



Article Electrochemical Behavior of Nickel Aluminide Coatings Produced by CAFSY Method in Aqueous NaCl Solution

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Abstract: Combustion-assisted flame spraying (CAFSY) is a novel method that allows in-flight synthesis of alloys during flame spraying. The in-flight synthesis of alloys by the CAFSY method during flame spraying combines two different methods: the self-propagating high-temperature synthesis (SHS) and flame spraying (FS). The present work studies the corrosion performance (by cyclic polarization and chronoamperometry in aerated 3.5 wt.% NaCl) of NiAl coatings fabricated by the CAFSY technique in relation to main process parameters (composition of the initial feedstock, spraying distance, substrate temperature, postdeposition heat treatment) and their effect on the microstructure and porosity of the coatings. Most of the coatings exhibited limited susceptibility to localized corrosion. In all cases, the steel substrate remained intact despite corrosion had the form of pitting and/or crevice corrosion in the coating that propagated dissolving Al and Al-rich nickel aluminides along coating defects. Substrate preheating and postdeposition heat treatment negatively affected the corrosion resistance. A short spraying distance (1.5 inch) increased the corrosion resistance of the coatings.

Keywords: combustion-assisted flame spraying (CAFSY); in-flight synthesis; flame spraying; SHS; intermetallic phases; coatings; corrosion resistance; cyclic polarization; chronoamperometry

1. Introduction

The intermetallic compounds (IC) of NiAl and Ni₃Al are important for the industry, owing to their outstanding properties as protective coatings [1,2]. Because of their high melting points, these intermetallic compounds are used in high-temperature applications, such as heat treatment furnaces, gas turbines, aircraft connectors, automotive turbochargers, pistons and valves, tools, and permanent molds [3]. The application of nickel aluminide coatings on metals and alloys has a beneficial effect on the high-temperature performance of boilers and turbines that operate at high temperatures [4]. The intermetallic compounds of the Ni-Al system are known for their high-temperature mechanical strength and can improve the resistance to oxidation and corrosion by forming a protective outer alumina film [5]. It has also been reported that the two-phase material Ni₃Al + NiAl exhibits a synergistic beneficial effect on the properties of these alloys and has been used in aerospace engines [6]. In addition, intermetallic compounds in the Ni-Al system, as well as the Ti-Al system, are considered strong candidates as new alternative structural systems for high-temperature applications [7–10].

The in-flight synthesis of alloys by the CAFSY method during flame spraying combines two different methods: the self-propagating high-temperature synthesis (SHS) and flame spraying (FS) [11,12]. During CAFSY, the initial mixture of base-metal powders



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). is introduced into the flame, and, during the flight stage, the base-metal powders react exothermically, producing in situ intermetallic coatings on the substrate [13].

In the past, a similar in-flight synthesis during thermal spraying was demonstrated only by plasma spraying due to the very high temperatures that can be reached [14–17]. However, plasma spraying significantly increases the cost of such composite coatings due to a high consumption of electricity [18]. The need to synthesize low-cost coatings in an oxygen-acetylene flame was the main impetus that led to the development of the CAFSY method by the authors of the present work [19,20].

The in-flight flame spraying method is an economical and portable method of synthesis of coatings of various compositions using pure conventional powders (powder particle size: 40–250 mm). The first efforts to synthesize nickel aluminides in-flight from pure Ni and Al powders were described in previous works [19,20]. The exothermic reactions during flight increase the available energy; thereby, the required reaction time between Ni and Al is reduced, resulting in a rapid synthesis of the NiAl and Ni₃Al intermetallics [19,20]. The Ni-Al system was selected because the intermetallic compounds of the system (particularly NiAl and Ni₃Al) are widely used in industry as built-up and bond coats, as well as for high-temperature applications [1,21].

Since commercial Ni and Al powders are widely available and very inexpensive, CAFSY eliminates the need to use the expensive pre-alloyed powders generally used for thermal spraying and hard coatings [22,23].

During CAFSY of various Ni and Al powder mixtures in air, many different compounds form (NiAl₃, Ni₂Al₃, NiAl, Ni₃Al, NiO, Al₂O₃, NiAl₂O₄) by mostly exothermic combustion reactions, which have originally been described by Naiborodenko et al. [24]. Unfortunately, the formation of nickel aluminides is accompanied by the generation of oxides and spinels within the final coating.

The process parameters are determined on the basis of one product stoichiometry (NiAl with a stoichiometric ratio of Ni-to-Al equal to 1:1). However, during SHS and even during the mechanical treatment of the Ni-Al system, complicated mechanisms occur with many parallel reactions that lead to multiphase products composed of mixtures of two or more from NiAl₃, Ni₂Al₃, NiAl, Ni₃Al and Ni [25–27].

Previous efforts [19,28] by the authors focused on the improvement of the process parameters. Parameter optimization led to high-quality coatings with low porosity (<3%), coherent structure, good adhesion strength to the substrate (>40 MPa) and a low erosion rate (2–8 mg/min) [19]. When the matrix of the coating consists of large amounts of Ni and Al, intermetallics do not significantly affect the erosion resistance. Instead, coatings with high amounts of NiAl and Ni₃Al and simultaneously low contents of brittle NiAl₃ and Ni₂Al₃ phases have shown improved resistance to airborne sand erosion [19,20]. It was also shown that the content of intermetallic phases in the coatings can be improved substantially by post-spraying heat treatments applied by repeated passes of the materials in the flame [28].

In many applications, coatings are required to combine high hardness and erosion resistance with high aqueous corrosion resistance. Many studies have been carried out on the corrosion behavior of Al-alloys and Ni-alloys; much fewer studies have addressed the corrosion performance of aluminides of transition metals (TMs). The bilayered structure of the passive film of Al is long known [29]. According to Bockris et Kang [30], the outer layer consists of Al-oxide, hydrated alumina and fibril-like AlOOH. The inner layer is mainly composed of Al₂O₃, with small amounts of fibril AlOOH. Several studies have reported that the passive film on Ni is bilayered, comprising an inner barrier NiO layer and an outer Ni(OH)₂ layer [31–33]. Oxides of alloying elements (such as Cr, Ta, Si, Ge) may benefit the localized corrosion resistance of Al and Fe-aluminides by blocking the Cl⁻ adsorption sites [30,34,35]. Mixed multilayered structures of hydroxides/oxy-hydroxides/oxides of Al and TMs have been reported to form on aluminides of TMs exposed to various electrolytes [34,36–42]. The inner layers are composed of anhydrous oxides that have a barrier character, whereas the outer layers are composed of mixed Al-TM hydroxides/oxy-

hydroxides. The presence of transition metals, such as Cr [43,44], W [30], Mo [30], Ta [30,45], Co [39,40,46], etc., in the Al₂O₃-based passivating layer reportedly improves the localized corrosion resistance in solutions containing Cl⁻. In many metals, aggressive anions, such as Cl⁻, are able to enhance the flux of cation vacancies through the barrier layer, such that under favorable conditions (voltage, pH, Cl⁻ concentration), vacancy condensation will occur at the metal/barrier layer interface and, hence, passivity breakdown will ensue [47].

Within the above framework, the present work presents results of the corrosion performance of nickel aluminide coatings fabricated by the CAFSY technique in relation to the process parameters and their effect on the microstructure and porosity of the coatings (both of paramount importance for the corrosion behavior of a material). An integrated evaluation of the above coatings has the final objective to open the way for the synthesis of coatings of other compositions by the CAFSY method.

2. Materials and Methods

Plates of 304L stainless steel (nominal size 4 cm \times 5 cm) were coated by the CAFSY method. The following powders were used as feedstock materials: Sulzer-Metco's 56C-NS (Ni) and pure aluminum (99.5%) from Aluminium Powder Company ALPOCO Ltd. (Rotherham, UK), with particle sizes of 45–75 µm and 45–90 µm, respectively. Flame spraying was conducted employing the 5P-II oxy-acetylene flame spraying gun. During CAFSY, the Ni and Al powder mixture reacted in an SHS synthesis regime, both in-flight and on the surface of coupons, producing various nickel aluminides. Table 1 presents the parameters employed in the present study, as previously determined [20,28]. Four different parameters were studied: (1) composition of the initial powder (COMPO), (2) distance of thermal spraying (DIST), (3) substrate temperature (SUBTEM) and (4) postheat treatment (COATR). The substrate temperature was measured by an infrared thermometer (UEI, INF 151) and was determined under identical conditions of passing the gun over the substrate without powder feeding and heating it up until the desired temperature was reached. Postheat treatment was carried out applying a number of gun passes after the coating deposition; the temperature was measured by an infrared thermometer.

