CORROSION RESISTANCE OF SELECTED CAST IRON GRADES UNDER DEPOSIT MINING CONDITIONS

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Abstract

The paper analyzes two types of alloyed cast iron used for pump impellers operated in mine working conditions. The research on corrosion resistance of two cast iron grades resistant to abrasive wear was presented. Tests were performed for chromium cast iron (HCCI) grade EN-GJN HV600 (XCr18) (acc. to EN 12513) and high-silicon cast iron HSCI Grade 1 (acc. to ASTM A 518/ A 518M - 99). Deposit mining is characterized by variable working conditions. Both types of cast iron are resistant to abrasive wear and are suitable for loaded elements (e.g. pump impellers). The paper presents a metallographic analysis of selected cast iron grades based on light microscopy. The chemical composition of the tested cast irons was determined with the Leco GDS 500 spectrometer; C and S content was determined with the CS125 Leco Carbon–Sulfur Determinator. The Si content for HSCI Grade 1 was determined by gravimetric method. Corrosion tests were performed under laboratory conditions. In-service tests of cast impellers were performed under real conditions (working mines applications). Corrosion resistance tests were measured with VoltaLab® Potentiostat (PGP 201). Performed tests resulted in the determination of the usefulness of materials used for dewatering pump impellers in mine working conditions. The results of laboratory tests were verified under the operating conditions of cast impellers. In the conditions of transporting a liquid-solid mixture at the moment of appearance of impurities (e.g. chlorine impurities) in the liquid, the impellers from cast iron HCCI revealed a tendency to pitting corrosion, which explains the exploitation results collected in the mining. After laboratory tests for sample from HCCI, the low value of breakdown potential E_b and repassivation E_{cp} was concluded which says about the absence of pitting corrosion resistance.

Keywords: corrosion resistance, silicon cast iron, chromium cast iron, pitting corrosion, abrasive wear

Introduction

Rotodynamic, centrifugal, single-stage, and horizontal pumps with single-suction impellers are designed for pumping contaminated liquids containing sand, ores, coal, slag, etc., in high concentrations. Due to the special pump design, the flow system can be operated for a long time, maintaining high hydraulic efficiency. Heavy liquid pumps are used to pump highly contaminated liquids containing abrasive materials such as sand, quartz, metal ores, waste rock, and coal. The pumps are made of highly abrasion-resistant materials. Solid content by weight in the pumped medium must not exceed 60%. The maximum density of

the pumped liquid is 2200 kg/m³. Possible applications for high-power pumps are dewatering of mining workings extracting minerals using the opencast method, including the pumping of surface water, which periodically, during heavy rainfall, may contain significant amounts of solids (e.g. sand). Therefore, all pumps operated in such conditions work at a nominal speed of 1500 rpm, which significantly increases their resistance to wear caused by the presence of solids in the pumped liquid.[1,2]

Medium- and highly alloyed chromium cast irons are widely used in industry for castings used in high temperatures and in conditions requiring high resistance to abrasive wear or corrosion. Chromium cast iron is melted in electric furnaces. This material has a good castability and in this respect does not cause any major technological

problems; however, casting shrinkage is about 2%. Medium- and high-chromium cast irons are characterized by carbide microstructure, but their mechanical properties and elasticity are much better than in the case of unalloyed white cast iron with cementite. The Fe–C–Cr phase equilibrium system determined for high chromium cast irons[3–6] shows that the microstructure of high chromium cast iron may consist of mixtures of different phases: α dendrites, γ dendrites, γ dendrites, peritectic $(\gamma + {}_7C_3)$, peritectic $(\gamma + M_3C)$, eutectic $(\gamma + M_7C_3)$, eutectic $(\gamma + M_3C)$, and primary carbides M_3C and $M_{23}C_6$.

