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Application of reaction synthesis principles to thermal spray coatings

S. C. DEEVI*, V. K. SIKKA
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA
C. J. SWINDEMAN, R. D. SEALS
Thermal Spray Technology Center, Oak Ridge Centers for Manufacturing Technology, Oak Ridge, TN, USA

Reaction synthesis principles have been extended to plasma spraying to obtain coatings consisting of mixed oxide phases and iron aluminides. Elemental powders of iron and aluminium were fed through a d.c. plasma torch to deposit intermetallic coatings on carbon steel substrates. Carbon steel substrates were also pre-heated with a plasma flame to create an iron oxide surface on the substrate such that an exothermic thermite reaction takes place when molten splats of aluminium impinge the pre-heated substrate at sub- or supersonic velocities. A thermite reaction between iron oxide and aluminium allowed the formation of alumina, $FeAl_2O_4$, iron, and iron aluminide phases. The presence of $FeAl_2O_4$ and Al_2O_3 increased the surface hardnesses of the coating, and the hardnesses of the coatings are significantly higher than the hardnesses of steel substrate, and aluminium particles. X-ray analysis of the coatings, microstructural observations, and microhardness measurements suggest that plasma spraying conditions can be tailored to obtain coatings with high hardness values with *in situ* synthesized reinforcements (spinel and alumina) or iron aluminide phases. Aluminium-rich phases were observed in the as-deposited coatings when a mixture of aluminium and iron or aluminium and nickel were fed through the plasma gun in ratios equivalent to Fe_3Al, FeAl, Ni_3Al, and NiAl. In some cases, annealing allowed the formation of iron-rich or nickel-rich aluminide phases. High solidification rates of molten splats allowed very limited diffusional reactions between the splats of aluminium and iron, or aluminium and nickel because the available diffusional time for exothermic interfacial reactions is limited to a fraction of a second at best. Oxidation of part of the aluminium led to the formation of alumina in the as-deposited coatings, and therefore, a vacuum plasma spraying technique is desirable to obtain intermetallic phases. The results suggest that reactive spraying will allow deposition of coatings by utilizing the heats of reaction between the constituents, and reactive spraying will broaden the engineering applications of reaction synthesis techniques.

1. Introduction

During the last several decades, ordered intermetallics based on aluminides and silicides of transition metals such as nickel, iron, titanium, niobium, cobalt and molybdenum have been under investigation for their possible use as structural materials and as protective coatings against high-temperature oxidation, corrosion and sulfidation [1–6]. However, monolithic intermetallics have been used on a limited basis because of one or all the following possible reasons: low room-temperature ductility, low high-temperature strength and higher creep rates [7–11].

By thermally spraying iron aluminides on stronger base materials, the attributes of the coating material can be realized with less concern for its poor room-temperature ductility and low high-temperature strength. Thermal spraying offers a potentially economical method of depositing nickel and iron aluminides at relatively high deposition rates as coatings or near net-shape components. However, limited information exists on thermally sprayed coatings of aluminides, even though coatings based on NiCrAlY and FeCrAlY have been widely used throughout the industry.

Intermetallics, in general, release significant amounts of energy during their formation.

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* Author to whom all correspondence should be addressed. *Permanent address*: Research and Development Center, Philip Morris USA, 4201 Commerce Road, Richmond, VA 23234, USA.

Combustion synthesis, reaction synthesis, and reactive hot pressing depend on the heat of formation to combine both the synthesis and densification of intermetallics. Intermetallics such as Fe_3Al, FeAl, NiAl, CoAl, $MoSi_2$, and Ti_5Si_3 can be obtained by igniting the mixtures of elemental powders [12–15]. Ignition of a mixture generates a combustion wave, and an exothermic combustion wave passes through the elemental powders leading to the synthesis of intermetallics. In the case of aluminides, molten aluminium reacts with the transition metal either slowly (as in FeAl) or at an extremely high rate (as in NiAl or CoAl) depending on the heat of formation and specific heat of the mixture. The exothermicity of the reaction between iron and aluminium (see Table I) can be utilized in thermal spray coatings by feeding elemental powders or unalloyed material such that experimental conditions leading to an exothermic reaction can be favoured either before or after the powders are deposited on a substrate by controlling the velocity, power and plasma torch design. Plasma transfers intense heat to the feed material as it passes through the torch, and the heat transfer is generally sufficient to bring the particles to a molten state. Molten metal particles may react in the plasma before or after deposition on a substrate. A variety of coating techniques such as plasma spraying, vacuum plasma spraying, flame spraying, arc spraying, etc., fall broadly under the category of thermal spray techniques, and important parameters such as plasma temperature, feed rate, and quality of the coatings depend on the attributes of the technique. Therefore, thermal spray technology offers another avenue to apply the principles of combustion synthesis or reaction synthesis for surface modification or to produce *in situ* intermetallic coatings on the substrate. The use of thermal spraying to obtain intermetallic coatings and their composites *in situ*, using unalloyed materials or at least one elemental powder, is hereafter termed reactive spraying. In some cases, annealing of the coating may be required to homogenize and stabilize the microstructure or to facilitate thermite reactions.

Because the temperatures generated in the plasma are several thousand degrees, and the velocities are either sub- or supersonic, a carbon steel substrate can be heated very quickly by adjusting the distance between the torch and the substrate, the plasma temperature, and the velocities. The heating of carbon steel substrates in air should result in the formation of iron oxides because carbon steel is primarily composed of iron, and plasma spraying of aluminium on to an oxidized substrate should initiate a thermite reaction between an iron oxide and molten aluminium particles. A thermite reaction between iron oxide and aluminium is known for decades, and several reactions fall in the category of thermite reactions. In general, thermite reactions release significant amounts of energy due to the formation of a stable Al_2O_3 [16, 17]. Several reactions based on aluminium as the reducing agent have been studied during the last several decades, and some are widely used in a variety of commercial applications [16]. A feature common to all the thermite reactions is release of significant amounts of heat, which can raise the temperatures of the reactants to several thousand degrees. The exothermicity of the reaction propagates a self-sustaining combustion wave through the reactants forming *in situ* composites, and synthesis of composites such as $TiC–Al_2O_3$, $TiB_2–Al_2O_3$, $SiC–Al_2O_3$, $Fe–Al_2O_3$ have been reported in the literature [16–19].

TABLE I Heats of formation, aluminium content, densities and melting points of iron aluminides

Intermetallic	Heat of formation to ΔH_{f298} (kcal mol^{-1})	Density (g cm^{-3})	(wt %)	Melting point (°C)
Fe_3Al	− 16.0	6.648	13.87	1502
FeAl	− 12.0	5.585	32.57	1215
Fe_2Al_5	− 34.3	3.963	54.70	1171

In this paper, we discuss some of our results on the phase identification carried out by X-ray diffraction, microstructures, and hardnesses of the coatings obtained by reactive spraying of aluminium on to pre-heated carbon steel substrates. Pre-heating was carried out to obtain an iron oxide on the substrate to initiate a thermite reaction between iron oxide and plasma-sprayed aluminium powder. The study is also extended to determine if iron aluminides can be formed by reactive spraying a mixture of iron and aluminium under different conditions. X-ray phases obtained from the coatings of iron and aluminium mixtures are compared with the phases observed in the coatings of nickel and aluminium mixtures.

