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Improving the corrosion wear resistance of AISI 316L stainless steel by particulate reinforced Ni matrix composite alloying layer

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Abstract

In order to overcome the problem of corrosion wear of AISI 316L stainless steel (SS), two kinds of composite alloying layers were prepared by a duplex treatment, consisting of Ni/nano-SiC and Ni/nano-SiO₂ predeposited by brush plating, respectively, and subsequent surface alloying with Ni-Cr-Mo-Cu by a double glow process. The microstructure of the two kinds of nanoparticle reinforced Ni-based composite alloying layers was investigated by means of SEM and TEM. The electrochemical corrosion behaviour of composite alloying layers compared with the Ni-based alloying layer and 316L SS under different conditions was characterized by potentiodynamic polarization test and electrochemical impedance spectroscopy. Results showed that under alloying temperature (1000 °C) conditions, amorphous nano-SiO₂ particles still retained the amorphous structure, whereas nano-SiC particles were decomposed and Ni, Cr reacted with SiC to form $Cr_{6.5}Ni_{2.5}Si$ and $Cr_{2.3}C_{6.5}In$ static acidic solution, the corrosion resistance of the composite alloying layer with the brush plating Ni/nano-SiO₂ particles interlayer is lower than that of the Ni-based alloying layer. However, the corrosion resistance of the composite alloying layer with the brush plating Ni/nano-SiO₂ particles interlayer is prominently superior to that of the Ni-based alloying layer under acidic flow medium condition and acidic slurry flow condition. The corrosion resistance of the composite alloying layer with the brush plating Ni/nano-SiC particles interlayer is evidently lower than that of the Ni-based alloying layer, but higher than that of 316L SS under all test conditions. The results show that the highly dispersive nano-SiO₂ particles are helpful in improving the corrosion wear resistance of the Ni-based alloying layer, whereas carbides and silicide phase are deleterious to that of the Ni-based alloying layer due to the fact that the preferential removal of the matrix around the precipitated phase takes place by the chemical attack of an aggressive medium.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

AISI 316L stainless steel (SS), as one of the most commonly selected structural alloys for use in corrosion environments, has

received special attention in the last years due to its inherent corrosion resistance properties attributed to the continuous formation of a thin, adherent and self-healing passive film on the surface [1,2]. Consequently, AISI 316L SS is widely used in food and chemical processing, biomaterials application and petrochemical as well as in nuclear industries.

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However, the application of this material in many cases is severely limited by very poor wear and friction behaviour, when it is subjected to both erosive and corrosive conditions. For example, in chemical plants, the conveying components of valves and pumps which transport various slurries fail quickly [3]. Corrosion wear is known to promote the premature failure of materials when exposed to wear in a corrosive environment. The rate of materials loss during the combined action of corrosion and wear is much higher than the sum of the individual contribution of wear and corrosion [4-8]. Corrosion and wear are essentially surface-dependent degradation related to the microstructure and composition of only the near-surface To date, a wide variety of surface modification region. of austenitic SSs, such as gas nitriding [9], ion nitriding [10], physical vapour deposition (PVD) and ion implantation [11–13], have been undertaken for improving their corrosion or tribological properties. However, in the literature, there are very limited studies on the corrosion wear behaviour of coatings applied over austenitic SS. Neville et al [12] studied the erosion-corrosion behaviour of WC-based MMCs in an aggressive slurry environment simulating recycled cooling water. They found that the UNS S31603 exhibited superior performance to the MMCs when tested against coarse sand, whilst it suffered the highest mass loss against fine sand. Dong et al [13] investigated the erosion-corrosion behaviour of low-temperature plasma surface alloyed AISI 316 SS using a slurry pot erosion-corrosion apparatus containing a slurry comprising 20 wt% silica sand and 3.5%NaCl at 40 °C. They concluded that the erosion-corrosion resistance of AISI 316 SS can be effectively improved by low-temperature plasma alloying with carbon (carburizing) and nitrogen (nitriding) by 50% and 70%, respectively. The double glow surface alloying technique is a unique and hybrid plasma surface treatment process which is the evolution of both plasma nitriding and sputtering techniques and developed in response to the need for higher quality alloy layers on the surface of cheap materials. This technology employs a low-temperature plasma produced by a glow discharge. During the alloying process, the desired alloying elements are sputtered from the source electrode, travelling towards the substrate, and subsequently the alloying elements deposit onto and diffuse into the substrate's surface. By using this technique, an alloying layer with special physical and chemical properties can be obtained on the surface of metallic materials. In recent years, various studies by the present authors have demonstrated that the corrosion resistance of the Ni-based alloying layer formed on the AISI 304 SS substrate by the double glow technique is better than that of the nickel-based alloy HastelloyC-2000 and 304 SS [14–16]. Furthermore, the novel duplex surface treatment, which consists of brush plating surface treatment and double glow plasma surface alloying, has been adopted to improve the corrosion resistance of the alloying layer formed on low carbon steel [17]. This duplex surface treatment technology provides a feasible route for fabricating particulate reinforced metal matrix composite coating and opens new possibilities for enhancing the wear resistance of the Ni-based alloying layer without compromising its corrosion resistance.