Rectangular coated coupons were cut with a diamond saw and used for electrochemical testing. The coupons were ground with a #1000 SiC grit to a final roughness of lower than 5 µm in order to avoid the formation of microgalvanic cells due to their initial roughness. Ultrasonically cleaned coupons were encapsulated in PTFE, leaving an exposed surface area of $\sim 1 \text{ cm}^2$ to be exposed to aerated 3.5 wt.% NaCl at 25 °C. A standard threeelectrode cell (reference electrode: Ag/AgCl (3.5 M KCl, $E_{AgCl} = E_{SHE} - 200$ mV), counter electrode: Pt gauge) was employed. All the electrochemical tests were performed using the Gill AC potentiostat/galvanostat by ACM instruments. The rest potential (E_{rest}) was determined after 4 h of immersion in 3.5% NaCl at 25 °C (open circuit state). Following the determination of the rest potential, potentiodynamic polarization tests were carried out at a scan rate of 10 mV/min. Tafel extrapolation [48] was used to determine the corrosion current densities. In this work, linear regression analysis (least squares method) was applied to the *E*-log (*i*) data starting from $E_{rest} \pm 50$ mV and extending over a current density range of at least one order of magnitude. The linear regression was computed by the statistical analysis tools of Microsoft Excel (LINEST and TREND functions). A reasonable accuracy was ensured by conforming to several criteria elaborately reported in previous works [49,50].

Reverse polarization tests were also conducted to study the susceptibility of the coatings to localized corrosion. This technique is based on the principle that pitting would occur if the current density of the anodic curve of the reverse scan is greater than the current density of the forward scan for the same anodic potential [51]. In that case, the so-called "negative hysteresis" results. More details can be found in a previous work [50]. Finally, chronoamperometry tests (2 h in 3.5% NaCl at 25 °C) were carried out in order to confirm the indications of the potentiodynamic polarization tests regarding the nature and the protection ability of the current limiting processes.

Sample Name $ ightarrow$																
Parameters of Thermal Spraying \downarrow	COMPO 1	COMPO 2	COMPO 3	COMPO 4	DIST 1	DIST 2	DIST 3	DIST 4	SUBTEM 1	SUBTEM 2	SUBTEM 3	SUBTEM 4	COATR 1	COATR 2	COATR 3	COATR 4
Composition Ni+Al,	42.1 Ni	59.3 Ni	65.1 Ni	86.8 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni	65.1 Ni
wt.%	57.9 Al	40.7 Al	34.9 Al	13.2 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al	34.9 Al
Particle size Al, µm	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100	75-100
Spray distance, cm (inch)	11.4 (4.5)	11.4 (4.5)	11.4 (4.5)	11.4 (4.5)	3.8 (1.5)	6.4 (2.5)	11.4 (4.5)	16.5 (6.5)	11.4 (4.5)	11.4 (4.5)	11.4 (4.5)	11.4 (4.5)	11.4 (4.5)	11.4 (4.5)	11.4 (4.5)	11.4 (4.5)
Ratio O_2/C_2H_2	1.56	1.56	1.56	1.56	2.39	2.39	2.39	2.39	1.52	1.52	1.52	1.52	1.56	1.56	1.56	1.56
Substrate temperature, °C	450	450	450	450	200	200	200	200	200	450	550	600	450	450	450	450
Number of gun passes for heat treatment	10	10	10	10	-	-	-	-	-	-	-	-	0	10	15	20

Table 1. Parameters of thermal spraying.

The microstructure of the specimens was examined by scanning electron microscopy (SEM), under secondary electron (SE) and back scattered image (BSE) modes, and energy dispersion X-ray (EDX) analysis in the Quanta Inspect FEI Inspect SEM. The surface phases in the coatings were identified by X-ray diffraction analysis (XRD). The development of the various intermetallics was monitored by calculating the peak ratios of intensities of particular XRD peaks. The peaks used were: for aluminum, *hkl*: 111; for NiAl, *hkl*: 220; for Ni₃Al, *hkl*: 311; and for NiAl₃, *hkl*: 112. These peaks were selected because they were uniquely assigned to their respective phases. The porosities of the coatings were determined by image analysis on polished cross-sections (×500 magnification); image analysis was carried out by thresholding the porosity in the field of view. Ten separate fields of view per sample were analyzed. The Leica image analysis method was used. Pores were identified by a process of color segmentation.

3. Results and Discussion

3.1. Microstructure of the As-Sprayed Coatings

3.1.1. Effect of Composition

Figure 1 illustrates cross-sections of coatings that were fabricated from powders of different Ni contents and were subjected to a heat treatment of 10 gun passes. Relatively high percentages of intermetallic compounds and scare unmelted particles were revealed. According to elemental quantitative EDX, the intermetallics found correspond to NiAl, NiAl₃, Ni₂Al₃ and Ni₃Al. Heat treatment significantly increased the coating temperature, favoring solid–liquid phase reactions between intermetallic compounds and Al, as well as solid-phase reactions [26].



Figure 1. Cont.



Figure 1. SEM (SE mode) micrographs of coatings (cross-sections) with an initial mixture composition of: (a) 42.1% Ni-COMPO 1; (b) 59.3% Ni-COMPO 2; (c) 65.1% Ni-COMPO 3; (d) 86.8% Ni-COMPO 4 and (e–h) phase identification by EDX. All coatings have been subjected to 10 gun passes of heat treatment. Based on data of [52].

X-ray diffraction analysis in Figure 2a (using data of [52]) shows that coatings COMPO 1, COMPO 2 and COMPO 3 (42.1 wt.%, 59.3 wt.% and 65.1 wt.% Ni) consisted of Ni, NiAl, NiAl₃, Ni₂Al₃, Ni₃Al, Al, NiO, NiAl₂O₄ and Al₂O₃ phases. Coating COMPO 4 (86.8 wt.% Ni) displayed only traces of NiAl₃, while no Al and Al₂O₃ were detected. It is clear that as the concentration of Ni in the initial mixture increased up to 65.1 wt.%, the amount of the Ni₃Al phase increased. The non-detection of an Al phase in the final product of COMPO 4 indicates that Ni₃Al was rather the product of reaction between NiAl and Ni than reaction between Ni and Al.

As shown in Figure 2b, the concentration of each Ni_xAl_y phase (as a function of the Ni percentage) appears to be maximum in the Ni composition corresponding to the stoichiometry of the respective reaction between Ni and Al (42.1 wt.% Ni is the percentage that corresponds to the NiAl₃ stoichiometry during reaction Ni + 3Al \rightarrow NiAl₃; 59.3 wt.% Ni corresponds to the Ni₂Al₃ stoichiometry during reaction 2Ni + 3Al \rightarrow NiAl₃; and 65.1 wt.% Ni corresponds to the NiAl stoichiometry during reaction Ni + Al \rightarrow NiAl). On the other hand, the concentration of Ni₃Al in the coating with 86.8 wt.% Ni (corresponding to the Ni₃Al stoichiometry during reaction in the initial mixture. For such a low Al concentration in the initial mixture, the reaction between three Ni particles and one Al particle to produce Ni₃Al during flight is perplexing, whereas Al sublimation in the flame deteriorated the yield of reaction $3Ni + Al \rightarrow Ni_3Al$. Figure 2 also shows that the porosity of the coating decreased with increasing the percentage of Ni. As the Ni percentage increased, less aluminum became available to sublime and, hence, less Al₂O gas could be trapped between coating splats.





Figure 2. (a) XRD pattern of the surfaces formed after different initial composition of the powder before CAFSY (using data of [52]) and (b) coating porosity and semiquantitative analysis of the intermetallic phases present in the coatings as functions of the Ni content in the initial feedstock mixture.

3.1.2. Effect of Thermal Spraying Distance

SEM examination of cross-sections of the coatings (Figure 3) shows that as the spraying distance decreased, the amount of the intermetallic compounds formed (intermediate contrast regions) increased. At the distance of about 3.8 cm (Figure 3a), the Al phase (darkgray contrast) appears drastically reduced, while there is a strong presence of intermetallic compounds. Quantitative EDX analysis identified the presence of NiAl₃, NiAl and Ni₂Al₃ intermetallics. An increase in the spraying distance led to an increase in the remaining Al phase in the final product because by moving the gun away from the substrate, the substrate temperature decreased. At close spraying distances, the substrate temperature reached high values, enhancing the complete melting of the aluminium particles. When the fully melted particles impacted the substrate, the droplets backscattered and did not adhere to the substrate, creating cavities. As a result, the porosity of the coating increased.



Figure 3. SEM (SE mode) micrographs of the cross-sections of the coatings produced at various thermal spraying distances: (a) 1.5 inch (3.8 cm): DIST 1, (b) 2.5 inch (6.4 cm): DIST 2, (c) 4.5 inch (11.4 cm): DIST 3 and (d) 6.5 inch (16.5 cm): DIST 4 and phase identification by EDX.

