

Review

# Recent Advances in the Deposition of Aluminide Coatings on Nickel-Based Superalloys: A Synthetic Review (2019–2023)

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**Abstract:** Thermal barrier coatings (TBCs) are widely used to improve the oxidation resistance and high-temperature performance of nickel-based superalloys operating in aggressive environments. Among the TBCs, aluminide coatings (ACs) are commonly utilized to protect the structural parts of jet engines against high-temperature oxidation and corrosion. They can be deposited by different techniques, including pack cementation (PC), slurry aluminizing or chemical vapor deposition (CVD). Although the mentioned deposition techniques have been known for years, the constant developments in materials sciences and processing stimulates progress in terms of ACs. Therefore, this review paper aims to summarize recent advances in the AC field that have been reported between 2019 and 2023. The review focuses on recent advances involving improved corrosion resistance in salty environments as well as against high temperatures ranging between 1000 °C and 1200 °C under both continuous isothermal high-temperature exposure for up to 1000 h and cyclic oxidation resulting from AC application. Additionally, the beneficial effects of enhanced mechanical properties, including hardness, fatigue performance and wear, are discussed.

**Keywords:** high-temperature corrosion; aggressive environment; coating deposition; nickel alloys



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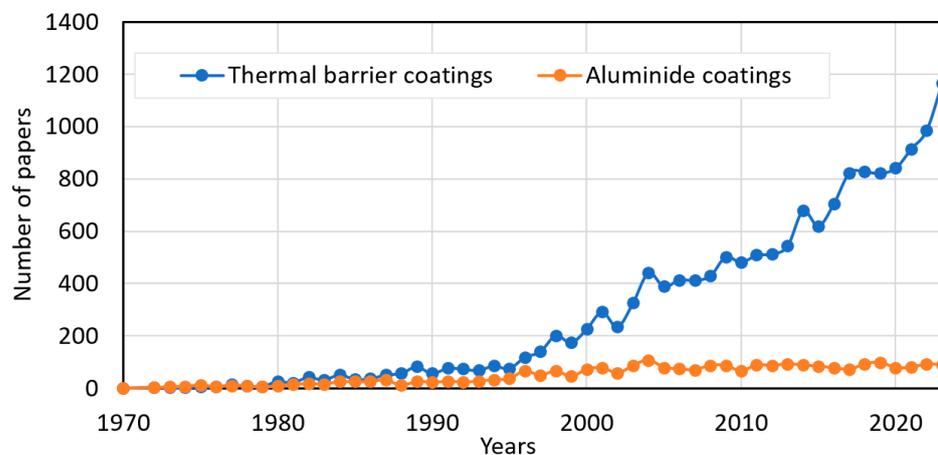
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## 1. Introduction

Nickel-based superalloys are a group of high-performance materials that are used in applications requiring excellent strength, oxidation resistance, and creep resistance at elevated temperatures [1]. These superalloys are commonly used in aircraft, aerospace, nuclear, and other industries where materials suffer from high-temperature exposure and harsh operating conditions [2]. They are classified into four groups: commercially pure nickel-based alloys (I), nickel–copper alloys (Monel) (II), non-heat treatable nickel–chromium–iron alloys (Incoloy, Hastelloy) (III) and heat treatable nickel–chromium–iron alloys (Inconel, Nimonic, Waspaloy) (IV). Although they are characterized by outstanding properties at high temperatures, the recent demands of the aerospace and aircraft industries require further increasing the operational conditions of critical elements working in the engines [3]. Thus, aluminide coatings are often deposited on nickel superalloys to improve their oxidation and wear resistance [4]. They are a cost-effective and efficient way to enhance the performance and durability of nickel superalloys in high-temperature applications [5]. Since the application of aluminide coatings has remained stable over the years, it is worth summarizing the recent advances in this field. The constant development in aircraft industries requires proper modification of aluminizing processes in order to further increase the operating parameters of coated engine parts.

One should emphasize the importance of TBCs in different industrial sectors, also represented by the increasing number of publications concerning their high-temperature and -corrosion performance (Figure 1). Among the TBCs, the interest in ACs has remained stable over the years, with less than 100 papers each year since their invention in 1970, which is directly related to their commercialization and widespread application in the aircraft and power-engineering sectors. The increasing demands of these sectors enforce the use of

critical service parameters of engines and turbine elements, which significantly reduce their service life. Therefore, ACs are usually applied on the structural parts made of nickel-based superalloys to improve their corrosion resistance and high-temperature performance.



**Figure 1.** The number of publications on thermal barrier coatings and aluminide coatings over the years based on the Scopus database.

The main aim of this review is to introduce and summarize the recent achievements related to AC deposition by using conventional techniques, including pack cementation (PC), slurry aluminizing and chemical vapor deposition (CVD). Additionally, some non-standard approaches for coating deposition are discussed. The review highlights studies in which significant corrosion resistance improvement was achieved. Additionally, the positive impact of AC application on the mechanical properties of Ni-alloys with a special emphasis on hardness, fatigue performance, and wear resistance is discussed.

