
Transition Metal Aluminide Coatings and Initial Steps on Additive Manufacturing

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Abstract

During the last decades, Fe-, Ni- and Ti-based aluminides have been studied in terms of bulk materials with an effort to develop alloying and processing strategies to overcome their low ductilities and toughness compared to conventional alloys. Whenever significant improvements can be addressed in this direction, they will be opened to an extensive range of industrial applications, especially those related to high temperature resistance requirements. In parallel, progressing interest has also been focused on their application as protective layers. This chapter is intended to provide a review of the evolution that has been made mainly during the last two decades of the several coating technologies devoted for this purpose. From thick to thin coatings are revised, with insight into coating microstructures and properties as well. Lack of space has forced the selection of those technologies arising most interest within last years; therefore, the content will follow this order: joining (laser cladding and electrospark deposition), thermal spraying (high velocity oxygen fuel and cold spraying) and physical vapor deposition (magnetron sputtering and cathodic arc deposition).

Keywords: intermetallic, coating, overlay, repair, corrosion, wear

1. Introduction

Due to their intrinsic outstanding properties, intermetallic compounds (IMCs) have found application to coat other materials, either to improve surface resistance of an industrial substrate component to environmental attack or to create a beneficial intermediate layer between the substrate and another coating material [1, 2]. As coatings, a wide range of techniques have been employed to deposit them, either at low temperatures such as plating or at high temperatures by hot dipping, joining, thermal spraying and so on. Many intermetallic coatings have been produced for a wide range of applications and different technological interest; however, the scientific community has been mainly focusing during the last decades on the study of

those coatings for high temperature protection of industrial components. One of the primary users of high-temperature coatings is the gas turbine engine industry for commercial and military aircraft, industrial power generation and marine applications. One possible application could therefore be for the protection against oxidation of external and internal surfaces of turbine blades and vanes to fight oxidation and hot corrosion. Other applications would include turbines for coal gasification combined cycle power plants in components of fast breeder reactors or superheater tubes in the incinerator of waste to energy plants. Those IMC coating materials of interest rely on aluminide, chromide or silicide intermetallics because they can form protective oxide films of Al_2O_3 , Cr_2O_3 or SiO_2 [1–3].

Transition metal aluminides as bulk materials are seen as potential candidates for future substitution of superalloys since they can also offer significant reductions in density. Within this group, Fe, Ni and Ti aluminides are mainly considered, although Co-Al, Nb-Al, Pt-Al, Ru-Al alloys as well as other trialuminide alloys (Al_3X where X can be Ti, Zr, Hf, V, Nb or Ta) are also reviewed, even with some works dealing with coatings [4–8].

Nickel and iron aluminides especially provide excellent oxidation resistance in the range 1100–1400°C due to their high aluminum contents and high melting points, although many times spallation problems can be important [9, 10]. **Table 1** provides the critical ordering temperature ($T < T_c$ long-range order while $T > T_c$ short-range order), melting temperature and the maximum use temperatures of the main compounds of potential industrial interest. As it can be seen, their corrosion resistance extends to temperatures at which these alloys have limited or poor mechanical strength. Because of the limitation on balancing loading capabilities with high temperature corrosion resistance, together with poor room temperature ductility, some processing problems, as well as low strength and creep properties at high temperatures of some intermetallics [11], their commercialization is still limited; therefore, their use as coatings to provide resistance to other materials offers increasing suitable possibilities. The purpose of the present chapter is to offer an overview of the most recent advances on this topic.

Table 2 presents the main characteristics of the most usual coating techniques employed for the production of intermetallic coatings. The use of pack cementation, slurry, hot dipping and chemical vapor deposition was the first initially established [12]; the fundamentals of such

Intermetallic	Critical ordering T	Melting point	Maximum use temperature (°C)	
			Strength limit	Corrosion limit
Ni_3Al	1390	1390	1100	1150
NiAl	1640	1640	1200	1400
Fe_3Al	540/760	1540	700	1200
FeAl	1250	1250	800	1200
Ti_3Al	1100	1600	760	650
TiAl	1460	1460	1000	800

Table 1. Temperature limits for iron, nickel and titanium aluminides.

Slurry	Applying a powder mixture of aluminum or an aluminum alloy with an activator along with a binder either by spraying or by brushing followed by a diffusion heat treatment at a temperature of 1000–1200°C
Hot dipping	Immersion of the substrate into a molten metal pool and diffusion in the solid state during dipping or subsequent thermal treatment
Pack cementation	<i>In situ</i> chemical vapor deposition (CVD) batch process where the substrate is buried in a mixture of the master alloy powder (powder of the element or elements to be deposited on the surface of the parts, such as Cr and/or Al, Cr and/or Si), an halide salt activator and an inert filler powder
Chemical vapor deposition	Precursor gases (often diluted in carrier gases) are delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase and are deposited onto the substrate
Joining techniques	Welding processes where the powder in liquid phase, upon reaction with the substrate metal, forms the intermetallic compound. The coating material is melted in contact with the substrate
Thermal spraying	The feedstock coating material (in powder, wire or rod form) is heated to a molten or semimolten state some distance from the substrate. The resultant heated particles are accelerated and propelled toward a prepared surface by either process gases or atomization jets
Physical vapor deposition	A solid metal is vaporized in a high vacuum environment and deposited on the substrate

Table 2. Main characteristics of diffusion and overlay coatings.

technologies are based on the formation of the intermetallic through the interaction of a reactant that contains Al with the primary elements composing the substrate alloy. Many of these techniques have in common that rely on diffusion processes to form the intermetallic. The behavior of diffusion coatings strongly depends on the composition of the substrate alloys because the alloy participates in the formation of the coating. As a result, these coatings do not offer wide flexibility for the incorporation of minor elements. In order to face this limitation, the “overlay”-type coatings were developed with minimal direct contribution of the substrate alloys. The present chapter will thus mainly focus on these overlay processes such as thermal spraying, joining or physical vapor deposition that actually consist of an alloy of a specially designed composition, i.e. feedstock intermetallic, to be deposited on the component surface. The coating thicknesses deposited by the above overlay joining and thermal spray methods are of the order of ~200 μm and higher. Physical vapor deposition (PVD) techniques enable the deposition of coatings in the nanometer to micron thickness range. Thermal spraying and joining techniques can be considered as fusion processes. Each process results in different coating microstructures, thus also having a direct influence on the final properties (**Figure 1**).