2. Experimental procedure

Powders of iron and aluminium with compositions corresponding to Fe_3Al and FeAl were sprayed on to carbon steel substrates as follows: (1) powders with desired stoichiometry were blended and fed to a d.c. plasma torch; (2) powders of iron and aluminium were fed separately; and (3) aluminium was fed through the plasma torch on to a pre-heated substrate. Pre-heating was conducted in order to produce iron oxide/s on the substrate surface prior to plasma spraying of either aluminium or a mixture of iron and aluminium in the desired ratio with an objective of obtaining iron aluminides dispersed with an alumina phase. All the carbon steel substrates were cleaned and grit blasted to remove the oxides present on the surface prior to the plasma spraying experiments.

Coatings of various thicknesses were deposited on carbon steel substrates using various power levels, feed rates, velocities, and substrate pre-heat temperatures. Table II provides a list of spray parameters, and the thicknesses of the coatings obtained on the carbon steel substrates. Coatings with thicknesses ranging from 0.25–1 mm were obtained, and the coatings peeled off from the substrate above a coating thickness of 0.75 mm. Coatings were obtained by varying the power levels from 30–50 kW, and the velocities from sub-sonic to Mach I. Pre-heating was

TABLE II Spray parameters

Sample	Target Fe/Al ratio (wt %)	Method of mixing	Power (kW)	Velocity	Substrate temperature, (°C)	Average coating thickness (mm)
121394-5	86/14	Blended	30	Subsonic	–	0.25
121494-3	67/33	Blended	30	Subsonic	–	0.275
121594-11	67/33	Blended	32	Subsonic	–	0.25
121594-15	86/14	Blended	32	Mach I	–	0.25
40395-5	67/33	Blended	40	Subsonic	520–680	0.25
40795-2	1:1	Dual fed	48	Subsonic	480–615	1.5
40795-4	3:1	Dual fed	48	Subsonic	520–660	1.0

carried out by traversing the plasma across the substrate for a desired number of passes either to oxidize the surface or to attain a stable temperature prior to plasma spraying of either aluminium powder or a mixture of iron and aluminium powders. A thermocouple placed at the centre of the substrate allowed monitoring of the pre-heat temperature. Coated substrates were then annealed in argon for 1 h at 600 °C, heated to 800 °C for 1 h, heated again to 1100 °C for 1 h, and then cooled in the furnace.

X-ray diffractometry with CuK_α radiation was carried out to identify the phases present in the as-sprayed and annealed coatings. In some cases, X-ray diffraction patterns were plotted without full intensity to show the presence of minor and trace phases. Optical microscopy, and Vickers microhardness measurements were carried out on polished and etched cross-sections.

3. Results

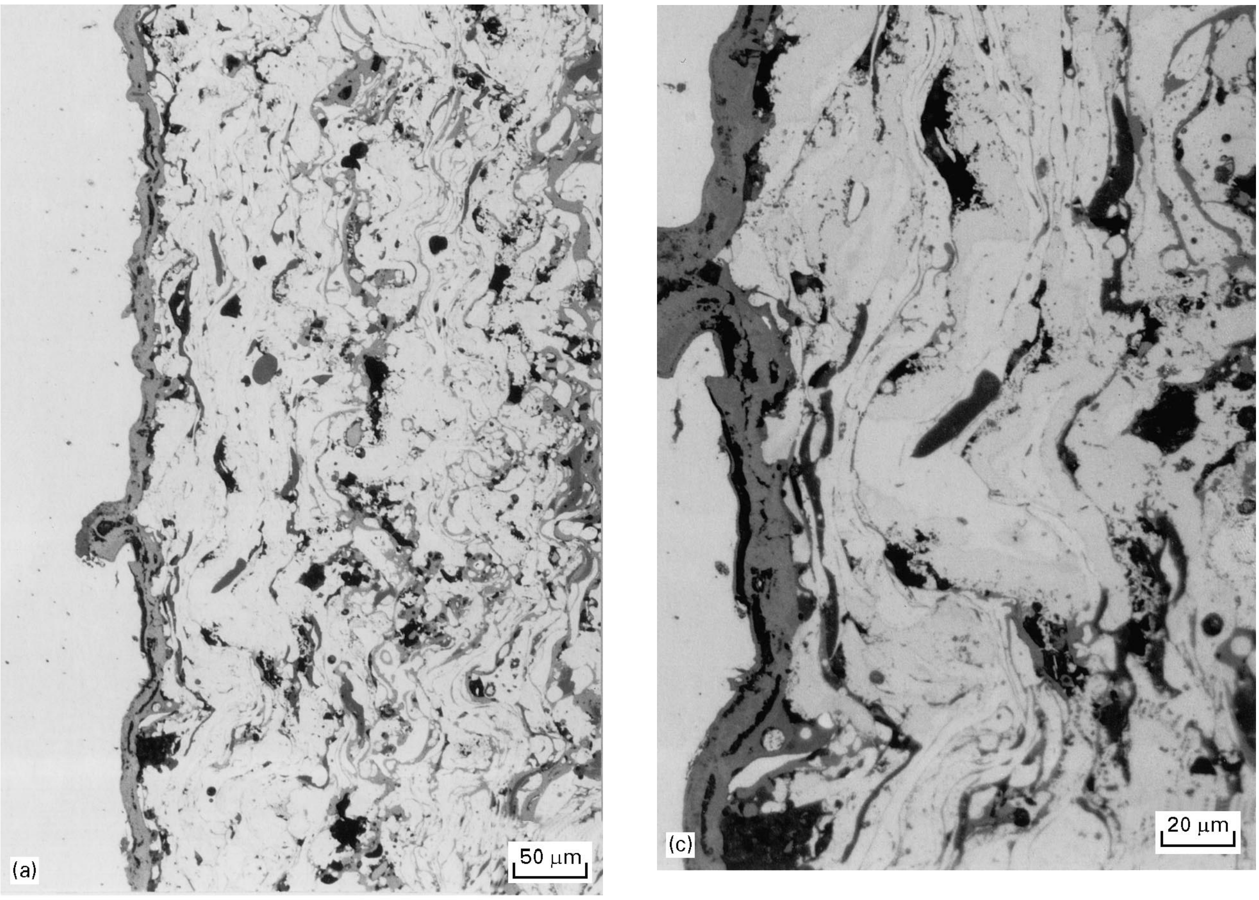
Cross-sections of coatings deposited on carbon steel substrates which were pre-heated to 690 °C in four passes and then plasma sprayed with aluminium in two passes, were examined for their microstructural features. The microstructures showed a grey phase next to the substrate with a Vickers microhardness value of 403 kg mm^{-2}, and an aluminium coating on top of this grey phase. The Vickers microhardness of the substrate and aluminium layer were 160 and 35 kg mm^{-2}, respectively.