Indeed, the porosity of coating DIST 1 (3.8 cm spraying distance, Figure 3a) appears to be higher than that of DIST 2 (6.4 cm spray distance, Figure 3b). Besides the aforementioned scattering of the droplets, a major reason for the increased porosity at the short spraying distance is the sublimation of Al inside the flame (higher temperatures enhance evaporation

of Al, leading to formation of Al_2O gas trapped between the splat of the coating) and on the surface of the substrate of DIST 1 (higher temperatures of the coating surface also lead to higher sublimation of Al at the surface).

The XRD analysis in Figure 4a shows that the coatings consisted of Ni, Al, NiAl, Ni₃Al, NiAl₃, Ni₂Al₃ and NiO phases. The DIST 1 coating sprayed at the lowest distance exhibited the lowest concentration of Al and the highest concentrations of NiAl₃ and Ni₂Al₃ (based on the relative intensities of the corresponding peaks [53,54]). Conversely, an increase in the spraying distance led to reduced peak intensities of the Ni-aluminides. Specifically, only traces of NiAl₃ were observed in the diffractograms of DIST 3 and DIST 4 coatings (11.4 and 16.5 cm distances, respectively), while the Ni₂Al₃ phase was not even detected in the diffractogram of coating DIST 4.



Figure 4. (a) XRD pattern of the surfaces formed after different thermal spraying distance and (b) coating porosity and semiquantitative analysis of the IC phases present in the coatings as functions of the thermal spraying distance.

In more detail, the semiquantitative presentation of the peak ratios (Al, *hkl*: 111, Ni *hkl*: 200, NiAl, *hkl*: 220, Ni₃Al, *hkl*: 311 and NiAl₃, *hkl*: 112 [55]) as functions of the thermal spraying distance in Figure 4b shows that as the spraying distance increased, the concentrations of NiAl, Ni₃Al and NiAl₃ decreased. The concentration of NiAl₃ shows a sharp drop, with distance increasing from 1.5 inch to 2.5 inch. The concentrations of the NiAl and Ni₃Al compounds appear to have stabilized at spraying distances greater than 2.5 inch, suggesting that more energy was needed to increase their concentration in the coating. This action can be performed by varying other spraying conditions.

During flame spraying, the substrate continues to be heated. As such, when the substrate is closer to the gun, the temperature of the coating and the substrate increases faster and continuously until the whole coating is sprayed. Therefore, at the spraying distance of 1.5 inch, the hot zone of the flame gun contacts the substrate, leading to a sharply increased coating/substrate temperature; consequently, the synthesis of intermetallic compounds is aided. However, this can be dangerous for the spray gun, as there is a risk of overheating due to the short distance from the substrate. Figure 4 (using data of [28]) also reveals that the porosity increases with increasing spray distance, while exhibiting a minimum value at the spraying distance of 2.5 inch. This can be attributed to the reduction of the fully melted particles when they impacted the substrate, resulting in fewer backscattered droplets, and hence, a smaller number of cavities. A further increase in the spraying distance (DIST 3 and DIST 4) led to the sublimation of smaller particles of Al inside the flame, having thus promoted the entrapment of gas (Al₂O) between the splats in the coating; hence, it resulted in a higher porosity.

3.1.3. Effect of Substrate Temperature

The SEM observation of the coatings in cross-sections (Figure 5) shows that the low preheating temperature (200 °C-SUBTEM 1, Figure 5a) led to distinct splats with rough boundaries. Once the semi-molten particle impacted the "cold" surface, it solidified faster, preventing its spreading and smoothing at the top. The SUBTEM 2 coating (Figure 5b) seems more uniform than the rest; porosity is significantly reduced, and formation of splats is uniform. It is also observed in Figure 5b that the amount of intermetallics (intermediate contrast areas) formed during the first passes (close to the coating/substrate interface) is increased relative to the succeeding passes. This suggests that preheating of the substrate to 450 °C promoted the formation of the ICs. Preheating the substrate to 550 °C and 600 °C led to a slightly increased porosity (red circles in Figure 5c,d), attributed to the backscattering of particles. The molten particles impacted the substrate, which cannot be cooled on time to form a uniform splat. As such, the cooling rate of the molten particle decreased, while the impact velocity remained high. Especially, as far as SUBTEM 4 is concerned, the substrate temperature is high enough and, in fact, close to the melting temperature of Al, thus resulting in prolonged reactions throughout the coating and, hence, more reaction products, i.e., ICs and, possibly, gaseous Al₂O.

The diffractograms of Figure 6a show an increase in the peak intensities of the ICs, with the substrate temperature increasing (NiAl₃ primarily and Ni₃Al secondarily). This increase is observed especially in NiAl₃ because Al melted evenly on the surface of the coating, enabling a further reaction to form NiAl₃, which is intermetallic with the highest concentration in the metal having the fastest diffusion rate, i.e., Al. Generally, the XRD analysis shows that all the coatings consisted of Ni, Al, NiAl₃, NiAl, Ni₃Al, NiO and NiAl₂O₄.



Figure 5. SEM (SE mode) micrographs of cross-sections of the coatings with various substrate temperatures: (a) 200 °C: SUBTEM 1, (b) 450 °C: SUBTEM 2, (c) 550 °C: SUBTEM 3 and (d) 600 °C: SUBTEM 4 and phase identification by EDX. Red circles enclose porosity of the coatings.

Semiquantitative analysis based on the peak ratios (Al, *hkl*: 111, Ni *hkl*: 200, NiAl, *hkl*: 220, Ni₃Al, *hkl*: 311 and NiAl₃, *hkl*: 112 [55]) in Figure 6 (using data of [28]) confirms that an increase in the substrate temperature caused an increase in the concentration of the intermetallic compounds. NiAl₃ manifests the largest increase since, as mentioned above, heating of the substrate at temperatures over 550 °C increased the reactivity of Al, especially when the temperature is close to the melting point. A small but noticeable increase in the content of Ni₃Al with substrate temperature is observed. The higher the temperature of the substrate, the faster the temperature increase in the coating. The coating temperature probably reached levels that promoted the formation of Ni₃Al (by facilitating diffusion of Ni).



Figure 6. (a) XRD pattern of the surfaces formed with different substrate temperatures and (b) coating porosity and semiquantitative analysis of the intermetallic phases present in the coating as functions of the substrate temperature.

3.1.4. Effect of Heat Treatment of the Coating

SEM examination of cross-sections of the coatings (Figure 7) suggests a proliferation of reactions by increasing the heat input (the greater the number of gun passes, the higher the postdeposition coating temperature). In further detail, Figure 7a–c reveal a decrease in the percentage of Ni as the number of gun passes (after coating deposition) increased from 0 to 15 passes of the flame. This suggests that the temperature increased, encouraging the reaction of the remaining Al with Ni. In fact, it appears that the coating subjected to 15 passes contains almost 95 vol.% (estimated by image analysis) of intermetallic compounds.



Figure 7. SEM (SE mode) micrographs of the coatings (in cross-section) at various levels of postdeposition heat treatment using the flame spraying gun; (**a**) 0 gun passes: COATR 1, (**b**) 10 gun passes: COATR 2, (**c**) 15 gun passes: COATR 3 and (**d**) 20 passes: COATR 4, corresponding to surface temperatures of about 400 °C, 500 °C, 600 °C and 700 °C, respectively. Based on data of [28].

The XRD analysis (using data of [28]) presented in Figure 8a indicates that the COATR 1 coating (as-sprayed) consisted of Ni, Al, NiAl₃, NiAl, Ni₂Al₃, NiO, NiAl₂O₄ and traces of Ni₃Al. In contrast with COATR 1, coating COATR 4 (20 heat-treatment passes) resulted in an absence of Al, NiAl₃, NiAl₂O₄, Ni_{42.2}Al₉ and Al₂O₃.



Figure 8. (a) XRD pattern of the surfaces changing the postdeposition heat treatment (using data of [28]) and (b) coating porosity and semiquantitative analysis of the intermetallic phases in the coatings as functions of the postdeposition heat treatment of the coating: 0 passes: COATR 1; 10 passes: COATR 2; 15 passes: COATR 3; 20 passes: COATR 4.

The influence of the postdeposition heat treatment on the contents of NiAl, Ni₂Al₃, Ni₃Al and NiAl₃ in relation to the remaining unreacted Ni is illustrated in Figure 8b (based on data of [28]). The semiquantitative analysis in Figure 8 shows that heat treatment of 10 passes notably decreased the NiAl₃ concentration, while it notably increased the Ni₂Al₃ concentration; hence, it is concluded that the coating temperature attained by 10 gun passes was suitable to form Ni₂Al₃ by the reaction of NiAl₃ + Ni \rightarrow Ni₂Al₃. Further increasing gun passes from 10 to 20 led to the extinction of NiAl₃ and a small increase in the concentration of NiAl and Ni₃Al (as compared to the as-sprayed coating). Multiple passes of the gun on the coating led to an increase in the temperature of the coating itself. Thus, it is indicated that in the final coating (COATR 8), NiAl₃ completely reacted with the remaining free Ni to form the NiAl and Ni₃Al phases.