Chromium cast irons containing 11–23% chromium in their chemical composition are classified according to the standards as wear-resistant cast irons. An important factor influencing the abrasion resistance of chromium cast iron is the Cr/C ratio, which, according to the literature, should be in the range of 3–10, which determines the crystallization of the complex M_7C_3 carbides, desired in the microstructure. Formation of this type of carbide significantly contributes to the hardness of the alloy and its resistance to abrasive wear. Increasing the carbon content of chromium cast iron results in an increase in the proportion of the carbide phase in the alloy microstructure, which increases the abrasion resistance of chromium cast iron, but can lead to the formation of M_3C carbide networks which impair impact resistance and reduce crack resistance. At a sufficiently high cooling rate in chromium cast iron, an austenitic matrix with M_7C_3 carbide precipitations can be obtained after casting. In contrast to cementite in unalloyed white cast iron, M_7C_3 carbides do not form a network sensitive to brittle fracture. Therefore, chromium cast irons can work in impact and abrasive conditions. Obtaining austenitic matrix results in increased wear resistance of cast iron. This is particularly important when making large-size castings, e.g. large pump bodies difficult to harden in order to obtain a martensitic matrix resistant to abrasive wear. Abrasion-resistant chromium cast irons are used, among others, for castings of flail strips in spindle mill, flails in hammer mills, armor plates, and balls in ball mills, rollers, parts of pumps, and screw cleaners.[3,5,7] To increase the hardness, heat treatment is often performed which leads to the formation of a martensitic structure, and various alloying additives are used to increase wear resistance of chromium cast iron.[8–10] With chromium contents over 25%, only chromium ferrite is present in the cast iron matrix, which results in the lower hardness of the cast iron. The wear resistance of the alloy decreases, but corrosion and heat resistance increase. Cast iron containing 26–36% chromium has very good resistance to mineral acids, oxidizing acids, seawater, mine waters, and various sea salt solutions. The corrosion resistance of chromium cast iron comes from the formation of a thin passive film of chromium oxides on the casting surface. The formation of the oxide film is associated with an appropriate chromium content in the cast iron matrix (above 12%). The formation of the chromium oxide layer may also be promoted by the corrosive medium. Chromium cast iron reacts to nitric acid similarly to silicone cast iron; however, chromium cast iron can only be active in acids of lower concentration, as opposed to silicon cast iron, which is resistant to nitric acid of high concentration.[3]

The corrosion resistance of high-silicon cast iron increases with the increase in silicon content in the alloy, while only ca. 14% concentration of this element about gives a material with sufficient corrosion resistance.[11] The resistance to acid attack of high-silicone cast iron is determined by the formation of a SiO_2 layer on the casting surface. Iron atoms are washed out from the surface of a crystalline network of silicon ferrite, and the remaining atoms combine with oxygen to form a protective layer. The oxidizing environment strengthens the protective properties of the layer, whereas in case of its mechanical damage the layer may regenerate under the influence of oxidants.[3]

With lyes, silicon dioxide forms soluble silicates (Na_2SiO_3. K_2SiO_3) and with hydrogen fluoride–gaseous SiF_4 silicon tetrafluoride. The formation of these compounds results in the lack of resistance of high-silicon cast iron to the media in which these compounds occur.[3] High-silicon cast iron is resistant to an oxidizing effect of inorganic (nitric, sulphuric, chromium, etc.) acids and their solutions with organic acids at different values of their concentration and temperature, maintaining, in some cases (e.g. HNO_3), this resistance at boiling temperature.[3] High-silicon cast iron not only has good resistance to acids but is also resistant to abrasion; hence, the alloy is used in the production of pumps transporting sludge.[11] Frequently, when the silicon content drops below 12.5%, we obtain better castability of the material and better mechanical properties, especially plasticity. However, corrosion resistance decreases.[12] Corrosion resistance decreases with an increase in carbon content and an increase in the size of graphite precipitates. The form of graphite in high-silicon cast iron also plays a significant role. The material with spheroidal graphite has higher corrosion resistance in comparison with the alloy with flake graphite.[12] Corrosion of flake graphite progresses deep into the material after separation of graphite because oxygen penetrates into the casting mainly along graphite flakes, causing oxidation of the alloy with all its consequences.[3,11] Another unfavourable phenomenon is the segregation of Si in particular (local differences in chemical composition). It causes differences in a passive layer produced on the surface of the alloy in the form of a variable thickness and formation rate. Such conditions promote electrochemical corrosion.[13]

Along with a decrease in grain size, the corrosion resistance of the material increases. Therefore, castings made in permanent moulds always have higher corrosion resistance in comparison with castings made in sand moulds.[3,14]

