

Corrosion resistance of PPTA Ni-based hardfacing layers

Research Article

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Abstract: In this study, the corrosion resistance of four different hardfacing layers in a 3.5% NaCl solution was tested. Using 316L steel as a reference material, NiCrBSi, NiCrBSi + 35 wt% WC, and NiCrCuMo were deposited onto a structural steel S235JR substrate using the plasma powder transferred arc technology and prepared samples in a disc form for testing. The purpose of this investigation was to propose an alternative material to the commonly known anti-corrosion protection product of 316L steel simultaneously with better wear resistance. Its corrosion damage mechanism was assessed based on electrochemical examination and is related to changes in the microstructure of the sample surface investigated by using a potentiostat and a scanning electron microscope. Polarization tests were carried out, which confirmed that all proposed overlayers provide effective anti-corrosion protection. For all samples, the corrosion current density did not exceed $0.3 \mu\text{A}/\text{cm}^2$, and the corrosion potential was not less than -290.9 mV , which were considered positive results.

Keywords: *Hardfacing layers • PPTA • Corrosion resistance • Electrochemical properties*

1. Introduction

The plasma transferred arc (PTA) coating process was developed for the rebuilding and repair of worn parts and the manufacturing of hardfacing layers of parts exposed to extreme working conditions. Common steel parts with an appropriate PTA coating can exhibit superior corrosion and wear behavior when compared to specific alloys [1]. The PTA is a cost-effective method that is easily operated and offers a wide range of selected forms of filler materials, making it a popular choice for fabricating coatings with a large surface area, high thickness, and high quality [2]. In industry, hardfacing is a low-cost method for depositing materials resistant to harsh factors usually on metal surfaces with components to extend the service life. It is not only used to restore worn parts to usable conditions but also applied to new components for preventive purposes, with the aim of extending the service life even in aggressive working environments, thereby reducing the cost of maintenance [3,4]. In this way, surfacing by the PTA is used to manufacture protective

layers which could protect the products' surface against different types of damage [5,6] among others against the corrosion effect, as well as against the cavitation erosion [7]. This is due to the fact that thick coatings provide very good protection possibilities in aggressive industrial environments [8].

The corrosion is an important cause of damage in industry which has triggered much investigation (e.g., Lachowicz and Swietlicki et al. [9,10]). One of the crucial solutions to the challenges posed by this phenomenon is nickel-based alloys [11]. NiCrBSi coatings are widely employed to improve the quality of components whose surface are subjected to corrosion and wear [3,12]. Layers made of Ni-based alloys are also fixed on many industrial components to improve tribological properties. The NiCrBSi feedstock powder is a well-known material used to deposit hardfacing layers [13,14]. It is also renowned for excellent wear and corrosion resistance under high temperature working conditions [15]. Because of these important advantages, Ni-based alloys are widely used as coating materials [16,17]. Despite the significant advantages, there is a need to constantly search for a material that is reliable even in more difficult operating conditions. The

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common possibility to improve the mechanical and functional properties of NiCrBSi is often the addition of tungsten carbide (WC) or other hard materials [13,17–19]. Tungsten carbide is corrosion resistant to many kinds of media, except for the mixture of hydrofluoric acid and nitric acid at elevated temperatures [20], which should have a positive influence on corrosion resistance of coatings based on Ni-alloys with WC addition. It is also an outstanding addition to composites, which excellently improved their wear resistance [21].

In cases in which the key property is corrosion resistance, the 316L steel is a highly valued material. This type of stainless steel has excellent corrosion resistance, processability, high strength, and high durability [22,23]. Because of the above-mentioned advantages, this material is used even in nuclear power primary circuits [24]. In the literature, some information about manufacturing powder metallurgy methods of stainless steel could be found [25,26], which confirms the application of this form of material as potential protective layers. Corrosion-resistant steel is also used in the plating process as protective material, mainly for low-carbon steel [27]. In comparison with all earlier described materials, less information can be found about the adoption and the properties of NiCrCuMo material, despite it being a good candidate for protective coatings as well [28,29]. Although there are only a few articles about NiCrCuMo, these alloys find applications in various industries, including aerospace, chemical processing, marine engineering, and electronics, wherein corrosion resistance, high-temperature strength, and oxidation resistance are crucial requirements. The NiCrCuMo alloy shows excellent properties and is also

widely used for pipeline transportation, corrosion-resistant valves, and key components of aircraft carrier shafts and pumps in the environments of hydrofluoric acid, hydrochloric acid, alkali salts, and reducing acid media [30]. This alloy is significantly corrosion resistant, which has been widely applied in extremely harsh environments [31].

The main purpose of this article was to manufacture different types of hardfacing layers based on Ni–Cr and investigate them in terms of corrosion resistance. For this, polarization tests and microstructural analysis were performed.

2. Materials and methods

Four types of commercial feedstock powders were used to weld-deposit hardfacing layers by powder PTA (PPTA): 316L (Castolin Eutectic), NiCrBSi (Durum Wear Protection GmbH), NiCrBSi + 35% WC (Höganäs AB), and NiCrCuMo (Durum Wear Protection GmbH). The chemical composition and the particle size distribution (PSD) of powders are presented in Tables 1 and 2.

Preliminary studies were used in order to obtain a set of optimal parameters for each type of feedstock material. The overlayers were manufactured using a EuTronic Gap 3511 DC (Castolin Eutectic, Gliwice, Poland). The elected and used parameters are listed in Table 3. The structural steel S235JR plates (100 mm × 160 mm × 10 mm) were used as the substrate. Their chemical composition is presented in Table 4. Before the hardfacing process, the steel plates were prepared by grinding followed by cleaning with ethanol.