Considering the above microstructure analysis and the negative values of free enthalpy of formation of various Ni_xAl_y phases (Table 2), it is suggested that all intermetallic compounds in the Ni-Al system can be formed by exothermic reactions in the CAFSY method. The more negative the Gibbs free energy of formation (ΔG_f^0), the higher the formation tendency of the IC. Accordingly, when nickel reacts with aluminium, Ni₂Al₃ is produced first, followed by Ni₃Al, NiAl₃ and NiAl.

Table 2. Gibbs free energies of formation and free enthalpies of formation of some nickel aluminides [53,54,56,57].

Reaction	Gibbs Free Energy of Formation ΔG_f^0 (kJ·mol ⁻¹)	Free Enthalpy of Formation ΔH_{f}^{0} (kJ/mol), T = 298 K				
$Ni + 3Al \rightarrow NiAl_3$	-166.8	-114.4				
$2Ni + 3Al \rightarrow Ni_2Al_3$	-311.0	-170.9				
$Ni + NiAl_3 \rightarrow Ni_2Al_3$	-144.1	-				
$Ni + Al \rightarrow NiAl$	-133.0	-117.4				
$3Ni + Al \rightarrow Ni_3Al$	-167.8	-153.3				

3.2. Cyclic Polarization Experiments

3.2.1. Effect of Composition

Figure 9 and Table 3 show that increasing the Ni content from 59.3% to 86.8% did not have any significant effect on the anodic polarization curves of the coatings.

Table 3. Electrochemical values of the coatings immersed in 3.5% NaCl at 25 °C: Effect of powder composition.

Sample	Initial Mixture Ni + Al, wt.%	E _{corr} (mV vs. Ag/AgCl)	E _{a/c tr} (mV vs. Ag/AgCl)	E _{cp} (mV vs. Ag/AgCl)	E _b (mV vs. Ag/AgCl)	E _r (mV vs. Ag/AgCl)	i _{cor} (mA/cm²)	R ²	b _c (mV/decade)
Compo 1	42.1 Ni 57.9 Al	-595 (±120)	-456 (±108)	-441 (±95)	-203 (±67)	-	0.047 (±0.021)	0.982 ± 0.004	-663
Compo 2	59.3 Ni 40.7 Al	-344 (±45)	-382 (±34)	-	340 (±41)	339 (±35)	0.011 (±0.005)	0.992 ± 0.008	-684
Compo 3	65.1 Ni 34.9 Al	-326 (±28)	-375 (±33)	-	-	-105 (±19)	0.023 (±0.007)	0.980 ± 0.002	148
Compo 4	86.8 Ni 13.2 Al	-337 (±26)	-371 (±29)	-250 (±18)	-192 (±23)	-108 (±11)	0.035 (±0.010)	0.970 ± 0.009	47

 E_{cor} : corrosion potential; $E_{a/c}t_r$: anodic-to-cathodic transition potential; E_{cp} : critical "passivation" potential; E_b : breakdown potential; E_r : potential at which positive hysteresis turns to negative; i_{cor} : corrosion current density; R^2 : regression coefficient of the linear fit; b_c : cathodic Tafel slope.

The anodic forward polarization curves of the three coatings present more or less distinct deflections in their gradients at the breakdown potential (E_b), leading to almost flat gradients, which are sustained for about two orders of magnitude of current. Moreover, the hysteresis upon reverse polarization at potentials lower than E_r becomes negative (Figure 9b). Hence, it is suggested that the three coatings have been subjected to localized corrosion.



Figure 9. Effect of Ni content in the initial feedstock on the cyclic polarization behavior of nickel aluminide coatings. (a) Forward polarization curves; (b) cyclic (forward and reverse) polarization curves (3.5% NaCl, 25 °C).

The anodic forward polarization curves of the three coatings present final current stabilization stages at very high current densities. The latter imply the deposition of unstable (heavily hydrated surface compounds) and/or high concentration of cations in the anolyte. Despite the high current densities, the positive hysteresis loop (Figure 9b) upon reverse polarization through the final current limiting stage suggests a temporary protective effect lasting from the anodic potential of scan reversal to a potential E_r nearly equal to E_b (where the positive hysteresis turns to negative).

A different polarization behavior is exhibited by the Al-42.1% Ni coating, as shown in Figure 9 and Table 3. This coating presents the highest corrosion current density due to having the highest porosity (Figure 2), the highest surface area of Al (Figure 1a) and

the lowest corrosion potential as a result of the significant presences of Al and NiAl₃ (the IC with the highest ratio of Al/Ni), which are hardly present in alloys COMPO 3 and COMPO 4. Moreover, the residual stresses due to trapping of Al₂O gas are also responsible for the comparatively low corrosion potential of COMPO 1 [40]. The positive hysteresis loop and the nobler anodic-to-cathodic potential ($E_{a/c}$ tr) value as compared to the corrosion potential (E_{corr}) (implying nobler surfaces at $E_{a/c}$ tr upon reverse scanning) suggest non-susceptibility to pitting. The paradox of high resistance (Figure 9b, COMPO 1) to localized corrosion despite the high porosity indicates that pores are not interconnected, being blocked by the complex microstructure features (splat boundaries, phase boundaries, interlayer boundaries, etc.). Moreover, the high amount of aluminides with low Ni content (NiAl₃) led to a weak galvanic effect between Al and aluminides. Finally, it is possible that the high amount of unreacted Al led to well-melted splats that fit well to their substrates and did not form distinct boundaries with their matrix. As such, splats were not efficient stress concentrators, and they did not favor localized stress-corrosion processes.

It should be noted that the microstructures of the coatings were too complex to justify any strong and consistent trends in the electrochemical values. The many corrosion-resistant intermetallic phases competed against abundant cell inducers, such as interlayer boundaries, phase boundaries, splat interfaces, pores and oxides. The net resultants are similar electrochemical values and corrosion mechanisms governed by localized phenomena at the aforementioned defects.

The different shapes and the large shifts of the cathodic curves in Figure 9 are justified by the different number, distribution, types and particle sizes of the cathodic intermetallic phases. COMPO 4 presents the highest cathodic current densities, possibly due to the presence of large areas of Ni₃Al and NiAl that could effectively support cathodic reactions with adjacent ICs of higher Al or metal elements.

3.2.2. Effect of Thermal Spraying Distance

Figure 10 and Table 4 show that increasing the thermal spraying distance from 2.5 to 6.5 inch did not have any significant effect on the polarization curves of the coatings.

Sample	Spray Distance, cm (inch)	E _{cor} (mV vs. Ag/AgCl)	E _{a/c tr} (mV vs. Ag/AgCl)	E _r (mV vs. Ag/AgCl)	i _{cor} (mA/cm ²)	R ²	b _c (mV/decades)
DIST 1	3.8 (1.5)	-626 (±112)	-592 (±129)	-	0.023 (±0.014)	0.994 ± 0.005	-437 (±54)
DIST 2	6.4 (2.5)	-600 (±46)	-641 (±22)	-511 (±25)	0.015 (±0.004)	0.998 ± 0.002	-333 (±87)
DIST 3	11.4 (4.5)	-540 (±62)	$-638 (\pm 58)$	-327 (±49)	0.021 (±0.003)	0.994 ± 0.006	-473 (±32)
DIST 4	16.5 (6.5)	-591 (±29)	-644 (±36)	-318 (±23)	0.058 (±0.011)	0.996 ± 0.003	-244 (±112)

Table 4. Electrochemical values of the coatings immersed in 3.5% NaCl at 25 °C: Effect of spray distance.

 E_{cor} : corrosion potential; $E_{a/c tr}$: anodic-to-cathodic transition potential; E_r : potential at which positive hysteresis turns to negative; i_{cor} : corrosion current density; R^2 : regression coefficient of the linear fit; b_c : cathodic Tafel slope.

All coatings (except DIST 1) show negative hysteresis loops at $E < E_r$, suggesting susceptibility to localized corrosion. However, the reverse anodic scan of DIST 1 (1.5 inch) does not section the forward anodic scan, resulting in higher $E_{a/c tr}$ as compared to E_{corr} . The latter indicates nobler surfaces at $E_{a/c tr}$ upon reverse polarization relative to the surface at E_{corr} upon forward polarization.

The relatively high resistance to localized corrosion exhibited by the coating sprayed at the lowest distance (DIST 1) can be justified by the high contents of NiAl₃ and Ni₂Al₃. The high portion of Al in these aluminides reduces the galvanic effect between the Al matrix and adjacent aluminides. Moreover, porosity is also relatively low (Figure 4). Here, it should be noted that the differences between E_{corr} and $E_{a/c tr}$ for DIST 2 (which exhibits the lowest porosity—Figure 4) are small and within experimental error, also suggesting a good behavior toward localized corrosion.