Purpose of Research

High chromium cast iron (HCCI), from which some of the pump impellers for the mine workings in question were made, should have good corrosion resistance, but in few cases, it is not required. Due to the above requirements, some of the pump impellers are made of such material. Their operation was relatively failure-free, so there was no demand for improvement of their quality. Unfortunately, deposits of water-rich in chlorides and other chemical compounds increasing the risk of corrosion began to appear periodically in the mine working. As a result, the impellers were subject to very rapid abrasive and corrosive wear. Such an impeller is shown in Figure 1a. An alternative to this type of load system is a casting made of HSCI Grade 1, which in its untreated state is shown in Figure 1c. The weight of the casting from HSCI alloy in the raw state was 30 kg. The height of the casting was 200 mm, and the diameter was 400 mm. Therefore, this paper analyses two types of alloyed cast iron used for pump impellers operated in mine working conditions. Due to the requirement of confidentiality, the paper does not mention the name of the mining plant in which the analyzed castings were used. The pictures show impellers made of chromium cast iron after the operational term (Figure 1a, b) and impellers made of untreated silicon cast iron after removing from the mould (Figure 1c).

Research Results

Chemical Composition

Tests were performed for high chromium cast iron grade EN-GJN HV600(XCr18) (HCCI) according to EN 12513 and high-silicon cast iron HSCI Grade 1 according to ASTM A 518/ A 518M - 99). The chemical composition of the tested castings is presented in Table 1. Chemical composition was determined, using Leco GDS 500 Spectrometer. C and S contents were determined, using Leco Carbon–Sulfur Determinator CS125. Si content was determined by gravimetric method (for HSCI Grade 1 with flake graphite).

Metallographic Testing

Metallographic examination was performed with Nikon Eclipse LV150N light microscope. Test samples in the form of metallographic specimens were subjected to metallographic evaluation. A chromium cast iron specimen was subjected to etching in iron chloride. A silicon cast iron specimen was examined in the as-polished condition. The obtained microstructures are shown below in Figure 2. Figure 2 a-b shows microstructures of high-silicon cast iron with type II black graphite secretions (according to PN-EN ISO 945) on a bright background of silicon ferrite. The darker lenticular component in the metal matrix is the Fe_5Si_3 phase.[15] The photomicrographs in (Figure 2. c-d) show visible eutectic of M_7C_3 carbide[16] in the austenitic

Table 1. Chemical Composition of the Tested Cast Irons.

Alloy cast iron	Chemical composition, wt%							
	C	Cr	Si	Mn	Mo	Ni	P	S
HCCI	2.85	20.4	0.657	0.385	0.565	1.48	0.049	0.032
HSCI Grade 1	0.87	0.0	14.71	0.34	0.02	0.0	0.02	0.001