X-ray diffraction analysis of the coating revealed the presence of small quantities of Al_5Fe_2 and $Al_{86}Fe_{14}$ along with $FeAl_2O_4$ as the major product phase. The Vickers microhardness values, and the presence of both $FeAl_2O_4$ and iron aluminides, suggest that a thermite reaction between aluminium and iron oxide occurred as a result of plasma-spraying of aluminium on to a pre-heated substrate.

The thickness of the grey phase formed next to the substrate was found to depend on the pre-heat temperature of the substrate. Increase of pre-heat temperature and the number of pre-heat passes allowed extensive oxidation of the surface, and iron oxide formed on the substrate reacted with the plasma-sprayed aluminium. For example, Fig. 1 shows the microstructures obtained after pre-heating the substrate to 700 °C in one pass, followed by plasma spraying of aluminium in three passes. In this case, Vickers microhardness of the coating next to the substrate was only 281 kg mm^{-2} with a standard deviation of 35 kg mm^{-2}. Hardnesses of the substrate and aluminium were close to 160 and 35 kg mm^{-2}, respectively.

Systematically increasing the pre-heat time and the substrate temperature resulted in the formation of different oxides. The microstructures of a coated substrate heated to 1100 °C in five passes and maintained at that temperature for a minute prior to plasma spraying of aluminium in two passes is shown in Fig. 2. The Vickers microhardness of the grey phase in the coating is 639 kg mm^{-2} with a standard deviation of 265 kg mm^{-2}, which is four times that of the base substrate hardness of 156 kg mm^{-2}. A layering of the product phases can be observed in Fig. 2, and the separation of product from the substrate can be attributed to the differences in thermal expansion coefficients of the product phase/s and the substrate. The exothermic thermite reaction was observed to be violent, and excess aluminium bubbled within seconds after it was deposited on the substrate. X-ray diffraction analysis of the coating revealed that the product phases consisted of $FeAl_2O_4$ and Al_2O_3. The large variation in the Vickers microhardness can be attributed to the distribution of Al_2O_3 and $FeAl_2O_4$ in the coating. The Vickers microhardness of the coating increased to 729 kg mm^{-2} with a standard deviation of 132 kg mm^{-2} when aluminium was plasma sprayed on to a substrate pre-heated to 1200 °C prior to plasma spraying of aluminium.

The X-ray diffraction pattern of a coating obtained on a substrate pre-heated to 850 °C in three passes and sprayed with aluminium in one pass is shown in Fig. 3. It is interesting to note the presence of aluminium along with the FeO, Fe_3O_4, and iron phases, which clearly indicates that pre-heating results in formation of oxides. The presence of iron along with a trace amount of FeAl, and unreacted aluminium suggests that iron oxide was reduced by aluminium, resulting in metallic iron, small amounts of FeAl and alumina phases. Some of the peaks identified by JCPDS (Joint Committee on Powder Diffraction Standards) are compared with the X-ray pattern, and are plotted in Fig. 3 with JCPDS comparisons. Plasma spraying of aluminium in two passes on to a substrate heated to 1100 °C shows a very complex X-ray pattern with



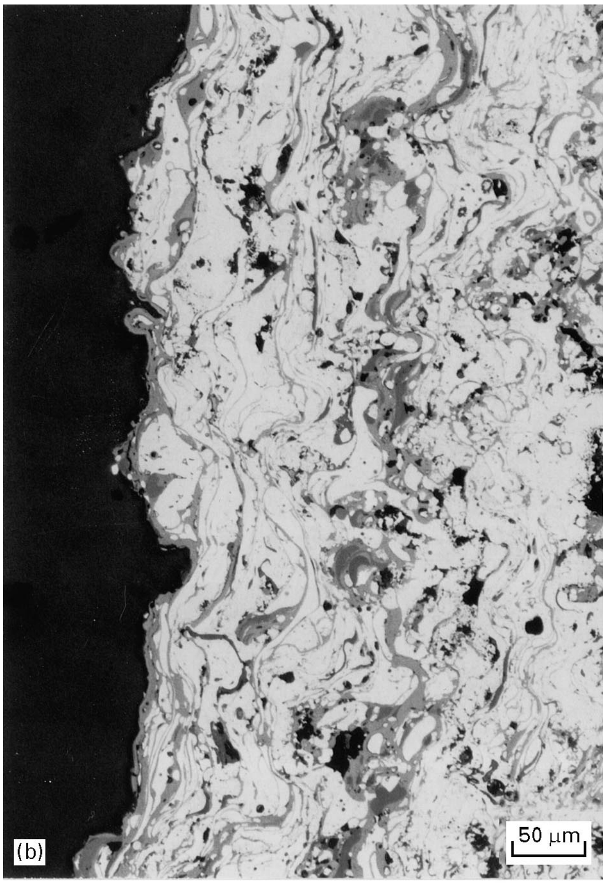


Figure 1 Microstructure of a plasma-sprayed coating of aluminium on a pre-heated carbon steel substrate. Substrate was pre-heated to 700 °C in one pass, and aluminium was sprayed in three passes: (a) 200 ×, (b) 200 ×, (c) 500 ×.

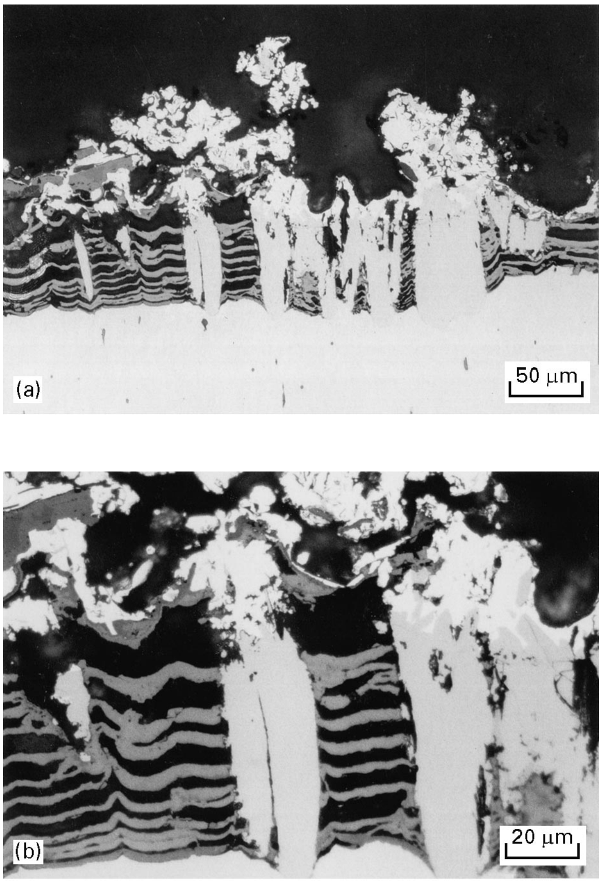


Figure 2 Microstructure of a plasma-sprayed coating of aluminium on a pre-heated carbon steel substrate. Substrate was pre-heated to 1100 °C in five passes, and aluminium was sprayed in two passes: (a) 200 ×, (b) 500 ×.