We will also explore the concepts of rapid prototyping and additive manufacturing applied to IMCs, which are acquiring relevant interest. The conventional production process for bulk components on intermetallic compounds is casting, which leads to a partial oxidation and grain growth owing to aging at high temperature for a long time [9, 10]. The direct manufacturing of 3D articles of these materials is complex due to the brittleness at low temperatures inherent in intermetallics. Moreover, the subsequent sample machining leads to a noticeable wear of the cutting tool.

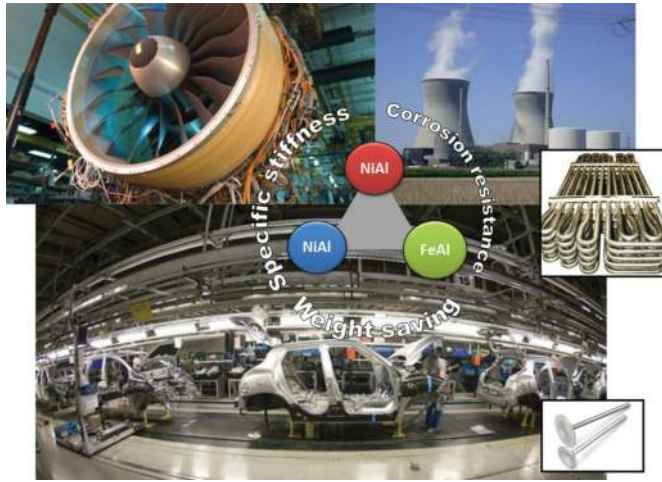


Figure 1. Fields of application where intermetallic coatings can be applied.

On that concern, rapid prototyping actually refers to the rapid production of prototypes for several objectives, including ergonomic and visual trials, assessment of functional performance and supporting parts to other processes. By contrast, additive manufacture technologies (AMTs) involve any manufacturing process using layer-by-layer or drop-by-drop processes. Usually, these AMTs are used for obtaining prototypes, rather than large-scale production. However, recently, more and more AMTs are employed for final components, especially when complex geometries need to be produced, or for the incorporation of special functionalities [13]. Some of the above-mentioned processes can also then be regarded as potential technologies for additive manufacturing, which can outperform conventional hot-pressing consolidation of powder due to their less complexity, lower energy consumption, higher productivity and therefore lower production costs [14].

2. Overlay coatings

2.1. Joining techniques

Welding involves a range of technologies suitable for the application of thick coatings, from 1 to 50 mm or more, of metallic materials. The available processes are manual metal arc (MMA), metal inert gas (MIG), tungsten inert gas (TIG), plasma transferred arc (PTA), etc.; Çam et al. [15] reviewed the use of these techniques for intermetallics. A part from improving the surface properties, they can be used for cosmetic repair of casting defects as well as for the assembly of components. Alternatively, the laser cladding process is increasingly used instead of PTA (Plasma Transferred Arc) welding and uses a laser as source of heat. It outperforms conventional welding methods like TIG for advanced weld repair applications. Typically coatings from 0.5 to 3 mm thicknesses can be build-up with laser cladding. Instead

of using a filler rod, consumable electrode or a previously applied paste, it uses powder as feedstock material to form the coating, which is carried into the melt pool by an inert gas through a powder nozzle.

Although PTA and laser cladding are technologies dating from about the same period, i.e. the 1960s, laser cladding has received more attention in this decade for possible production of additive manufacturing of aluminides; therefore, in order to avoid overextension of the present chapter, the emphasis is highlighted on laser cladding and references to PTA intermetallic coatings can be found in the literature as reported at the beginning of this section.

Laser cladding uses a powder-fed or wire-fed system and the resulting coatings possess extremely dense and pore-free microstructures. They are bonded to the substrate through an excellent metallurgical union, have uniform composition and coating thickness. Laser coating also produces very low dilution and small affected zone to the base material [16]. Laser cladding will be here revised as an option for additive manufacturing purposes. Also other wire feeding systems have appeared to be suitable for the build-up of intermetallic structures such as the so-called wire-arc additive manufacturing (WAAM) process [17, 18].

Furthermore, for repair purposes, electrospark deposition (ESD) has also been used to deposit intermetallics and this will briefly be revised; this is a process based on pulsed micro-welding, working slower than previous processes and with maximum thicknesses of about 2-3 mm. In order to deposit the electrode material, electrical pulses of short duration are used [19].