Figure 10. Effect of thermal spraying distance on the cyclic polarization behavior of nickel aluminide coatings. (a) Forward polarization curves; (b) cyclic (forward and reverse) polarization curves (3.5% NaCl, 25 °C).

The relatively high (general) corrosion rate (i_{cor}) of DIST 4 can be justified by the high porosity (Figure 4) and the high amounts of unreacted Ni and Al (Figures 3d and 4). The differences in the E_{corr} values are small and within experimental error. It should be mentioned that the extremely complex (multiphase, multilayer, multidefect) microstructure is considered responsible for the large standard deviations observed in some cases (e.g., DIST 1).

3.2.3. Effect of Substrate Temperature

The polarization curves of all coatings (Figure 11) present positive hysteresis loops of large surface areas, suggesting a high resistance to localized corrosion. Surface films deposited during the final current limiting stage, although highly conductive and probably hydrated, seem to protect the coatings at $E > E_r$. Even the coatings deposited on hotter substrates (550 °C and 600 °C) show a good localized corrosion resistance despite their relatively high porosities (Figure 6) and the less-uniform microstructures (compare

Figure 5b with Figure 5c,d). It seems that the porosity shown in Figure 5c,d, as well as Figure 6, was filled up with surface depositions (formed during the current limiting stage upon forward polarization) that were not dissolved during almost the entire anodic part of reverse polarization. Additionally, porosity is not interconnected, as it is intercepted by the abundant different microstructural features (along with the high percentage of intermetallics), not allowing the electrolyte to access the substrate. However, hysteresis turns to negative at $E < E_r$, suggesting that localized corrosion may occur at low anodic E_s .



Figure 11. Effect of substrate temperature on the cyclic polarization behavior of nickel aluminide coatings. (a) Forward polarization curves; (b) cyclic (forward and reverse) polarization curves (3.5% NaCl, 25 °C).

Despite their relatively high porosities, SUBTEM 3 and SUBTEM 4 sprayed on the hottest substrates (550 °C and 600 °C) display high resistance to localized corrosion with

 $E_{a/c tr}$ nobler or equally noble to E_{corr} (Table 5). It is postulated that the reduced presence of Al induces limited localized corrosion occurrence. Additionally, the highly increased presence of NiAl₃ mediated the galvanic effect between Ni and Al, forming weak galvanic couples between Al and NiAl₃. Similarly, the increased presence of NiAl₃ mediated the galvanic effect between of NiAl₃ mediated the galvanic effect between Ni and Al, forming weak galvanic effect between Ni and Al, forming weak galvanic couples with Ni.

Table 5. Electrochemical values of the coatings immersed in 3.5% NaCl at 25 °C: Effect of substrate temperature.

Sample	Substrate Temperature, °C	E _{cor} (mV vs. Ag/AgCl)	E _{a/c tr} (mV vs. Ag/AgCl)	E _r (mV vs. Ag/AgCl)	E _b (mV vs. Ag/AgCl)	E _{cp} (mV vs. Ag/AgCl)	i _{cor} (mA/cm²)	R ²	b _c (mV/decades)
SUBTEM 1	200 °C	-602 (±98)	-640 (±110)	-474 (±40)	-	-	0.013 (±0.005)	0.997 (±0.003)	-351 (±34)
SUBTEM 2	450 °C	-617 (±74)	-655 (±86)	-557 (±53)	-	-	0.016 (±0.006)	0.989 (±0.007)	-437 (±48)
SUBTEM 3	550 °C	-607 (±112)	-607 (±99)	-	-	177 (±71)	0.022 (±0.010)	0.993 (±0.005)	-401 (±26)
SUBTEM 4	600 °C	-598 (±88)	-514 (±94)	-	-283 (±34)	-	0.022 (±0.012)	0.992 (±0.008)	-478 (±19)

 E_{cor} : corrosion potential; $E_{a/c tr}$: anodic-to-cathodic transition potential; E_r : potential at which positive hysteresis turns to negative; E_b : breakdown potential; E_{cp} : critical "passivation" potential; i_{cor} : corrosion current density; R^2 : regression coefficient of the linear fit; b_c : cathodic Tafel slope.

However, hotter substrates seem to have led to relatively high corrosion current density values (slightly higher, though within experimental error), as shown in Table 5. This trend can be attributed to the increased porosity (Figure 6) as well as the presence of small anodic areas (Al) adjacent to large cathodic areas (NiAl₃), as illustrated in Figure 5c,d.

3.2.4. Effect of Thermal Treatment of the Coating

The different shape and electrochemical values of the polarization curve of the assprayed coating (COATR-1) in Figure 12 and Table 6 suggest that the postdeposition heat treatment in the form of gun passes led to a different corrosion response. On the other hand, not many differences are observed in the polarization performance of the coatings as a function of the number of gun passes (10–25 passes).



Figure 12. Cont.



Figure 12. Effect of heat treatment of the coatings after thermal spraying on the cyclic polarization behavior of nickel aluminide coatings. (a) Forward polarization curves; (b) cyclic (forward and reverse) polarization curves (3.5% NaCl, 25 °C).

Table 6. Electrochemical values of the coatings immersed in 3.5% NaCl at 25 °C: Effect of heat treatment.

Sample	Thermal Treatment (Gun Passes)	E _{cor} (mV vs. Ag/AgCl)	E _{a/c tr} (mV vs. Ag/AgCl)	E _b (mV vs. Ag/AgCl)	E _r (mV vs. Ag/AgCl)	i _p (mA/cm ²)
COATR 1	0	$-574 (\pm 78)$	-416 (±82)	-247 (±39)	-	20 (±3)
COATR 2	10	-291 (±65)	-383 (±68)	-238 (±45)	-69 (±11)	22 (±5)
COATR 3	15	$-289 (\pm 48)$	-376 (±56)	-205 (±68)	-105 (±29)	23 (±6)
COATR 4	20	-298 (±53)	-391 (±69)	-188 (±44)	-34 (±13)	24 (±8)

 E_{cor} : corrosion potential; $E_{a/c tr}$: anodic-to-cathodic transition potential; E_b : breakdown potential; E_r : potential at which positive hysteresis turns to negative; i_p : current density range in the middle of the final pseudopassive region. (i_{cor} could not be determined because of low R^2 values).

The sustainable flat gradients of the anodic forward portions of the heat treated specimens (Figure 12a) corresponding to negative hysteresis loops of considerable surface areas and the fact that $E_{a/c tr}$ values are less noble than the E_{cor} values by approximately 100 mV manifest the occurrence of localized degradation. On the other hand, the positive hysteresis loop of accountable surface area along with the nobler $E_{a/c tr}$ relative to the E_{cor} by ~160 mV suggest a high resistance to localized corrosion for the as-sprayed coating.

It would be expected that heat treatment of 15 passes (COATR 3) would lead to the best behavior toward localized corrosion due to the lowest porosity and the high amount of aluminides. However, the particularly high amount of the Al-rich aluminides NiAl₃ and Ni₂Al₃ may have led to a strong galvanic coupling between Ni and intermetallics, favoring pitting and crevicing at the interfaces. Moreover, Figure 7c reveals small anodic areas (Ni) in contact with large cathodic areas (NiAl₃, Ni₂Al₃), a combination that accelerates the dissolution of Ni at the interfaces.

On the other hand, the untreated coating (COATR 1) presents an equally low porosity with COATR 3 but higher amounts of Ni and Al. The presence of high amounts of Al-rich aluminides (NiAl₃, Ni₂Al₃), which are contained in accountable quantities (Figures 7a and 8) combined with relatively large surface areas of anodic Al, may lead to the formation of weak galvanic couples. Figure 7a also illustrates large surface areas of Ni (anodic) next to smaller zones of intermetallics, suggesting relatively weak galvanic coupling.

Finally, the nobler E_{cor} of the heat-treated coatings as compared to the E_{cor} of the as-sprayed coating may be explained by the absence of Al (10, 20 passes) and the extremely high amount of intermetallics (15 passes).

3.3. Chronoamperometry

Chronoamperometry testing was performed to confirm the deposition of surface films indicated at the high anodic E_s of the potentiodynamic curves. The potentiostatic measurements were performed by polarization of the specimens at potential values corresponding to the pseudopassive regions for 2 h (Figure 13).



Figure 13. Chronoamperometry plots of the nickel aluminide coatings at pseudopassive potentials (as determined by potentiodynamic polarization) varying: (**a**) the initial mixture composition (%wt. Ni), (**b**) the thermal spraying distance, (**c**) the substrate temperature and (**d**) the thermal treatment of the coating. All specimens were immersed in 3.5% NaCl at 25 °C.

