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Effect of Corrosion on Wear Resistance of the Composite Based on GX120Mn13 Cast Steel Zonally Reinforced with Particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$)

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Abstract

The subject of the work are modern composite materials with increased wear resistance intended for elements of machines operating in difficult conditions in the construction and mining industries. The study determined the effect of zone reinforcement of GX120Mn13 cast steel with macroparticles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) on the corrosion resistance and abrasion wear of the composite thus obtained. SEM studies have shown that at interface between two phases, and more precisely on the surface of particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) a durable diffusion layers are formed. During the corrosion tests, no significant differences were found between the obtained parameters defining the corrosion processes of GX120Mn13 cast steel and GX120Mn13 with particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) composite. No intergranular corrosion was observed in the matrix of the composite material, nor traces of pitting corrosion at both phases interface. This is very important in terms of tested material's service life. Reinforcement of cast steel with particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) resulted in a very significant improvement in the abrasion resistance of the composite – by about 70%. After corrosion tests, both materials were subjected to further operational investigations. These examinations consisted in determining the impact of corrosion processes on the durability of the composite in terms of abrasion. The obtained results indicate that corrosion processes did not significantly deteriorate the wear resistance of both the cast steel and the composite.

Keywords: Abrasive wear, Cast steel, Ceramics, Composites, Corrosion

1. Introduction

Abrasive and corrosive wear of materials, due to the complexity of processes and technological and economic importance, has been the subject of research for many years [1–3]. This works show that it is not possible to develop a universal material that guarantees high abrasion resistance, while at the same time increased corrosion resistance, in all operating conditions. However, it was found that usually the higher the hardness of the

material, the higher the abrasion resistance [1–5]. At the same time, increasing the hardness of the material causes a deterioration of its impact strength most often [5]. It seems that the solution to this problem may be the use of composite materials that combine the features of the components used in them. This is particularly effective when strengthening is required only in specific places of the manufactured elements.

Local strengthening of castings is used primarily in the case of nonferrous metal alloys, mainly Al-alloys. They are obtained by means of porous moldings made of SiC or Al_2O_3 particles and



fibers [6–8]. However, their porosity is so small that they must be pressure infiltrated in the process of casting production [5–9]. It is therefore a method that cannot be used for the production of large-size iron-carbon castings. In that cases, methods of surface saturation of castings with alloying elements are mainly used or creation of bimetallic layer castings i.e. surface-reinforced [10,11]. It allows you to strengthen only the top layer of the casting, a few millimeters thick.

However, the degree of wear of machine elements working in the mining industry as well as in civil engineering, is usually several centimeters. Therefore, such a solution was proposed, Hadfield's cast steel GX120Mn13 was used as the matrix, which was reinforced with particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) in zones. As a result, the casting areas subjected to intensive abrasion were strengthened, while the increased mechanical properties of the base cast steel were maintained in the remaining zones. It can therefore be assumed that a composite was obtained combining the advantages of Hadfield cast steel (high toughness and impact strength) and corundum (very high hardness and resistance to abrasive wear).

On the other hand, components of working machines, apart from intensive abrasive wear, they are also exposed to aggressive corrosive environments, especially during downtime. Alloys composed of different phases with a large difference in electrochemical potentials usually have lower corrosion resistance compared to single-phase alloys [4,12–14]. The greater the difference of these potentials, the greater the value of the SEM, which is an indicator of the progress of corrosion processes. The proposed solution seems to meet these requirements, because the values of the electrochemical potential of the phases used do not show much difference.

The studies carried out so far have shown that the reinforcing phase of the composite made of Hadfield cast steel can be ordinary corundum [13]. In this work, an attempt was made to determine whether the change of reinforcing phase from ordinary corundum to particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$ – greater so-called „ductility”), while maintaining the same zone reinforcement method, will allow to obtain an equally durable composite. And also, will the corrosion processes (in conditions of machine downtime) significantly affect the durability of the composite in terms of later resistance to abrasive wear?