In this work, in order to overcome the problem of corrosion wear of AISI 316L SS, two kinds of composite alloying layers were prepared by a duplex treatment, consisting of Ni/nano-SiC and Ni/nano-SiO₂ being predeposited by brush plating, respectively, and subsequent surface alloying with Ni–Cr–Mo–Cu by a double glow process. Potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) were measured to study the effects of the different particulates on corrosion and corrosion wear behaviour of the Ni-based alloying layer in an aggressive slurry environment simulating valves and pumps used to transfer acid-containing slurries. The corrosion wear properties of AISI 316L SS and Ni-based alloying layer formed on AISI 316L SS by double glow plasmas technology were also evaluated in order to compare them with the results obtained for the two kinds of composite alloying layers.

2. Experimental method

An AISI 316L SS plate with dimensions of $50 \text{ mm} \times 10 \text{ mm} \times$ 5 mm was used as the substrate. The chemical composition of the AISI 316L SS in wt% was Ni : 11.54; Mo : 2.59; Cr : 16.39; C: <0.03 Si: <1.00 Mn: <2.00 P: <0.04 S: <0.03 and the balance: Fe. Before brush plating, the surfaces were ground to a surface finish of $Ra = 0.2 \,\mu m$ and rinsed with ethanol followed by acetone. DSD-75-S direct current power was used. The plating tool was soaked in the plating solution and then brushed against the surface of the substrate material that was to be finished. The plating solution was delivered to the work area by a porous, absorbent cover wrapped over the anode of the plating tool. The composition of the electric brush Ni/nano-SiC or Ni/nano-SiO₂ solution was $420 \text{ g} \text{ l}^{-1}$ NiSO₄·7H₂O, $105 \text{ g} \text{ l}^{-1}$ NH₃·H₂O, $2 \text{ g} \text{ l}^{-1}$ MnSO₄·H₂O, $5 \text{ g} \text{ l}^{-1}$ NaF, $56 \text{ g} \text{ l}^{-1}$ (NH₄)₃C₆H₃O₇, $23 \text{ g} \text{ l}^{-1}$ CH₃COONH₄, 0.1 g l^{-1} (COONH₄)₂·H₂O and 20 g l^{-1} SiC or SiO₂ particulate.

For this series of experiments, the value of pH of the plating bath was 7.2 and the average size of SiC or SiO₂ particles was 20-30 nm. Electric brush plating was operated at a working voltage of 12-14 V and the relative velocity between the positive electrode (plating tool) and the negative electrode (substrate materials) was 11 m min⁻¹. The Ni/nano-SiC or Ni/nano-SiO₂ plating coating with a deposit thickness of 30–40 μ m was obtained as shown. The alloying processes of the as-deposited samples were performed in a double glow surface alloying device. In the double glow process, one cathode is the source (target) cathode, which was fabricated from the desired sputtering materials, and the other cathode is the substrate material. When two different voltages are applied to the two cathodes, a glow discharge appears. The double glow processing parameters were base pressure: 4×10^{-4} Pa; target electrode voltage: 1000 V; substrate voltage: 270 V; working pressure: 35 Pa; alloying temperature: 1000 °C; the parallel distance between the source electrode and the substrate: 15 mm and a treatment time of 3 h. A superalloy Hastelloy C-2000 (the composition is Cr 23, Mo 16, Cu 1.6, Ni 59 in wt%) plate (200 mm \times 150 mm \times 5 mm) were used as the target material for supplying the alloying elements. In this study, the composite alloying layer with the brush plating



1 computer, 2 CHI660b, 3 counter electrode (platinum foil), 4 reference electrode (saturated calomel electrode), 5 working electrode (test samples), 6 salt bridge, 7 rotator, 8 samples, 9 test solution, 10 PTFE wafer

Figure 1. Experiment apparatus for corrosion wear test.

Ni/nano-SiO₂ particles interlayer and the composite alloying layer with the brush plating Ni/nano-SiC particles interlayer were designated as composite alloying layer A and composite alloying layer B, respectively.