All curves of Figure 13a,b correspond to anodic potentials in the final current limiting stage, where hysteresis is positive. In general, the i vs. t curves present shapes typical of a current-limiting behavior. Current density initially decreased quickly, attaining a minimum value. Thereafter, it relaxed either to steady values or values that gradually decreased. The above trend signifies the build-up of surface films to a maximum thickness and extent. The maximum surface layer volume was further maintained or slightly and gradually increased. However, the high current density values in compatibility with the high current density values in the current limiting stages of the voltammograms (Figures 9–12) imply heavily hydrated products. Indeed, as mentioned in the Introduction,

it is well-established that all the major phases participating in the coatings, i.e., Al, Ni and aluminides, form bilayered surface films during immersion in aqueous chlorides with a defective inner oxide (barrier) layer adjacent to the metal and an outer layer that is composed of oxyhydroxides/hydroxides formed by cations that have been ejected from the barrier layer into the solution.

The paradox of high current density values despite the good protection ability of the surface depositions suggested by the positive hysteresis can be explained by the bilayered structure of the surface films, where the inner layer is anhydrous and has barrier abilities but the outer layer is hydrated and, thus, highly conductive, as reported in the Introduction.

COMPO 2, COMPO 3 and COMPO 4 present a slow but consistent decrease in current as a function of time, which is evidence of a slow but consistent deposition of surface products on the active surfaces. The higher current density values of COMPO 1 (42.1% Ni in the initial feedstock—the lowest Ni content) as compared to COMPO 2 (both polarized at 150 mV vs. Ag/AgCl) are in compatibility with the differences in the current density values of COMPO 1 and COMPO 2 at 150 mV during forward potentiodynamic polarization. They can mainly be ascribed to the high porosity of COMPO 1. COMPO 1 exhibits an initial sharp drop of i vs. t, most likely justified by the relatively high content of unreacted Al, which is subjected to spontaneous "passivation" as soon as it is immersed in the electrolyte. The succeeding current increase can be attributed to the anodic activity of the defective film (pores, interfaces, etc.).

The relatively low current density values of DIST 1 (Figure 13b) are rather due to the relatively low overpotential, as the concentration of Cl^- in the exposed defective surfaces increases with increasing potential [39]. Moreover, the DIST 1 coating, sprayed at the lowest spraying distance, contains the highest amount of Ni-aluminides, especially Ni₃Al, (Figure 4), as shown in Figure 5. As such, it may be postulated that the surface films are the richest in Ni, which, as a transition metal, is expected to improve the resistance of the Al₂O₃-based film to Cl^- , according to the aforementioned literature. Hence, the lowest conductivity of the surface film on DIST 1 conforms with the highest resistance to localized corrosion, indicated in Figure 10.

The jagged shape of the current density vs. time curve of SUBTEM 4 (highest substrate temperature), polarized at -350 mV (Figure 13c), is compatible with the metastable pitting suggested by the jagged "pseudopassive" portion of the voltammogram in Figure 11. High porosity (Figure 6) along with a variety of IC and metal phases (Al, Ni, Ni₃Al, NiAl, NiAl₃) favored the formation of differential aeration cells. Nevertheless, it is postulated that the increased NiAl₃ and Ni₃Al (Figure 6) caused an enrichment of the surface films with Ni; thus, the surface films became more stable with time, inhibiting stabilization of the pits. Based on the above postulation, the shape of the curve at -350 mV can be explained by the above considerations, namely, active corrosion was succeeded by the formation of unstable products on the active sites, which were formed with the same rate at which they were dissolved, resulting in a jagged plateau, and maintained up to 650 s of immersion. Then, a slow but consistent drop of current follows, suggesting alternative regrowth and dissolution, where the regrowth takes place at an increasingly higher rate as compared to the dissolution. Eventually, the film thickness and extent are stabilized. Metastable pitting is shown in all cases of substrate preheating (indicated by the jagged shape of the i vs. t curves). Nevertheless, in all cases, the dropping trend of current eventually became a current stabilization trend, manifesting a pseudopassive activity ascribed to thick, hydrated Al₂O₃-based films.

All the i vs. t curves of Figure 13d exhibit a gradual current drop with time, eventually leading to current stabilization (except COATR 4). Current oscillations and high current density values suggest soluble surface films, which grew with time until attainment of a constant thickness. However, the as-sprayed coating (COATR 1) exhibits a different behavior during polarization at -300 mV vs. Ag/AgCl, a potential corresponding to the first current limiting stage in the respective voltammogram of Figure 12. The initial sharp drop of current followed by current stabilization at very low values implies a passive-like

behavior. This behavior confirms the occurrence of a first current limiting stage shown in Figure 12. A deeper investigation on the nature of this stage is out of the scope of this paper; however, on a first approximation, it could be associated with passivation of Al, which is the phase with the highest passivation tendency for passivation. Indeed, the Gibbs free energies of formation of Al-oxide-based compounds are more negative (-1562.7 kJ/mol) than the Gibbs energies of formation of Ni-oxide-based compounds (-211.7 kJ/mol) [58]. Of course, the potential of -380 mV vs. Ag/AgCl is higher than the pitting potential of Al ($\sim-660 \text{ mV}$ [39–41]), and this probably explains the metastable pitting situation during potentiodynamic polarization (Figure 12).

The metastable pitting that did not evolve to stable pitting raises the possibility that Ni dissolved in Al stabilized the Al₂O₃-based film of Al. The solubility of Ni in Al is negligible under equilibrium conditions: 0.023 at% Ni (~0.05 wt. %) [59]; however, under the rapid solidification conditions of thermal spraying, the solubility of Ni in Al may be increased to 1.5 at% Ni (~3.0 wt. %) [60]. Indeed, SEM/EDX quantitative analysis of the Al phase in the coatings revealed dissolved Ni up to 1.4 at% (~2.8 wt.%).

The intense current fluctuations along with the plateau of i vs. t up to 2000 s, for the coating post-heat-treated by 15 gun passes (COATR 7), confirm the consideration stemming from the potentiodynamic polarization findings that indicated a strong galvanic coupling between Ni and Al-rich aluminides that favored pitting/crevicing at the interfaces.

The high current density values recorded for the coatings heat-treated by 10 and 20 gun passes as compared to the 15 gun passes heat-treated coating can be justified by the relatively high porosities that constitute sites of increased Cl^- concentration.

3.4. Microstructure of Corrosion

Figure 14 presents the microstructure of COATR 3 after cyclic polarization. COATR 3 (15 passes of heat treatment) showed low resistance to localized corrosion in Figure 12.

The presence of both oxide products of Al and Ni in the surface of the coatings agrees with previous studies on the corrosion of intermetallic compounds of Al with transition metals [36–39,42].

Each phase of the coating exhibited a different behavior to corrosion. From the observation of the cross-section of coating COATR 3 by SEM/EDS (Figure 14) after cyclic polarization, it seems that the corrosion propagated through phases containing a high percentage of Al (Figure 14, points 1–3).



Figure 14. Cont.





Figure 14. Cont.



Figure 14. SEM of cross-section and EDX analysis of points 1–7 of nickel aluminide coating (COATR 7) after cyclic polarization in 3.5 wt.% NaCl at 25 °C. (**a**) low magnification for a general view, (**b**) magnification of the "square area" of (**a**), (**c**) magnification of the "square" area of (**b**), (**d**) area below the crevice of (**c**), (1–7)—EDX spectra of respective points in (**c**,**d**).

Figure 14a shows an overview of the cross-section of COATR 3. The pits propagated through the dark phase in the coating, as shown in Figure 14b. It is observed that lighter phases are protected during polarization. EDX analysis (Figure 14c, points 1–3) suggests that the dark areas correspond to the NiAl₃ intermetallic compound, while the white areas (Figure 14c, point 4) correspond to Ni. It is seen that the electrolyte did not reach the interface with the substrate. It was reported that at high temperatures, corrosion of NiAl may occur by diffusion of Al and formation of a surface Al_2O_3 -based film. When the proportion of Al is reduced below the minimum level necessary for the formation of Al_2O_3 , corrosion penetrates the substrate, resulting in formation of brittle phases [61,62].

Thus, it appears that Ni was protected in the presence of the NiAl₃ phase, which was oxidized first; the formed film was probably not stable enough to stop the penetration of the electrolyte into the coating. Close to the pit, the phases of Ni₂Al₃ (Figure 14d, point 5), NiAl (Figure 14d, point 6) and Ni₃Al (Figure 14d, point 7) are observed. The oxidation trend most likely follows the order: NiAl₃ > Ni₂Al₃ > NiAl > Ni₃Al, in analogy to their Al content. Moon et al. [63] stated that the NiAl coatings exhibited lower corrosion rates than the Ni₂Al₃ coatings in a carbonate fuel solution (molten carbonate fuel cell, MCFC). It is also established that in aerated solutions containing halogen ions, among which Cl⁻ is the most common, aluminum is highly susceptible to pitting corrosion [39,40].

