izbere podatke, ki ležijo v območju ±20 mV glede na korozijski potencial. Pred vsako meritvijo smo testno površino brusili z brusnim papirjem iz

and the mold temperature was 130 °C -140 °C. The cast balls were kept in the mold for 3 minutes and, subsequently, taken out and cooled in ambient air. Casting and testing of HCWCI "base alloy" (chemical composition defined by ASTM A532-IIE) were performed under the same conditions, in order to compare with properties of as-cast balls, produced with Al5Ti1B inoculant.

The samples were tested in the as-cast temper. The microstructure was investigated by optical and scanning electron microscopy. The corrosion behavior of HCWCI alloys was analyzed using Ametek Versa 3 potentiostat/galvanostat. The VersaStudio software (version 2.62.2.0) was used for all electrochemical data analysis. A standard cell composed of a specimen as a working electrode, graphite counter electrode and Ag/AgCl electrode as a reference electrode was used in the corrosion tests. Tafel polarization tests were carried out using the routine that automatically selects the data that lies within the Tafel region (±250 mV with respect to the corrosion potential). The linear polarization tests were performed under the routine that automatically selects the data that lies within the region ±20 mV concerning the corrosion potential. Before each measurement, the test surface was ground with silicon carbide papers and rinsed with acetone. Electrochemical silicijevega karbida in jo oprali z acetonom. Elektrokemične preskuse smo opravili v 0,1 M NaCl in sladki vodi (HCO_3 =74,5 mg/l; K^+ < 0,5 mg/l; Mg^{2+} <0,1 mg/l; Na^+ = 48,3 mg/l; Ca^{2+} < 3 mg/l; SiO_2 =45 mg/l). Trdoto zlitin smo preskusili z Rockwellovo metodo (HRC; obremenitev: manjša 10 kg, večja 150 kg; čas: 10 s), pri čemer smo izračunali povprečne vrednosti za prerez krogel za mletje.

3 Rezultati in razprava

Mikrostrukture ulitih krogel za mletje v litem stanju z različnimi vsebnostmi cepiva Al5Ti1B ob površini in v sredinskih conah prerezov so predstavljene na optičnih mikrografijah na Sliki 1. Predstavljena je tudi mikrostruktura osnovne zlitine HCWCI, in sicer z namenom opazovanja sprememb, ki jih povzroči dodajanje različnih vsebnosti Al5Ti1B. Mikrostruktura v vseh preiskovanih zlitinah je sestavljena iz dendritov primarnega avstenita in evtektičnih kolonij, ki so v sestavljene iz mešanice karbidov in avstenita M_7C_3. Mikrogrami SEM, ki prikazujejo mikrostrukturo osnovne zlitine HCWCI in zlitine z dodatkom 1,0 wt.% Al5Ti1B, so prikazani na Sliki 2. Na podlagi analize mikrostrukture (Sliki 1 in 2) je jasno razvidno, da lahko z modifikacijo HCWCI z dodatkom inokulanta Al5Ti1B zagotovimo bistveno bolj fino strukturo. Struktura postane bolj fina, velikost primarnih avstenitnih dendritov in evtektičnega karbida M_7C_3 pa se v HCWCI z 0,5 wt.% Al5TiB1 v primerjavi z osnovno zlitino zmanjša. Zlitina HCWCI, modificirana z 1,0 wt.% Al5Ti1B, ima nekoliko bolj grobo strukturo kot zlitina z 0,5 wt.% Al5Ti1B. Z nadaljnjim povečanjem deleža Al5Ti1B do 2,0 wt.% postane struktura v primerjavi z drugimi modificiranimi zlitinami bolj groba, vendar še vedno bolj fina v primerjavi z osnovno zlitino

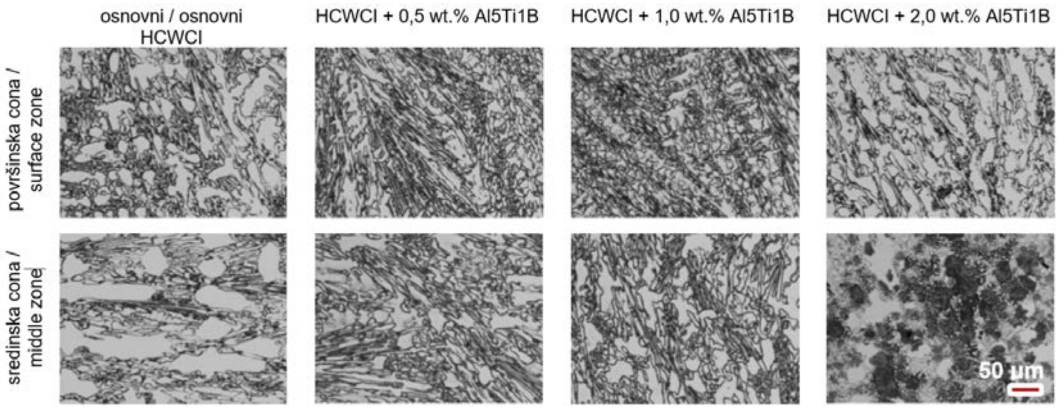
tests were conducted in 0,1 M NaCl and freshwater (HCO_3=74,5 mg/l; K^+ < 0,5 mg/l; Mg^{2+} <0,1 mg/l; Na^+ = 48,3 mg/l; Ca^{2+} < 3 mg/l; SiO_2 =45 mg/l). The hardness of alloys was tested by the Rockwell method (HRC; load applied: minor 10 kg, major 150 kg; time: 10 s), with calculating the average values for the cross-section of the grinding balls.