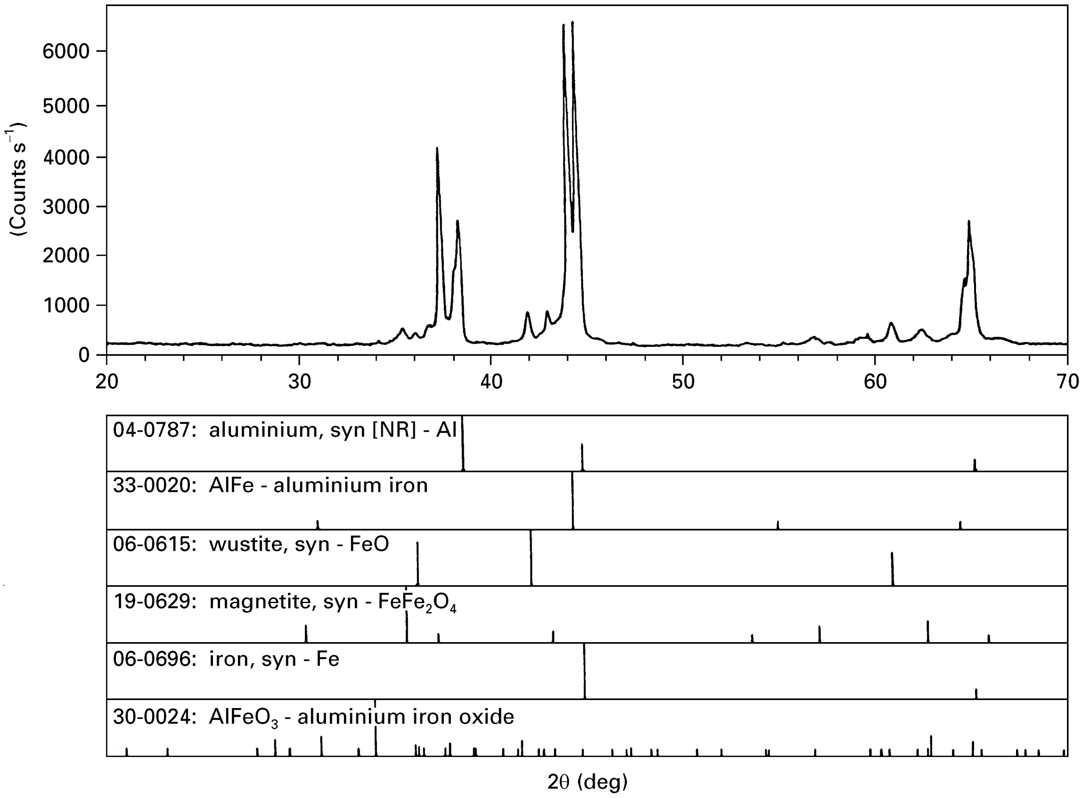


Figure 3 X-ray diffraction pattern of a coating obtained on a carbon steel substrate by pre-heating the substrate to 850 °C in three passes prior to plasma spraying of aluminium in one pass.

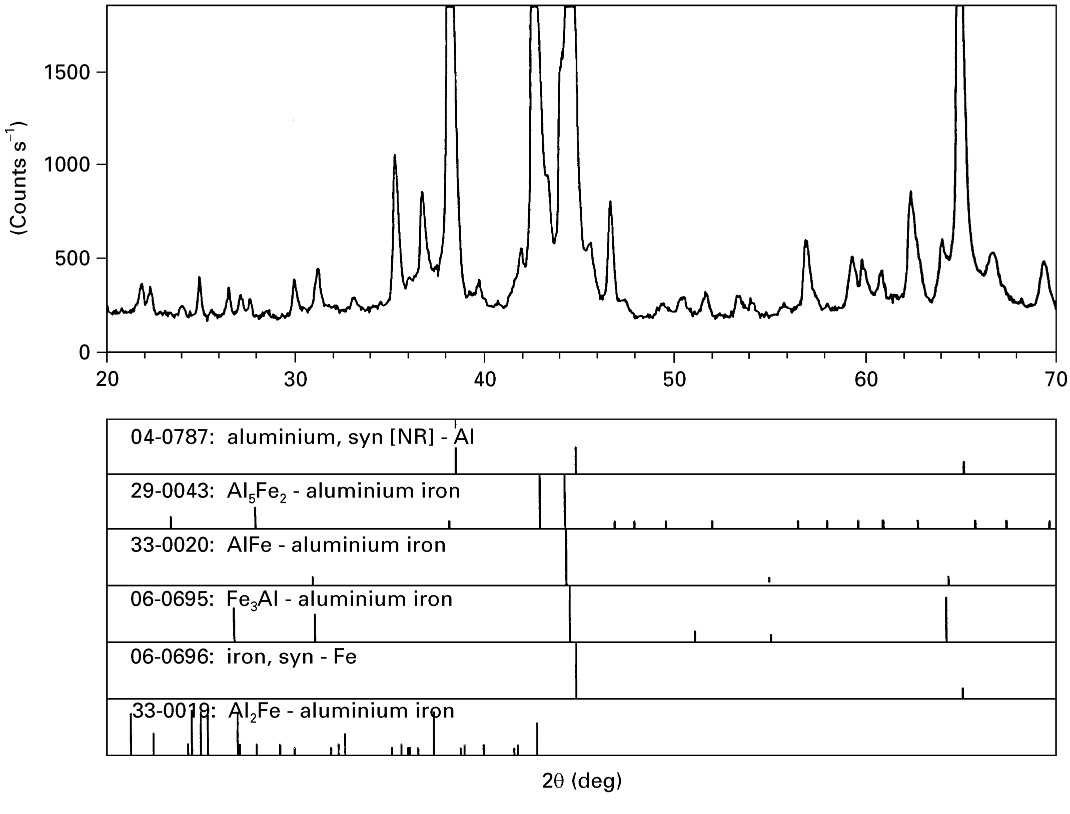


Figure 4 X-ray diffraction pattern of a coating obtained on a carbon steel substrate by pre-heating the substrate to 1100 °C in five passes prior to plasma spraying of aluminium in two passes.

several different phases. Some of the non-oxide phases are compared with JCPDS patterns in Fig. 4.