A likely localized corrosion mechanism involves selective dissolution of the Al and NiAl₃ phase. Pits started from the phase of Al and propagated sequentially through NiAl₃ (phase rich in Al) and then through Ni₂Al₃. This sequence occurred in areas highly susceptible to localized corrosion, such as pores, splats boundaries and unmelted particles. The phases of Ni and Ni₃Al adjacent to NiAl₃ remained protected.

4. Conclusions

- The corrosion behavior of the nickel aluminide coatings is complicated because of the complex microstructure, characterized by the coexistence of various intermetallic phases (Ni-aluminides of various stoichiometries) with unreacted Ni and Al, along with thermal spraying defects (pores, splats, unmelted particles, oxide inclusions, etc.). As a consequence, no clear trends could be extracted from the electrochemical behavior of the coatings as a function of the fabrication (composition of the initial feedstock, spraying distance, substrate temperature, postdeposition heat treatment) parameters.
- 2. Most of the coatings have exhibited limited susceptibility to localized corrosion. In all cases, the steel substrate remained intact despite corrosion.
- 3. The main effects of the fabricating parameters on the corrosion behavior of the coatings are as follows. Effect of initial powder mixture composition: the coating with the lowest Ni content in the initial powder feedstock (42.1 wt.% Ni) exhibited the lowest resistance to general corrosion but the highest resistance to localized corrosion. Effect

of spraying distance: the coating sprayed at the shortest distance presented the highest resistance to localized corrosion. Effect of substrate temperature: hotter substrates have led to lower resistances to general corrosion. Effect of postdeposition heat treatment: heat treatment led to an increased susceptibility to localized corrosion.

- 4. Interconnected porosity seems to be the main parameter accelerating uniform corrosion. An increase in porosity from 1.3 vol.% to 5.0 vol.% resulted in a tripling of the corrosion current density.
- 5. Nickel aluminides appeared oxidized after polarization.
- 6. Chronoamperometry experiments at pseudopassive potentials confirmed findings 3 and 4 of the potentiodynamic polarization experiments.
- 7. Localized corrosion had the form of pitting and/or crevice corrosion in the coating and propagated dissolving Al and Al-rich nickel aluminides along coating defects.
- The low susceptibility to localized corrosion and the intactness of the substrate suggest that the CAFSY method is prospective for the production of corrosion-resistant nickel aluminide coatings.

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References

- Frommeyer, G.; Rablbauer, R. High Temperature Materials Based on the Intermetallic Compound NiAl Reinforced by Refractory Metals for Advanced Energy Conversion Technologies. *Steel Res. Int.* 2008, 79, 507–512. [CrossRef]
- Dey, G.K.; Tewari, R.; Roa, P.; Wadekar, S.L.; Mukhopadhyay, P. Precipitation hardening in nickel copper alloy monel K500. *Metall. Trans. A* 1993, 24, 2709–2719. [CrossRef]
- 3. Davis, J.R. *Nickel Cobalt and Their Alloys, ASM Specialty Handbook;* ASM International: Materials Park, OH, USA, 2000.
- 4. Sidhu, T.S.; Prakash, S.; Agrawal, R.D. Hot corrosion and performance of nickel-based coatings. Curr. Sci. 2006, 90, 41–47.
- Buta, S.S.; Prakash, S. Evaluation of the Corrosion Behavior of Plasma Sprayed Ni₃Al Coatings on Steel in Oxidation and Molten Salt Environments at 900 °C. Surf. Coat. Technol. 2003, 166, 89–100.
- 6. Hussey, T.S.; Koczak, M.J.; Smith, R.W.; Kalidindi, S.R. Synthesis of nickel aluminides by vacuum plasma spraying and exothermic in-situ reactions. *Mater. Sci. Eng. A* **1997**, 229, 137–146. [CrossRef]
- Vershinnikov, V.I.; Borovinskaya, I.P. Self-propagating high-temperature synthesis of titanium and nickel aluminides with additives. *Powder Metall. Met. Ceram.* 2009, 48, 533–539. [CrossRef]
- 8. Yamaguchi, M.; Inui, H.; Ito, K. High-temperature structural intermetallintermetallics. Acta Mater. 2000, 48, 307–322. [CrossRef]
- 9. Sauthoff, G. Multiphase intermetallic alloys for structural applications. Intermetallics 2000, 8, 1101–1109. [CrossRef]
- 10. Scheppe, F.; Sahm, P.R.; Hermann, W.; Paul, U.; Preuhs, J. Nickel aluminides: A step toward industrial application. *Mater. Sci. Eng. A* 2002, 329–331, 596–601. [CrossRef]
- 11. Makino, A. Fundamental aspects of the heterogeneous flame in the self-propagating high-temperature synthesis (SHS) process. *Prog. Energy Combust. Sci.* **2001**, *27*, 1–74. [CrossRef]
- 12. Pawlowski, L. The Science and Engineering of Thermal Spray Coatings; John Wiley and Sons: Hoboken, NJ, USA, 1995.
- 13. Xanthopoulou, G. Catalytic Properties of the SHS products. Rev. Adv. Sci. Technol. 2010, 63, 287–296.
- Kozerski, S. The Oxide Reduction in the Plasma Sprayed Ni-A1 Layers, Advances in Thermal Spraying. In Proceedings of the Eleventh International Thermal Spray Conference, Montreal, QC, Canada, 8–12 December 1986; Pergamon Press: Oxford, UK, 1986; pp. 845–852.
- 15. Zhang, Q.; Li, C.J.; Wang, X.R.; Ren, Z.L.; Li, C.X.; Yang, G.J. Formation of NiAl Intermetallic Compound by Cold Spraying of Ball-Milled Ni/Al Alloy Powder Through Postannealing Treatment. *J. Therm. Spray Technol.* **2008**, *17*, 715–720. [CrossRef]
- Deevi, S.C.; Sikka, V.K.; Swindeman, C.J.; Seals, R.D. Reactive Spraying of NickeI-Aluminide Coatings. J. Therm. Spray Technol. 1997, 6, 335–344. [CrossRef]