Two discs were cut from each hardfacing sample. The discs had a thickness of 5 mm and a diameter of 14.8 mm. Before starting the experiments, cut samples were mechanically ground with 800, 1,200, and 2,000 SiC emery papers and then polished using diamond suspensions, as mentioned above.

For all samples, microscopy examinations were carried out before and after the electrochemical process using

Feedstock material	Sample code	PSD (μm)
316L	S1	–150 + 45
NiCrBSi	S2	–125 + 45
NiCrBSi + 35 wt% WC	S3	–125 + 22
NiCrCuMo	S4	–125 + 45

Table 1. Sample code and the PSD of powders [32].

Feedstock	Elemental content (wt%)								
	C	Si	Cr	B	Ni	Mo	Cu	Fe	W
S1	0.03	—	18.00	—	13.00	2.7	—	bal.	—
S2	0.95	3.80	16.50	3.30	Bal.	—	—	—	—
S3	2.35	3.80	16.50	3.30	Bal.	—	—	—	25.00
S4	0.50	4.00	16.00	4.00	Bal.	3.0	3.0	—	—

Table 2. Chemical composition of feedstock powders (material no. from Table 1).

Sample code	Parameters		
	Current intensity (A)	Torch speed (mm/s)	Powder feed rate (g/min)
S1	100	0.8	9.7
S2	80	0.8	9.0
S3	100	1.6	11.0
S4	80	0.8	9.0

Table 3. Parameters used for hardfacing of the overlays.

C	Mn	P	S	Cu	N	Fe
0.17	1.40	0.035	0.035	0.55	0.012	Bal.

Table 4. Chemical composition of S235JR steel (in wt%) [33].

a scanning electron microscope, Tescan Vega3 (Tescan Orsay Holding), and a digital microscope, Keyence. The aim of this procedure was to identify the surface features after electrochemical corrosion investigation in 3.5% NaCl solution. Additionally, energy-dispersive X-ray spectroscopy (EDS or EDX) analysis of the tested samples was carried out after potentiostatic measurements. Finally, the microstructure investigation on the sample cross-sections was carried out.

After preparing the samples in the form of discs as well as the research set-up consisting of three-electrode cells with a potentiostat (ATLAS 0531 ELEKTROCHEMICAL UNIT & IMPEDANCE ANALYSER, Atlas-Sollich, Gdańsk, Poland), the polarization test began. The auxiliary electrode was made of austenitic stainless steel, and the reference electrode was a saturated Ag/AgCl. The potential value of the Ag/AgCl electrode compared to the standard hydrogen electrode was +0.196 V according to the ISO 17475:2010 standard [34]. The surface area of the working electrode (the sample) was 0.785 cm². Before starting the experiments, each sample was immersed for 30 min in a 3.5% NaCl solution at room temperature. Then, the open circuit potential (E_{OCP}) was measured. Polarization tests were conducted in the same solution by stepping the potential in the anodic direction using a scanning rate of 1 mV/s. Two anodic and cathodic polarization curves were recorded for the tested materials. Among them, it was chosen as the representative one. The initial potential value was 200 mV lower than the E_{OCP} value. The polarization of each tested sample was terminated at different potential values. The polarization curves were plotted using an automatic data acquisition system, and the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were estimated by Tafel plot extrapolation.

3. Results and discussion

3.1 Microstructure characterization of the tested material surface

The obtained overlays before and after electrochemical corrosion are characterized by smooth surfaces without clear pores and pits. To evaluate the quality of the deposited hardfacing layers after the corrosion process, optical microscopy (OM) images of the interface line were analyzed (Figure 1). The tested materials were compared with the reference overlayer – 316L – which is widely recognized as a proven anti-corrosion protection alloy [22,23,35]. The images were taken using a scale of 500 µm and a scale of 200 µm, presenting a fragment of the interface layer–substrate area at a higher magnification.

In all cases, the interface line was clear, without delamination, or any other small destructions. The overlayers filled the substrate very well, which proved the strong adhesion between hardfacing layers and the substrate. As expected, dense and great bonded layers were obtained using the PPTA process [36,37] (Figure 2).

Figure 3 shows the detailed observation of unaffected by corrosion materials and inspection of them after the process.

The presented images of the surface of Ni-alloy matrix-based materials taken by a scanning electron microscope before and after electrochemical corrosion seem to be confusingly similar. The analysis performed at 1,000× magnification did not prove significant corrosion damage to any of the tested samples. It may seem promising that the quality of the obtained overlayers based on the Ni-alloy is characterized by slightly better corrosion resistance than when using a micro-beam plasma arc [38]. It should be noted that Ni-based coatings exhibit excellent corrosion resistance [39]. The aim of additions is to improve other functional properties.

Figure 4 shows the SEM images of the interface between overlayers (Figure 4a, c and e) and characteristic EDX spectra obtained from the surface of examined hardfacing layers after the electrochemical corrosion process. Thanks to these examinations, it was determined which phases are likely to be present in the obtained overlayers and whether the corrosion process contributed significantly to their surface oxidation. In addition, observation of the cross-sections confirmed the good interface condition (Figure 4b, d and f).

Using the information in Figure 4 and Table 2 and also the considerations of other researchers working on Ni-

based composites included in the literature [3,29,40], the probable presence of the following phases was indicated.