3 Results and Discussion

Microstructures of as-cast grinding balls with different contents of Al5Ti1B inoculant, near the surface and in the central zones of the cross-sections, are presented in optical micrographs in Fig. 1. The microstructure of the base HCWCI alloy is also presented to observe the changes caused by the addition of different Al5Ti1B contents. The microstructure in all investigated alloys consists of dendrites of primary austenite and eutectic colonies, which are essentially a mixture of M_7C_3 carbides and austenite. SEM micrographs showing the microstructure of the base HCWCI alloy and the alloy with the addition of 1,0 wt.% Al5Ti1B is shown in Figure 2. Based on the microstructure analysis (Fig. 1 and Fig. 2), it is clearly seen that a much finer structure can be obtained by modifying of HCWCIs with the addition of Al5Ti1B inoculant. The structure becomes finer, and the size of the primary austenite dendrites and eutectic M_7C_3 carbide are decreased in HCWCI with 0,5 wt.% of Al5TiB1 if compared to the base alloy. The HCWCI was modified with 1,0 wt.% Al5Ti1B has a slightly coarser structure than the alloy with 0,5 wt.% of Al5Ti1B. With a further increase of the Al5Ti1B up to 2,0 wt.%, the structure becomes coarser if compared to the other modified alloys, but still finer compared to the base HCWCI alloy. The size, morphology and volume

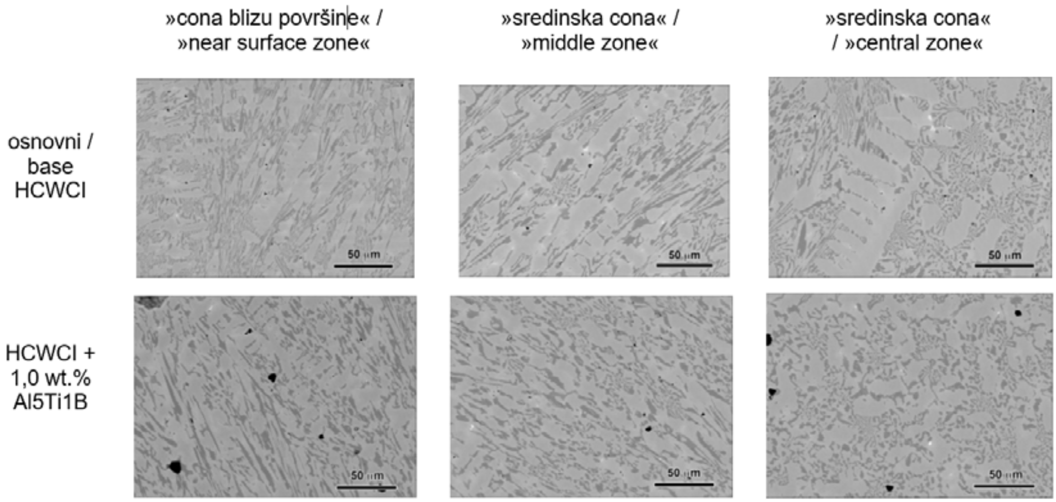
HCWCI. Velikost, morfologija in volumski delež faz v površinskih in sredinskih conah se pri vseh preiskovanih zlitinah razlikujejo. Vendar so s povečevanjem vsebnosti

fraction of the phases in the surface and central zones differ in all investigated alloys. However, with an increase in the Al5Ti1B content, the differences in the structure



Slika 1. Optične mikrografije mikrostrukture kroglic za mletje v litem stanju z različnimi vsebnostmi inokulanta Al5Ti1B

Figure 1. Optical micrographs of the as-cast microstructure of grinding balls produced with different contents of Al5Ti1B inoculant



Slika 2. Mikrogrami SEM, ki prikazujejo mikrostrukturo osnovne zlitine HCWCI in zlitine HCWCI z dodatkom 1,0 wt.% cepiva Al5Ti1B, glede na oddaljenost od površine preskušenih krogel za mletje

Figure 2. SEM micrographs showing the as-cast microstructure of base HCWCI and HCWCI alloy with the addition of 1,0 wt.% of Al5Ti1B inoculant, depending on the distance from the surface of the tested grinding balls

Al5Ti1B razlike v strukturi od površine do sredine ulitih krogel manj izrazite, struktura pa je bolj homogena. V osnovni zlitini HCWCI in HCWCI z 0,5 % Al5Ti1B je opazna prisotnost martenzita, predvsem v mejni coni primarnega in evtektičnega avstenita ter evtektičnih karbidov M_7C_3 karbidov (Slika 1). Poleg tega se volumski delež martenzita zmanjšuje od površine proti sredini, Slika 3.