Figure 1. Pump impeller with visible traces of abrasive wear and pitting corrosion after a period of operation in an environment rich in chlorides—chromium cast iron (a), pump impeller after the period of operation with visible traces of abrasive wear after the period of operation in the absence of corrosive factors—chromium cast iron (b), and pump impeller after casting in the raw state—silicon cast iron (c).
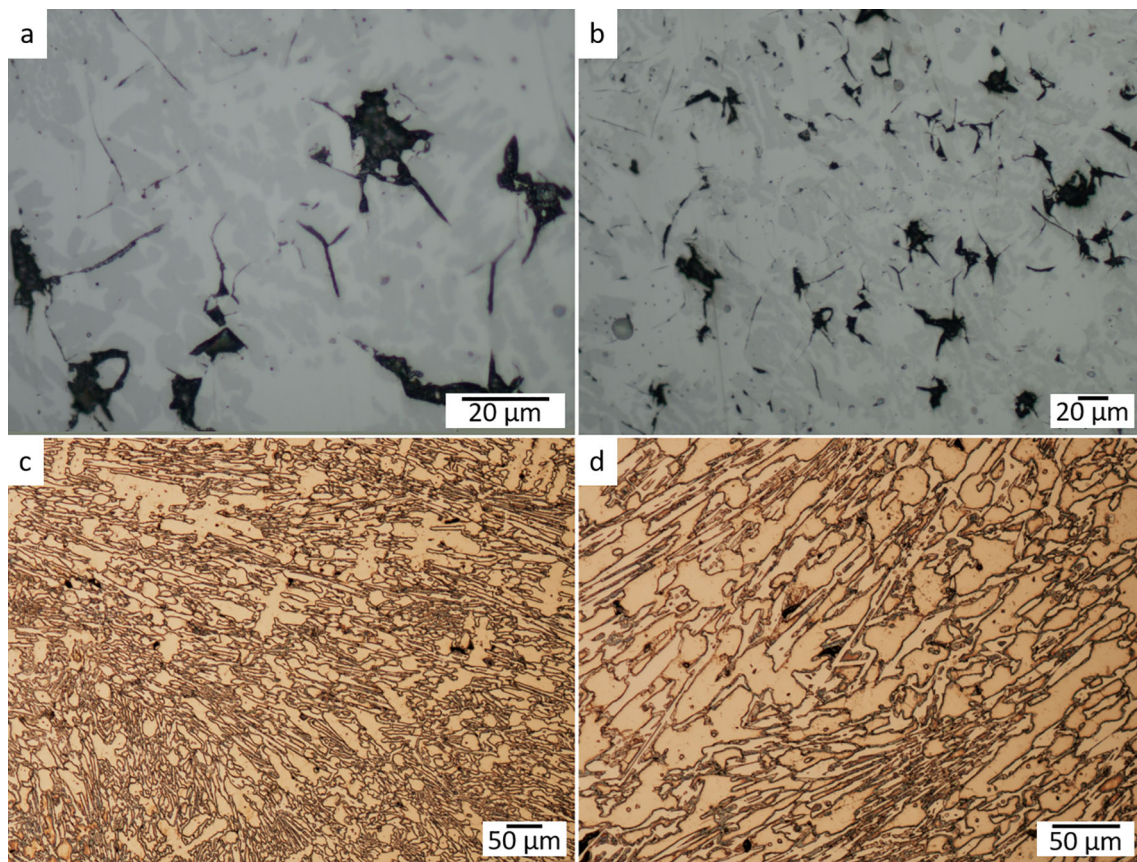
Figure 2. *The microstructure of HSCI Grade 1, un-polished specimen (a, b). The microstructure of high chromium cast iron HCCl, specimen etched with ferric chloride (c, d).*

Table 2. Results of Potentiodynamic Tests—Mean Values

Alloy cast iron	Corrosion test parameters											
	$*E_{corr}$, mV	STD	$*E_b$, mV	STD	$*E_{cp}$, mV	STD	$*E_{tr}$, mV	STD	$*R_p$, k$\Omega \cdot$cm^2	STD	$*I$corr, μA/ cm^2	STD
EN-GJN HV600(XCr18)	− 457.1	± 5.5	− 179	± 10.5	− 500.6	± 0.2	−	−	3.77	± 1.71	11.0	± 1.1
HSCI Grade 1	− 257.9	± 20.2	−	−	−	−	1546	± 44	23.76	± 0.72	1.6	± 0.6

*Description of symbols used in the table: E_{corr}—corrosion potential, E_b—breakdown potential, E_{cp}—repassivation potential, E_{tr}—transpassivation potential, R_p—polarization resistance, I_{corr}—corrosion current, STD—standard deviation

matrix. In contrast to cementite in white unalloyed cast iron, these carbides do not form a network sensitive to brittle fracture.

Corrosion Testing

A test stand for corrosion tests consisted of the following elements: VoltaLab Potentiostat (PGP 201), auxiliary electrode (PtP-201 Platinum electrode), reference electrode (saturated calomel electrode (SCE) of KP-113 type), anode (tested specimen), and computer recording system with