## 2. Review Methodology

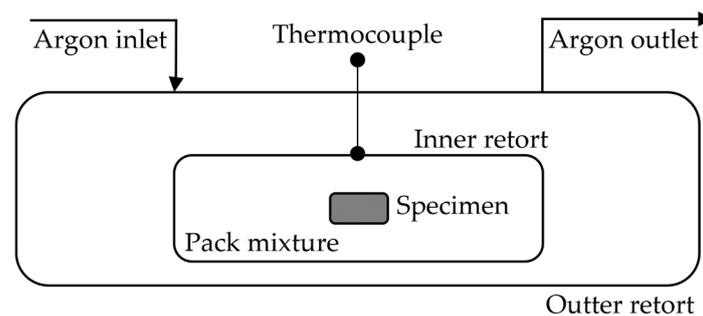
This literature review involved the detailed investigation of aluminide coatings applied on nickel-based superalloys with an emphasis on their deposition methods and high-temperature performance. The review was conducted based on the Web of Science, Scopus, PubMed, ERIC, IEEE Xplore and ScienceDirect databases and scientific papers published between 2019 and 2023, among which “aluminide coatings” and “nickel alloys” were the main phrases used for paper scanning. The period of the last 5 years was selected to highlight the recent achievements in the field of AC application for Ni-based superalloys since the continued development of deposition techniques and characterization methods in recent years has revealed new possibilities and trends that were not reported as yet. A total of 250 scientific papers and conference proceedings were identified via the electronic databases. They were evaluated in terms of their eligibility by examining the title, abstract, and summary of each paper based on specific inclusion and exclusion criteria. Following this, papers that did not meet the inclusion criteria were not discussed. In order to avoid potential similarities, the review papers were not considered or analyzed. Finally, 72 papers were deemed relevant and included in the review. They were divided by specific topics into sections devoted to each deposition technique.

## 3. Deposition of Aluminide Coatings

### 3.1. Pack Cementation (PC) and above the Pack/Vapor-Phase Aluminizing

Pack cementation is a process in which metal parts or components are placed in a container filled with a mixture of powdered metal and a chemical activator, typically argon or nitrogen [6]. The container is then sealed and heated to a high temperature, allowing the powdered metal to diffuse onto the surface of the parts, and consequently forming a hard, wear-resistant coating (Figure 2). This process is commonly used in industries such as automotive, aerospace, and tool manufacturing to improve the surface properties of metal

parts, such as the hardness, wear resistance, and corrosion resistance. Pack cementation can be used to apply a variety of coatings, such as nitriding, carburizing, and boronizing, depending on the specific requirements of the application. On the other hand, above the pack/vapor-phase aluminizing is a surface treatment process used to enhance the wear resistance, corrosion resistance, and high-temperature performance of metal components. In this process, the metal component is placed in a container with aluminum powder and then heated to a temperature above its melting point. The aluminum vaporizes and diffuses onto the surface of the metal, forming a thin layer of aluminum-rich alloy. This process is commonly used in aerospace, automotive, and other industries where components are subjected to high temperatures and harsh environments.



**Figure 2.** Schematics of PC technology.

Although PC is commonly used as a conventional process in different industries, there are many new reports that provide new insights into such methodology. Cojocaru et al. [6] used pack cementation to deposit an NiAl coating on Inconel 718. The formed NiAl layer was well adhered to the substrate material and was characterized by improved hardness of 40HRC due to the precipitation of the  $\delta$ -Ni<sub>3</sub>Nb-hardening phase inside the grains of the solid solution  $\gamma$ . Gloria et al. [7] presented optimized halide-activated pack cementation technology for the Mar-M246 alloy, the effectiveness of which was assessed through high-temperature oxidation tests in air up to 1000 °C. The coated nickel-based superalloy exhibited superior oxidation resistance as compared to its wrought state. Recently, Morgiel et al. [8] proposed a novel pack cementation approach during which the NiAl coating system was modified with rare earth elements. The studies confirmed the successful formation of a very thin (<10 nm) amorphous layer of Yb<sub>2</sub>O<sub>3</sub> that may decrease the cavitation erosion and oxidation. On the other hand, Zahedi et al. [9] modified the NiAl coating by the addition of cerium oxide. The obtained coating deposited on Rene 80 was characterized by the dense Al-rich NiAl surface layer with uniformly distributed cerium. Zhang and Zhou [10] proposed an Si-modified coating consisting of an Al-rich Ni<sub>0.9</sub>Al<sub>1.1</sub> layer with the dispersion of minor Ni<sub>2</sub>Al<sub>3</sub> and Cr-rich phases of Al<sub>13</sub>Cr<sub>2</sub> and Cr<sub>5</sub>Si<sub>3</sub> [10]. It exhibited a lower oxidation rate and improved alumina scale adhesion in air at 1100 °C as compared to conventionally aluminized specimens. Furthermore, it was also characterized by an extended service life. It was stressed that while specimens after simple aluminide lost their scale, the Si-modified aluminide coatings retained their protective capabilities even after 300 h. Such behavior was also reported for Inconel 738LC protected with a Ce-Si-modified NiAl coating obtained by using PC [11]. It was found that the simultaneous addition of 1% cerium and 6% silicon led to the formation of Ce<sub>1</sub>Si<sub>6</sub>, which limits the oxygen diffusion, promotes the growth of the continuous Al<sub>2</sub>O<sub>3</sub> layer, and further enhances the hot-oxidation resistance of the coating. A similar improvement in the hot-temperature corrosion resistance was reported for aluminized Incoloy 825 [12], Inconel 625 [13], and Inconel 600 [14]. One should mention that PC could also significantly improve the mechanical behavior of the protected substrate. It was reported that  $\delta$ -Ni<sub>2</sub>Al<sub>3</sub> and  $\beta$ -NiAl coatings deposited on pure nickel significantly increase the tribological properties up to 600 °C [15].

Furthermore,  $\beta$ -NiAl coatings were effective in enhancing the high-temperature oxidation resistance up to 1100 °C of Rene 108DS [16] and CMSX-4 [17]. It has been reported that the NiAl coatings doped with zirconia [18–20] and hafnium [21] also reduce the oxidation rate of nickel-based superalloys since the addition of these elements leads to the formation of stable oxides, inhibiting aluminum depletion. Other significant studies report that a functional NiCoCrAlY coating improves the hot-corrosion resistance of Inconel 738L exposed to air for 100 h at 700 °C [22]. It is worth mentioning that aluminide coatings also improve the high-temperature corrosion resistance of Inconel 718 in a salty environment [23]. This interesting fact is related to the microstructure of the coating itself. Khan et al. [24] reported that an ultrafine-grained Ni<sub>2</sub>Al<sub>3</sub> coating significantly enhances the oxidation resistance in air at 900 °C as compared to the same coating in a coarse-grained state [24]. A summary of the pack cementation research concerning the coating, deposition method and main advantages is presented in Table 1.