As can be seen in the SEM images of the composition of all investigated samples, there is enough nickel content for the formation of the γ -Ni phase [3,40]. Despite the absence of iron content in the chemical composition of feedstock powders based on the Ni-alloy, the element iron appears in the EDX analysis. Because of that, in NiCrBSi and NiCrBSi + 35 wt% WC, FeNi₃ and Fe₂Si phases could be found [3]. In addition, Ni₃B, CrB, Cr₇C₃, and Cr₂₃C₆ phases can occur in these materials. In NiCrBSi + 35 wt% WC, the decarburization phenomenon associated with W₂C phase formation could take place [3,40].

The conditions of the melt pool solidification during cladding with high-energy density methods result in the

formation of non-equilibrium structures. This should be associated with rapid heating and subsequent cooling and solidification [40,41]. Makarov *et al.* [42,43] found that the microstructure of NiCrBSi coating consists of the γ -Ni solid solution, eutectic γ + Ni₃B, and main strengthening phases, i.e., chromium carbide (Cr₇C₃) and chromium boride (CrB). In the case of NiCrBSi coating with the addition of WC, the coating microstructure also consists of large particles of W (C,B) carbides, which are formed by the reaction of WC carbides with boron during the melting of the NiBSi powder during laser cladding.

In the NiCrCuMo material, there is a tendency to combine chemical compounds and create phases by the elements: copper with nickel and chromium with molybdenum. Moreover, Cr₆C and Cr₂₃C₆ can be expected in

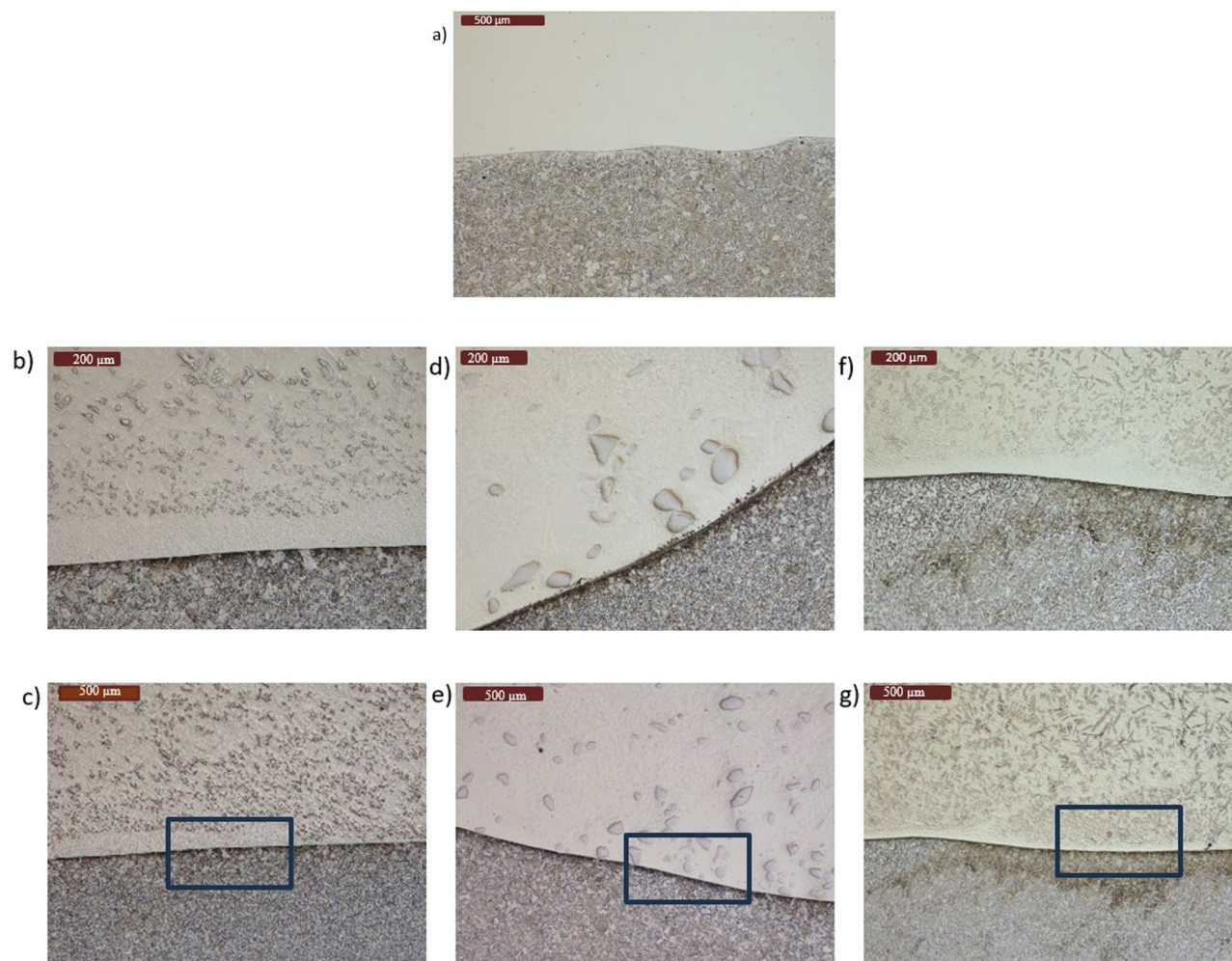


Figure 1. OM images after 3% nital etching of the interface line (cross-section): reference material S1 (a), S2 (b and c), S3 (d and e), and S4 (f and g).