V površinskih conah je perlit prisoten v zelo majhnih količinah, medtem ko je v sredinski coni opazen nekoliko večji volumski delež, Slika 3. Stopnja pretvorbe avstenita v perlit je bistveno višja v zlitinah HCWCI, modificiranih z dodatkom 2,0 wt.% Al5Ti1B (Slika 1 in Slika 3), pri čemer se volumski delež perlita povečuje od površine proti sredini ulitih kroglic (Slika 1).

Vpliv dodatka Al5Ti1B na trdoto ulitih kroglic je prikazan na Sliki 4. Dodatek 0,5 wt.% Al5Ti1B povzroči povečanje povprečne vrednosti trdote za 1,5 HRC v primerjavi z osnovnim HCWCI, pri čemer se z nadaljnjim večanjem vsebnosti Al5Ti1B do 2 wt.% trdota ne spremeni bistveno in se giblje med 53,8 in 54,1 HRC.

from the surface to the center of the as-cast balls are less pronounced, and the structure is more homogeneous. The presence of martensite, mainly in the boundary zone of both primary and eutectic austenite and eutectic M_7C_3 carbides, is observed in base HCWCI alloy and in HCWCI with 0.5% Al5Ti1B (Fig. 1). Additionally, the volume fraction of martensite decreases from the surface to the center, Fig.3.

Pearlite is present in very small amounts in the surface zones, while in the central zone, a slightly larger volume fraction can be observed, Fig. 3. The degree of transformation of austenite into pearlite is significantly higher in HCWCI alloys modified by the addition of 2,0 wt.% Al5Ti1B (Fig. 1 and Fig. 3), noting that the volume fraction of pearlite increases from the surface to the center of the as-cast balls (Fig. 1).

The influence of the Al5Ti1B addition on the hardness of the as-cast balls is illustrated in Fig.4. The addition of 0,5 wt.% Al5Ti1B causes an increase in the average hardness value of 1,5 HRC, if compared to the base HCWCI, noting that with further

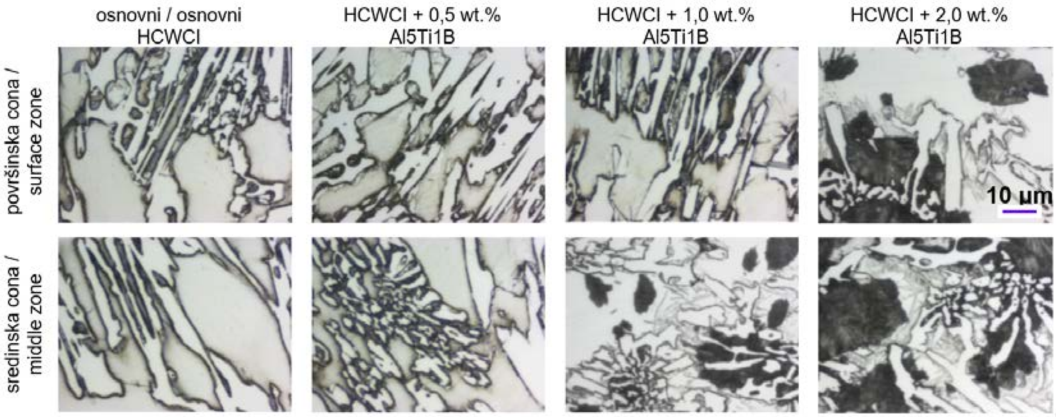
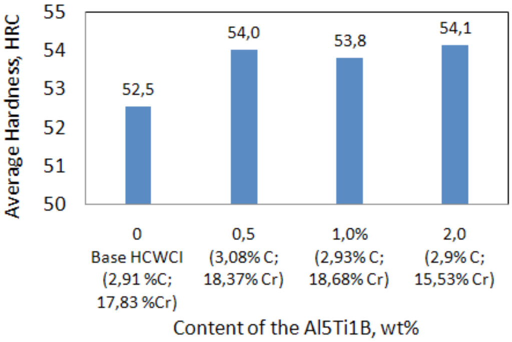


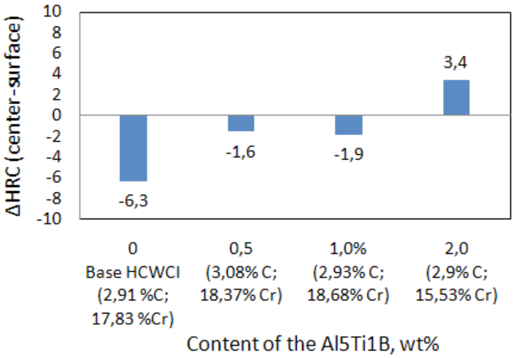
Figure 3. Optical micrographs of the as-cast microstructure of grinding balls produced with different contents of Al5Ti1B, “near-surface zone” and “central zone”