**Table 1.** A summary of the pack cementation-related research [6–24].

Substrate	Coating/Technology	Main Features	Ref.
Inconel 178	NiAl/PC	Perfectly adherent; precipitation of the $\delta$ -Ni <sub>3</sub> Nb-hardening phase inside the grains of solid solution $\gamma$ increases the matrix hardness to 40 HRC	[6]
MAR-M46	NiAl/halide-activated PC	Superior behavior in oxidation at high temperatures up to 1000 °C.	[7]
Haynes 263	NiAl + Yb <sub>2</sub> O <sub>3</sub> /PC	Formation of a very thin (<10 nm) amorphous layer of Yb <sub>2</sub> O <sub>3</sub> that may decrease the cavitation erosion and oxidation	[8]
Rene 80	NiAl + CeO <sub>2</sub> /PC	Formation of a dense Al-rich NiAl surface layer with cerium distributed in the coating suitable for high-temperature applications	[9]
K438	Ni <sub>0.9</sub> Al <sub>1.1</sub> + Ni <sub>2</sub> Al <sub>3</sub> /Al <sub>13</sub> Cr <sub>2</sub> /Cr <sub>5</sub> Si <sub>3</sub> /Hybrid Slurry/PC	A lower oxidation rate and improved alumina scale adhesion in air at 1100 °C; a longer service life compared to the conventionally aluminized coatings; retained its protective nature after 300 h	[10]
Inconel 738LC	Ce-Si-Modified NiAl/PC	Cerium addition up to 1% increases oxidation resistance during the cyclic oxidation test at 1100 °C	[11]
Incoloy 825	NiAl/PC	Improved oxidation resistance	[12]
Inconel 625	NiAl/PC	Homogeneous and continuous coating of 60 $\mu$ m thickness characterized by improved oxidation resistance and hardness	[13]
Inconel 600	NiAl/PC	The aluminide coating obtained from 20 wt% Al had the best hot-corrosion resistance, which was attributed to the formation of Al <sub>2</sub> O <sub>3</sub> surface scale	[14]
Nickel	$\delta$ -Ni <sub>2</sub> Al <sub>3</sub> and $\beta$ -NiAl/PC	Significantly improved the tribological properties up to 600 °C	[15]
Rene 108DS	Al-rich $\beta$ -NiAl/HTLA PC	Improved hot-corrosion resistance at 1050 °C, negligible mass variations after 200 h of high-temperature exposure to aggressive NaCl and Na <sub>2</sub> SO <sub>4</sub> salts	[16]
CMSX-4	$\beta$ NiAl/PC	Improved oxidation resistance at 1150 °C for 100 h due to $\beta \rightarrow \gamma'$ transformation	[17]

Table 1. Cont.

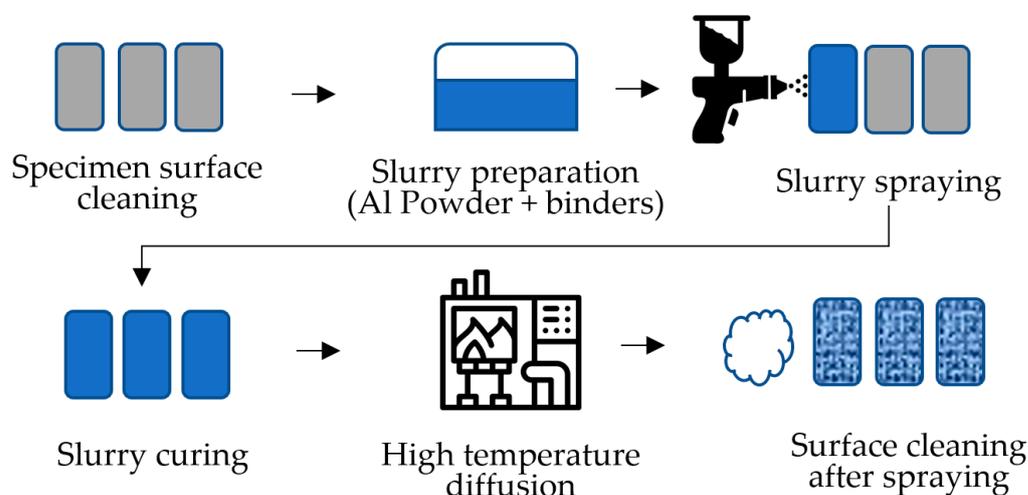
Substrate	Coating/Technology	Main Features	Ref.
Rene 80	NiAl + Zr/HAPC	Formation of high-density Zr-rich phases ( $\text{AlNi}_2\text{Zr}$ and $\text{Al}_{2-x}\text{Ni}_x\text{Zr}$ ) and Al-rich nickel aluminides ( $\beta\text{Al}$ and $\text{Ni}_2\text{Al}_3$ ) restricts the out-diffusion of Ni and triggers the changing of the stoichiometry of the surface NiAl in favor of Al	[18]
Inconel 738L	NiAl + Zr/HAPC	Excellent scale adhesion, a slow oxidation rate and lower amounts of Ti and Cr in its oxide layer, leading to a pure aluminide oxide layer at 1000 °C in air	[19]
Nimonic 75	CrAl + Zr/PC	High oxidation resistance due to the formation of the stable $\alpha\text{-Al}_2\text{O}_3$ phase, improved the adherence of the oxide scales and reduced void formation at the coating/metal interface and inhibited the outward diffusion of Al, resulting in a lower oxidation rate	[20]
Nickel	NiAl + Hf/PC	Formed $\text{HfO}_2$ acts as a diffusion barrier to prevent inter-diffusion during cyclic oxidation; the surface rumpling extent is much relieved due to a slower Al depletion rate and higher creep resistance by Hf addition	[21]
Inconel 738L	NiCoCrAlY/PC	Improved hot-corrosion resistance at 700 °C	[22]
Inconel 718	NiAl/PC	Aluminized surface reduced the hot corrosion by 50% at 700 °C in an NaCl environment	[23]
Nickel	$\text{Ni}_2\text{Al}_3$ /PC	Ultrafine-grained $\text{Ni}_2\text{Al}_3$ coating significantly enhances the oxidation resistance in air at 900 °C	[24]