The structure and chemical composition of the samples were determined by x-ray diffraction (XRD, D8ADVANCE with Cu K α radiation), scanning electron microscopy (SEM, Quanta200, FEI Company), transmission electron microscopy (TEM, Tecnai G²20, FEI Company) and energy-dispersive x-ray spectroscopy (EDX). To prepare TEM specimens, 0.5 mm thick slices were cut from the sample surface. After mechanically grinding to 50 μ m from the cutting side of the slice, 3 mm diameter discs were punched out from the thin foils, which were prepared by jet electropolishing from the untreated side of the substrate. The microhardness was measured with a load of 200 g using a HX-200 micro-Vickers machine.

The corrosion wear tests were conducted in two different environments, namely, a 10% HCl solution and slurry solution (10% HCl + 10% quartz sand). Sand particles with an average size of 500 μ m were suspended in the solution to make the severe corrosive wear condition. The schematic diagram of the corrosion wear experimental apparatus designed by the authors is shown in figure 1. This apparatus facilitates the measurement of the electrochemical corrosion rate of the material in static, liquid impingement and liquid-solid impingement conditions. The apparatus is a rotating disc with four specimen holders on its edge. It consists of three parts: speed regulating system, electrochemical measurement system and slurry pot accessories. The rotating velocity was adjustable in the range 0–4000 rpm. Block samples (measuring $22 \text{ mm} \times 8 \text{ mm} \times 10^{-4} \text{ mm}$ 3 mm) were mounted in non-conducting epoxy resin with the $20 \text{ mm} \times 5 \text{ mm}$ face being exposed to the test solution. Specimens were fixed at the periphery of a non-conducting disc at a radial distance of 3 cm. The back of the samples was electrically connected to the terminals of the potentiostat to enable electrochemical measurements. All wetted parts in the container were manufactured using non-metallic materials. A platinum foil served as a counter electrode and a saturated calomel electrode (SCE) was employed as the reference electrode, connected by a salt bridge placed in the side cylinder.

Potentiodynamic polarization and EIS were employed here using a CHI660b electrochemical analyzer (Shanghai, China) to evaluate the corrosion protection performance of the developed composite alloying layers on 316L SS at room temperature (20 °C). The potentiodynamic polarizations were carried out under static, sand-free acidic flow and acidic slurry flow condition with a sweep rate of 30 mV min⁻¹. All the samples were immersed in the slurry for 10 min before starting the potential scan. When the corrosion wear tests were carried out at a rotational speed of 600 rpm, the motor drove the samples to rotate in the acidic flow solution (with or without sand particles), corresponding to linear speeds of samples $1.884 \,\mathrm{m \, s^{-1}}$. EIS tests were done in three groups: (1) after 20 h immersion in acidic solution (10% HCl solution); (2) after a 20 h corrosion wear test in sand-free acidic flow (10% HCl solution) and (3) after a 20 h corrosion wear test in acidic slurry (10% HCl + 10% quartz sand). The EIS measurements were carried out in static condition applying 5 mV sinusoidal perturbations in the 100 kHz to 10 mHz frequency range in deaerated aqueous solution.

3. Results

3.1. Microstructures of composite alloying layer

Typical microstructures of the Ni/SiO₂ brush plating layer, the Ni/SiC brush plating layer and composite alloying layers A and B formed on 316L SS are shown in figure 2. It can be seen from the figures that the two kinds of composite alloying layers with a thickness of about 50–60 μ m are continuous and compact without any visible metallurgy flaw. Shown in figure 3(a) are the bright-field TEM images of composite alloying layer A. It can be clearly seen that spherical-shaped nano-SiO₂ particles with sizes in the range 10-30 nm are dispersed and homogeneously distributed in the austenite matrix of composite alloying layer A. Shown in figure 3(b) is a magnified view (bright-field image) of the interface between SiO₂ and the matrix; it can be found that the interface is clean and free from deleterious interfacial reaction products. Figure 3(c) shows a selected area diffraction (SAD) pattern of nano-SiO₂ particles in composite alloying layer A. The SAD pattern confirms that nano-SiO₂ particles still retain the amorphous structure in the composite alloying layer A after double glow surface alloying. Figure 4(a) shows a bright-field image of composite alloying layer B. The microstructure of composite alloying layer B reveals that larger, spherical-shaped and small, strip-like particles are distributed inside the crystal grain and grain boundary of the Ni-based alloying matrix, respectively. The large, spherical-shaped particles are found to have sizes in the range 30-80 nm whereas the size of the small, strip-like particles is in the range 30-50 nm. The volume fraction of the particles is qualitatively determined under TEM by comparing the number density of large, spherical-shaped particles with that of small, strip-like ones in a specified area at the same magnification for a number of times. The volume fraction of former particles is found to be greater than the latter. SAD patterns shown in figures 4(b) and (c) are taken from the two kinds of particles. After analysing the SAD patterns, the large, spherical-shaped particles are identified



Figure 2. The cross-section views of Ni/SiO₂ brush plating layer (*a*), Ni/SiC brush plating layer (*b*), composite alloying layer A (*a*) and composite alloying layer B (*b*).