VoltaMaster 4 software. The corrosion tests started with establishing the open circuit potential E_{OCP} at currentless conditions during the time $t = 120$ min. Polarization curves were recorded from the initial potential value $E_{start} = E_{OCP} − 100$ mV. The potential was increased in the anode direction at the rate of 3 mV/s. After reaching an anode current density of 10 mA/cm^2, the polarization direction was changed. Based on the obtained curves, the corrosive potential E_{corr}, breakdown potential E_b, repassivation potential E_{cp}, and transpassivation potential E_{tr} were determined. Additionally, a value of polarization resistance R_p and corrosion current i_{corr} was determined with the Stern
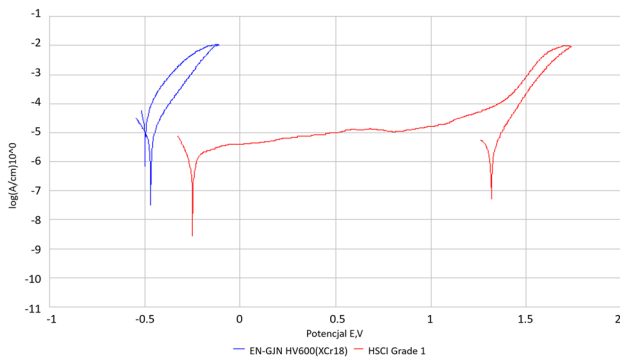
Figure 3. Polarization curves for tested alloys. Blue cast iron HCCI, red HSCI Grade 1.

and Tafel method. The pitting corrosion resistance test was performed in 3% NaCl solution at 24 °C.

The results of the pitting corrosion resistance potentiodynamic test are presented in Table 2 and Figure 3.

Based on the obtained results, it was found that the corrosive potential of E_{corr} for the HCCI alloy samples (1) was − 457.1 mV, whereas for high-silicon cast iron samples it was − 257.9 mV. For sample, HCCI was concluded the low value of breakdown potential E_b (− 179 mV) and repassivation Ecp (− 500.6 mV) (Table 2) which says about the absence of pitting corrosion resistance. While in the case of a high-silicon cast iron specimen, it was found transpassivation potential E_{tr} was favourable, amounting to about 1546 mV (Table 2). The high-silicon cast iron displayed a high polarization resistance value (Table 2) and a reduced in the corrosive current value to 1.6 μA/cm^2 in comparison with the chromium cast iron alloy (11 μA/cm^2). A long plateau section on the polarization diagrams (Figure 3) indicates the presence of a passive layer on the surface of the specimen made of high-silicon cast iron, which significantly improves corrosion resistance in comparison with the chromium cast iron alloy.

Summary and Discussion

The chemical composition of mine waters was not examined in terms of the content of chemical elements promoting corrosion due to restrictions on access to the mine working that occurred in the analyzed case. In specific cases (working conditions without corrosive factors), high chromium cast iron HCCI may be used as a heavily loaded element. However, literature sources and results of studies show that corrosion resistance of chromium cast iron is strictly dependent on Cr content in the alloy. Authors of work[17] developed a map for quick identification of alloy compositions (C and Cr content) that may be suited for wear or corrosion conditions. The map is presented in Figure 4.
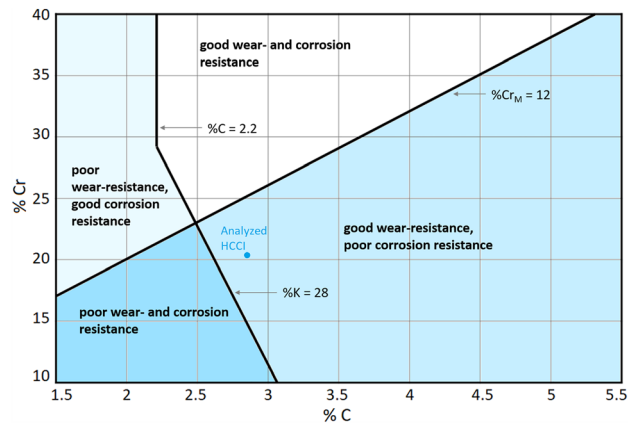

Figure 4. Wear- and corrosion resistance map for chromium cast iron dependent of C and Cr content in alloy composition.