### 3.2. Slurry Aluminizing

The slurry-aluminizing process is the technology in which the substrate is protected with a slurry containing aluminum particles. The slurry typically consists of aluminum powder mixed with a binder, such as a polymer or a solvent. The substrate is first cleaned and prepared to ensure good adhesion of the aluminized coating. It is then applied to the surface of the substrate using techniques such as dipping, spraying, or brushing. After the slurry is applied, the coated substrate is dried and then heated in a furnace to sinter the aluminum particles. This process bonds the aluminum particles to the substrate, forming a uniform and durable aluminized coating (Figure 3).

The slurry method offers several advantages as compared to other methods [25]. This involves a shorter thermal cycle during the coating preparation and the possibility of precise protection of large parts. Due to these benefits, the slurry method is widely used in obtaining diffusion aluminide coatings for engine jet parts. Li et al. [25] confirmed that smooth coating with a surface roughness  $R_a < 4.5 \mu\text{m}$  could be obtained on a nickel-based substrate by using slurry aluminizing. Besides the precise and uniform nature of these coatings, they are characterized by excellent high-temperature corrosion resistance either in molten NaCl–KCl at 700 °C [26], air [27,28] and in the absence of salt [29]. Slurry-aluminized coatings are also effective under extreme service conditions. Bortoluci Ormastroni et al. [30] reported that the CMSX-4 Plus alloy with an NiAl coating exhibited improved fatigue life as compared to the AM1, CMSX-4 and Rene N5 alloys for the same applied alternating stress (180 MPa) at a high temperature (1000 °C) and under fully reversed conditions ( $R_\epsilon = -1$ ). Recently, some effective ultrafast slurry-aluminizing techniques were reported for pure nickel [31,32]. It was proved that during a very short coating process of 5 min, a defect-free coating with a microstructure and features similar to the ones obtained using conventional

gas-aluminizing processes (CVD-like) could be formed. Other interesting approaches involve the successful addition of different alloying elements. Pillai et al. [33] added the iron to NiAl coating to reduce its manufacturing cost and maintain its resistance to cyclic oxidation in air +10% H<sub>2</sub>O at 900 °C for 1000 h. Galetz et al. [34] have used a modified NiGeAl-aluminized coating to increase the high-temperature performance of the 602 CA alloy at 1200 °C. Hatami et al. [35] successfully applied a silico-aluminide layer containing a  $\beta$ -(Ni, Co)Al phase on Hastelloy-X/NiCoCrAlY by the slurry technique after heat treatment in argon. It was found that the NiCoCrAlY(HVOF)/silico-aluminide (slurry) coating was more resistant to high-temperature oxidation at 1000 °C than the NiCoCrAlY coating. Such interesting findings confirm that even an already coated nickel-based superalloy could be additionally protected by an aluminized layer, which enhances its corrosion resistance. Mahmoudi et al. [36] developed a new plasma paste-aluminizing process to deposit an Ni/Cr/Ti-Al coating on Inconel 738. The main finding of this study was that the growth activation energy equal to 83 kJ/mol was lower than the values provided in the literature for the conventional aluminizing techniques.



**Figure 3.** Schematics of slurry-aluminizing technology.

A summary of the slurry-aluminizing research concerning the coating, deposition method and main advantages is presented in Table 2. It could be observed that most studies aimed to increase the operating temperature [28,30–33] and improve the high-temperature corrosion resistance in either air [28,30], molten salts [26,29] or water vapor [33].

**Table 2.** A summary of the slurry-aluminizing-related research [25–34].

Substrate	Coating	Main Features	Ref.
DZ22B	NiAl	Smooth coating with a surface roughness $R_a < 4.5 \mu\text{m}$	[25]
Inconel 600/pure nickel	NiAl	Corrosion resistance in molten NaCl–KCl at 700 °C for 100 h under argon	[26]
Ni20Cr/CM-247 LC	NiAl + Cr	New slurry coating design offers new opportunities to coat gas turbine components with complex geometry	[27]
Pure nickel	NiAl + Cr	$\beta$ -NiAl coating with undissolved Cr particles for high-temperature applications	[28]
Pure nickel	NiAl	Considerably increased the oxidation–sulfidation resistance of nickel in a salty environment	[29]

Table 2. Cont.

Substrate	Coating	Main Features	Ref.
CMSX4Plus, AM1, CMSX-4, Rene N5	NiAl	CMSX-4 Plus exhibited an improved fatigue response compared to AM1, CMSX-4 and Rene N5 for the same applied alternating stress (180 MPa) at a high temperature (1000 °C) and under fully reversed conditions ( $R\epsilon = -1$ )	[30]
Pure nickel	$Ni_2Al_3 + NiAl$	Ultrafast (35 min) slurry-aluminized pure nickel was characterized by improved oxidation resistance between 900 °C and 1100 °C in air for 100 h	[31]
Pure nickel	$\beta$ -NiAl	Ultrafast (5 min annealing) aluminizing to reduce the coating time	[32]
DA-1	Al-rich $\beta$ -(NiFe)Al	A significant fraction of the phase was retained in the coating after cyclic oxidation behavior in air +10% $H_2O$ at 900 °C for 1000 h	[33]
602 CA	NiAl + Ge	Maintains its integrity and protective behavior at 1200 °C	[34]
Hastelloy-X + NiCoCrAlY	SiAl	NiCoCrAlY (HVOF)/silico-aluminide (slurry) coating is more resistant to high-temperature oxidation at 1000 °C than NiCoCrAlY coating	[35]
Inconel 738	Ni/Cr/Ti-Al	The growth activation energy of about 83 kJ/mol was less than the values provided in the literature for the conventional aluminizing techniques	[36]