2. Subject, scope and methodology

The subject of the work are high-quality castings (made in industrial conditions, by gravity casting into sand moulds) of Hadfield cast steel GX120Mn13 according to EN 10349:2011 standard (with a chemical composition: 1.30 %C; 13,25 %Mn; 1.15 %Cr; 0,85 %Ni 0,04 %P; 0,03 %S and hardness approx. 210 HB), zone-reinforced to a depth of 5 cm from the face of the reinforcement by particles (72–78% $\text{Al}_2\text{O}_3 + 23$ –25% ZrO_2). The granularity of the particles ranges from 0.5 to 2.5 mm.

In the case of composite materials, strong and durable connections between phases guarantee increased resistance to external forces and prevent the particles of the reinforcing phase from chipping off during friction. However, these connections can be weakened not only by abrasion but also by corrosion. Therefore, wear tests were carried out: abrasive and corrosive. In addition, a series of microscopic observations and analyzes of the chemical

composition at the junction of the two phases of the composite were carried out.

Macroscopic examinations were carried out using an optical stereoscopic microscope OZL 963 by Kern Optics, while for microscopic examinations a scanning electron microscopes TM 3000 by Hitachi and Quanta 250 by FEI were used.

The chemical composition of the matrix of the analyzed samples was determined by two methods, i.e. spectral and energy dispersive spectroscopy. GDS 750 QDP Leco glow analyzer and EDX by Oxford Instruments detector in SEM by FEI, were used, for this purpose.

In order to obtain reliable results, the corrosion tests were carried out using two methods: gravimetric and potentiodynamic. In both cases, an aerated 3% NaCl aqueous solution was used as the corrosion medium [4,12–14]. Corrosion resistance was determined as its rate based on weight loss of tested samples in relation to their surface over time (V_C). On this basis, the linear corrosion rate (V_P) was determined using the following formula [4,12]:

$$V_P = 0,0365 \cdot V_C / d \text{ [mm/year]}, \quad (1)$$

where:

V_C – sample weight loss over time [$\text{mg}/(\text{dm}^2 \cdot \text{day})$],

d – metal matrix density [g/cm^3] for GX120Mn13 ($7.9 \text{ g}/\text{cm}^3$).

Gravimetric research consisted in placing samples in a Corr-Eco 108 salt spray chamber by Corr-Lab. In turn, the SP-300 potentiostat by BioLogic, was used for potentiodynamic studies. The potentiodynamic tests were carried out at a rate of 1 mV/s, and in each case the polarization was carried out in the anodic direction. The potential was determined with respect to a saturated calomel electrode, using a platinum electrode as the auxiliary electrode. The following electrochemical parameters were determined as corrosion resistance indicators: cathode-anode transition potentials (E_{K-A}), open cell potential (E_{OC}), corrosion current density (i_{corr}) and polarization resistance (R_p) [4,12–13].

Abrasive wear research were carried out using the T-07 tester (Institute of Technology and Operation – National Research Institute in Radom, Poland). According to standard GOST 23.208 –79 loose abrasive was used - corundum F90 (acc. to ISO 8486:1998), a sliding type of movement ensuring dry technical friction at constant load. The pressure F of the sample (dimensions $30 \times 30 \times 3$ mm) against the counter-sample (a metal disc (roll) covered with rubber with a hardness of 78–85 °Sh, rotating at a speed of 60 ± 2 rpm) was exerted with weights using a lever system and amounted to 44 N. The tests lasted 10 minutes.

All examinations were carried out on at least three properly prepared samples taken from different castings. The samples were taken from the reinforcement zone, which was about 5 cm (from the surface to the inside of the casting, more precisely in the middle of this zone), using different cutting techniques (electro-spark and precision, liquid-cooled).

3. Results and discussion

3.1. Macroscopic observations

Macroscopic observations showed that the casting process was carried out correctly – Fig. 1. Castings of this type are subjected to strong dynamic loads and intensive abrasive wear of the front surface. Therefore, the subject of research is a composite with a GX120Mn13 cast steel matrix (high impact strength) reinforced with particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) (high abrasion resistance), obtained by casting.