2.1.1. Laser cladding

2.1.1.1. Fe-Al coatings

Previous works with gas tungsten arc (GTA) and gas metal arc (GMA) welding techniques indicate that when the clad has an aluminum content above 10 wt.%, cold cracking in the iron aluminide cladding occurs in a similar manner to that observed in bulk samples [20, 21]. High-quality clads were produced by proper optimization of the pulsed laser-assisted powder deposition (LAPD) process conditions on mild steel; however, since Al plus Fe powders were used as feedstock, inhomogeneous phase distribution was obtained rather than the stoichiometric Fe_3Al or FeAl phases which are the ones of interest for possessing enough Al content to form a continuous oxide surface layer [22]; notice then that those works required the mixing of the two base metals. Cheng and He [23] produced real overlays as defined before when employing Fe_3Al powders; they observed a fine dendritic structure with some cracking in the coatings, whereas none when using a mixed powder of Fe and Al, as well as Bax et al. [24], who achieved completely crack-free single-phase Fe_3Al and FeAl coatings with hardness values HV0.1–300 on mild steel and HV0.1–500 on pure nickel, respectively. The shift in composition in comparison to the initial powder composition (45/55 at.% ratio) is reported to be caused during the mixing or laser cladding process.

In addition, FeAl intermetallic matrix composite coatings with TiC as reinforcement have been produced for wear resistance at high temperatures [25, 26]; TiC is found to be a suitable reinforcement because of its excellent high temperature stability, high hardness and low density;

a transition from abrasive wear to adhesive wear was found when the load was increased for such tested coatings.

Whereas previous cited works usually dealt with coatings deposited on steel substrates, Tomida and Nakata [27] deposited on A5052 commercial Al-Mg alloy substrate to improve its surface hardness and wear resistance for possible application in automobile industry, railway cars, aircraft, etc.

Abboud et al. [28] as well as Chen and Wang [25] used a one-step process instead of preplac-ing the powder on the substrate and then passing the laser, which offers higher flexibility enabling the use of such technique for rapid prototyping. Apart from coating, laser cladding has therefore gained importance within this decade for 3D manufacturing purposes. This might be a good solution to solve the drawbacks encountered for bulk processing, also when problems concerning porosity, bond strength and thermal expansion coefficients mismatch between the coating and the substrate may arise.

There are some reports on additive manufacturing of iron aluminides, i.e. 3D laser cladding, laser metal deposition (LMD), laser engineered net shaping (LENS) and selective laser melting (SLM) processes [29–36]. SLM derives from the selective laser sintering (SLS) process because instead of sintering or partial melting, complete melting of powder occurs; also for SLS post-processing is required. Song et al. [29] reached a hardness value in SLM pieces about 750 HV0.3, harder than those FeAl coatings deposited by high velocity oxy-fuel spraying and also higher than hot forging (680 HV0.3) or by mechanical milling + explosive shock wave consolidation (683 HV0.5) [37]. A large-scale collaborative German project explored the possibilities for the production of parts from iron aluminide-based alloys by ALM for automotive, aeronautics and energy conversion applications by means of SLM and LMD with a Fe-28 at.% Al feedstock powder. Defect-free samples were produced whose mechanical properties are highly dependent on the internal stresses. SLM samples were only ductile above 200°C while LMD samples

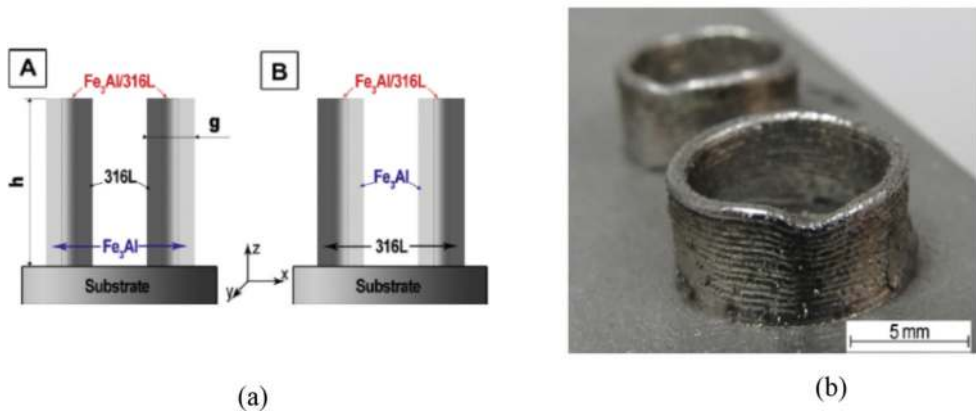


Figure 2. Laser clad tubes: (a) scheme of the composition of each structural component: A—316 L/Fe₃Al and B—Fe₃Al/316 L, and (b) first technological trials [34].

are already ductile at room temperature [29]. Michalcová et al. [36] recently explored three different strategies for strengthening iron aluminides at high temperatures using LAM: (i) increasing the ordering temperature $D03 \leftrightarrow B2$ Fe–30Al–10Ti (at.%), (ii) precipitation of borides (Fe–30Al–5Ti–0.7B) and (iii) generation of coherent A2 + L21 microstructures (Fe–22Al–5Ti). Dense samples could be generated with yield stress and compressive creep strength matching that of the as-cast alloys above 600°C and even higher at lower temperatures, being dependent on the building direction. No general improvement of ductility was observed.

LENS has been mostly used for obtaining functionally graded materials (FGMs), either Fe₃Al/SS316L or Fe/FeAl [30, 33, 34], allowing to produce tubes with good shape and a high metallurgical quality (**Figure 2**). LENS enables the production of metal components through a process of metal powder sintering aided with pre-designed three-dimensional computer-aided design (CAD) models. On account of the “layer by layer” building mode, the chemistry of each layer being build-up can be different, and thus, the LENS technique can produce composition gradients in near-net-shape components without using any additional intermediate steps.