Feeding of iron and aluminium powders into the plasma with iron and aluminium in a ratio of 1:1 (corresponding to FeAl) resulted in a coating consisting of aluminium, iron, $FeAl_2O_4$ and iron aluminide phases, as shown in Fig. 5. Subsequent annealing in argon for 1 h at 600 °C, 1 h at 800 °C, and 1 h at 1100 °C reduced the intensity of the aluminium peak and increased the intensity of the iron peak

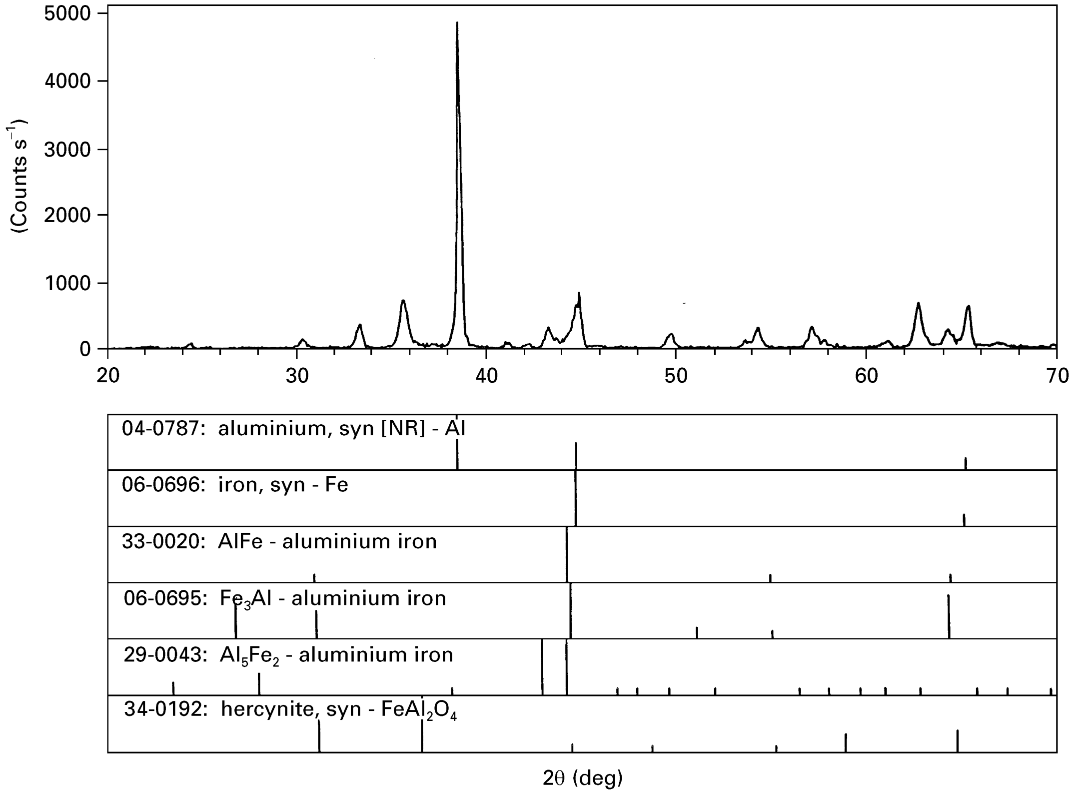


Figure 5 X-ray pattern of a coating obtained with iron and aluminium in a ratio of 1:1 (corresponding to FeAl, dual fed) with 50 kW power and at subsonic conditions.

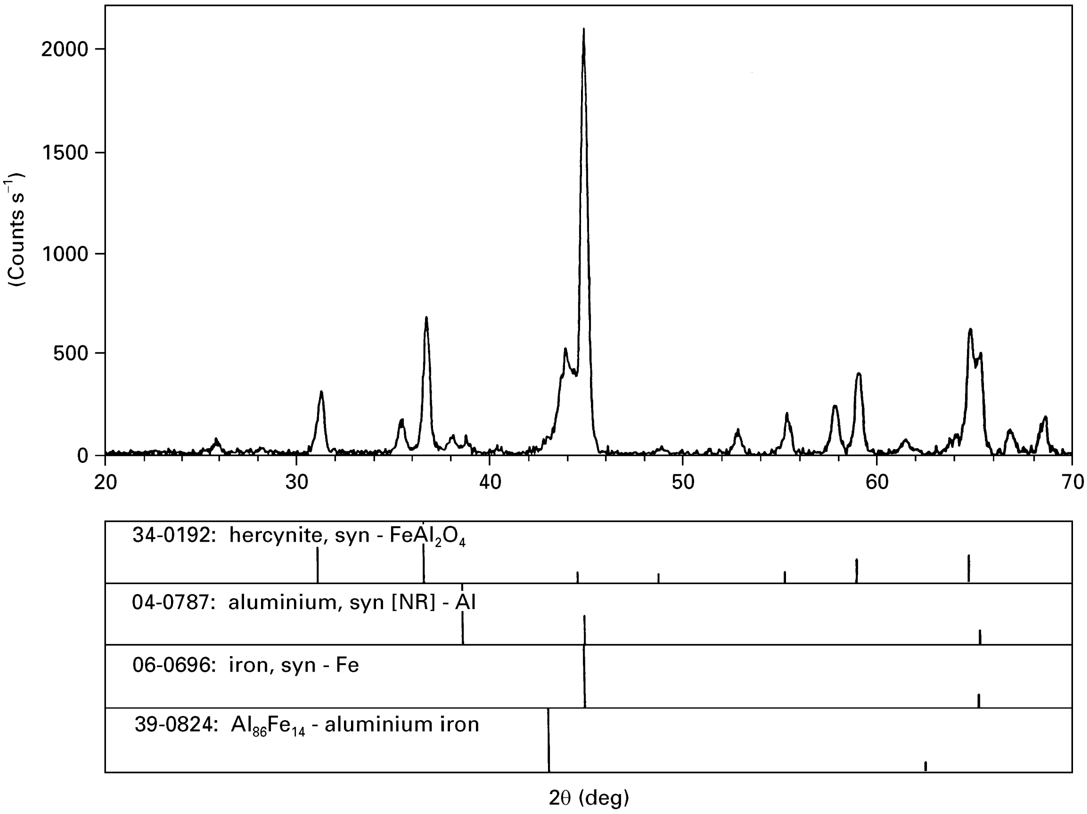


Figure 6 Annealing of the coating obtained with iron and aluminium in a ratio of 1:1 (corresponding to FeAl, dual fed) with 50 kW power and at subsonic conditions. (Compare Figs 5 and 6).

significantly. This can be attributed to the reaction of aluminium with the oxidized substrate. The $FeAl_2O_4$ content increased after heating, as can be seen by comparison of the relative intensities of $FeAl_2O_4$ to the aluminium peaks (compare Figs 5 and 6). Plasma spraying a mixture of iron and aluminium by increasing the ratio of Fe/Al to 3/1 (corresponding to Fe_3Al) resulted in $FeAl_2O_4$, $Al_{86}Fe_{14}$, iron, and aluminium phases (in decreasing order). Annealing of the coating resulted in an increase of $Al_{86}Fe_{14}$, and a decrease of $FeAl_2O_4$ with very little free iron or aluminium present.

Table III shows a list of phases observed under different spraying conditions. The variety of phases produced are influenced by the aluminium and iron concentrations, the pre-heat temperatures, and the power levels. The presence of phases such as $FeAl_2O_4$ and iron aluminides such as $Al_{86}Fe_{14}$, FeAl suggests that exothermic diffusional reactions can take place on the substrate after plasma spraying of either aluminium or a mixture of iron and aluminium powders. The high Vickers microhardnesses of the coatings can be attributed to the presence of alumina, and mixed spinel phases based on alumina and iron oxide.