### 3.3. Gas-Phase Deposition

Chemical vapor deposition (CVD) is a process in which a thin film of material is deposited onto a substrate by chemical reactions in the vapor phase. In this process, a precursor gas is introduced into a chamber, where it reacts to form a solid film on the substrate surface (Figure 4). Since CVD is a commonly used process in the industry, the recent advances related to this deposition technique are mainly related to its successful application on different grades of nickel-based superalloys (Table 3) [1–3,5,37–55]. It was reported that NiAl coatings were effectively deposited on MAR 247 [1–3,37,39,43,49–51], Inconel 740 [5], Inconel 738 [38,45], Inconel 713 [39,41,52], CMSX 4 [42,44,46], Inconel 100 [39], K-403 [47], K444 [51], pure nickel [48] and even on additively manufactured Haynes 282 [55].

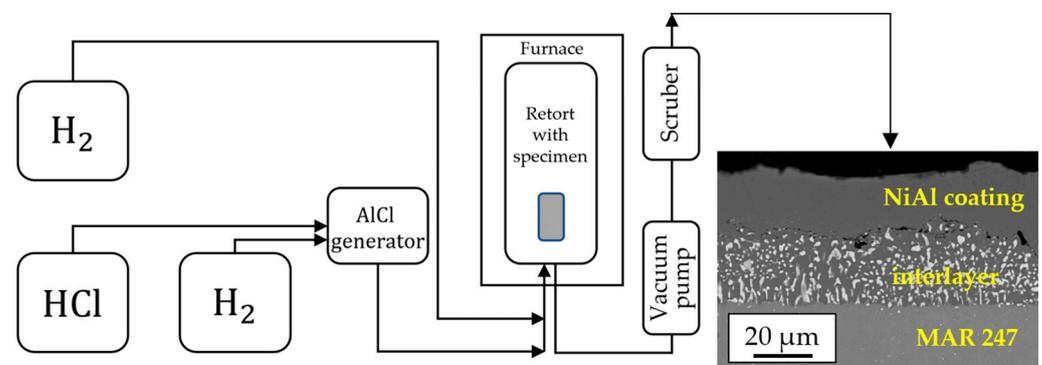


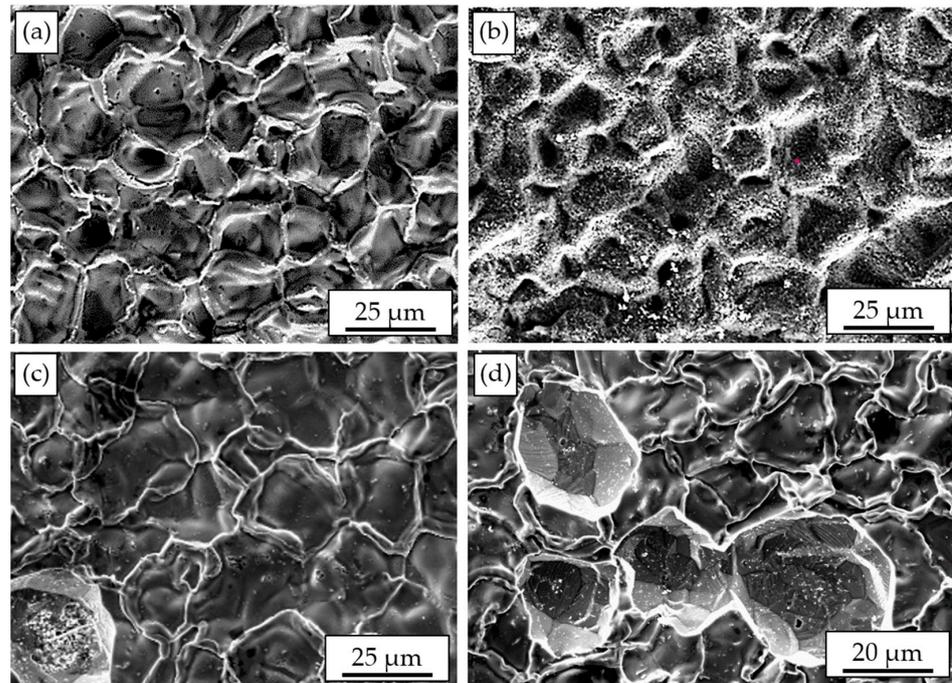
Figure 4. Schematics of CVD technology with exemplary NiAl coatings deposited on MAR 247.