Figure 3. TEM micrograph of composite alloying layer A: (*a*) bright-field image; (*b*) interface between the particle and matrix (dark-field image); (*c*) SAD pattern of SiO₂ particle.



Figure 4. TEM micrograph of composite alloying layer B: (*a*) bright-field image; (*b*) SAD patterns of $Cr_{6.5}Ni_{2.5}Si$ phase; (*c*) SAD patterns of $Cr_{23}C_6$.



Figure 5. Polarization curves for composite alloying layer A (*a*), Ni-based alloying layer (*b*), 316L SS (*c*) and composite alloying layer B (*d*) under static state condition (10% HCl solution), acidic flow condition (10% HCl solution) and acidic slurry flow condition (10% HCl solution + 10% quartz sand) at a velocity of 1.884 m s^{-1} .

as σ -Cr_{6.5}Ni_{2.5}Si having a tetragonal structure whereas the small, strip-like particles are identified as Cr₂₃C₆ having face-centred cubic structure. In the literature, it has been reported that the reaction kinetics of SiC/Ni is fast during isothermal annealing at (and above) 1000 °C, resulting in decomposition of SiC [18, 19]. Under double glow alloying temperature (1000 °C) condition, Ni and Cr can diffuse into the SiC particle resulting in a severe degradation of SiC and simultaneously react with SiC to form thermodynamically more stable ternary element silicide phase and binary element carbide. Based upon the above analysis, it can be inferred from the reaction mode representing the SiC/Ni, Cr that Ni, Cr react

with SiC to form $Cr_{6.5}Ni_{2.5}Si$ and free carbon following the equation

$$SiC + 6.5Cr + 2.5Ni = Cr_{6.5}Ni_{2.5}Si + C.$$
 (1)

Meanwhile, Cr reacts with free C to form $Cr_{23}C_6$, which is expressed by

$$23Cr + 6C = Cr_{23}C_6.$$
(2)

3.2. Potentiodynamic polarization measurements

Figure 5 shows the potentiodynamic polarization curves obtained for composite alloying layers A and B. For

Table 1. Electrochemical parameters calculated from polarization measured on 316L SS, composite alloying layers A, B and Ni-based alloying layer in static state, acidic flow condition (10% HCl solution) and acidic slurry flow condition (10% HCl solution + 10% quartz sand).

Samples	Condition	$E_{\rm corr}$ (V)	$i_{\rm corr}$ (A cm ⁻²)	$R_{\rm p}$ (Ω)
316L stainless steel	Static state Acidic flow Acidic slurry flow	-0.361 -0.414 -0.448	1.031e-4 6.711e-3 1.77e-2	183 11 2
Composite alloying layer A	Static state Acidic flow Acidic slurry flow	$-0.281 \\ -0.305 \\ -0.339$	3.498e-5 4.837e-5 5.977e-4	1026 627 387
Composite alloying layer B	Static state Acidic flow Acidic slurry flow	$-0.241 \\ -0.289 \\ -0.336$	5.167e-5 9.222e-5 1.571e-3	597 316 25
Ni-based alloying layer	Static state Acidic flow Acidic slurry flow	-0.273 -0.322 -0.369	2.662e-5 5.130e-5 7.405e-4	1323 508 281

comparison Ni-based alloying layer and AISI 316L SS polarization curves under identical conditions are presented. Three different curves in every diagram are presented for each material, corresponding to three different conditions: static state, sand-free acidic flow and acidic slurry flow.

In corrosion, quantitative information on corrosion currents and corrosion potentials can be extracted from the slope of the curves, using the Stern–Geary equation [20], as follows:

$$i_{\rm corr} = \frac{1}{2.303 R_{\rm p}} \left(\frac{\beta_{\rm a} \times \beta_{\rm c}}{\beta_{\rm a} + \beta_{\rm c}} \right),\tag{3}$$

where β_a and β_c are, respectively, the anodic and cathodic Tafel slopes and R_p is the polarization resistance. The corrosion potential (E_{corr}) , corrosion current density (i_{corr}) and polarization resistance (R_p) which were obtained from the polarization curves are given in table 1.