2.1.1.2. Ni-Al coatings

Mostly nickel [28, 38–40] and steel [28, 41–45] substrates were employed for the fabrication of laser cladding nickel aluminide coatings, the composition being either controlled by using two powder feeders and selecting the powder feeder rates [28] or by mixing the desired amount of nickel and aluminum powders that are preplaced on the substrate and then selecting the laser power density to generate the melt pool [45]; from the first work, a compositional gradient was obtained, whereas single-phase adherent NiAl coatings free from pores and cracks could be produced afterwards. Depending on the operating conditions, a dendritic, cellular or equiaxial structure can be obtained, and the optimum one has resulted that leading to a dense and fine dendrite microstructure that leads to improved wear rates, i.e. about 14×10^{-5} mm³/Nm under sliding conditions. Up to a hardness value of 750 HV0.2 could be pursued by the addition of phosphorous, also resulting in a refined cellular microstructure (Ni₃Al + Ni₃P) near the interface; in that case, the microstructure of the coating was however composed of γ -Ni, Ni₃Al and NiAl rather than a uniform single phase [40]. Also by the increased yttrium addition, the dendrites were gradually refined [46].

As well as for iron aluminides, a great focus has been done on the preparation of intermetallic composite coatings with TiC or WC particulate reinforcement. Chen et al. [35, 36] tried with a 35 and 20 at.% Al ratios in the raw material of elemental powder blends resulting in NiAl-Ni₃(Al,Ti,C) and NiAl-Ni₃Al-TiC composition with dendritic structure and a hardness around 650 and 750 HV0.2, respectively. The NiAl-Ni₃Al-TiC laser clad coating exhibited excellent wear resistance not only at room temperature but also at 600°C in dry sliding wear test conditions. The adhesive wear seems to be prevented thank to the high strength of the interatomic bonds of the intermetallic matrix, providing a firm support for TiC particles and resisting metallic adhesion during metallic dry sliding wear. The cavitation erosion resistance of laser clad nickel aluminide composite coatings is also ameliorated by the use of TiC as well as the work hardening ability of the NiAl-Ni₃Al [43, 44].

LENS was employed to obtain not only nickel aluminides with various compositions but also with composition gradient [47]; cracking problems were solved by preheating the substrate. Due to problems in mixing with a single feeder, two feeders were used for the Ni and Al powders, so that the in situ reactive alloying was successful.

2.1.1.3. *Ti-Al coatings*

Titanium aluminide intermetallic coatings produced by laser cladding were employed to protect titanium and aluminum specimens. On aluminum substrates, Ti + Al powders were preplaced to produce Al_3Ti reinforced with TiB_2 , TiC and SiC so that the wear resistance could be improved; in order to produce an adherent layer, the process was optimized to minimize the melting of the base material [48]. On titanium substrates, either pure Ti or its alloys, such as Ti6Al4V, which are extensively used in aeronautical, marine and chemical industries, the use of intermetallic layers is aimed at improving its wear and oxidation resistance at temperatures above 500°C [49–55]. In most of the cases, just by preplacing the Al powder in the right portion, Ti_3Al , TiAl or TiAl₃ layers can be achieved [52, 53], but this implies a high dilution with the base material. Guo et al. [50] found the following hardness order $\text{Ti}_3\text{Al} > \text{TiAl} > \text{TiAl}_3$ and the main conclusions derived from their studies are that, under the same sliding conditions, the wear resistance tendency followed the same order as the hardness, with the higher Ti content exhibiting the highest resistance.

Other authors used Ti + Al powders [29, 49, 51] and some observed an increase in hardness when increasing the Al content, contrarily to what is reported in the previous paragraph. The wear rate and mechanisms change according to normal load and composition [54].

Few used TiAl alloy powders, i.e. TiAl₃ [54] or TiAl [55, 56] compositions; Li et al. [54] also uses TiB_2 , Al_2O_3 and nano- Y_2O_3 but the best results on the volume wear loss approach to 2 mm³, whereas by using TiC, TiN or SiC, one order of magnitude lower is reached.

Zhang et al. [56] also used TiAl alloys, i.e. Ti482Nb0.4Ta and Ti48Al2Cr2Nb (at.%) powders to be deposited onto stainless steel, a Nb alloy, a Ti alloy and TiAl alloy and produced 3D components through the LENS technology; final microstructure, either an equiaxed, metastable α_2 -Ti₃Al or massive γ , is very influenced by the processing parameters. Also LMD was used for building up components from Ti-47Al-2.5 V-1Cr and Ti-40Al-2Cr (at.%) intermetallic alloys. Fully lamellar (FL) microstructure consisted of γ -TiAl and α_2 -Ti₃Al was formed in the as-laser deposited γ -TiAl samples [57].

However, with laser cladding, the quality of the coating may vary significantly due to small changes in the process variables such as laser power, beam velocity and powder feed rate. Optimizing the set of parameters is of crucial importance for the control of the microstructure. Therefore, for prototyping operations, its use is still limited. However, undergoing developments in high-power diode lasers (HPDL), fiber lasers and control units based on knowledge offers promising capabilities for industrial benefits.

On the other hand, the ability to have automatization control of the laser/material feed system, precise thermal energy dosing and coating integrity makes laser cladding suitable over other processes such as high velocity oxy-fuel (HVOF) and cold spray (CS).

2.1.2. *Electrospark deposition*

FeAl compound has proved to be resistant in corrosion environments such as in molten salts. Therefore, their use for corrosion protection of austenitic stainless steels used as bipolar plates and cell housing materials appears to be promising. Frangini and Masci [58] were pioneers on directly depositing FeAl through ESD with no apparent oxide content or crack formation within the layer; its corrosion in (Li + K) carbonate molten salts showed some degradation at long exposure times. More recently, these coatings were oxidized by using a DC plasma oxidation technique to grow alumina films, which despite being the metastable gamma alumina, it presented very good barrier properties [59]. Lower interest has been devoted to the Ni-Al system where instead pure alloyed layers, Ni-Cr-NiAl [60] and Al-NiAl₃ [61], have been produced.