When a mixture of iron and aluminium were sprayed at a sonic velocity at 40 kW, the resultant coating consisted of iron, $FeAl_2O_4$, aluminium and a small amount of Al_5Fe_2 phase (Fig. 7). After annealing the coating at 600 °C for 1 h, 800 °C for 1 h, and 1100 °C for 1 h, the iron content decreased dramatically and FeAl became the major phase. The disappearance of aluminium and $FeAl_2O_4$ to trace levels suggests that annealing resulted in the formation of iron aluminide phases and the reduction of spinel phase (Fig. 8). The presence of spinel can be inferred by comparing Figs 7 and 8 to the previous figures.

4. Discussion

The Fe–Al phase diagram (see Fig. 9) shows that at least five equilibrium iron aluminide phases can be obtained, depending on the temperature and the relative concentration of aluminium [20]. Iron aluminide phases of Fe_3Al and FeAl have been studied extensively during the last decade due to their high melting points, and good mechanical properties, as compared to the other iron aluminides such as $FeAl_2$, Fe_2Al_5, and $FeAl_3$. Increasing the aluminium content beyond the FeAl phase boundary results in iron aluminides with melting points lower than FeAl (by as much as 300 °C), and some of the compounds have very limited phase boundaries. It is important to note from the experiments that aluminium-rich iron aluminides formed initially, and further annealing resulted in the formation of either FeAl or Fe_3Al. Formation of aluminium-rich iron aluminide ($FeAl_3$) was also observed by Rabin and co-workers [21, 22] in the reaction synthesis of iron aluminides, and the iron-rich aluminide

TABLE III Observed phases in selected plasma-sprayed coatings obtained on carbon steel substrates

Sample	Target Fe/Al ratio (wt %)	Method of mixing	Power (kW)	Velocity	Pre-heat or post-spray annealing	Average coating thickness (mm)	Observed phases[a]
94-2090	100 Al	NA[b]	–	Subsonic	900 °C pre-heat	–	$FeAl_2O_4$
32395-20	86:14	Blended	40	Subsonic	–	0.225	Fe^{vs}, Al^{s}, $FeAl_2O_4^{w}$, $Al_2O_3^{vw}$
32395-16	86:14	Blended	44	Mach I	–	0.200	Fe^{vs}, $FeAl_2O_4^{s}$, Al^{w}
32395-16	86:14	Blended	44	Mach I	Post-spray 1 h, 600 °C 1 h, 800 °C 1 h, 1100 °C furnace cool	0.200	$AlFe^{vs}$, Fe^{s} $FeAl_2O_4^{vw}$, $Al_2O_3^{w}$, Al^{t}
41895-4	1.2:1	Dual fed	50	Subsonic	800 °C pre-heat	0.750	$FeAl_2O_4^{vs}$, $Al_{86}Fe_{14}^{s}$, Fe^{vw}, Al^{t}
41895-2	1.2:1	Dual fed	50	Subsonic	800 °C pre-heat post-spray 1 h, 600 °C 1 h, 800 °C 1 h, 1100 °C furnace cool	0.750	$Al_{86}Fe_{14}^{vs}$, $FeAl_2O_4^{s}$, Fe^{vw}, Al^{t}
41895-11	1:1	Dual fed	50	Subsonic	–	0.475	Al^{vs}, Fe^{s}, $FeAl_2O_4^{w}$, $Al_5Fe_2^{vw}$, Fe_3Al^{t}
41895-8	1:1	Dual fed	50	Subsonic	Post-spray 1 h, 600 °C 1 h, 800 °C 1 h, 1100 °C	0.475	Fe^{vs}, $FeAl_2O_4^{s}$, $Al_{86}Fe_{14}^{w}$, Al^{t}

[a] vs = very strong, s = strong, w = weak, vw = very weak, and t = trace.
[b] NA = non applicable.

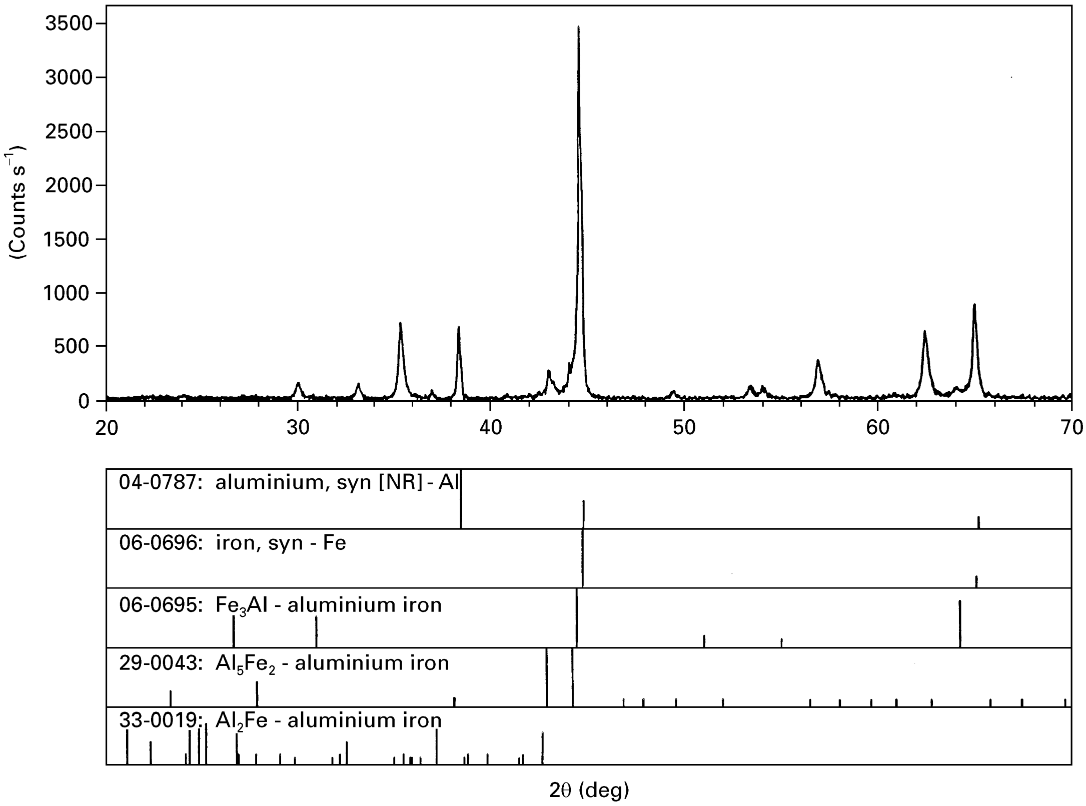


Figure 7 X-ray pattern of a coating obtained with blended iron and aluminium in a weight per cent ratio of 86/14 (corresponding to Fe_3Al) with 44 kW power and at Mach I conditions.