Slika 3. Optične mikrografije mikrostrukture kroglic za mletje, izdelanih z različno vsebnostjo Al5Ti1B, »cona blizu površine« in »sredinska cona«



Slika 4. Vpliv dodatka Al5Ti1B na trdoto krogel v litem stanju

Figure 4. The influence of the Al5Ti1B addition on the hardness of as-cast balls



Slika 5. Vpliv dodatka Al5Ti1B na razliko v trdoti v sredinski coni površine

Figure 5. The influence of the Al5Ti1B addition on the hardness difference in the center-surface zone

Trdota vseh preskušenih krogel v litem stanju se zmanjšuje v smeri od površine do sredine, razen pri zlitini z 2,0 wt.% Al5Ti1B, kjer je opaziti rahlo povečanje trdote v smeri od površine do sredine, Slika 5. Razlika v trdoti med površino in sredino pri osnovni HCWCI je 6,3 HRC. Dodatek 0,5 wt.% Al5Ti1B to razliko zmanjša na 1,6 HRC, Slika 5, kar pomeni, da dodatek 0,5 wt.% Al5Ti1B ne samo poveča povprečno vrednost trdote, temveč tudi znatno zmanjša razpršenost vrednosti trdote na prerezu krogel, kar je posledica bolj homogene strukture. HCWCI, modificirana z 1,0 wt.% Al5Ti1B, ima bolj fino strukturo, transformacija avstenita v martenzit je bolj enakomerna po celotnem prerezu, v primerjavi z osnovno zlitino pa je v sredinski coni opazna zelo majhna količina perlita (Slika 3). S tem se poveča povprečna trdota in zmanjša razlika v trdoti med površino in sredino. Pri HCWCI z 2,0 % Al5Ti1B smo opazili nasprotno težnjo (povečanje trdote v smeri od površine proti sredini) kot posledico povečanja stopnje transformacije avstenita v zelo fin perlit in martenzit (Sliki 1 in 3) z majhnimi deleži preostalega avstenita.

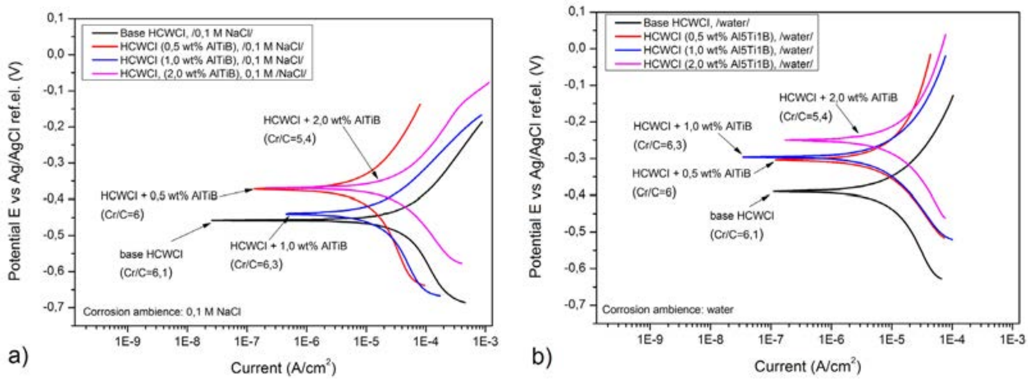
increase in the content of Al5Ti1B up to 2 wt.%, hardness remains approximately the same, and ranges between 53,8 and 54,1 HRC.

The hardness of all tested as-cast balls decreases in direction surface-center, except for the alloy with 2,0 wt.% Al5Ti1B, where a slight increase in surface-center hardness is observed, Fig. 5. The difference in surface-center hardness in the base HCWCI is 6,3 HRC. The addition of 0,5 wt.% of Al5Ti1B decreases this difference to 1,6 HRC, Fig. 5, noting that the addition of 0,5 wt.% of Al5Ti1B not only increases the average hardness value, but also significantly reduces the dispersion of hardness values on the cross-section of the balls, as a consequence of a more homogeneous structure. The HCWCI modified with 1,0 wt.% of Al5Ti1B has a finer structure, the transformation of austenite into martensite is more uniform across the cross-section, and a very small amount of pearlite is noticeable in the central zone (Fig. 3) if compared to the base alloy. This increases the average hardness and decreases the difference in surface-center