Gradual titanium aluminide coatings onto γ -TiAl substrates were produced by Li et al. [62], mainly presenting TiAl₃ on the top with a good oxidation resistance at 800°C but less at 900°C. Electrospark deposition has been recently explored in combination with ultrasonic impact treatment reaching up to 540 HV.

2.2. Thermal spray

One of the major advantages of thermal spray technologies compared to the previous ones is the minimum heat input to the substrate, the so-called heat affected zone present in welding processes, here is absent. Thus, materials with very high melting points can be applied without modifying the properties of the component and without excessive thermal distortion of the part. An additional advantage is the capability of recoating damaged deposits without changing previous dimensions or properties.

The raw material (in powder, wire or rod form) is deposited onto the substrate by propelling the energetic particles by means of high-pressure carrier gas. The particles can be fully or partially melted on impact with the substrate creating cohesive bonds with each other and adhesive bonds with the substrate. The resulting microstructure is lamellar with the characteristic "splats," which attach each other after undergoing very high cooling rates.

Thermal spray processes can be classified according to the energy source, differing from the respective characteristic gas temperatures and particle velocities. When a combustion is used to heat up the material, the existing processes are detonation gun, flame spray and high-velocity oxygen fuel, whereas when it is based on electric energy, plasma spray and arc spray are found. Further modifications of those such as vacuum plasma spray (VPS), high-velocity suspension flame spraying (HVSFS) or suspension plasma spraying (SPS) also exist [63].

More lately, cold spray (CS) has raised the interest of many scientists. Unlike the previous processes, CS is a solid-state process, which offers many advantages in front of conventional thermal spraying: avoids oxidation and undesirable phases, retains the properties of the starting materials, induces low residual stresses, results in a cold-worked microstructure with high-density and high-hardness, allows spraying of thermally sensitive materials, requires minimum surface preparation and implies a safer process due to the absence of high-temperature gas jets, radiation and explosive gases [63].

Recently, the principal findings on thermal spraying of transition metal aluminides were reviewed [64]. Since the larger production of intermetallic coatings has been produced by means of HVOF, the last studies are here reported, as well as those of CS, whose goal is trying to resemble to bulk structures.

2.2.1. High-velocity oxygen fuel

2.2.1.1. Fe-Al coatings

Fe_3Al and FeAl coatings were produced by HVOF with the aim to improve oxidation and wear performance. They have been mostly applied on steel substrates as well as light alloys [65–69]. A wide range of feedstock compositions have been investigated along the years; different alloying elements have been introduced to the feedstock powders, i.e. Cr, Zr, B, Mo, Ni, as well as ceramic particles such as CeO_2 , WC, TiC, TiN, TiB_2 for different purposes, from decreasing the spallation phenomena during high temperature oxidation to introduce ceramic reinforcement to decrease wear rates.

Typical microstructural features that can be found are the occurrence of molten or partially melted FeAl or Fe_3Al particles, with different amount of Al-depletion, intersplat oxidation and porosity depending on the spraying parameters. Playing with different ranges of particle sizes also results in quite different structures but, mostly, molten splat areas exhibit columnar grains while the rest is equiaxed.

Up to 479 HV0.4 and even 520 HV0.5 hardness values were achieved for iron aluminides, while even 650 HV0.2 can be reached when ceramic particles are introduced [65]. Usually, the higher the microhardness is, the higher the wear resistance. Performance in sliding, abrasive and erosion testing conditions has been investigated, and the wear resistance is governed by the wear mechanisms taking place, i.e. adhesive through material transfer, delamination by fatigue, abrasive and oxidation wear can be encountered depending on the load, sliding speed, counterpart material and so on [68–70]. Dry sliding has been ultimately investigated also at high temperatures with rates in the order of $2.11 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ at 400°C and unnoticeable wear track at 800°C with a Si_3N_4 counterpart ball and 5 N load [70]. The use of intermetallic matrix for composite coatings has also been studied here as a good strategy for improving wear as it was reviewed for laser cladding coatings; in this case, not only TiC [65] but also WC [69], CeO_2 [68] and TiN- TiB_2 [66] cermets have been synthesized. One of the best wear performances was the coating where 10 wt.% of BN and 20 wt.% of Ti were added to starting Fe_3Al powder leading to $8 \times 10^{-7} \text{ mm}^3/\text{Nm}$ with an alumina ball and 10 N load.

The performance of iron aluminide in gaseous corrosion, molten salt corrosion, erosion-corrosion, aqueous corrosion, oxidizing, carburizing and sulfidizing properties has been quite investigated. The moderate and high temperature conditions have been the mostly studied. They possess the ability to form compact aluminum oxide layers due to their high Al content; at high temperatures (>900°C), the occurrence of a stable $\alpha\text{-Al}_2\text{O}_3$ layer is highly desirable, but some spallation can be induced if less stable oxides are present; the relative diffusion kinetics of Fe and Al upon exposure can induce the formation of voids at the coating-oxide layer interface [64].

At high oxidizing temperatures, additional points to consider are: ability to suppress cracking when external stresses are applied or induced thermally, as well as mismatch in the coefficient thermal expansion of the coating and substrate. Also, lower porosity reduces the effective surface area and increases the life service.

Thermal spray iron aluminide coatings have been tested in high temperature gaseous environments [64], but to the author's knowledge, very few findings were observed concerning their use in hot corrosion conditions [71]. These authors reported that no degradation (corrosion and wear) was noticed on the Fe-25% Al-Zr plasma and HVOF coatings sprayed onto low carbon steel heat exchanger tubes tested in a new industrial plant burning very poor fuel; however, this work is not explicit on the coating structures and corrosion evolution. Coal combustion atmospheres can be simulated by testing the coatings in sulfidizing mixture of gases. Coating microstructure can strongly affect its resistance to sulfur penetration [72]. By adding CeO_2 , the sulfidation resistance was improved [73].