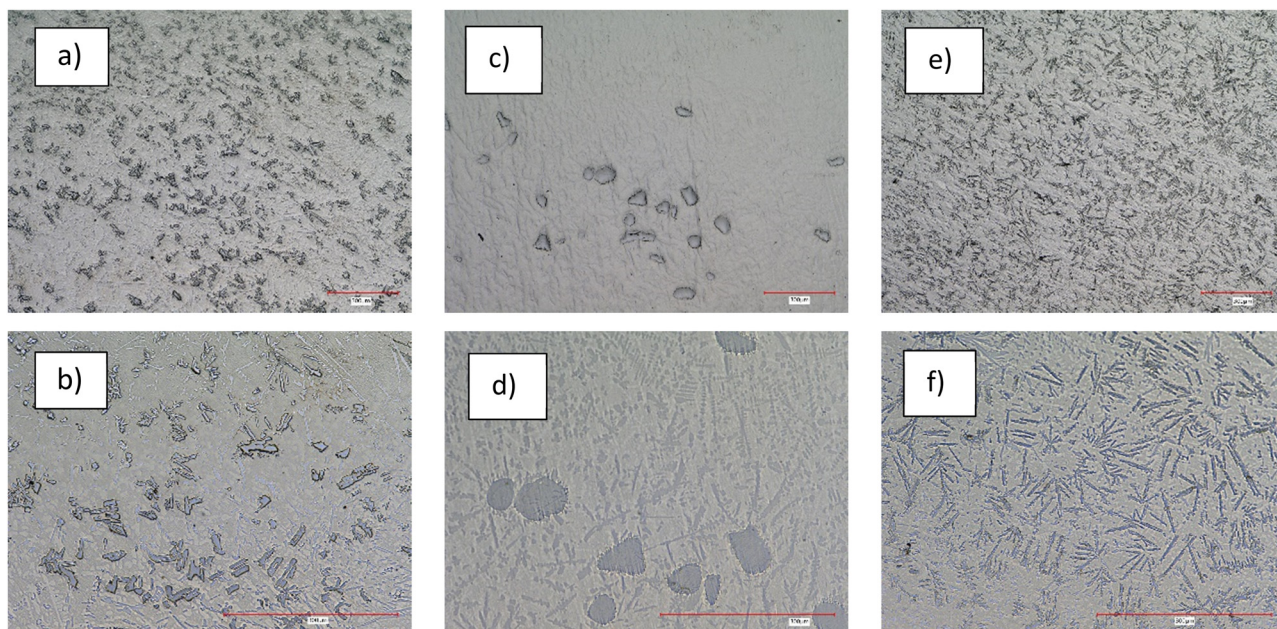


Figure 2. Cross-sections of the hardfacing layers at lower magnifications (200 $\times$) (S2 (a), S3 (c), and S4 (e)) and higher magnifications (500 $\times$) (S2 (b), S3 (d), and S4 (f)).