**Table 3.** A summary of the CVD-related research [1–3,5,35–53].

Substrate	Coating	Main Features	Ref.
MAR 247	NiAl	Improved hardness and fatigue performance at room temperature and at 900 °C, wear and oxidation resistance	[1–3,37]
Inconel 740	NiAl	Improved fatigue performance at room temperature and oxidation resistance at 1000 °C in air	[5]
Inconel 738	NiAl	Surface modification by grift blasting improves the adherence of the coating and enhances the high-temperature corrosion resistance during shocking test with cycles of 2 h heating and 15 min cooling, with pressurized air at 1120 °C in the air	[38]
Inconel 100 Inconel 713 MAR M247	NiAl	Excellent corrosion resistance during cyclic oxidation test at 1100 °C	[39]
Inconel 713LC	NiAl	Improved low-cycle fatigue behavior at 800 °C	[40]
Inconel 740H	NiAl	Improved corrosion resistance in 0.1 M Na <sub>2</sub> SO <sub>4</sub> solution	[41]
CMSX 4	NiAl	Coatings with hardness greater than 1000 HV due to the presence of TCP precipitates	[42]
MAR M247	NiAl	Improved corrosion resistance after oxidation at 1100 °C for 1040 h	[43]
CMSX 4	NiAl + Rh	Improved corrosion resistance during cyclic oxidation tests at 1100 °C/20 h/10 cycles in air	[44]
Inconel 738 LC	NiCoCrAlY	The MCrAlY layer is microstructurally similar to the superalloy substrate and effectively reduces the mismatch between their thermal properties	[45]
CMSX 4	NiAl + Pd/Zr	Pd + Zr co-doping improved the oxidation resistance after 250 h at 1100 °C	[46]
K-403	NiAl	A novel diffusion barrier of pure Al-rich β-NiAl bond coat with promising properties for high-temperature applications for aircraft engine turbine components	[47]
Pure nickel	Ni <sub>2</sub> Al <sub>3</sub>	Nano-alumina-modified NiAl coating improves the oxidation resistance at 1000 °C	[48]
MAR 247	NiAl + Pt, Pd, Zr and Hf	Fully adhered coatings for high-temperature applications	[49,50]
K444	NiAl	Successfully deposited coating for high-temperature applications	[51]
Inconel 713	NiAl + Rh/Pt	Improved oxidation resistance at 1100 °C under the atmospheric pressure	[52]
Ni <sub>3</sub> Al-based single crystal superalloy	NiCrAlYSi	Improved oxidation resistance at 1200 °C	[53,54]
Haynes 282	NiAl	Additively manufactured Haynes 282 with successfully deposited NiAl coating	[55]

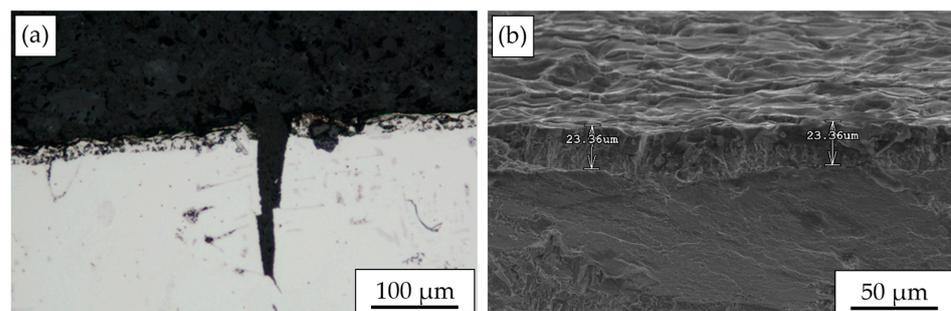
One can observe that NiAl coatings applied on different nickel-based superalloys have mainly been used to improve the corrosion resistance against high temperatures ranging between 1000 °C [5,38,39,43,44,46,48,52] and 1200 °C [53,54]. It should be stressed that such coatings exhibited excellent corrosion resistance under continuous isothermal high-temperature exposure [5,43,46,48,52], during cyclic oxidation [38,39,44] as well as in salty environments [41].

The effectiveness of the CVD technology for corrosion protection was confirmed for the MAR247 nickel-based superalloy with a CVD coating obtained at 1040 °C during deposition for 12 h in a hydrogen-protective atmosphere (Figure 5a). It was found that the surface after 24 cycles of 1 h exposure to air atmosphere at 1100 °C (Figure 5b) and after corrosion tests in a 0.3 M NaCl (Figure 5c) and 0.9 M NaCl (Figure 5d) solutions was still tight, without visible cracks and spallation products. Furthermore, NiAl coatings could also be effectively used to improve the mechanical properties of nickel-based superalloys, including the hardness [1–3,42], fatigue performance [5,40] and wear [3].



**Figure 5.** Exemplary morphology of the MAR247 nickel-based superalloy with a CVD coating (1040 °C/12 h/hydrogen-protective atmosphere): as-deposited surface (a); the surface after 24 cycles of 1 h exposure to air atmosphere at 1100 °C (b); and after corrosion tests in a 0.3 M NaCl (c) and 0.9 M NaCl (d) solutions.

One should mention that the NiAl coatings deposited on MAR 247 exhibited excellent adherence to the base material, as even after the specimen subjected to cyclic loading fractured, no cracks were detected in the area near the fracture (Figure 6a) and the coating was still well connected with the base material (Figure 6b). Recently, some new approaches were reported to increase the operating temperature of NiAl coatings above 1200 °C. These involve the addition of platinum, palladium, zirconium and hafnium [44,46,49,51].



**Figure 6.** Exemplary crack tip of an MAR247 specimen with a CVD coating (a); the cross-sectional view of a well-adhered coating after specimen fracture (b).