Finally, Shankar highlights the interest on aqueous corrosion mainly for two reasons [74]; firstly, to test durability of these alloys when they are either stored ideally or during working conditions in a corrosive atmosphere. Secondly, since these materials are less expensive compared to conventional stainless steels, they are also considered for room temperature applications in replacement of stainless steels, such as pipes and tubes for heating elements, and in distillation and desalination plants. It is also worth to consider that in order to avoid the use of strategic elements, such as Cr and Ni, these materials are also considered for biomaterials applications, for example bone joints and surgical instruments. Primarily then, their low temperature electrochemical behavior has been tested in simulated human body fluids (Hank's solutions) [75], NaCl [76], H_2SO_4 [77] and NaOH [78]. For thermal sprayed coatings, just few authors have dealt with the topic [79, 80].

2.2.1.2. Ni-Al coatings

In analogy to the Fe-Al system, nickel aluminide coatings also intend to produce uniform coatings with target NiAl or Ni_3Al compositions. Like it occurred in the microstructure of Fe-Al-based coatings, HVOF NiAl and Ni_3Al coatings typically present Ni-rich regions along the splat boundaries, as well as oxides and the intermetallic at the splat core.

Concerning mechanical properties, up to 470 HV0.1 of hardness value was obtained for NiAl HVOF coatings [81] and even higher up to 750 HV0.1 when nanocrystalline powders are used [82], which have made them also attractive for wear resistance even in slurry conditions [83]. Recently, Benegra et al. [84] compared the abrasive behavior of HVOF and PTA NiAl coatings and reported similar results. At room temperature and dry sliding conditions, friction coefficients as low as 0.3 at 90 N can be obtained with a AISI 52100 steel pin [85]. Like FeAl, nickel aluminides have been proposed as matrix phases for wear performance at high temperatures [86–88]; in erosion conditions, NiAl–40Al₂O₃ coatings showed lower sensitivity to the test temperature in front of chromium carbide cermet coatings. Wang et al. [89] investigated the high temperature wear behavior (600–900°C) of NiAl–Al₂O₃–TiC composites against SiC under dry sliding conditions on a ball-on-disc test; they exhibited excellent self-lubricating property.

α -Al₂O₃, nickel spinels and oxides were formed during oxidation of HVOF NiAl coatings above 900°C [90]. The addition of ceria was also used for the improvement of carburization resistance, by creating corrosion products acting as diffusion barrier [91], but giving lower efficiency for the erosion resistance compared to nonheat-treated coatings [92].

To the author knowledge, no aqueous corrosion works have been found for NiAl HVOF coatings; some exist for plasma-sprayed deposits in 0.01 M H₂SO₄ electrolyte solution at ambient temperature [93], with lower current densities and higher aluminum content.

2.2.1.3. Ti-Al coatings

Few articles have dealt on HVOF spraying of titanium aluminides and those few ones are based mainly on the TiAl with additions of Cr, Fe [94–97] or even Al₂O₃ incorporation [98]. TiAl-based alloys can be more sensitive to the high temperature oxidation occurring within the flame resulting in high oxidation [99].

The hardness and wear performance of plane titanium aluminide HVOF coatings have not been much investigated unlike other of the conventional processes such as plasma spraying, whose hardness values can reach 589 HV at room temperature [100]. As in the other reviewed cases, the use of such intermetallics has also been used to form composite coatings to improve the wear resistance of Ti6Al4V substrates [101]. The sliding wear resistance is reported to be higher for γ -TiAl-Al₂O₃ HVOF, followed by γ -TiAl-Al₂O₃ APS and, finally, by γ -TiAl APS. In addition, HVOF γ -TiAl-Al₂O₃ coatings exhibited lower wear rate at 700°C compared to uncoated hardened H13 tool steels [102]. Under non-lubricated conditions, the wear resistance of γ -TiAl-Al₂O₃ HVOF at RT is higher than γ -TiAl-Al₂O₃ HVOF at 700°C, and this, in turn, higher than RT H13 at RT. Also, carbide reinforcement was introduced but for APS coatings.

As far as the oxidation resistance is concerned, mixed Al₂O₃-TiO₂ layers are usually formed on titanium aluminides, resulting in less protection capabilities than Al₂O₃ scales. By alloying further elements to Ti₃Al and TiAl, this can be improved [103]. Also TiAl₃ + Al coatings have been sprayed to achieve better sprayability avoiding the brittleness of the intermetallic and reporting improved performance at 700°C. APS, VPS and HVOF coatings were also tested under cyclic and isothermal oxidation tests at 700 and 900°C [104]. HVOF coatings have shown good cyclic oxidation resistance, reporting that service temperature might be increased by 150°C more than the steel substrate material. No spallation was there observed, while some studies concerning LPPS (low pressure plasma spray) coatings, indicated cracking failure during deposition or early oxidation testing, when coatings are applied on Ti and TiAl [105].

Ti-Al blends were also sprayed by warm spraying, which has been lately studied for the deposition of titanium aluminides given their sensitivity to oxidation. This allows working at decreased temperatures of combustion gas via mixing with nitrogen. After heat treatments, Ti₃Al, TiAl and TiAl₃ were formed with significant porosity that developed during the heat treatment was caused mainly by Kirkendall effect [106].