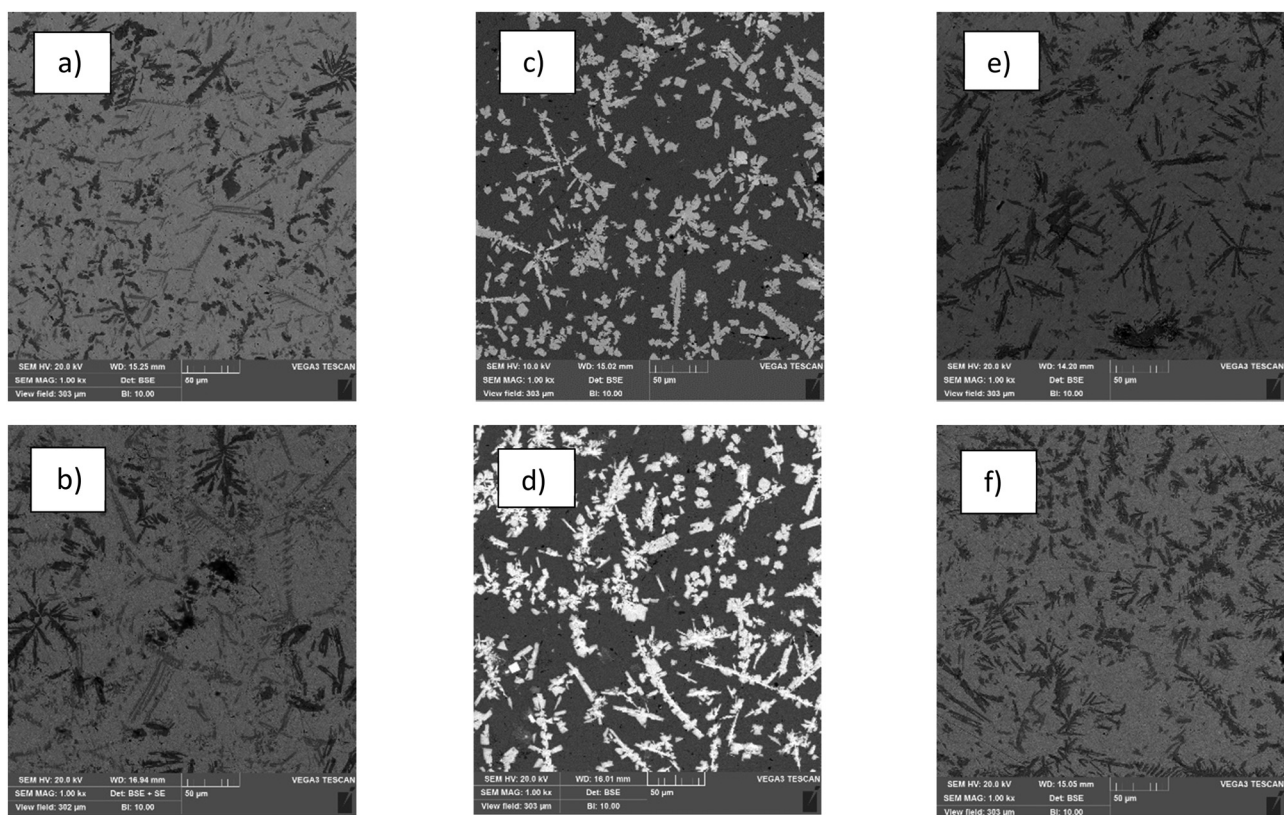


Figure 3. Top view SEM images of tested materials before the electrochemical corrosion (S2 (a), S3 (c), and S4 (e)) and after the process (S2 (b), S3 (d), and S4 (f)); magnification: 1,000 $\times$.

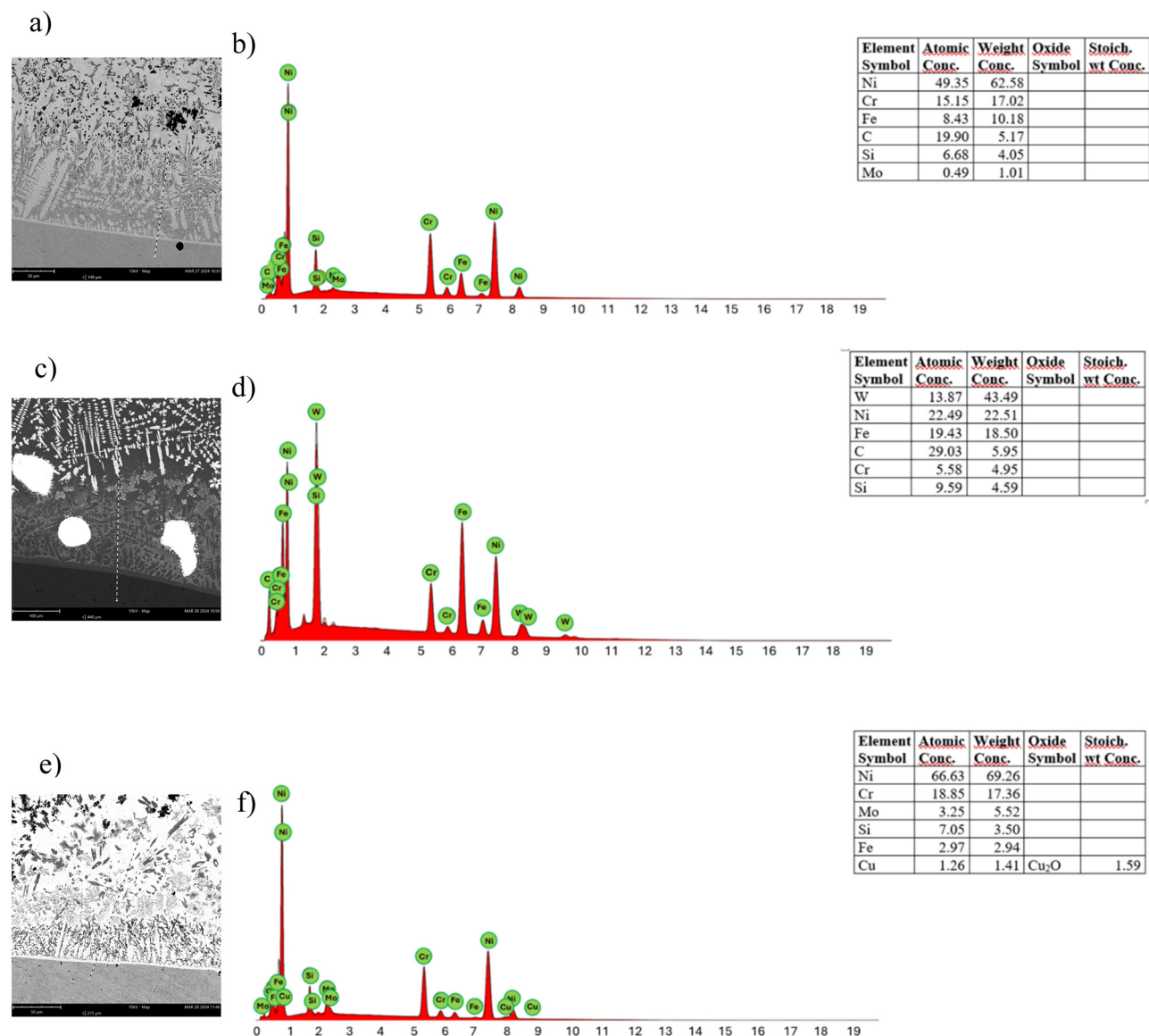


Figure 4. SEM images of the cross-section of S2 (a), S3 (c), and S4 (e) samples. EDS spectra of the characteristic obtained from the surface of S2 (b), S3 (d), and S4 (f) samples.

the described hardfacing layer [3,29]. No significant oxidation phenomenon was detected in the described study for any of the overlays.