Taflove krivulje preskušenih HCWCI v 0,1 M NaCl so prikazane na Sliki 6.a skupaj z ustreznimi korozijskimi podatki, Preglednici 2. Dodatek Al5Ti1B zlitinam HCWCI premakne Taflove krivulje modificiranih belih železz visoko vsebnostjo kroma k manj negativnim vrednostim potencialov v okolju kloridne korozije, Slika 6.a. Premiku Taflovih krivulj proti bolj žlahtnim vrednostim potenciala zaradi modifikacije z Al5Ti1B sledi zmanjšanje vrednosti gostot korozijskih tokov v primerjavi z osnovno nemodificirano osnovno zlitino, Preglednica 2. Pri »osnovni zlitini« (Cr/C=6,1) so bile zabeležene najvišje vrednosti gostote korozijskega toka (71,1 μA/cm2) in najbolj negativen potencial $E_{(I=0)}$ (-458 mV) v primerjavi z vsemi drugimi preskušenimi modificiranimi zlitinami HCWCI v 0,1 M NaCl. Pri zlitini HCWCI z 0,5 wt.% Al5Ti1B (Cr/C=6) so bile zabeležene najnižje vrednosti gostote korozijskega toka v 0,1 M NaCl (23,3 μA/cm^2) in izračunana vrednost korozijske hitrosti (0,2 mm/leto). Podobne vrednosti korozijskih tokov (in hitrosti korozije) za zlitine HCWCI z dodatkom 0,5 wt.% Al5Ti1B (Cr/C=6) in 1,0 wt.% Al5Ti1B (Cr/C=6,3) so zabeležene v 0,1 M NaCl. Enakovredno vedenje zlitin HCWCI je razvidno iz preskušanja v sladki vodi, Slika 6.b. Taflove krivulje modificiranih belih železz visoko vsebnostjo kroma so v primerjavi s Taflovo krivuljo osnovne zlitine v poljih manjših negativnih vrednosti potencialov. Pri osnovni zlitini HCWCI (Cr/C=6,1) so bile zabeležene vrednost gostote korozijskega toka 21,5 μA/cm2 in najbolj negativen potencial $E_{(I=0)}$ (-389 mV) v primerjavi z vsemi modificiranimi zlitinami HCWCI, Preglednica 2. Podobne vrednosti $E_{(I=0)}$ za zlitine HCWCI, ki vsebujejo 0,5 wt.% (Cr/C=6) in 1,0 wt.% (Cr/C=6,3) Al5Ti1B, so bile zabeležene tudi pri korozijskih preskusih v 0,1 M NaCl.

hardness. The opposite tendency was observed in the HCWCI with 2.0% Al5Ti1B (an increase in hardness in the direction surface-center) as a result of an increase in the degree of transformation of austenite into very fine pearlite and martensite (Fig. 1 and 3) with small fractions of residual austenite.

The Tafel curves of tested HCWCIs in 0,1 M NaCl are shown in Fig. 6.a. with corresponding corrosion data given in Table 2. The addition of Al5Ti1B into the HCWCI alloys shifts the Tafel curves of modified high-chromium white irons toward less negative values of potentials in chloride corrosion ambiance, Fig.6. a. The shift of the Tafel curves toward more noble values of the potential due to modifying with Al5Ti1B is followed by a decrease in the values of the corrosion current densities, compared to the basic unmodified base alloy, Table 2. The “base alloy” (Cr/C=6,1) recorded the highest values of corrosion current density (71,1 μA/cm^2) followed by the most negative potential $E_{(I=0)}$ (-458 mV) if compared to all other tested modified HCWCI alloys in 0,1 M NaCl. The HCWCI alloy with 0,5 wt.% Al5Ti1B (Cr/C=6) recorded the lowest values of corrosion current density in 0,1 M NaCl (23,3 μA/cm2) and calculated the value of corrosion rate (0,2 mm/year). Similar values of corrosion currents (and corrosion rates) for HCWCI alloys with the addition of 0,5 wt.% Al5Ti1B (Cr/C=6) and 1,0 wt.% Al5Ti1B (Cr/C=6,3) are recorded in 0,1 M NaCl. The equivalent behavior of HCWCI alloys is indicated by testing in fresh water, Fig. 6.b. Tafel curves of modified high-chromium white irons are placed in the fields of les negative values of potentials compared to the Tafel curve of the base alloy. The base HCWCI alloy (Cr/C=6,1) recorded the value of corrosion current density of 21,5 μA/cm2 followed by the most negative potential $E_{(I=0)}$ (-389 mV)



Slika 6. Taflove krivulje osnovnih in modificiranih zlitin HCWCI v (a) 0,1 M NaCl in (b) sladki vodi

Figure 6. Tafel curves of HCWCI base and modified alloys in (a) 0,1 M NaCl and (b) fresh wate

Preglednica 2. Rezultati korozije zlitin HCWCI v 0,1 M NaCl in vodi; Taflove ekstrapolacije

Table. 2. Corrosion results of HCWCI alloys in 0,1 M NaCl and water; Tafel extrapolations

Vrsta zlitine / Type of alloy	Korozijsko okolje / Corrosion ambiance: 0,1 M NaCl			
	OCP [mV]	Stopnja korozije [mm/leto] / Corrosion rate [mm/year]	$E_{(I=0)}$, [mV]	I_{corr},[μA/cm^2]
Osnovni / Base HCWCI	-436	0,637	-458	71,1
HCWCI + 0,5 wt.% AlTiB	-388	0,200	-372	23,3
HCWCI + 1,0 wt.% AlTiB	-418	0,210	-440	23,5
HCWCI + 2,0 wt.% AlTiB	-327	0,353	-359	40,6
Vrsta zlitine / Type of alloy	Korozijsko okolje: voda / Corrosion ambience: water			
	OCP [mV]	Stopnja kor. [mm/leto] / Corrosion rate [mm/year]	$E_{(I=0)}$, [mV]	I_{corr},[μA/cm^2]
Osnovni / Base HCWCI	-387	0,192	-389	21,54
HCWCI + 0,5 wt.% AlTiB	-266	0,118	-304	13,52
HCWCI + 1,0 wt.% AlTiB	-271	0,174	-297	19,93
HCWCI + 2,0 wt.% AlTiB	-212	0,347	-250	39,87