Fig. 1. Casting with visible reinforcement zone: (a) from the front, (b) fragment perpendicular to the reinforcement axis (cut and broken)

During casting, the corundum inserts were completely infiltrated with liquid cast steel in amplification areas. This fact is indicated by the photo of cross-section of the fragments of the reinforced casting, shown in the Fig. 1. Continuity of the structure was found at interface between two phases of composite.

3.2. Microscopic observations

Microscopic examinations consisted in SEM observations of the contact areas of both components of the composite, i.e. the matrix of cast steel and corundum. The results of the observations confirmed the lack of discontinuities at the interface of both phases. This is clearly visible in the SEM image in Fig. 2.

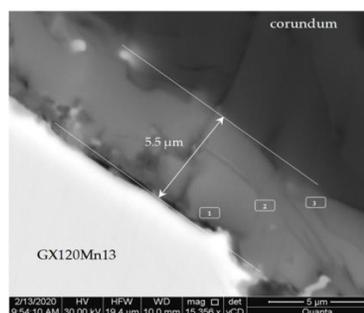


Fig. 2. The boundary area between GX120Mn13 cast steel and particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) elements distribution

A thin layer with a thickness of about 5.5 μm was observed at the surface of particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) (Fig. 2). The formation of this layer could be the result of diffusion processes taking place

during solidification and cooling of castings, similar to the previous studies, during which as the reinforcing material Al_2O_3 particles was used [13]. Straight segregation of manganese and reverse segregation of iron and chromium it was also found (Figs. 2–3). These elements could diffuse from the alloy to the surface layer of particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) both during pouring and during casting cooling. At the same time, the movement of aluminum, zirconium and oxygen into the interior of the particles was observed. These issues will be the subject of further, more detailed studies.

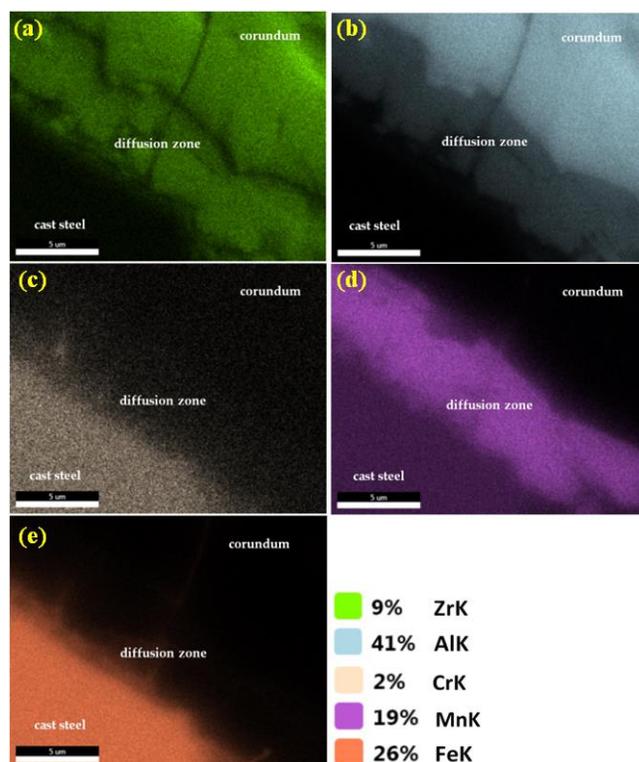


Fig. 3. Mapping of the distribution of individual elements in the composite: (a) Zr, (b) Al, (c) Cr, (d) Mn, (e) Fe

The obtained results confirm that a diffusion interface on surface of corundum grains is formed containing elements derived from cast steel, mainly manganese, as well as chromium and iron. The enrichment of this layer with these elements resulted in a simultaneous decrease in the aluminum content in this area.