Although the analysis of elements of austenitic stainless steel was not carried out, 316L steel is an alloy of Fe–Cr–Ni, where Fe–Cr is linked to the ferrite phase, whereas nickel is linked to the austenitic phase. The equilibrium phases depend on the proportion of the three aforementioned elements, and they can take forms like MC, M₆C, and M₂₃C₆ [44]. The properties of austenitic steels are influenced by the presence of other phases in the

microstructure. Due to the deterioration of mechanical properties and corrosion resistance in many applications, the presence of carbides is either completely avoided or allowed in an appropriate proportion with an acceptable morphology. The chromium depletion caused by the formation of chromium carbides at the grain boundaries is defined as sensitization. This results in intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC) of austenitic stainless steel [45,46]. The degree of sensitization can be influenced by several parameters such as chemical composition, cold work, grain size,

microstructure, and heating/cooling rate [47]. The formation of carbides will be facilitated by the diffusion of elements from the substrate material [48]. This also applies to carbon. The presence of carbides and their morphology can be suitably controlled by heat treatment. The $M_{23}C_6$ -type carbides are mainly observed. The M_7C_3 -type carbides occur mainly in austenitic steels with increased carbon content. The M_6C -type carbides are practically not observed, and the MC-type carbides occur in low carbon alloys containing titanium, niobium, vanadium, or zirconium [44,49,50]. Dissolution is the most commonly used heat treatment to dissolve phases, especially carbides [50]. AISI 316L steel can also contain 5–10% residual delta ferrite [46,51,52]. Many studies show that selective dissolution of the second phase (delta ferrite, sigma phase) can occur in austenitic steel. The presence of these phases reduces the corrosion resistance of these steels [51,53–55].

3.2 Electrochemical examination

Figure 5 presents a comparison between the polarization representative curves of investigated samples, while the results obtained during measurement with the Tafel extrapolation method are collected in Table 5. All hardfacing layers show a passive range and a lower potential value to the mild steel

Sample code	E_{OC} (mV)	E_{corr} vs Ag/AgCl (mV)	I_{corr} ($\mu A/cm^2$)	R_p ($k\Omega cm^2$)	E_p (mV)
Average result					
S1	-87.8	-159.7	0.1	213.7	845
S2	-262.0	-290.9	0.3	108.8	535
S3	-234.9	-237.1	0.2	146.8	483
S4	-194.4	-200.3	0.1	210.0	438

Table 5. Electrochemical parameters obtained for all samples.

substrate material and therefore have an anodic character in relation to it. They are characterized by a low value of pitting potential, which indicates the lack of pitting corrosion, but instead indicates the presence of uniform corrosion. For the 316L overlay, the corrosion potentials (average, -159.7 mV) were higher than for the other three tested materials. The largest potential difference concerning the substrate material occurred for NiCrBSi (average, -290.9 mV), and the smallest potential difference occurred immediately after reference coating for NiCrCuMo (average, -200.3 mV). The NiCrCuMo hardfacing layer had a similar corrosion current value to the reference material, which is due to

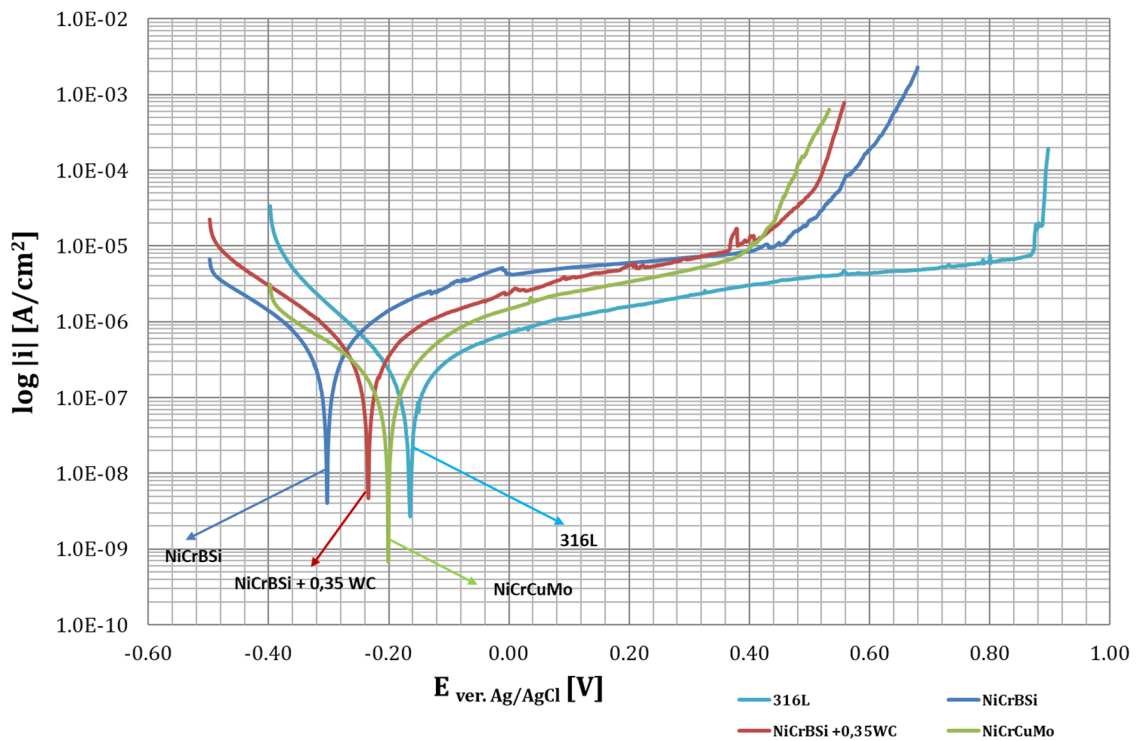


Figure 5. Representative potentiodynamic polarization curves of hardfacing layers examined in 3.5% NaCl solution.