Based on the presented map developed according to the research and authors' studies, it can be assumed that examined HCCI alloy cannot exhibit good wear resistance properties, especially in an aggressive environment. In the conditions of transporting a liquid-solid mixture at the moment of appearance of impurities (e.g. chlorine impurities) in the liquid, the impellers from HCCI have a tendency to pitting corrosion, which is confirmed by the exploitation results collected in the mining plant (Figure 1a) and the results of laboratory corrosion resistance tests. In the case of chromium cast iron, it was found that values of breakdown potentials E_b and repassivation potentials E_{cp} were low (see Table 2). Such results indicate no resistance to pitting corrosion. It is suggested that impellers for use in the mine workings in question should be manufactured with a surface layer resistant to abrasive wear and corrosion from high-silicon cast iron or to use chromium cast iron alloys resistant to corrosion and abrasive wear (alloys with Cr content above 25%). According to other authors' research[18], not only wear resistance but also the corrosion behaviour of chromium cast iron strongly depends on Cr/C ratio. It is important to keep a high level of Cr/C ratio, which should provide a proper content of Cr in the metal matrix that allows required corrosion resistance. If the Cr/C ratio is too small, most of Cr is concentrated in M_7C_3 carbides and corrosion resistance decreases. The studies of Abd El-Aziz at all[18] show that only the alloy with the Cr/C ratio equal 13 revealed increased corrosion properties in comparison with other investigated alloys with Cr/C ratio of about 7 and 9. In the presented work, the Cr/C ratio is 10, which may be also too low to achieve the required corrosion resistance of analysed chromium white cast iron. This also leads to the conclusion that higher Cr content is necessary for the improvement of corrosion resistance.

The controlled electrochemical experimental methods were used to characterize the corrosion properties of HCCI/HSCI alloys castings in combination with 3%NaCl

electrolyte solutions. The use of the potentiodynamic experiment allowed to provide a series of data related to pitting, the phenomenon of passivation for specific sample-solution combinations. As the potential for HCCI alloy increases, the phenomenon of pitting corrosion starts at a certain value of E_b. For HCCI alloy, the value of the lowest E_b potential is -179 mV, at which pitting occurs.

HSCI Grade 1 has a favourable transpassivation potential of approximately 1546 mV (Table 2). The addition of silicon to the HSCI Grade 1 alloy increased the polarization resistance value (Table 2) and a decrease in the corrosive current value to 1.6 μA/cm^2 in comparison with the chromium cast iron alloy (11 μA/cm^2). It indicates that a passive layer was created on the surface of the tested material. The researchers[19] determined that even a little amount of Si content in cast iron leads to the formation of SiO_2 as the major component of the formed surface layer in corrosion tests. They concluded that it may be caused by near-surface silicon diffusion and the corrosion resistance is strictly connected with the appearance of SiO_2 on the casting surface. According to the research[20] during the immersion in the solution, Si may dissolve into the solution and form SiO_2 oxides on the surface of HSCI. The presence of SiO_2 passive layer may increase the corrosion resistance and reduces the corrosion rate of high silicon cast iron.

The resistance to passive layer breakdown and pit initiation for chromium cast iron may be increased with the higher amount of Cr. According to researchers, more than 10% Cr_2O_3 content in the HCCI matrix surface film should facilitate the development of the passive layer.[21] Unfortunately, it was reported that there is an impaired passivity of the matrix near carbide boundaries, because of the Cr content depletion in this area. Authors of studies[22] suggested that this may cause the local passivity breakdowns on the HCCI surface in specific environments.

Conclusions

- The analyzed HCCI does not meet the requirements for application in the examined corrosive conditions.
- To avoid the corrosive wear of HCCI during the work in presented conditions, it is suggested to increase the Cr content above 25% and the level of C above 2.5%, but it is important to obtain the proper Cr/C ratio and to keep the possibly highest amount of fine M_7C_3 carbides in the metal matrix to maintain abrasive wear resistance.
- In the conditions of transporting a liquid-solid mixture at the moment of appearance of impurities (e.g. chlorine impurities) in the liquid, the impellers from cast iron HCCI have a tendency to pitting corrosion, which is confirmed by the exploitation results collected in the mining plant

(Figure 1a) and the results of laboratory corrosion resistance tests.

- In the case of chromium cast iron, it was found that values of breakdown potentials E_b and repassivation potentials Ecp were low (see Table 2). Such results indicate no resistance to pitting corrosion.
- HSCI Grade 1 has a favourable transpassivation potential of approximately 1546 mV.
- The HSCI Grade 1 alloy displayed and exhibited an increased polarization resistance value (Table 2) and a decrease in the corrosive current value to 1.6 μA/cm^2 in comparison with the chromium cast iron alloy (11 μA/cm^2). The low corrosion current value indicates that a passive layer was created on the surface of the HSCI material.

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