3.3. Corrosion investigations

Gravimetric studies

Gravimetric tests lasted for 24 days. Measurements were made after the following times of keeping the samples in 3% aqueous NaCl solution: 1, 2, 6, 8, 12, 16 and 24 days. Each time, the samples were weighed after having been cleaned of corrosion products. The obtained data were used to calculate the corrosion rate index V_c and then V_p using the relation (1) – Table 1. The results indicate a slight difference in corrosion resistance between the tested cast steel and the composite.

Table 1.

Cast	V_P [mm/year] after time [day]						
	1	2	6	8	12	16	24
GX120Mn13	0.55	0.58	0.54	0.52	0.46	0.44	0.37
GX120Mn13 + particles	0.58	0.61	0.54	0.51	0.46	0.40	0.36

After 1 day of exposure of the samples to the corrosive solution, the corrosion index V_P of both materials ranged from 0.55 to 0.58 mm/year. Initially, extending the exposure of both the steel and the composite did not cause significant changes in the values of the V_P index. Only keeping the samples in the corrosive solution for more than 2 days resulted in a successive reduction of the corrosion rate. Corrosion products formed on surface of the samples to some extent constituted a barrier for the corrosion solution. This proved beneficial and resulted in improved corrosion resistance and increased surface stability of both metallic castings. After 24 days of testing, corrosion rate was 0.36-0.37 mm/year. A decrease in the corrosion rate of about 35 (+/-) 5% compared to the initial values was found. Obtained results allow to conclude that the strengthening of cast steel GX120Mn13 with particles ($Al_2O_3 + ZrO_2$) did not result in significant changes in the corrosion rate determined by gravimetric method.

It can therefore be said, that the replacement of ordinary brown corundum [13] with particles ($Al_2O_3 + ZrO_2$) did not cause any significant changes in the corrosion resistance of the composite, determined gravimetrically.

Potentiodynamic studies

Electrochemical investigation consisted in the polarization of samples after different times of staying in a sodium chloride solution. The investigation results are listed in Table 2.

Table 2.

Electrochemical factors determining corrosion resistance						
Casting	Holding time [h] in 3% aqueous NaCl solution	E_{OC} [mV]	E_{K-A} [mV]	i_{corr} [$\times 10^{-5}$ $\mu A/cm^2$]	R_p [$k\Omega \cdot cm^2$]	
GX120Mn13	0.25	-565.4	-496.0	13.8	1879.5	
	24	-659.6	-791.5	95.6	2720.3	
	120	-669.3	-833.5	75.9	3408.2	
	168	-644.1	-860.2	63.4	513.5	
	360	-673.5	-769.3	59.5	2666.1	
	3600	-675.7	-717.6	40.5	641.5	
GX120Mn13 + particles	0.25	-545.5	-545.2	240.1	1083.4	
	24	-550.4	-750.6	342	757.7	
	120	-555.3	-805.2	244	1065.2	
	168	-566.2	-780.3	265	988.3	
	360	-550.8	-715.4	404	650.9	
	3600	-588.3	-750.8	365	718.5	

The results of potentiodynamic studies after a 15-minute exposure in 3% NaCl indicate slight differences in the E_{OC} potential values between the cast steel and the composite. They were around 20 mV. This means that the introduction of ceramic material to the cast steel did not cause significant changes in the so-called "nobleness" of the metal matrix. It also means not large chance of formation of a corrosive cells at the contact of cast steel / corundum (Table 2). The results obtained for the samples stored in a corrosive solution for 1 day indicate a comparable character of the processes

occurring on the surface of both materials. The electrode processes were analogous in both cases, however, some differences were found in changes of specific electrochemical indicators (Table 2). Clear changes in the value of E_{OC} amounting to about 100 mV were found primarily for GX120Mn13. It was clearly noticeable especially at the beginning of research, and more precisely after 24 hours (1 day) of exposure – Table 2. Extending the time to 3600 hours (150 days) resulted in only minor changes in the E_{OC} values. On the other hand, for the composite, changes in E_{OC} values were slight. Regardless of keeping time of samples, they were about 40 mV (Table 2). Comparable results indicate the stability of the tested surfaces from the point of view of corrosion resistance.