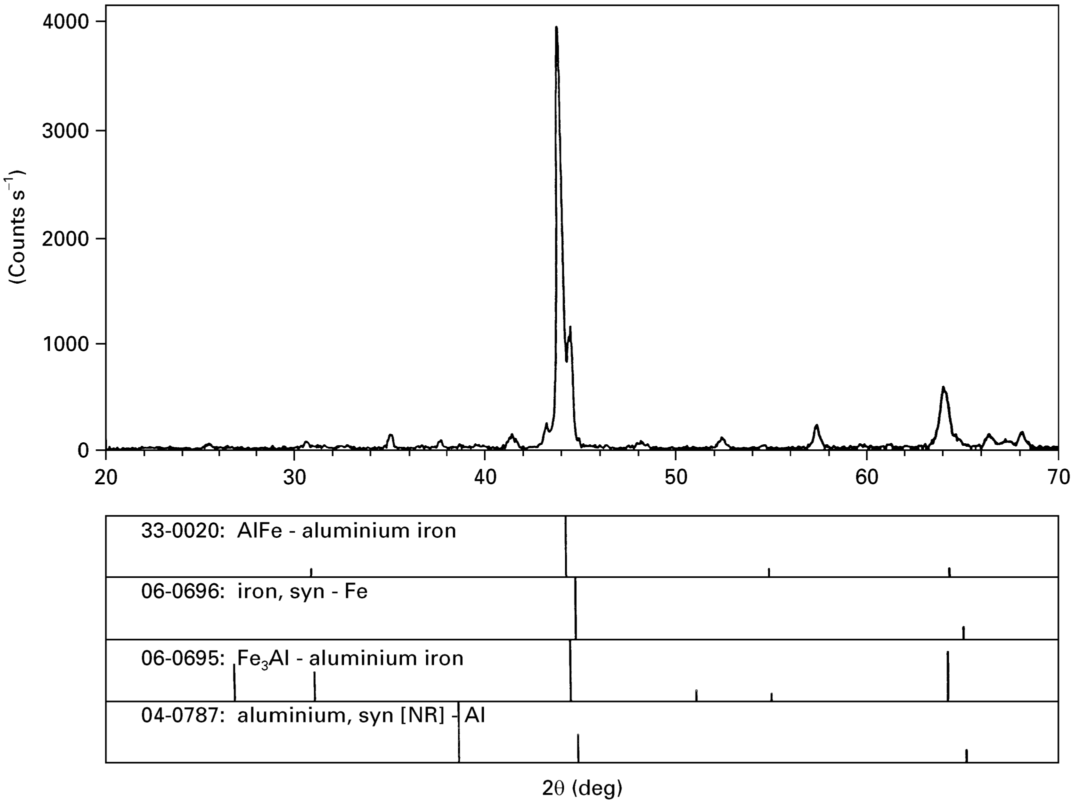


Figure 8 Annealing of the coating obtained with blended iron and aluminium in a weight per cent ratio of 86/14 (corresponding to Fe_3Al) with 44 kW power and at Mach I conditions.

precipitated only after more iron dissolved into the particles. Joslin *et al.* [23] also observed the formation of $FeAl_3$, and $FeAl_2$ during the reaction synthesis of iron aluminides of Fe–35.8 at % Al. The formation of aluminium-rich compounds were also observed even when nickel and aluminium were vacuum plasma sprayed by Chen and Herman [24], and by Deevi *et al.* [25] in plasma spraying of nickel and aluminium

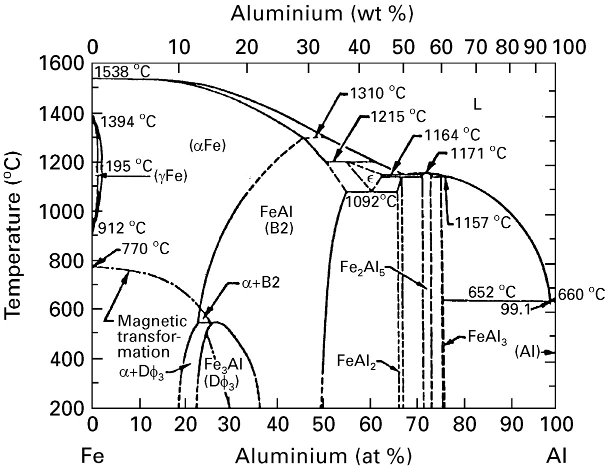


Figure 9 Equilibrium phase diagram of the Fe–Al system.

on to carbon steel substrates. To identify the similarities between the nickel and iron aluminides, a list of plasma-spray parameters and the associated X-ray phases observed in the as-sprayed coatings from a mixture of nickel and aluminium [25] are provided in Table IV.

Unlike in the case of combustion synthesis experiments, plasma spraying requires the use of larger particle sizes of iron and aluminium powders to ensure uniform flow through the powder feeders, and through the plasma gun at either sub- or supersonic velocities. Some of the non-uniformity observed in the microstructures implies that the density differences between iron and aluminium lead to screening of powders. Also, the intense heat available in the plasma can generally melt the particles, and the reaction between the constituents can take place in molten conditions. Therefore, in plasma spraying, the reaction between iron and aluminium can occur between a splat of molten aluminium and molten iron. Once a product layer is formed, further reaction of aluminium with iron is controlled by the diffusional coefficients of aluminium through the product layer. The fast cooling rates of plasma-sprayed coatings may hinder the diffusional reaction/s. The solidification rates of plasma-sprayed coatings are at least two to three orders of magnitude higher than the cooling rates observed in the combustion synthesis of FeAl and Fe_3Al compounds [26]. Therefore, annealing of coatings is required to facilitate further diffusional reaction.

The presence of Al_2O_3 in the as-sprayed coatings obtained from a mixture of iron and aluminium without any pre-heating of the substrate suggests that part of the aluminium oxidizes due to the oxygen present in the plasma spray chamber. It may be difficult to control the oxidation of aluminium in a plasma spray technique because the reaction of aluminium with oxygen is highly exothermic and releases 400 kcal mol^{-1} energy. Oxidation of aluminium can be prevented by depositing the coatings in a vacuum chamber as in the case of a vacuum plasma spray technique. The vacuum plasma spray technique may

TABLE IV Observed phases in selected plasma-sprayed coatings of nickel aluminides obtained on carbon steel substrates

Sample	Target Ni/Al ratio (wt %)	Method of mixing	Power (kW)	Velocity	Spray annealing	Average coating thickness (mm)	Observed phases[a]
32395-32	87:13	Blended	40	Subsonic	–	0.225	Ni^{vs}, Al_3Ni^{s}, Al^{w}, $Al_3Ni_2^{vw}$
32395-32	87:13	Blended	40	Subsonic	Post-spray 1 h, 600 °C 1 h, 800 °C 1 h, 1100 °C furnace cool	0.225	Ni^{vs}, $AlNi_3^{s}$ Al_3Ni^{w}, Al^{vw}
32395-4	87:13	Blended	44	Mach I	–	0.200	Ni^{vs}, Al^{s}, Al_3Ni^{w}, $Ni_5Al_3^{vw}$
32395-4	87:13	Blended	44	Mach I	Post-spray 1 h, 600 °C 1 h, 800 °C 1 h, 1100 °C furnace cool	0.200	$NiAl_3^{vs}$, Al^{s}
41895-12	1:1	Dual fed	45	Subsonic	–	0.775	Ni^{vs}, Al_3Ni^{s}, Al^{w}, $Ni_5Al_3^{vw}$, $Al_{0.42}Ni_{0.58}^{t}$
40795-9	95:5	Encapsulated powder	37	Subsonic	Preheat	0.150	Ni^{vs}, Al^{s}, $Al_3Ni_2^{t}$
40795-9	95:5	Encapsulated powder	37	Subsonic	100° preheat post-spray 1 h, 600 °C 1 h, 800 °C 1 h, 1100 °C	0.150	Ni^{vs}, $AlNi_3^{s}$, Al^{w}