2.2.2. Cold spray

2.2.2.1. Fe-Al coatings

CS of iron aluminide coatings has been produced with feedstock compositions Fe + Al, Fe(Al) and FeAl. The easiest way is by co-spraying the elemental powders or ball-milled powders with a solid solution composition, thus avoiding the challenges of the high strength and brittleness of the intermetallic compound, but this needs annealing post-processing to achieve the desired composition [107]. Direct cold spraying of intermetallic Fe 40 at.% Al particles has been just attempted by Cinca et al. [108], and dense coatings have been achieved (**Figure 3a**). The study of the spraying parameters revealed that in order to obtain good deposition, a narrow window of selected parameters need to be selected. More investigations need to be pursued concerning the influence of the anomaly yield strength behavior of this material as well as the performance under the typical high strain rates of the cold spray process; some studies in this direction are being undergone through the analysis of the as-sprayed deposits by the EBSD technique, which is showing considerable grain refinement not only at particle boundaries but also all along the upper part of the coating (**Figure 3b**) [109], probably because those particles are impinging on the first layers which are stiffer compared to the stainless steel substrate; splats of individual powder particles can be suspected; some examples are indicated by dotted ellipses. Assuming that, the large deformed grains are primarily located inside the splashes, which are surrounded by fine-grained material due to high strain rate deformation at the intersplat boundaries. Fracture surface features indicate the presence of ductile fracture most probably induced by softening (**Figure 3c**).

The cavitation wear and corrosion resistance of such Fe 40 at.% Al coatings have been characterized [110]. They exhibited reasonably good cavitation performance in fresh water with a low wear rate. In addition, the isothermal and cyclic oxidation at 900°C up to 300 h has shown that the coating keeps unaltered; most promising, **Figure 3d** shows the coating cross section

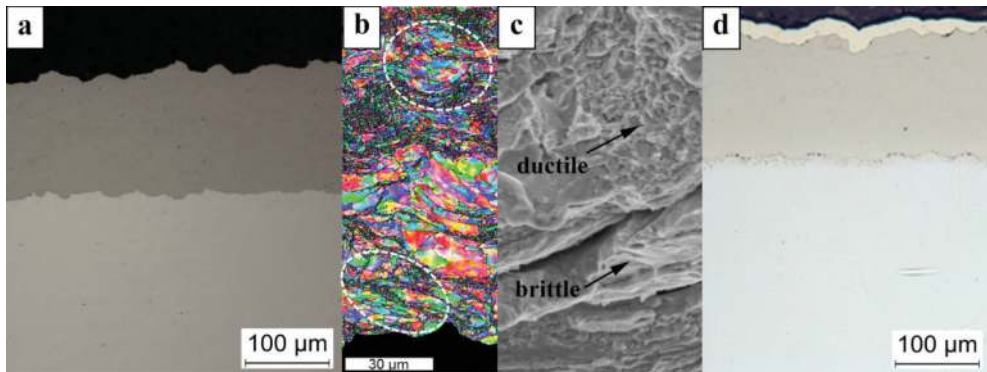


Figure 3. Cold sprayed Fe 40 at.% Al coating: (a) as-sprayed cross section, (b) orientation distribution map—EBSD, (c) fracture surface and (d) cross section after exposure at chlorinating environment.

after exposure at 650°C for 500 h in $N_2 + 6\% H_2O + 15\% CO_2 + 4\% O_2 + 0.1\% SO_2 + 500$ ppm HCl, indicating no damage at all (**Figure 3d**), which evidences the great capabilities of such materials under aggressive industrial environments [111].

2.2.2.2. Ni-Al coatings

Also, blends of elemental powders and ball-milled Ni + Al powders were deposited by cold spray [112–114]. When a mixture of powders is used as feedstock, the microstructure is non-homogeneous in composition and an annealing treatment is required afterwards [112], while the composition along the coating is more homogeneous when starting from the mechanically alloyed powders [113]. The microstructure of cold-sprayed NiAl deposits was also compared to that of HVOF and APS coatings through electrical measurements, proving that their resistivity values strongly depend on splat interface areas and porosity distribution; the presence of interparticle porosity within CS deposits results in higher electrical resistivities [115].

More recently, Azarmi et al. [116] investigated the performance of cold sprayed Ni–Ni₃Al composite coatings on aluminum substrates as an industrial material can be used under harsh service conditions. The compound coatings presented higher strength as well as elastic modulus values compared to pure Ni coatings given the increased amount of dislocations and hardening in Ni₃Al.

2.2.2.3. Ti-Al coatings

In order to improve high-temperature oxidation resistance, orthorhombic Ti₂AlNb alloy substrates, promising lightweight materials for the aeronautic industry, were coated with TiAl₃-Al composite coatings; the feedstock was a blend and needed a heat treatment of the as-sprayed deposit to enable the formation of the composite. During oxidation at 650, 800 and 950°C for 1200 h, the aluminum led to alumina; less protective intermetallics resulting from Al depletion of the TiAl₃ alloy and (Ti, Nb)Al_x compounds were formed [117–120]. Also, Ti-46Al-8.5Nb-1Ta (at.%) particles were deposited on a commercial alloy IMI-834 and the metastable phases present in the feedstock later transformed to the equilibrium ordered γ -TiAl and α_2 -Ti₃Al phases when heat treatment was applied to the as-sprayed deposit [121].

2.3. Physical vapor deposition

In PVD processes, reduced pressures are necessary for the coating deposition by condensation from neutral or ionized atoms of metals. Of all the possible PVD techniques, magnetron sputtering and cathodic arc vapor deposition usually result in adherent and dense thin layers at relatively low temperatures. In addition to the dense structure, PVD layers exhibit a nanocrystalline microstructure, which further enhances the adhesion and hardness properties of thin protective coatings.

Intermetallic aluminide coatings produced by PVD processes are mainly investigated to increase oxidation and corrosion resistance of several steel materials, rather than for improving the wear resistance as has been reported in previous coating technologies.