The polarization curves obtained for cast steel (Fig. 4a) and those obtained for composite (Fig. 4b) indicate that extending the time of keeping the samples in a NaCl solution causes their shift. E_{K-A} values are moving towards more negative values. This indicates differences in the electrode processes taking place on their surfaces.

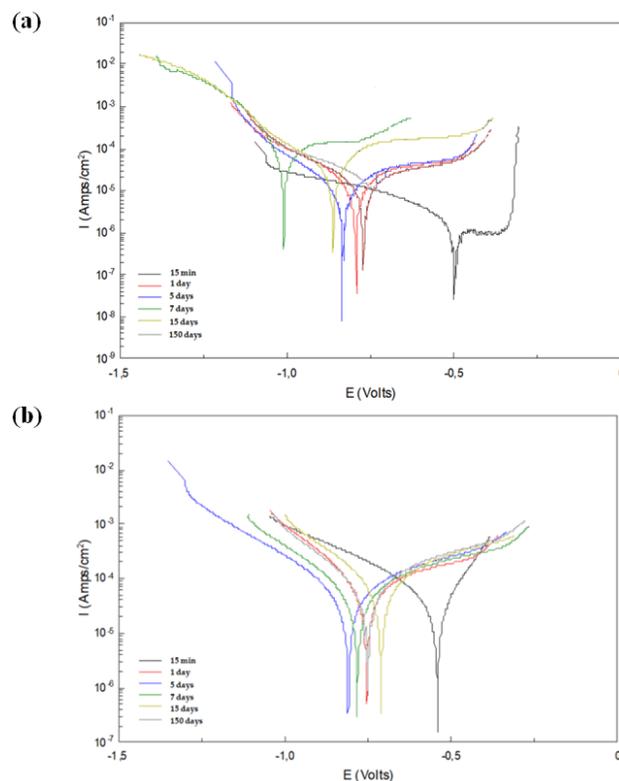


Fig. 4. Polarization curves obtained for: (a) cast steel GX120Mn13, (b) GX120Mn13 + particles ($Al_2O_3 + ZrO_2$) composite

In the case of GX120Mn13, the biggest changes in the E_{K-A} value were found after 1 day of storage in a corrosion medium – about 300 mV (Table 2, Fig. 4). In turn, for the composite after the same time, the difference in the E_{K-A} value was about 200 mV (Table 2). Further extension of time did not result in such clear changes in the E_{K-A} values for both materials (Table 2, Fig. 4). It follows that the corrosion processes occurred most intensively in the first phase of the research. Extending the time of keeping the samples in the corrosive solution "stabilized" the surfaces of the samples in terms of their resistance to corrosion. This is probably

due to the formation of a barrier on the surface of the samples composed of oxides of elements with a high electrochemical potential, capable of passivation.

The course of the polarization curves for GX120Mn13 indicates differences in their shape, as well as in the density of the corrosion current between particular times. This is due to differences in intensity of electrode processes running on the surface of analyzed material (Fig. 4). On the other hand, regardless of the exposure time, the corrosion current density in the anode area shows comparable values (Fig. 4). This confirms that the corrosion products on the surface of both analyzed materials can inhibit the electrode processes. This fact is confirmed also by the mild courses of the polarization curves in the anode areas after prolonged exposure to the corrosive agent. The differences in course of polarization curves affect the differences in values of polarization resistance (R_p) and corrosion current density (i_{corr}). This is indicated by data in Table 2. R_p index value of GX120Mn13 after a quarter of exposure was approx. $1879.5 \text{ k}\Omega\text{cm}^2$, and the corrosion rate was approx. $13.8 \times 10^{-5} \text{ A/cm}^2$.