From figure 5, it is found that the corrosion potentials $(E_{\rm corr})$ of all the measured specimens are shifted to more negative values under acidic flow corrosion condition. Furthermore with the electrode rotating in sand-free acidic flow solution and acidic slurry flow condition, a significant increase in the anodic and cathodic current density is seen. A further decrease in $E_{\rm corr}$ occurs upon the addition of sand particles in the acidic solution. It is worth mentioning here that the corrosion resistance of the composite alloying layers A, B and the Ni-based alloying layer has been improved compared with 316L SS. There is an obvious difference in the material electrochemical characteristics. Composite alloying layer A and Ni-based alloying layer (figures 5(a) and (b)) exhibit a typical active-passive transition in the 10% HCl solution at both static state and sand-free acidic flow conditions, whereas there are no clear passive regions under corrosion wear condition. Polarization curves (figures 5(c) and (d)) confirm the absence of a passive region in the composite alloying layer B and 316L SS under both static state and acidic flow solutions with or without sand conditions. This is in agreement with the results of López et al [21] using the slurry erosion equipment in the slurry composed of 3.5% NaCl with 10 wt% of quartz particles.

Accompanied by the flow of acidic solution and the addition of sand particles, the polarization resistance $(R_{\rm p})$ decreases (shown in table 1). These data clearly indicate that the Ni-based alloying layer has the highest corrosion resistance in static acidic solution, which is slightly higher than that of composite alloying layer A. In contrast, under hydrodynamic condition with or without sand particles, composite alloying layer A has the highest corrosion resistance. Under all the test conditions, the corrosion resistances of composite alloying layer B are better than that of AISI 316L SS, but much lower than that of composite alloying layer A and the Ni-based alloying layer.

3.3. EIS measurement

EIS analyses provide insight into the kinetics of electrode processes as well as the surface properties of the investigated systems [22]. To verify the surface properties after 20 h of immersion in acidic solution, corrosion wear test in sand-free acidic flow and in acidic slurry, EIS measurements were carried out at OCP. Figures 6-8 show that the EIS of all the specimens consisted of two capacitive impedance loops.

According to the EIS results (figure 6) obtained after 20 h of immersion in 10% HCl solution in static condition, the surface resistance of 316L SS is $79 \,\Omega \,\text{cm}^2$. The surface resistance of the Ni-based alloying layer improves sharply to $1625 \,\Omega \,\mathrm{cm}^2$ which is 20 times higher than that obtained from the 316L SS. For composite alloying layer A, the surface resistance decreased slightly to 1335 Ω cm² with respect to the Ni-based alloying layer, whereas that of composite alloying layer B decreases sharply to $170 \,\Omega \,\mathrm{cm}^2$, which is equal to about double the surface resistance shown by 316L SS.

Figure 7 shows that the surface resistance of the investigated materials decreased dramatically after 20 h of test with a rotating specimen in sand-free acidic flow medium. It is noteworthy that the remarkable change is that the surface resistance of the Ni-based alloying layer is lower than that of composite alloying layer A compared with that obtained in static condition. Under such hydrodynamic condition, the surface resistance of test samples decreases in the order of



Figure 6. Nyquist diagrams of impedance spectrum for composite alloying layers A, B, Ni-based alloying layer and 316L SS after 20h of immersion in 10% HCl solution.



Figure 7. Nyquist diagrams of impedance spectrum for composite alloying layers A, B, Ni-based alloying layer and 316L SS after 20h of corrosion test in acidic flow condition (10% HCl solution).

composite alloying layer A > Ni-based alloying layer > composite alloying layer B > 316L SS. Figure 8 indicates a further decrease in the impedance in the capacitive loop with the presence of sand particles in acidic flow. The changing trend of surface resistance obtained in acidic slurry is analogous to that obtained in sand-free acidic solution.

The measured impedance data obtained after 20 h corrosion wear test in acidic slurry were analysed by using the ZsimpWin software. There are two well-defined time constants in Bode plots (figure 9). The high frequency part of the spectrum is usually related to the barrier properties of the test samples, while the low frequency segment reflects the corrosion activity on the metal surface [23]. An equivalent circuit consisting of two *RC* circuits shown in figure 10 is proposed [24]. R_e is the electrolyte resistance; R_{ct} and C_{dl} are the charge transfer resistance and double layer capacitance; R_{pit} and Q_{pit} are the pitting resistance and constant phase element (CPE) of composite alloying layers. CPE is substituted for the capacitive element to give a more



Figure 8. Nyquist diagrams of impedance spectrum for composite alloying layers A, B, Ni-based alloying layer and 316L SS after 20 h of corrosion wear test in acidic slurry flow (10% HCl + 10% quartz sand).