### 3.4. Non-Conventional Deposition Approaches

Regardless of the conventional techniques used in the deposition of NiAl coatings, many interesting attempts have been made to improve the high-temperature performance of coated nickel-based superalloys (Table 4). Genova et al. [56] designed a new modified diffusion coating for Rene 108DS through electroless deposition of a thick nickel layer, which improved the high-temperature corrosion resistance of the substrate material at 1050 °C. Mazur et al. [57] proposed in situ processing of Ni<sub>3</sub>Al through a plasma-transferred arc to increase the elastic modulus, hardness and oxidation resistance of Inconel 625 at 1300 °C. Enrique et al. [58] developed an electrospray deposition technique for Inconel 625, which reduced the surface roughness and near-surface porosity. Furthermore, the coating increased the surface hardness up to 900% and density of 99.2%. Sarraf et al. [59] presented the reactive air-aluminizing (RAA) methodology as a low-cost method with high efficiency in forming an aluminide coating on Inconel 738LC. Zhang et al. [60] reported that the 5Hf-NiAl coating deposited on a nickel-based superalloy by arc-ion plating exhibited superior hot-corrosion resistance in comparison to a conventional NiAl coating. Such behavior was related to the addition of Hf, which promoted the formation of a protective oxide scale and reduced the growth rate of the oxide scale. Golshan and Ganjali [61] deposited a NiAl coating on Inconel 738 by using injection laser cladding. The coating exposed to hot-corrosion tests at 800 °C was characterized by high resistance against corrosive salt, even after 480 h, due to the formation of a thick and protective Al<sub>2</sub>O<sub>3</sub> scale. Barjesteh et al. [62] proposed a mixed methodology consisting of Pt electroplating and low-temperature high-activity to deposit a PtAl coating on Rene 80. Although the successful methodology was presented, the improvement in the high-temperature low-cycle fatigue (HTLCF) was only about 5% as compared to the uncoated substrate material. Ullah et al. [63] studied the initial oxidation behavior of an NiCoCrAlY coating deposited on a second-generation single-crystal nickel-based superalloy by using arc-ion plating in air at 900 °C, 1000 °C and 1100 °C. The authors highlighted that the oxide scale in the initial stage was mainly composed of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> at 900 °C, while  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> emerged with an increasing oxidation temperature. Furthermore, the beneficial effect of Y addition was reflected by its segregation at the scale/coating interface, which led to less cavity formation and hence improved the oxide scale adherence. Wu et al. [64] described the corrosion mechanisms of NiAl-coated pure nickel under a KCl deposition environment (95%N<sub>2</sub> + 5%O<sub>2</sub>) alone or with 15% or 30% water vapor at 700 °C. It was reported that the coatings were susceptible to slight surface and intergranular corrosion attacks without water vapor. However, the increase in water vapor to 30% led to the effective oxidation-decomposition reaction, resulting in severe degradation of the coatings. Góral et al. [65] proposed a new concept of thermal barrier coating for MAR M247 with a Pt + Pd/Zr/Hf-modified aluminide bond coat and a ceramic layer formed by the PS-PVD method, which was found to be an attractive alternative to conventional coatings produced using the expensive electron beam physical vapor deposition (EB-PVD) method. Shademani et al. [66] reported positive effects of rejuvenation heat treatment performed before pack cementation of ZHS32. The deposited  $\beta$ -NiAl coating was characterized by improved nanohardness, microhardness and elastic modulus as compared to the non-heat-treated substrate. Khan et al. [67] proposed a two-step electrodeposition + aluminizing process to deposit a NiAl coating with Cr<sub>2</sub>O<sub>3</sub> nanoparticles on pure nickel, which effectively improved its high-temperature corrosion resistance at 900 °C. Fatemi and Nogorani [68] studied the halide-activated pack cementation process in which a NiAl coating was doped with Ce, Y, La, and Zr. The successfully coated Inconel 738LC exhibited protective behavior against hot corrosion at 900 °C in a Na<sub>2</sub>SO<sub>4</sub>-NaCl-V<sub>2</sub>O<sub>5</sub> mixture. Liu et al. [69] found that a combined electroplating and gaseous-aluminizing process during which an (Ni, Pt)Al coating is doped with Re led to the improved cyclic and isothermal oxidation behavior of a nickel-based single-crystal superalloy at 1100 °C for 500 cycles and 1000 h, respectively, as compared to an (Ni,Pt)Al undoped coating. On the other hand, Li et al. [70] proposed a pre-oxidation treatment for an (Ni, Pt)Al coating under pressure  $5 \times 10^2$  at 1050 °C for

4 h to form a uniform, dense and compact  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale. The authors found that the pre-oxidized coating exhibited improved corrosion resistance at 1000 °C under a simulated marine environment (NaCl + water vapor) compared with the one without pre-oxidation due to the formation of a stable and thick alumina oxide. Similarly to [69], Li et al. [71] also reported the beneficial effects of Re doping in terms of the improvement of the cyclic oxidation resistance of 1Re-(Ni,Pt)Al coating. Furthermore, the addition of an Ni/Ni-Re layer also reduces the oxidation rate of protected material at 1150 °C. The improved resistance to cyclic oxidation at 1150 °C was also reported for the Rene N5 alloy following the addition of Hf/Zr during electron beam physical vapor deposition [72].