[a] vs = very strong, s = strong, w = weak, vw = very weak, and t = trace.

also favour the formation of the desired intermetallic phases from a mixture of elemental powders because the substrate temperature is generally around 800–900 °C, whereas the substrate temperature in a plasma spray technique is at best 300 °C, unless the substrate is intentionally pre-heated by traversing the plasma gun, as is done in the present work.

It is also interesting to note that the iron oxide present on the surface can be reduced by plasma spraying of aluminium, and the reduction leads to the *in situ* formation of iron and Al_2O_3, as shown by the reaction

$$Fe_2O_3 + 2\,Al \rightarrow Fe + Al_2O_3 \qquad (1)$$

In situ formed iron can react with the molten aluminium splat, forming an iron aluminide phase of either FeAl or some other iron aluminide phase [18, 19]. As described earlier, the presence of oxides and the reaction of aluminium with the oxides on the substrate results in coatings with high hardnesses.

The experimental observations suggest that *in situ* thermite reactions with reactive spraying can be used to harden the metallic surfaces and may allow deposition of coatings for aggressive environments. Some of the coatings may also act as bond coats between the substrate and a variety of other thermal spray coatings. Currently, we are exploring innovative plasma torch designs to enhance the residence times of the powders within the plasma, and are also optimizing process parameters for depositing desired intermetallic phases. High-velocity oxy-fuel (HVOF) spraying may also allow the formation of desired intermetallic coatings because mixtures of fine powders with average particle sizes in the range of 6–10 μm can be fed through an HVOF gun. Reaction synthesis principles can be implemented by a variety of manufacturing processes as shown in Fig. 10, and optimization of reactive spray process parameters may yield unique coatings on the substrate for protection against wear, oxidation, and corrosion. An understanding of the process parameters controlling the reactive spraying will also aid and extend the reaction synthesis principles to thermal spray coatings.

5. Conclusions

1. Plasma spraying technique can be used to initiate a thermite reaction on the surface of an oxidized carbon steel substrate and molten aluminium splats.
2. Thermite reactions resulted in the formation of oxide phases, and the presence of oxide phases led to a significant increase in the hardnesses of the coatings.
3. Feeding a mixture of iron and aluminium led to the formation of aluminium-rich iron aluminide coatings. Subsequent annealing of the coatings resulted in iron-rich aluminide phases.

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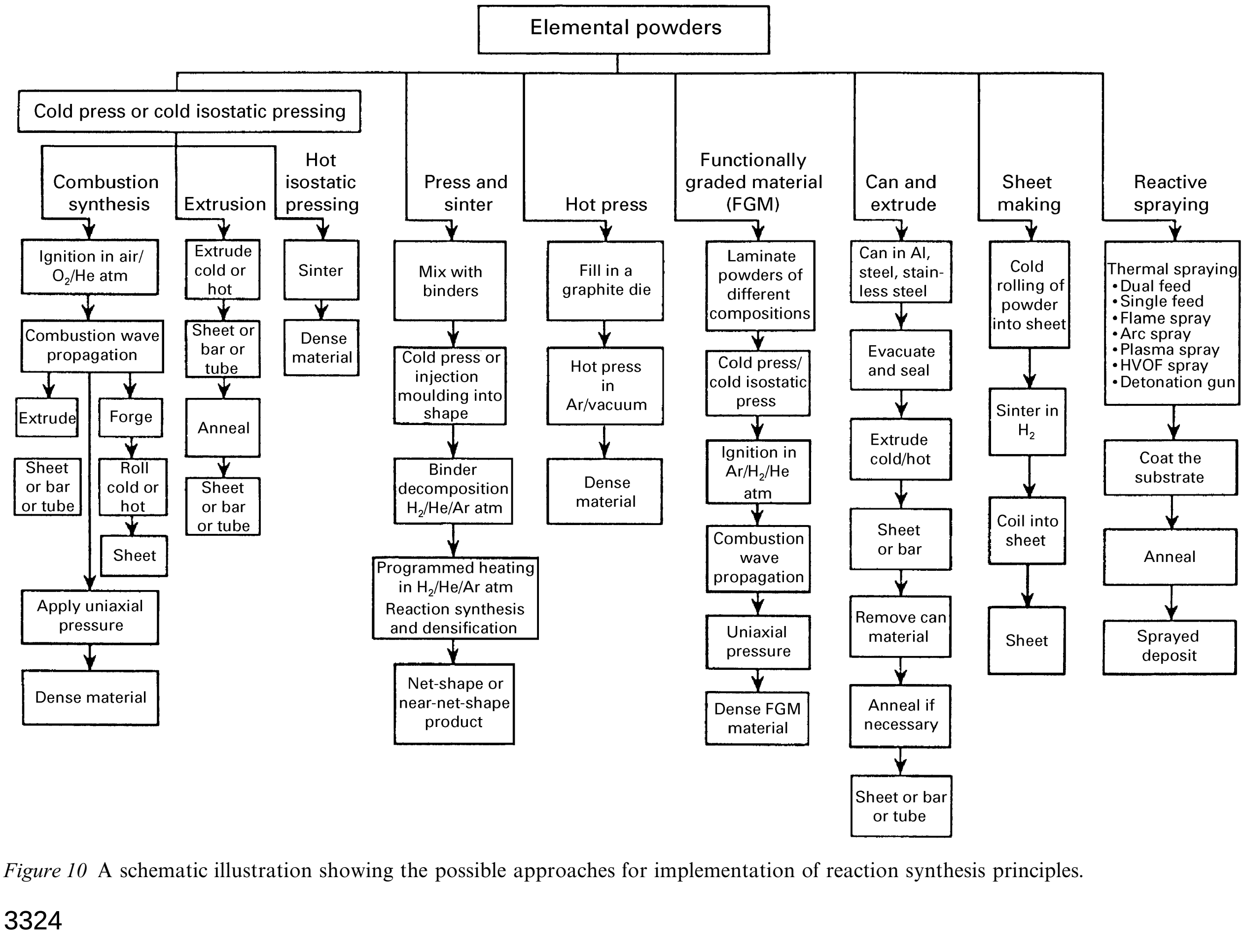

Figure 10 A schematic illustration showing the possible approaches for implementation of reaction synthesis principles.

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