Figure 9. Bode diagrams of impedance spectrum for composite alloying layers A, B, Ni-based alloying layer and 316L SS after 20 h of corrosion wear test in acidic slurry flow (10% HCl + 10% quartz sand).



Figure 10. Equivalent circuit diagram used to fit the EIS data obtained for composite alloying layers A, B, Ni-based alloying layer and 316L SS after 20 h corrosion wear test in acidic slurry flow (10% HCl + 10% quartz sand).

accurate fit [25], as the obtained capacitive loop is a depressed semi-circle rather than a regular one. The impedance of CPE is expressed as

$$Z_{\rm CPE} = [Y_0(j\omega)^n]^{-1},$$
 (4)

where Y_0 is the admittance magnitude of the CPE and *n* is the exponential term. Generally, 0 < n < 1, where n = 1, it is an ideal capacitance, and when n = 0, it is a resistance. The

Table 2. Impedance fitting values of the composite alloying layers A and B, Ni-based alloying layer and 316L stainless steel after 20 h of corrosion wear test in acidic slurry flow (10% HCl + 10% quartz sand).

Samples	316L stainless steel	Composite alloying layer A	Composite alloying layer B	Ni-based alloying layer
$\frac{R_{\rm e}}{(\Omega{\rm cm}^2)}$	0.112	0.112	0.104	0.097
$C_{\rm dl}$ ($\mu \rm F cm^{-2}$)	4346	71.42	559.4	106.1
$R_{\rm ct}$ ($\Omega {\rm cm}^2$)	0.91	21	3.6	9.6
$Y_{0-dl} \times 10^{-6}$ (s ⁿ ω^{-1} cm ⁻²)	93.1	242	118	265.4
n _{dl}	0.87	0.91	0.88	0.90
$R_{\rm pit}$ ($\Omega {\rm cm}^2$)	35.33	257.6	43.75	225.8

fitted data match the experimental results very well, with an average error of below 5%.

As shown in table 2, the R_{ct} of composite alloying A is the highest which implies that the corrosion product formed on the surface of composite alloying A is compact. The $R_{\rm ct}$ values of composite alloying layer B and 316L SS decrease by one order of magnitude compared with that of composite alloying layer A and the Ni-based alloying layer. The C_{dl} value is related to the surface morphology. The higher the C_{dl} value, the rougher the tested specimen surface. The C_{dl} value of 316L SS is the highest, followed by composite alloying layer B, the Ni-based alloying layer and composite alloying laver A has the lowest after 20h of corrosion wear test under acidic flow medium condition and acidic slurry flow condition. The R_{pit} value of the Ni-based alloying layer is smaller than that of composite alloying layer A, and the R_{pit} value of composite alloying layer B is lower than that of composite alloying layer A, but higher than that of 316L SS. In summary, the surface spectroscopy analyses indicate that the composite alloying layer A exhibits a greater ability to retard corrosion under flow acid slurry condition.

4. Discussion

From figures 5–8, we find that the flow acidic medium has great significance in E_{corr} , i_{corr} and surface resistance. In static state condition, it is known that the corrosion product over the mouth of a metastable pit acts as a diffusion barrier in the metastable stage [26]. When the specimens are tested in the sand-free acidic flow condition, the flow solution has two effects on the corrosion wear process. The first is that the flow solution enhances the transport of aggressive Cl⁻ and H⁺ to the surface. In the strongly acidic slurry medium, the cathodic reaction is as follows:

$$O_2 + 4H^+ + 4e^- \to 2H_2O,$$
 (5)

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \to \mathrm{H}_{2}, \tag{6}$$

which is given by Zhang *et al* [27] in the aerated condition. Owing to the depolarization of hydrogen ion and depolarization of oxygen, the surfaces of investigated samples were active and the cathodic reduction reaction was

enhanced. The second is that the flow solution also provides a better oxygen transfer, which is helpful for forming the oxide and hydroxide of Ni, Cr and Mo to retard the anodic dissolution process. Once the protective film is formed, it will protect the surface against the impact of acidic flow immediately. The protective film will be cracked and stripped off when eroded and is subsequently reformed on fresh metal due to repassivation. Apparently, a competition between the film removal and repair exists in this system. The result of competing processes between electrode oxidation and destabilization is determined by the test medium. Niu et al [28] have reported that the reactions on the surface of electrode were dominated by the oxidation or stabilization process due to the substantial supplement of oxidants in 50% ethylene glycol + 50% deionized water + 100 ppm Cl⁻ solution with increasing electrode rotation speed, resulting in the increase in corrosion potential and cathodic current density and the decrease in the anodic current density. Differing from the results obtained in the above-mentioned conditions, in this study, the predominant effect was the enhanced destabilization of the electrode under the acidic flow medium condition. Consequently, the corrosion potential decreased and the anodic and cathodic current density increased.