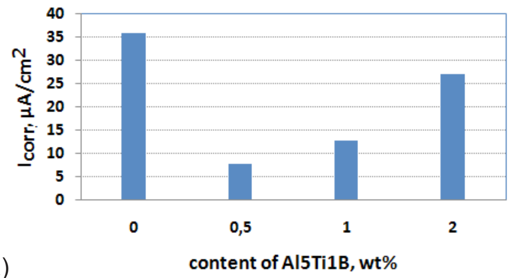
Korozijski podatki, pridobljeni z linearno polarizacijo zlitin HCWCI v 0,1 M NaCl in vodi, so prikazani v Preglednici 3. Tako kot pri preskušanju v raztopini natrijevega klorida se z dodatkom Al5Ti1B zlitinam HCWCI vrednosti $E_{(I=0)}$ vseh modificiranih zlitin v primerjavi z osnovno nemodificirano zlitino HCWCI v obeh korozijskih okoljih premaknejo k bolj žlahtnim vrednostim potencialov. Zaznanemu premiku potenciala E(I=0) proti žlahtnim vrednostim

if compared to all modified HCWCI alloys, Table 2. Similar values of $E_{(I=0)}$ for HCWCI alloys containing 0,5 wt.% (Cr/C=6) and 1,0 wt.% (Cr/C=6,3) of Al5Ti1B are also recorded, as well as in corrosion tests in 0,1M NaCl.

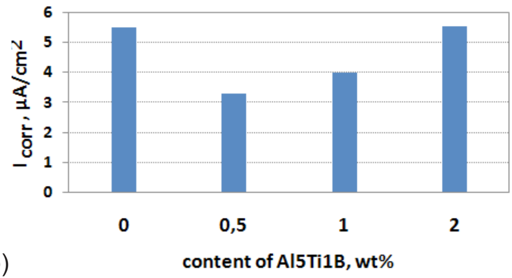
Corrosion data obtained by linear polarization of HCWCI alloys in 0,1 M NaCl and water are presented in Table 3. As well as when testing in a chloride solution, the addition of Al5Ti1B into the HCWCI potencialov sledijo nižji korozijski tokovi/ stopnje, izmerjeni v obeh uporabljenih korozijskih medijih, 0,1 M NaCl in sladki vodi, Preglednica 3 in Slika 7..

Zlitina HCWCI, ki vsebuje 0,5 wt.% Al5Ti1B, je imela najnižjo vrednost korozijskega toka v 0,1 M NaCl (7,59 μA/cm²) in v sladki vodi (3,29 μA/cm²), v primerjavi z osnovno zlitino HCWCI in drugimi modificiranimi zlitinami je bila manj

alloys shifts the values of E(I=0) of all modified alloys toward more noble values of potentials in both corrosion ambiances, compared to the base unmodified HCWCI alloy. The recorded shift of the potential E(I=0) towards noble potential values is followed by lower corrosion currents/rates measured in both used corrosion media, 0,1 M NaCl and fresh water, Table 3 and Fig.7.



a)



b)

Slika 7. Vpliv dodatka Al5Ti1B na I_{corr} zlitin HCWCI v (a) 0,1 M NaCl in (b) sladki vodi; linearna polarizacija

Figure 7. The influence of the Al5Ti1B addition on Icorr of HCWCI alloys, in (a) 0,1 M NaCl and (b) fresh water; linear polarization

Preglednica 3. Rezultati korozije zlitin HCWCI v 0,1 M NaCl in vodi; linearna polarizacija

Table. 3. Corrosion results of HCWCI alloys in 0,1 M NaCl and water; linear polarization

Vrsta zlitine / Type of alloy	Korozijsko okolje / Corrosion ambiance: 0,1 M NaCl			
	Stopnja kor. [mm/leto] / Corrosion rate [mm/year]	Rp, [kΩ]	$E_{(I=0)}$, [mV]	I_{corr},[μA/cm²]
Osnovni / Base HCWCI	0,319	0,609	-392	35,66
HCWCI + 0,5 wt.% AlTiB	0,066	2,861	-331	7,59
HCWCI + 1,0 wt.% AlTiB	0,110	1,721	-359	12,62
HCWCI + 2,0 wt.% AlTiB	0,234	0,807	-283	26,91
	Korozijsko okolje: voda / Corrosion ambience: water			
Vrsta zlitine / Type of alloy	Stopnja kor. [mm/leto] / Corrosion rate [mm/year]	Rp, [kΩ]	$E_{(I=0)}$, [mV]	I_{corr},[μA/cm²]
Osnovni / Base HCWCI	0,049	3,951	-348	5,50
HCWCI + 0,5 wt.% AlTiB	0,029	6,590	-226	3,29
HCWCI + 1,0 wt.% AlTiB	0,035	5,426	-235	4,00
HCWCI + 2,0 wt.% AlTiB	0,048	3,946	-178	5,51

korodirana. Osnovna zlitina HCWCI je imela najvišje vrednosti gostote korozijskega toka in je bila podvržena večji koroziji tako v 0,1 M NaCl kot v sladki vodi v primerjavi z vsemi preskušenimi zlitinami HCWC, modificiranimi z Al5Ti1B.