- 17. Zhu, H.; Abbaschian, R. Reactive processing of nickel-aluminide intermetallic compounds. J. Mater. Sci. 2003, 38, 3861–3870. [CrossRef]
- Vardelle, A.; Moreau, C.; Themelis, N.J.; Chazelas, C. A Perspective on Plasma Spray Technology. *Plasma Chem. Plasma Process.* 2015, 35, 491–509. [CrossRef]
- 19. Xanthopoulou, G.; Marinou, A.; Vekinis, G.; Lekatou, A.; Vardavoulias, M. Ni-Al and NiO-Al Composite Coatings by Combustion-Assisted Flame Spraying. *Coatings* **2014**, *4*, 231–252. [CrossRef]
- 20. Marinou, A. Synthesis of High Temperature Coatings Produced by the Novel CAFSY Method. Ph.D. Thesis, University of Ioannina, Ioannina, Greece, 2016.
- Kumar, K.G.; Sivarao, T.J.; Sahaya Anand, A. Novel Intermetallic Nickel Aluminide (Ni₃Al) as an Alternative Automotive Body Material. Int. J. Eng. Technol. 2011, 11, 17327197.
- 22. Sampath, S.; Bancke, G.A.; Herman, H.; Rangaswamy, S. Plasma Sprayed Ni–Al Coatings. J. Surf. Eng. 1989, 5, 293–298. [CrossRef]
- Oerlikon Metco. Material Data Sheet. Available online: https://www.oerlikon.com/ecoma/files/DSM-0271.2_Ni-Al.pdf (accessed on 10 October 2022).
- 24. Naiborodenko, Y.S.; Itin, V.I.; Savitskii, K.V. Exothermic effects during sintering of a mixture of nickel and aluminium powders. *Sov. Phys. J.* **1968**, *11*, 89–93. [CrossRef]
- Ozdemir, O.; Zeytin, S.; Bindal, C. A study on NiAl produced by pressure-assisted combustion synthesis. *Vacuum* 2010, *84*, 430–437. [CrossRef]
- 26. Curfs, C.; Turrillas, X.; Vaughan, G.B.M.; Terry, A.E.; Kvick, A.; Rodríguez, M.A. Al-Ni intermetallintermetallics obtained by SHS: A time-resolved X-ray diffraction study. *Intermetallics* **2007**, *15*, 1163–1171. [CrossRef]
- 27. Cui, H.Z.; Wei, N.; Zeng, L.L.; Wang, X.B.; Tang, H.J. Microstructure and formation mechanism of Ni-Al intermetallic compounds fabricated by reaction synthesis. *Trans. Nonferrous Met. Soc. China* **2013**, *23*, 1639–1645. [CrossRef]
- Marinou, A.; Xanthopoulou, G.; Vekinis, G.; Lekatou, A.; Vardavoulias, M. Synthesis and Heat Treatment of Sprayed High Temperature NiAl–Ni₃Al Coatings by In-Flight Combustion Synthesis (CAFSY). *Int. J. Self Propagating High Temp. Synth.* 2015, 24, 192–201. [CrossRef]
- 29. Hunter, M.S.; Fowle, P. Naturally and thermally formed oxide films on aluminum. *J. Electrochem. Soc.* **1956**, *103*, 482–485. [CrossRef]
- 30. Bockris, J.O.M.; Kang, Y. The protectivity of aluminum and its alloys with transition metals. *J. Solid State Electrochem.* **1997**, *1*, 17–35. [CrossRef]
- 31. Sikora, E. Nature of the passive film on nickel. *Electrochim. Acta* 2002, 48, 69–77. [CrossRef]
- 32. Melendres, C.A.; Pankuch, M. On the composition of the passive film on nickel: A surface-enhanced Raman spectroelectrochemical study. *J. Electroanal. Chem.* **1992**, 333, 103–113. [CrossRef]
- 33. Nishimura, R. Pitting Corrosion of Nickel in Borate and Phosphate Solutions. Corrosion 1987, 43, 486–492. [CrossRef]
- 34. Zamanzade, M.; Barnoush, A. Effect of chromium on the electrochemical properties of iron aluminide intermetallic intermetallics. *Corros. Sci.* **2014**, *78*, 223–232. [CrossRef]
- 35. Rosalbino, F.; Carlini, R.; Parodi, R.; Zanicchi, G.; Scavino, G. Investigation of passivity and its breakdown on Fe₃Al–Si and Fe₃Al–Ge intermetallintermetallics in chloride-containing solution. *Corros. Sci.* **2014**, *85*, 394–400. [CrossRef]
- Schaepers, D.; Strehblow, H.-H. An XPS and ISS Investigation of passive layers on Fe-Al alloys. *Corros. Sci.* 1997, 39, 2193–2213. [CrossRef]
- 37. Frangini, S.; de Cristofaro, N.B.; Mignone, A.; Lascovich, J.; Giorgi, R. A combined electrochemical and XPS study on the passivity of B2 iron aluminides in sulphuric acid solution. *Corros. Sci.* **1997**, *39*, 1431–1442. [CrossRef]
- 38. Shankar Rao, V. A review of the electrochemical corrosion behaviour of iron aluminides. *Electrochim. Acta* 2004, 49, 4533–4542.
- Lekatou, A.; Sfikas, A.K.; Karantzalis, A.E.; Sioulas, D. Microstructure and corrosion performance of Al-32%Co alloys. *Corros. Sci.* 2012, 63, 193–209. [CrossRef]
- 40. Lekatou, A.; Sfikas, A.K.; Petsa, C.; Karantzalis, A.E. Al-Co alloys prepared by vacuum arc melting: Correlating microstructure evolution and aqueous corrosion behavior with co content. *Metals* **2016**, *6*, 46. [CrossRef]
- 41. Palm, M.; Krieg, R. Neutral salt spray tests on Fe–Al and Fe–Al–X. Corros. Sci. 2012, 64, 74–81. [CrossRef]
- 42. Lekatou, A.; Marinou, A.; Patsalas, P.; Karakassides, M.A. Aqueous corrosion behaviour of Fe-Ni-B metal glasses. *J. Alloy Compd.* **2009**, *483*, 514–518. [CrossRef]
- Beni, A.; Ott, N.; Binczyk, E.U.; Rasinski, M.; Bauer, B.; Gille, P.; Ulrich, A.; Schmutz, P. Passivation and localised corrosion susceptibility of new Al–Cr–Fe complex metallic alloys in acidic NaCl electrolytes. *Electrochim. Acta* 2011, *56*, 10524–10532. [CrossRef]
- 44. Veys, D.; Rapin, C.; Li, X.; Aranda, L.; Fournee, V.; Dubois, J.M. Electrochemical behavior of approximant phases in the Al-(Cu)-Fe-Cr system. *J. Non-Cryst. Solids* **2004**, *347*, 1–10. [CrossRef]
- 45. Davis, G.D.; Shaw, B.A.; Rees, B.J.; Pecile, C.A. Electrochemical behavior and surface chemistry of nonequilibrium aluminumtantalum alloys: Solute-rich interphase model. *Surf. Interf. Anal.* **1995**, 23, 609–617. [CrossRef]
- Lekatou, A.G.; Sfikas, A.K.; Karantzalis, A.E. The influence of the fabrication route on the microstructure and surface degradation properties of Al reinforced by Al₉CO₂. *Materials* 2017, 200, 33–49.
- 47. Ahn, S.; Kwon, H.S.; Macclorand, D.D. Surface Oxide Films. In *ECS PV2003-25*; Birss, V., Burke, L., Hillman, A.R., Lillard, R.S., Eds.; ECS Publishing Group: Paris, France, 2003.

- Stern, A.L. Geary, Electrochemical Polarization I. A Theoretical Analysis of the Shape of Polarization Curves. J. Electrochem. Soc. 1957, 104, 56–61. [CrossRef]
- Lekatou, A.; Zois, D.; Karantzalis, A.E.; Grimanelis, D. Electrochemical behaviour of cermet coatings with a bond coat on Al7075: Pseudopassivity, localized corrosion and galvanic effect considerations in a saline environment. *Corros. Sci.* 2010, 52, 2616–2635. [CrossRef]
- 50. Lekatou, A.; Sioulas, D.; Karantzalis, A.E.; Grimanelis, D. A comparative study on the microstructure and surface property evaluation of coatings produced from nanostructured and conventional WC–Co powders HVOF-sprayed on Al7075. *Surf. Coat. Technol.* **2015**, *276*, 539–556. [CrossRef]
- Silverman, D.C. Practical corrosion prediction using electrochemical techniques. In Uhlig's Corrosion Handbook, 3rd ed.; Winston Revie, R., Ed.; Wiley & Sons: Hoboken, NJ, USA, 2011; pp. 1129–1166.
- 52. Xanthopoulou, G.; Marinou, A.; Karanasios, K.; Vekinis, G. Combustion Synthesis during Flame Spraying ("CAFSY") for the Production of Catalysts on Substrates. *Coatings* **2017**, *7*, 14. [CrossRef]
- 53. Rog, G.; Borchardt, G.; Wellen, M.; Lose, W.J. Determination of the activities in the (Ni + Al) alloys in the temperature range 870 K to 920 K by a solid-state galvanic cell using a CaF₂ electrolyte. *Chem. Thermodyn.* **2003**, *35*, 261–268. [CrossRef]
- Rog, G.; Kozłowska-Rog, A.; Borchardt, G.; Dorrer, L.; Loser, W. Determination of the standard Gibbs free energy of the intermetallic compound Ni₃Al in the temperature range (820 to 920) K by a solid-state galvanic cell method. *J. Chem. Thermodyn.* 2005, *37*, 97–100. [CrossRef]
- 55. Grote, K.-H.; Antonsson, E.K. (Eds.) Springer Handbook of Mechanical Engineering; Springer: New York, NY, USA, 2009.
- 56. Available online: http://www.tms.org/pubs/journals/JOM/9712/Kattner-9712.html (accessed on 30 September 2022).
- 57. Itin, V.Y.; Naiborodenko, U.S. *High Temperature Synthesis Intermetallic Compounds*; Tomsk University: Tomsk, Russia, 1989; pp. 1–212.
- 58. Dean, J.A. Lange's Handbook of Chemistry, 12th ed.; McGraw-Hill: New York, NY, USA, 1979.
- Gogebakan, M.; Uzun, O.; Karaaslan, T.; Keskin, M. Rapidly solidified Al-6.5 wt.% Ni alloy. J. Mater. Process. 2003, 142, 87–92. [CrossRef]
- 60. Afonso, C.R.M.; Spinelli, J.E.; Bolfarini, C.; Botta, W.J.; Kiminami, C.S.; Garcia, A. Rapid Solidification of an Al-5Ni Alloy Processed by Spray Forming. *Materials* **2012**, *15*, 779–785. [CrossRef]
- 61. Leyens, C.; Pint, B.A.; Wright, I.G. Effect of Composition on the Oxidation and Hot Corrosion Resistance of Ni-Al Doped with Precious Metals. *Surf. Coat. Technol.* **2000**, *133–134*, 15–22. [CrossRef]
- 62. Houngninou, C.; Chevalier, S.; Larpin, J.P. Synthesis and characterisation of pack cemented aluminide coatings on metals. *Appl. Surf. Sci.* **2004**, *236*, 256–269. [CrossRef]
- 63. Moon, Y.; Lee, D. Corrosion resistance of 316 L stainless steel with surface layer of Ni₂Al₃ or NiAl in molten carbonates. *J. Power Source* **2003**, *115*, 1–11. [CrossRef]