Under acidic slurry flow condition, the greater degree of increase in the corrosion rate is attributed to the impact particles. There exists a synergism of acidic fluid flow and sand impact on electrochemical corrosion behaviour of investigated materials. The impingement of a high speed acidic liquid-particle will cause severe plastic deformation on the investigated materials and result in inhomogeneous stress distribution and electrochemical properties [29]. The microcell of strain difference is formed between the high strain domains, such as plough ridge and protuberance at the pit edges and low strain domain. Hence, the electrode becomes more active under acidic slurry flow condition, which is in accord with the further increases in corrosion current densities and decreases in polarization resistance.

Any factor that can influence the nature of corrosion or corrosion wear mechanism of materials is pertinent to its microstructure characteristic and composition, including the type of reinforcement phase, the presence of an interfacial reaction product, the precipitated phase within the matrix and the concentration of corrosion resistant elements [30].



Figure 11. SEM micrographs of 316L SS (*a*) and (*b*), Ni-based alloying layer (*c*) and (*d*), composite alloying layer A (*e*) and (*f*) and composite alloying layer B (*g*) and (*h*) after 20 h of corrosion wear test in acidic flow solution and after 20 h of corrosion wear test in acidic slurry flow condition.

For SSs, pitting is a well-known phenomenon which is reported to take place preferentially at inclusions within the microstructure situated at the exposed metal/solution interface, most notably manganese sulphide (MnS) inclusions [31-35]. Figures 11(*a*) and (*b*) show typical surface morphologies of 316L SS after 20 h of exposure to acidic flow medium with or without quartz sand. Figure 11(a) shows pitting and substantial formation of craters on the specimen surface. In acidic slurry, severe plastic deformation and gouging type features with a great number of craters are observed in figure 11(b). It is obvious that the surface morphology is rougher than that in the acidic flow condition. Table 3 shows that the abilities of surface

Table 3. The hardness variation of measured materials before and after corrosion wear in acidic slurry flow condition.

Samples	Before corrosion wear/ $HV_{0.1}$	After corrosion wear/HV _{0.1}
316L stainless steel	235	326
Composite alloying layer A	330	458
Composite alloying layer B	311	438
Ni-based alloying layer	202	275

deformation strengthening of 316L SS are lower compared with composite alloying layers A and B. A good ability of surface deformation strengthening can obviously alleviate the impact effect of particles [36]. Consequently, 316L has the lowest corrosion wear resistance with respect to the other test samples.

The Ni-based alloying layer contains more corrosion resistant elements Cr, Ni and Mo, which can improve the corrosion resistance by the formation of protective oxides that act as a barrier against further corrosion [36]. Figure 11(c)shows that the surface is uniformly corroded under sand-free acidic flow condition. This confirms that materials removal from the Ni-based alloying layer occurs by continuous thinning layer by layer. It is well known that the rate of materials loss due to corrosion can be accelerated significantly when the passivity of any protective surface film is breached by mechanical action, especially for such passive alloys [37]. Owing to low abilities of surface deformation strengthening, the mechanical force by the micro-cutting of sand particles can weaken and break the passive film on the metal surface and results in the formation of 'strain difference cells'. As a result, there are some local grooves on the surface shown in figure 11(d).

Compared with the Ni-based alloying layer, composite alloying layer A presents a certain extent of reduction in corrosion resistance in static state condition. Pitting in the composite alloying layer was concentrated predominantly at the reinforcement-matrix interfaces. The influence of nano-SiO₂ particles on the corrosion behaviour of the composite alloying layer includes the following two aspects. On the one hand, as shown in figure 3(b), it can be found that the interface between the nano-SiO₂ particles and the matrix is clean without any interfacial reaction product and nano-SiO₂ particles in the matrix are chemically inert phases, which may impede the corrosive attack of the environment effectively. On the other hand, the SiO_2 particles in the matrix result in a higher probability of passive film disruption favouring more pitting sites. These two effects offset each other, resulting in a slight reduction in the corrosion resistance of composite alloying layer A compared with the Ni-based alloying layer. Under conditions of acidic slurry flow, nano-SiO₂ particles in composite alloying layer A are well bonded by the Nibased alloy matrix and are strong enough to withstand microcutting induced by the impact of sand particles. Furthermore, the microhardness was improved apparently after a 20 h