the presence of copper and molybdenum in the composition. In the case of this type of coating, the potential difference did not exceed 50 mV, which is important in the event of mechanical damage to the layer, because such a value is sufficient to initiate galvanic corrosion. The presence of WC in the NiCrBSi overlayer slightly improves the corrosion resistance of this material, which could be noticeable as a shift in the corrosion potential toward more positive values. Both NiCrBSi hardfacing layers (with and without tungsten carbide) showed higher values of corrosion current densities

compared to the 316L steel and NiCrCuMo materials. To sum up the abovementioned information, the 316L material has the best resistance to electrochemical corrosion among those tested, and NiCrCuMo is also the second promising material.

The obtained polarization curves are similar to those presented in the literature for austenitic steels [56–59]. The occurrence of local corrosion in the form of pitting is responsible for the rapid increase in current density at the pitting potential (E_p) [59]. Its value measured from potentiodynamic polarization depends on the scan rate [60]. For all

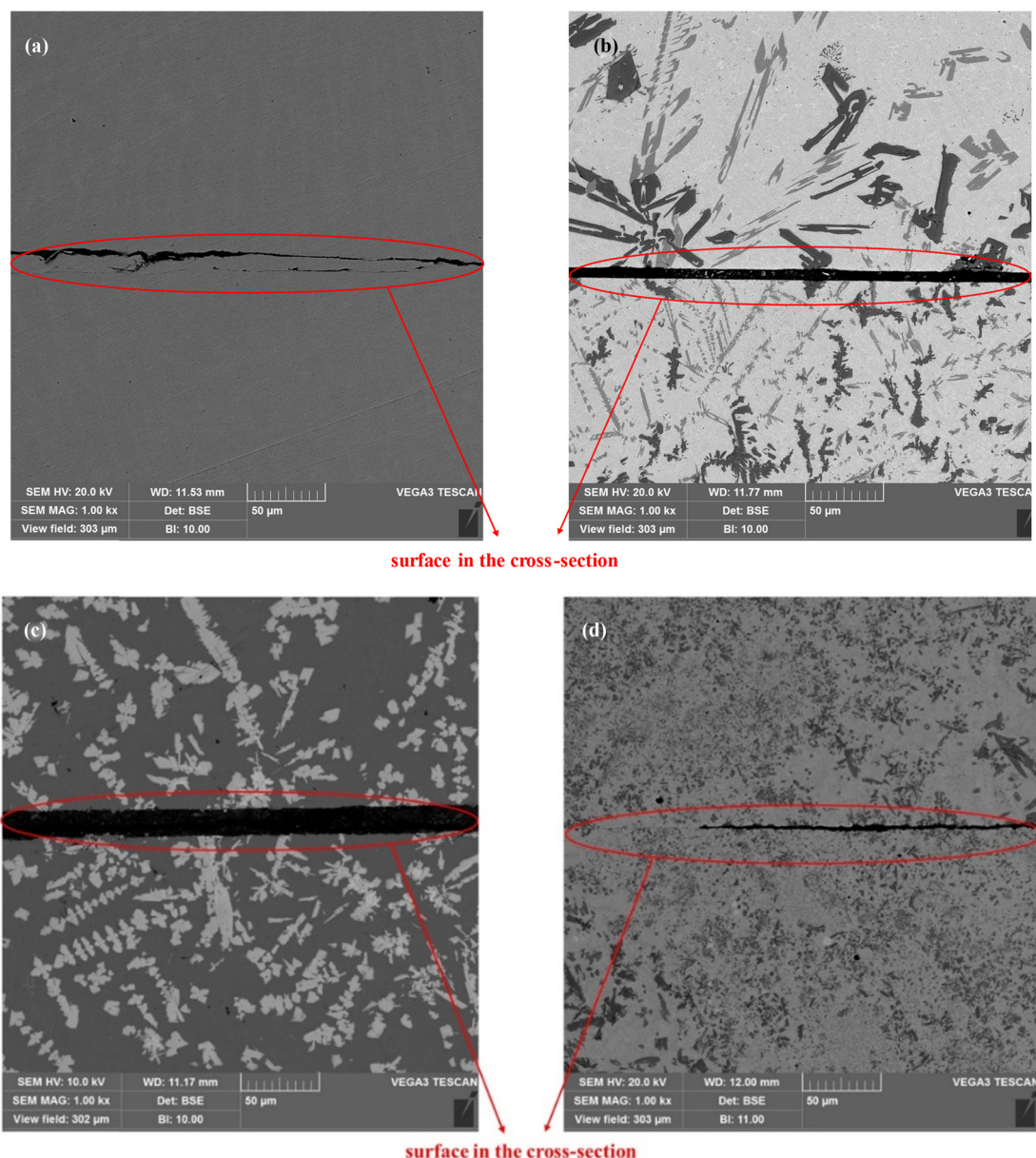


Figure 6. SEM images of the cross-section of the corroded surface of coatings: (a) S1, (b) S2, (c) S3, and (d) S4.