Dodatek 0,5 wt.% Al5Ti1B premakne potencial $E_{(I=0)}$ v bolj žlahtna območja (-226 mV), sledijo nižje vrednosti gostote korozijskega toka (3,29 μA/cm^2) v primerjavi z nemodificirano zlitino. Nadaljnje povečanje vsebnosti Al5Ti1B povzroči povečanje gostote korozijskega toka, pri čemer so bile za zlitino HCWC, ki vsebuje 2,0 wt.% Al5Ti1B, in osnovno zlitino zabeležene podobne vrednosti I_{corr}. Opaziti je mogoče, da so medsebojna razmerja med korozijskimi značilnostmi, pridobljena z linearnim polarizacijskim preskusom v sladki vodi, podobna razmerjem, zabeleženim s potenciodinamičnimi (Taflovimi) polarizacijskimi preskusi. Glede na zagotovljene korozijske lastnosti je zlitina HCWCI, modificirana z 0,5 wt.% Al5Ti1B, pokazala znatno zmanjšanje korozijskih izgub, z najboljšo korozijsko odpornostjo v primerjavi s preskušeno osnovno zlitino in drugimi modificiranimi zlitinami HCWCI.

4 Sklepi

Dodatek Al5Ti1B vpliva na postopek strjevanja krogel iz belega železa z visoko vsebnostjo kroma in na transformacije v trdnem stanju med ohlajanjem ulitih krogel. Z modifikacijo HCWCI z dodatkom inokulanta Al5Ti1B lahko zagotovimo bistveno bolj fino strukturo. Najbolj izrazit učinek je opazen pri dodatku 0,5 wt.% Al5TiB1.

Dodatek 0,5 wt.% Al5Ti1B povzroči povečanje povprečne vrednosti trdote v primerjavi z osnovnim HCWCI in zmanjša razpršenost vrednosti trdote na prerezu

The HCWCI alloy containing 0,5 wt.% of Al5Ti1B recorded the lowest value of corrosion current in 0,1 M NaCl (7,59 μA/cm^2) and in fresh water (3,29 μA/cm^2) and suffered less corrosion compared to the base HCWCI alloy and other modified alloys. The base HCWCI alloy had the highest values of corrosion current density and undergo more corrosion in both 0,1 M NaCl and fresh water compared to all tested HCWC alloys modified with Al5Ti1B.

The addition of 0,5 wt.% of Al5Ti1B shifts the potential $E_{(I=0)}$ towards more noble regions (-226 mV), followed by lower values of the corrosion current density (3,29 μA/cm^2) compared to the unmodified alloy. A further increase in the Al5Ti1B content causes an increase in the corrosion current density, noting that similar I_{corr} values were recorded for the HCWC alloy containing 2,0 wt.% Al5Ti1B and the base alloy. It is noticeable that the mutual relations between the corrosion characteristics obtained by the linear polarization test in fresh water are similar to the relations recorded by the potentiodynamic (Tafel) polarization tests. According to the obtained corrosion characteristics, the HCWCI alloy was modified with 0,5 wt.% Al5Ti1B showed a significant reduction in corrosion losses, with the best corrosion resistance compared to the tested base alloy and other modified HCWCI alloys.

4 Conclusion

The addition of Al5Ti1B affects the solidification process of high-chromium white iron balls and the transformations in the solid state during the cooling of the cast balls. A much finer structure can be obtained by modifying of HCWCIs with the addition of Al5Ti1B inoculant. The most pronounced krogel, kar je posledica bolj homogene strukture.

Dodatek Al5Ti1B zlitinam HCWCI premakne Taflove krivulje modificiranih HCWCI proti manj negativnim vrednostim potencialov v obeh uporabljenih korozijskih okoljih, sledi zmanjšanje vrednosti gostot korozijskih tokov v primerjavi z osnovno nemodificirano osnovno zlitino. Zlitina HCWCI z 0,5 %Al5Ti1B (Cr/C=6) je v obeh uporabljenih korozijskih okoljih (0,1 M NaCl in sladka voda) dosegla najnižje vrednosti gostote korozijskega toka in izračunane hitrosti korozije, prav tako je bila tudi najbolj korozijsko odporna izmed preizkušenih zlitin HCWCI.