Figure 12. TEM micrograph of the worn surface of composite alloying layer A after 20 h of corrosion wear in acidic slurry flow.

corrosion wear test in acidic slurry (table 3), which proves that composite alloying layer A exhibits a higher ability of surface deformation strengthening. Most of the published works on the theory of dispersion strengthening have shown that there are virtually two ways for the interaction of the nanoparticles (both shearable and non-shearable) with the dislocations [38–41]: (1) to cut through the nanoparticle or (2) to take a path around it. In the present research the second mechanism prevails due to the fact that the coarser nano-SiO₂ particles are coherent with the matrix. The gliding dislocation bows out between nanoparticles, then bypasses them leaving a loop around them. Dislocations are found to get trapped by nano-SiO₂ particles as shown in figure 12. Nano-SiO₂ particles in the matrix are obstacles for dislocation motion, and then the stress necessary for the motion of dislocations is increased. The microhardness of composite alloying layer A is increased after a 20 h corrosion wear test in acidic slurry, because the nano-SiO₂ particles in the composite layer can act as barriers to resist plastic deformation of the soft matrix. Figures 11(e) and (f) show the SEM micrographs of the corroded surfaces of composite A after a 20 h corrosion wear test in sand-free acidic flow and after a 20 h corrosion wear test in acidic slurry, respectively. Comparing figure 11(f) with figure 11(e), it is clear that surface morphology variation of composite A is negligible. Hence, composite alloying layer A with compatible higher abilities of surface deformation strengthening and corrosion resistance is a good candidate material for corrosion wear environment.

For composite alloying layer B, the corrosion resistance is inferior to that of the Ni-based alloying layer and composite alloying layer A, but is superior to that of 316L SS under all test conditions. The work reported here indicates that the added nano-SiC particle is deleterious to the corrosion resistance. Relatively severe corrosion occurs as a consequence of chromium depletion in regions close to grain boundaries and inside the crystal grains, which is associated with precipitation of dispersed $Cr_{6.5}Ni_{2.5}Si$ phase and $Cr_{23}C_6$ phase. As shown in figure 11(*g*), the corroded surface of composite alloying layer B reveals preferential attack at the interface of the cluster of grains and very small pitting pits inside the grains cluster, due to the fact that the Cr-depleted regions form along the grain boundaries and inside crystal grains. Cr depletion zones have anodic behaviour in relation to the adjacent zones that present higher Cr content (cathodic zones). Preferential removal of the matrix around the precipitated phase takes place through the chemical attack of the aggressive medium, leading to protrusion of relatively hard and inert precipitated phases (shown in figure 11(g)). Under acidic slurry flow condition, with evolution of the corrosion wear process, the area of matrix around the precipitated phase is constantly decreased, resulting in the precipitated phase in the microstructures of composite alloying B losing the support of the Ni-based alloy matrix. Ultimately, the precipitated phase is broken off and carried away by the impact of particles (shown in figure 11(h)). This is the reason why the corrosion wear resistance of composite alloying layer B is lower than that of composite alloying layer A and the Ni-based alloying layer.

5. Conclusion

- (1) During the double glow alloying process, the nano-SiO₂ particles still retained an amorphous structure at the alloying temperature (1000 °C), and spherical-shaped nano-SiO₂ particles with a size of about 10–30 nm were dispersed and uniformly distributed in composite alloying layer A, whereas the decomposition of nano-SiC particles occurred and nano-SiC particles reacted with Ni, Cr to form Cr_{6.5}Ni_{2.5}Si and Cr_{2.3}C₆.
- (2) Under acidic flow condition, potentiodynamic polarization curve measurement results exhibit an increase in corrosion current density and decrease in corrosion potential compared with those under static state condition, and a further increase in corrosion current and decrease in corrosion potential with the presence of sand particles in acidic flow solution.
- (3) In static acidic solution, the corrosion resistance of composite alloying layer A is lower than that of the Nibased alloying layer. However, the corrosion resistance of composite alloying layer A is prominently superior to that of Ni-based alloying layer under acidic flow medium condition and acidic slurry flow condition. The corrosion resistance of composite alloying layer B is evidently lower that of the Ni-based alloying layer, but higher than that of 316L SS under all test conditions.
- (4) EIS test results show that there are two capacitive impedance loops under all test conditions. Under sandfree acidic flow and acidic slurry flow condition, the significant decrease in the surface resistance indicates the decrease in the corrosion wear resistance of tested samples compared with that in static state medium. Under hydrodynamic conditions, the surface resistance of tested samples decreases in the order of composite alloying layer A > Ni-based alloying layer > composite alloying layer B > 316L SS.

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