The introduction of particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) to the metal matrix causes a decrease in polarization resistance by close $800 \text{ k}\Omega\text{cm}^2$, with a simultaneous increase in corrosion index i_{corr} to $24.1 \times 10^{-4} \text{ A/cm}^2$ (Table 2). 3600-hours (150 days) retention of both materials in a 3% NaCl solution does not cause significant differences in polarization resistance. This difference is approx. $75 \text{ k}\Omega\text{cm}^2$. In this respect, the corrosion current density of cast steel compared to composite is an order of magnitude higher.

The values obtained during measurements values of polarization resistance and corrosion current density, it can be assumed that the corrosion resistances of cast steel and composites does not differ significantly. This is extremely important in practical terms, because the introduction of particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) into Hadfield cast steel allows for a very significant improvement in resistance to abrasive wear, without sacrificing corrosion resistance.

Extending the exposure time of the samples in the corrosive solution above 1 day resulted in the stabilization of these parameters. This was certainly the result of the formation of more oxides containing Cr and Ni on the surface of the samples. This, in turn, favored the passivation of their surface and slowed down the progress of corrosion processes. However, this issue will be the subject of further more detailed tests.

Accordingly, it can be stated that, that the replacement of ordinary brown corundum [13] with particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) did not cause any significant changes in the corrosion resistance of the composite, determined by the potentiodynamic method.

3.4. Microscopic investigations after corrosion studies

After conducting potentiodynamic tests, the samples were examined using SEM (Fig. 5). On the surface of the cast steel (Fig. 5a) and the composite (Fig. 5b), the presence of a layer of corrosion products with a uniform distribution was found. EDS analysis of the surface of samples with corrosive products indicates the ability to passivate them (Fig. 6). This is due to the formation of oxides containing: Cr, Mn, Ni on their surface. In turn, Fig. 7 shows an SEM image of a composite (after cleaning), on the surface of which damages caused by corrosion are visible.

Microscopic examinations did not show corrosion damage in the form of deep pits at the interface between two phases (Fig. 7a). There were also no signs of intergranular corrosion (Fig. 7b). This is a positive phenomenon from the point of view of corrosion resistance and confirms the increased durability of the tested casting in terms of corrosion.

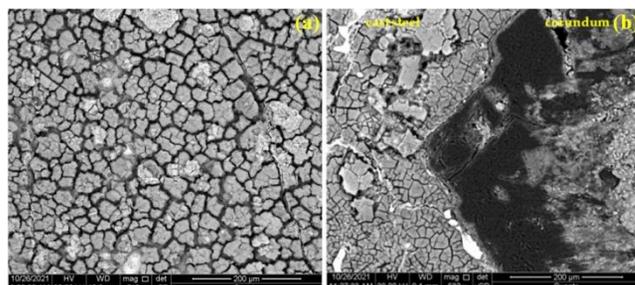


Fig. 5. The surface of the samples: (a) GX120Mn13, (b) GX120Mn13 + particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) after 150 days of being in a corrosive solution and after potentiodynamic tests