**Table 4.** A summary of the CVD-related research.

Substrate	Deposition	Coating	Main Advantages	Ref.
René 108DS	Electroless plating	Ni + $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Improved corrosion resistance after 1000 h of exposure at 1050 °C	[56]
Inconel 625	Plasma-transferred arc	NiAl	Increased elastic modulus, hardness and oxidation resistance at 1300 °C	[57]
Inconel 625	Electrospark deposition	NiAl	Reduces surface roughness and near-surface porosity, hardness increases up to 900% and density of 99.2%	[58]
Inconel 738LC	Reactive air-aluminizing	$\beta$ -NiAl	Successful application of low-cost methodology with high efficiency	[59]
Nickel-based superalloy	Arc-ion plating	5Hf-NiAl	Superior hot-corrosion resistance at 900 °C	[60]
Inconel 738	Injection laser cladding	NiAl	Corrosion resistance in a salty environment at 800 °C	[61]
Rene 80	Electroplating + low-temperature high-activity aluminizing	PtAl	Improvement of the HTLCF life	[62]
Second-generation nickel-based single-crystal superalloy	Arc-ion plating	NiCoCrAlY	Y segregation at the scale/coating interface resulted in less cavity formation and hence improved the oxide scale adherence	[63]
Pure nickel	Aluminizing	NiAl	Resistant to high-temperature corrosion attack after exposure at 700 °C for 168 h	[64]
MAR M247	Pt/Pd electroplating + CVD	Pt + Pd/Zr/Hf-NiAl	Alternative to conventional coatings produced by using EB-PVD method	[65]
ZHS32	Rejuvenation heat treatment + pack cementation	$\beta$ -NiAl	Improved nanohardness, microhardness and elastic modulus	[66]
Pure nickel	Electrodeposition + aluminizing	Cr <sub>2</sub> O <sub>3</sub> + Ni <sub>2</sub> Al <sub>3</sub>	Improved high-temperature corrosion resistance at 900 °C by the addition of Cr <sub>2</sub> O <sub>3</sub> nanoparticles	[67]
Inconel 738LC	Halide-activated pack cementation	NiAl + Ce, Y, La, and Zr	Protective behavior against hot corrosion at 900 °C in Na <sub>2</sub> SO <sub>4</sub> -NaCl-V <sub>2</sub> O <sub>5</sub> mixture	[68]
Nickel-based single crystal superalloy	Electroplating + gaseous aluminizing	(Ni,Pt)Al+ Re	Improved cyclic and isothermal oxidation behavior at 1100 °C for 500 cycles and 1000 h	[69]
Ni-based single crystal superalloy	Electroplating + above-pack aluminizing	(Ni,Pt)Al	Pre-oxidized coating exhibited improved corrosion resistance at 1000 °C under simulated marine-environment (NaCl + water vapor) compared with the one without pre-oxidation, due to the formation of a stable and exclusive $\alpha$ -Al <sub>2</sub> O <sub>3</sub> layer.	[70]
single-crystal nickel-based superalloy	Aluminizing	$\beta$ -(Ni,Pt)Al + Ni/Ni-Re	Addition of an Ni/Ni-Re layer reduced the oxidation rate during cyclic exposure at 1150 °C	[71]
René N5	Electron beam physical vapor deposition	Hf/Zr + $\beta$ -NiAl	Good oxide scale adhesion during the cyclic oxidation at 1150 °C	[72]

One should highlight the variety of modified deposition techniques used to enhance the high-temperature performance of nickel-based superalloys. Such processes usually involve pre-aluminizing treatments [61,64,67,69,70] and the addition of rare elements [58,64,68,69,71,72] or oxide nanoparticles [54,67] to increase the corrosion resistance of these alloys. The constant modification and improvement of conventionally used methods are directly related to the increasing demands of different industries to increase the operating conditions of elements made of nickel-based superalloys.

#### 4. Summary and Future Perspectives

In this review, different deposition techniques dedicated to nickel-based superalloys were presented and discussed. Although all of them were used to deposit NiAl coatings to improve some functional properties of the base materials, one can expose different approaches leading to the same findings. It could be noticed that PC methods are mainly used to deposit pure NiAl or  $\beta$ -NiAl coatings [6,7,12–17,23,24]. Some reports analyze the addition of different oxides [8,9] and Zr [18–20].

A similar tendency was found for the slurry-aluminizing [25,26,29–32] and CVD technologies [1–3,5,37–43,47,51,55], for which the deposition of NiAl coatings is still the main area of interest. Interestingly, the most frequently modified nickel-based alloys are those with the highest oxidation resistance, possessing high mechanical strength. These involve Rene 80 [8,18,63], Inconel 625 [13,57,58], Inconel 713 [39,40,52], Inconel 718 [41], Inconel 738L [11,19,22,36,45,59,61,65,68] and CMSX-4 [17,30,42,44,46]. One should highlight that the research involving conventional nickel-based superalloys is mainly dedicated to future high-temperature applications. Therefore, the suitability of deposited NiAl coatings is assessed not only in terms of the oxidation resistance but also regarding their mechanical performance. One should stress that such an approach is extremely important since the coating durability should be investigated together with the substrate material. The coating itself could possess superior oxidation resistance; however, if it is not well adhered to the base material, its industrial application is not possible.

Although there is no direct relation between the deposition technique and the corrosion resistance, the following trends have been observed. One should emphasize that NiAl coatings possess high oxidation resistance at high temperatures and in salty environments. Such unmodified coatings are widely deposited by using all the discussed methods. However, the coating modification was less frequently applied during slurry aluminizing. On the other hand, there is a general tendency to increase the service parameters of structural elements operating under aggressive conditions. Such trends enforce the need to enhance the durability of coatings as well. Therefore, rare earth elements, including zirconium [18–20], hafnium [21,60,66], palladium [46,66], rhenium [47,52,69] and platinum [49,51,52,63,66,69–71], are frequently added to significantly extend the service temperature of nickel-based superalloys up to 1300 °C. One can conclude that their addition is extremely beneficial as not only the operating temperature increase but also the material stability of the coating is improved.

It is clearly observed that recent research has focused on improving the deposition of aluminide coatings on nickel-based superalloys to enhance their oxidation and corrosion resistance at high temperatures. Researchers have explored various advanced deposition techniques, such as pack cementation, electrochemical deposition, and chemical vapor deposition (CVD), to improve the quality and properties of aluminide coatings on superalloys. Although these techniques have been used for many years, constant progress is maintained due to the introduction of new materials. The addition of other elements, such as chromium, yttrium, and silicon, has been studied to improve the performance of the coatings. The microstructure of aluminide coatings plays a crucial role in their performance, so studies have also focused on controlling the grain size, morphology, and distribution of phases in the coatings to improve their mechanical and protective properties. Apart from conventional AC containing a top coat and interlayer, some new multi-layered aluminide coatings, where different layers with varying compositions or structures are deposited on

the superalloy substrate, are of great interest. These multi-layered coatings offer enhanced protection against oxidation and corrosion, as well as improved adhesion to the substrate. One should stress that recent studies on the deposition of aluminide coatings on nickel-based superalloys have led to the improved performance and durability of these materials in high-temperature applications, such as gas turbines, aerospace components, and power generation systems.

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