As far as the Fe-Al system is concerned, Fe-40% Al [122] and Fe-45% Al [122–124] were produced, studying the high temperature oxidation resistance. Magnetron sputtered Fe-45% Al

coatings containing different nominal compositions ranging 6.5–45 wt.% Cr and 0.5% Zr were deposited on bulk FeAl and 304 stainless steel. The scale spallation was diminished by the addition of such alloying elements during thermal cycling at 1000 and 1100°C. The resistance to scale spallation was even superior than bulk iron aluminides. The nanostructure of PVD coatings has been reported to improve the oxide scale adherence due to the reduction of the thermal stresses and inducing an anchoring effect as result of the formed oxide intrusions.

Cathodes of Fe-40% Al and Fe-45% Al composition were used by Paldey and Deevi [122] to deposit iron aluminides by means of cathodic arc evaporation, which uses a higher energy input than PVD sputtering processes, and it was observed a reduction of the mass gain during isothermal oxidation at 800°C of 440C steel by four times and also improved the oxidation resistance up to 1000°C of 304SS.

The cyclic thermal oxidation was also evaluated for NiAl PVD coatings to be employed as bond coats in thermal barrier coating (TBC) systems [125]; such bond coats have the role of (i) reducing the mismatch in thermal expansion coating of typically superalloy substrates and ceramic upper coatings and (ii) improving the oxidation resistance. He et al. [125] investigated three routes for the Ni30Al70 deposition on 304 SS and Inconel 600 alloy plates, i.e. arc ion plating (AIP), electron beam evaporative ion plating (EBIP) and sputter ion plating (SIP); description of such techniques can be found elsewhere. The AIP was formed by NiAl₃ and Ni₂Al₃ phases; the SIP was dominated by NiAl₃ and less Ni₂Al₃, while EBIP was rather formed by minor Ni₂Al₃ in mainly Al. Although such differences in composition, the oxidation resistance was improved at 800 and 1100°C for the two substrates, although by means of different protection mechanisms. Another technique, here cathodic arc plasma (CAP), was used by Chang et al. [126] with the aim to improve the cavitation wear resistance of AISI 1045 steel substrates with Ni₃Al coating through the following target compositions: Ni52Al48, Ni60Al40 and Ni70Al30; the cavitation performance was ameliorated by 10 times to the bare substrate in fresh water and twice in 3.5 wt.% NaCl. Potentiodynamic polarization tests also indicated an improvement on the corrosion resulting in higher corrosion potentials and lower corrosion current densities.

Titanium aluminides seem to have been more extensively studied by PVD methods. Ti-51Al-12Cr at.% magnetron sputtered layers were applied to γ -TiAl substrates and then covered by yttria partially stabilized zirconia to form TBCs. Such layers did not provide long-term protection at 900°C [127].

Predominantly, (Al,Cr)₂O₃ films were found to be protective on the TiAlCrN, TiAl55CrSiYN and TiAl60CrSiYN layers deposited by PVD on titanium aluminide alloys, thus improving the isothermal oxidation resistance at 900°C [128].

Good thermal stabilities up to 700°C of titanium aluminide films on SiO₂ substrates prove them as candidates for materials for high temperature electronics [129].

When using sputtering, titanium aluminide thin films have been manufactured by the use of different targets: (i) a target of an Al disk mounted on a Ti disk, (ii) one target of titanium and another of aluminum, (iii) the intermetallic target [130–133]. A part from the high temperature performance, the microstructure evolution [131–133], crystallization kinetics [133] and mechanical properties [130] have also been investigated. In some cases, a proper annealing treatment was necessary to achieve the target composition within the deposited film.

3. Final remarks

To sum up, thick coating deposition techniques such as welding-related processes can provide significant advantages for repairing purposes and good adhesion being achieved due to the metallurgical bonding mechanism. However, as it is reviewed, uniform compositions are reached hardly, the heat affected zone can induce alteration in substrate microstructure and properties and surface cracking is common resulting from thermal mismatch between the coating and substrate due to their different crystal structure, especially for the Fe-Al and Ti-Al system.

Each depositing method results in its characteristic coating microstructure, also determining of the final properties. Given the interest regarding high temperature applications, usually thick transition aluminide coatings are required in order to form a continuous and stable Al_2O_3 layer, especially in the case of titanium aluminides, where thin layers often result in oxide scales containing large amounts of TiO_2 which exhibits limited protection. In that case, intermediate coating methods such as thermal spray technologies can be of interest, although good bond strength requires proper mechanical anchoring, also related to convenient matching of thermal expansion coefficients between the coating and substrate.

The oxidation performance up to 900°C in isothermal and cyclic testing conditions and even higher temperatures has raised an interest for nickel and iron aluminides for aeroengines and power generation industries, while that of titanium aluminides has been more focused also for automobile parts. Their degradation in other harsh environments as well as for wear resistance has become frequently investigated during the last decade, giving importance to the use of intermetallic as promising metal matrix for composite coatings in high temperature wear applications.

The use then of intermetallics as coatings can be expanded as long as new compositions can reach protection at more aggressive environments.

Finally, the manufacture of components via additive manufacture technologies occupies more and more references in the literature. Up to this moment, Ni-, Fe- and Ti-based aluminides have been investigated through laser processes. Clearly, this seems to be the trend for the future. Nowadays, additive manufacturing technologies are gaining more importance; especially for this type of materials, where several fabrication issues arising from conventional technologies might be a concern, the build-up of near net shape components through the use powders can be of great interest. The effort, however, is need to be focused on achieving uniform compositions without disparity of undesired phases that may lower the mechanical properties.

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