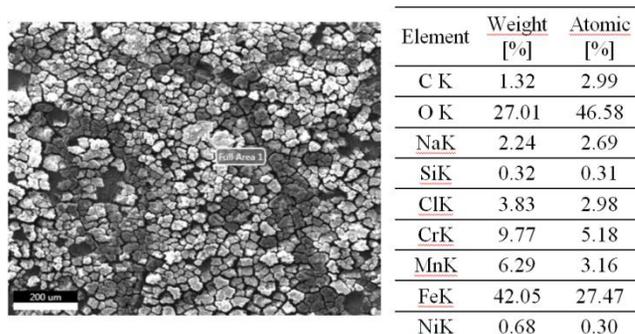


Fig. 6. EDS analysis of the uncleaned composite surface after corrosion tests

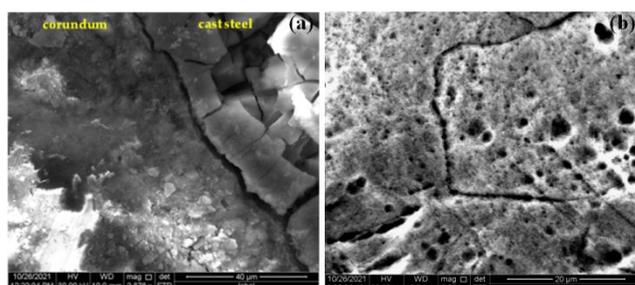


Fig. 7. The surface of GX120Mn13 + particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) after 150 days of keeping in a corrosive solution and after potentiodynamic tests: (a) contact area of both phases, (b) matrix surface

3.5. Abrasive wear tests

Abrasive tests showed a strong, positive effect of reinforcement on the abrasive wear resistance of castings. This resistance was expressed in the form of the abrasive wear rate [mg/m]. The value of this indicator for samples made of cast steel was on average 1.56 mg/m , in turn for samples with corundum-reinforced surface was

0.50 mg/m. Measurement results are presented in Table 3. The reinforcement increased the abrasion resistance of the composite compared to the cast steel by about 70%.

Table 3.
Measurement results of abrasive wear of cast steel and composite

Cast	Abrasive wear rate [mg/m]			
	Measurement results			Average value
GX120Mn13	1.53	1.58	1.57	1.56
GX120Mn13 + particles	0.51	0.52	0.51	0.50

After the potentiodynamic tests (after 150 days of keeping the samples in a corrosive solution), the samples of GX120Mn13 and the GX120Mn13 + particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) composite were subjected to further measurements of abrasive wear. The test results are shown in Table 3, but in Fig. 8 was presented SEM pictures of the samples after corrosion research and then abrasive wear tests. The results did not differ significantly from those obtained for the samples before the corrosion resistance tests. The value of the abrasive wear rate after potentiodynamic tests for cast steel GX120Mn13 samples was 1.58 mg/m on average (Table 4). In turn, this index for the samples of the GX120Mn13 + corundum composite (only in the reinforced area), subjected to abrasive abrasion, was 0.55 mg/m.

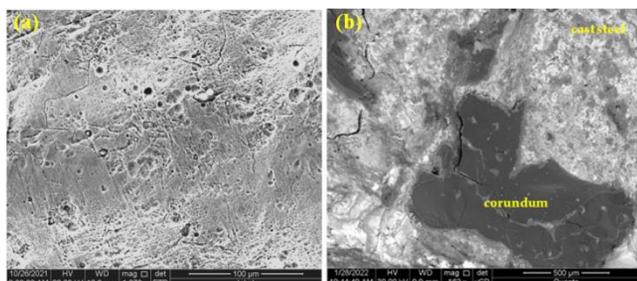


Fig. 8. Surface of samples initially subjected to potentiodynamic and then to abrasion tests: (a) matrix surface, (b) both phases

Table 4.
Measurement results of abrasive wear of cast steel and composite after corrosion tests

Cast	Abrasive wear rate (mg/m)			
	Measurement results			Average value
GX120Mn13	1.53	1.58	1.57	1.58
GX120Mn13 + particles	0.51	0.52	0.51	0.55

4. Conclusions

- SEM research confirmed that a diffusion layer is formed at the contact point between cast steel and particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$), significantly affecting the service life of the composite.
- Corrosion tests showed comparable corrosion resistance of cast steel and composite. No intercrystalline corrosion or pitting corrosion was observed at the interface between the two phases of the composite, which is very important for its durability.

- The replacement of particles from ordinary corundum with particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) with much better „ductility”, did not cause significant differences in the corrosion resistance of both composites.
- Reinforcement of Hadfield cast steel GX120Mn13 with particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) improved its resistance to abrasive wear by about 70%.
- The corrosion processes did not significantly affect the deterioration of the abrasive wear resistance of both GX120Mn13 cast steel and the GX120Mn13 + particles ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) composite.

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