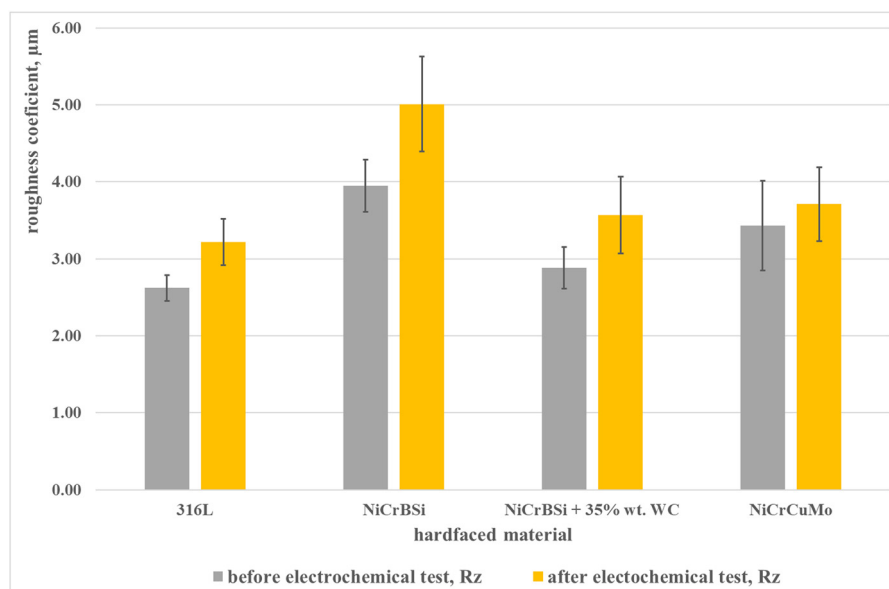


Figure 7. Average values of the roughness parameter measured with the stylus profilometer.

investigated samples, the tests were performed at the same scan rate, which allows for their comparison with each other. The initiation of pitting corrosion can be observed as sharp current density spikes on the polarization curves [61]. The different corrosion resistance also depends on the crystallographic orientation. This allows the shaping of properties by means of manufacturing methods [62]. In the case of austenitic steel, higher corrosion resistance was observed. It is commonly accepted that single-phase alloys are more resistant to corrosion than multi-phase alloys [63,64]. This effect is even greater if the chemical composition favors the formation of compact oxide layers with good protective properties. If there is more than one phase in the alloy microstructure, this leads to the formation of a corrosion microcell. This usually results in the lower resistance of two-phase alloys than single-phase alloys. The formation of corrosion microcells should be associated with the lower corrosion resistance of the overlays made of the tested nickel alloys, which were multi-phase materials. In multi-phase alloys, the corrosion mechanisms are determined by the difference in the potentials of both phases, their arrangement, and also the proportion of the cathodic to the anodic phase.

3.3 SEM surface evaluation

For detailed analysis of the surface conditions of the tested materials after the electrochemical process and checking the correctness of previous assumptions, an additional set

of images of the sample cross section was taken using a scanning electron microscope. Again, the microstructure of the investigated materials did not show any sign of visible surface damage caused by the electrochemical corrosion (Figure 6). Upon analyzing these images, it could be clearly seen that there is no difference.

All examined hardfacing layers after the corrosion process exhibit surfaces without pitting. Noticeable modification in the topography of the deposited materials occurred only for NiCrBSi, but it was small and amounted only to approximately 0.1 Ra and just over 1.0 for the roughness parameter Rz. The results of surface roughness obtained with a stylus profilometer (MarSurf PS 10) were according to the ISO 21920-3:2022-06 standard, and it was checked whether the roughness coefficient did not exceed 0.5 Ra for each sample before the test. To definitely prove the absence of corrosion pitting, the Rz profile was selected. The received outcomes of surface roughness measurements are shown in the form of a diagram (Figure 7). As mentioned above and as observed from the topography test, all conducted measurements proved that the corrosion of the investigated surfaces had an uniform and mild character.

4. Conclusions

In this study, deposition of four different feedstock material hardfacing layers was studied and described. The studied properties were corrosion resistance and

compatibility of the overlayers with the substrate. The key aim of the research was to compare the resistance of the tested materials and identify a potential replacement for 316L steel, which is a reputable protected material. Deductions based on conducted studies are summarized in the following points:

All tested materials have relatively good resistance to electrochemical corrosion. Surface observation and EDX analysis did not exhibit any clear change caused by corrosion.

SEM analyses of the cross-section after the electrochemical process did not indicate corrosion changes, like pitting, inside hardfacing layers.

The NiCrBSi material has the lowest value of corrosion potential, but no significant traces of corrosion were detected. Based on the obtained potentiodynamic polarization curves, it can be concluded that the addition of WC only slightly increases the corrosion resistance of this material.

Every tested overlayer showed a lower potential value in relation to the substrate material. The smallest potential difference was found in the case of the molybdenum and copper coating (NiCrCuMo) next to the reference material.

The NiCrCuMo hardfacing layer had the most congruent corrosion current value to the reference material among the three remaining deposited materials.

Although the tests confirmed the reliability of 316L steel in anti-corrosion protection, it was noticed that the NiCrCuMo coating may compete with it. Its very good corrosion resistance is largely due to the contents of Cu and Mo in the chemical composition.

Authors contributions

Monika Górnik: methodology, investigation, writing – original draft. Marzena Lachowicz: methodology, investigation, writing – review and editing. Leszek Łatka – conceptualization, methodology, investigation, writing – review and editing.

Conflict of interest statement

Authors state no conflict of interest.

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