Glede na zabeležene korozijske podatke in vrednosti trdote je zlitina, modificirana z 0,5 wt.% Al5Ti1B, zagotovila optimalno kombinacijo preskušenih lastnosti. Na podlagi rezultatov raziskave je prav tako mogoče sklepati, da je mogoče predzlitino Al5Ti1B uporabljati kot cepivo v belih litinah z visoko vsebnostjo kroma za krogle za mletje.

5 Zahvala

To delo sta podprla Ministrstvo za izobraževanje, znanost in tehnološki razvoj Republike Srbije in Ministrstvo za gospodarski razvoj Črne gore v okviru pogodbe št. E!13302CastBalls: White iron composition and processing design for highly efficient casted milling balls.

effect is observed in the case of the addition of 0,5 wt.% Al5TiB1.

The addition of 0,5 wt.% Al5Ti1B causes an increase in the average hardness value, if compared to the base HCWCI and reduces the dispersion of hardness values on the cross-section of the balls, as a consequence of a more homogeneous structure.

The addition of Al5Ti1B into the HCWCI alloys shifts the Tafel curves of modified HCWCIs toward less negative values of potentials in both used corrosion ambiances, followed by a decrease in the values of the corrosion current densities, compared to the basic unmodified base alloy. The HCWCI alloy with 0,5 %Al5Ti1B (Cr/C=6) recorded the lowest values of corrosion current densities, and calculated corrosion rates, in both used corrosion ambiances (0,1 M NaCl and fresh water), with the best corrosion resistance between tested HCWCI alloys.

According to recorded corrosion data and hardness values, the alloy was modified by 0,5 wt.% Al5Ti1B,showed the optimal combination of tested properties. Based on the obtained research results, it can be also concluded that Al5Ti1B master alloy can be used as a modifier in high-chromium white cast irons for grinding balls.

5 Acknowledgment

This work has been supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, and the Ministry of Economic Development of Montenegro, under contract No. E!13302CastBalls: White iron composition and processing design for highly efficient casted milling balls

Viri / References

1. S. O. Yilmaz, T. Teker, Effect of TiBAl inoculation and heat treatment on microstructure and mechanical properties of hypereutectic high chromium white cast iron, Journal of Alloys and Compounds 672 (2016) 324–331
2. Eternal Bliss Alloy Casting & Forging Co, Ltd. Technical Dept.: „Introduction and application of high chromium cast iron materials", https://ebcastworld.com/high-chromium-cast-iron/ December 20, 2019
3. High Alloy White Irons, Total Materia, ref. 13 December 20, 2002
4. JTH Pearce (2002) High-chromium cast irons to resist abrasive wear. Foundryman 95(4):156–16
5. A.E. Karantzalis, A. Lekatou, H. Mavros (2009) Microstructural modifications of As-cast high-chromium white iron by heat treatment. ASM Int JMEPEG 18:174–181
6. E. Zumelzu, I. Goyosb, C. Cabezas, O. Opitz, A. Parad (2002) Wear and corrosion behaviour of high-chromium (14–30% Cr) cast iron alloys. J Mater Process Technol 128:250–255
7. The hardness of grinding media ball,https://www.nghexin.com/the-hardness-of-grinding-media-ball/
8. A. Bedolla-Jacuinde, R. Correa, J.G. Quezada, C. Maldonado, Effect of titanium on the as-cast microstructure of a 16% chromium white iron, Mater. Sci. Eng. A 398 (2005) 297–308.
9. F. Han, S. Shen, D. Wang, X. Chen, X. Lu, Study on the structure and properties of a novel mini-sized high Cr mill balls, Wear 253 (2002) 640–649.
10. A. Wiengmoon, T. Chairuangsri, A. Brown, R. Brydson, D.V. Edmonds, J.T.H. Pearce, Microstructural and crystallographical study of carbides in 30wt..%Cr cast irons, Acta Mater 23 (2005) 4143–4154.
11. R.J. Llewellyn, S.K. Yick, K.F. Dolmanb, Scouring erosion resistance of metallic materials used in slurry pump service, Wear 256 (2004) 592–599.
12. B. Lu, J. Luo S. Chiovelli, Corrosion and wear resistance of chrome white irons—A correlation to their composition and microstructure Metallurgical and Materials Transactions A · Oktober 2006 DOI: 10.1007/s11661-006-0184-x https://www.researchgate.net/publication/226653636
13. Kh. Abd El-Aziz, Kh. Zohdy, D. Saber, H. E. M. Sallam, Wear and Corrosion Behavior of High-Cr White Cast Iron Alloys in Different Corrosive Media J Bio Tribo Corros (2015) 1:25, DOI 10.1007/s40735-015-0026-8
14. XH Tanga, R Chunga, CJ Panga, DY Li, B Hinckleyb, K Dolmanb (2011) Microstructure of high (45 wt.%) chromium cast irons and their resistances to wear and corrosion. Wear 271:1426–1431
15. A Wiengmoon, JTH Pearce, T. Chairuangsri (2011) Relationship between microstructure, hardness and corrosion resistance in 20 wt.% Cr, 27 wt.% Cr and 36 wt.% Cr high chromium cast irons. Mater Chem Phys 125:739–748.