Article

Ni-Al and NiO-Al Composite Coatings by Combustion-Assisted Flame Spraying

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Abstract: A new, cost-efficient and on-site-applicable thermal spraying process for depositing NiAl metallic overlay or bond-coat coatings for high temperature applications by synthesizing the desired intermetallic phases in-flight during oxy-acetylene flame spraying is presented. Base-metal powders were used for spraying and, by adjusting the spraying conditions, excellent NiAl-based coatings were achieved on various substrates, including mild steel, stainless steel and aluminium alloys. Expensive, pre-alloyed or agglomerated powders are avoided and the method is very promising for *in-situ* work and repairs. We call the new method "Combustion-Assisted Flame Spraying" (CAFSY) and its viability has been demonstrated at a pre-industrial level for coating metallic substrates. The NiAl-based coatings produced by CAFSY exhibit very high integrity with good adhesion, very low porosity, high surface hardness and high erosion resistance at a substantially lower cost than equivalent coatings using pre-prepared alloy powders.

Keywords: combustion-assisted flame spraying (CAFSY); combustion synthesis; flame spraying; intermetallic phases

1. State of the Art

Protective coatings can impart superior properties on a substrate and are used in a large number of engineering applications. Table 1 lists the principal coating processes, the typical coating thicknesses attainable, common coating materials, and some applications [1–6]. Not all processes are suitable for all coating materials and not all coating thicknesses are attainable with all methods. Beyond that, the equipment necessary for some processes can be quite complex and, therefore, costly, especially for plasma spraying. Cost analysis can determine whether a coating is a practical solution for a particular application. Present regulations [4] require that ecological criteria of the respective coating processes must also be examined, as not all methods are environmentally equivalent.

Table 1. Principal coating processes and their characteristics [4].

Coating Process	Typical Coating Thickness	Coating Material	Characteristics	Examples
PVD	1–5 μm	Ti(C,N)	Wear resistance	Machine tools
CVD	1–50 μm	SiC	Wear resistance	Fibre coatings
Thermal Spray Coating	0.04–3 mm	Ceramic & Metallic alloys	Wear resistance, Corrosion resistance	Bearings, axles
Hard Chromium Plating	10–100 μm	Chrome	Wear resistance	Rolls
Weld Overlay	0.5–5 mm	Steel, Stellite	Wear resistance	Valves
Galvanisation	1–5 μm	Zinc	Corrosion resistance	Steel sheet
Braze Overlay	10–100 μm	Ni-Cr-B-Si alloys	Very hard, dense surface	Shafts

Thermally sprayed hard coatings are extremely effective at increasing a metallic component's life and value, decreasing machinery down time and improving performance in a wide variety of applications, by imparting improved hardness, wear and corrosion resistance, lowering friction *etc.* Industries utilising thermal spray coatings include but are not limited to aerospace, agricultural, automotive, bio-medical, defence, electronics, energy, food processing, machinery, medical devices, oil and gas, paper making, printing, power generation, semiconductors and others [1].

Thermal spraying is applicable to a large range of coating materials, coating thicknesses and coating characteristics. Thermal spraying methods are grouped into three main categories: flame spraying, electric arc spraying and plasma arc spraying, referring to the energy sources producing the flame to heat the coating material to a molten or semi-molten state. The heated molten particles are accelerated and propelled towards a prepared surface by either the process gases or atomization jets. Upon impact [2], a bond forms with the substrate and the subsequent particles form a lamellar structure. Droplet size and injection velocity [3] are the most important parameters, whereas the injection angle is of lesser importance.

1.1. Flame Spray Coatings

Flame spraying is the most widespread method of imparting a hard protective coating on a metallic substrate. Its main characteristic distinguishing it from HVOF (High Velocity Oxy-Fuel) and plasma spraying is its lower cost and ease of use, although it generally gives lower quality coatings. The principle of operation is simple. A pre-alloyed wire or powder is melted by injection into a gaseous

oxygen-fuel flame at about 50 m/s. The fuel may be acetylene, propane or hydrogen and the flame temperature depends on the gas used; for an oxyacetylene flame it can reach about 3000 °C [2,4,7].

Oxygen-fuel flame spraying is capable of spraying rates of up to about 6 kg/h, although it has temperature and speed limitations. In addition, it relies on the availability of pre-alloyed powders, a fact which reduces its applicability both because of their high cost and their limited compositional range. Nevertheless, the lower cost of the equipment means that it is widely used, especially for repairs and other applications that require mobility.

The performance and applicability of flame spraying has been enhanced in this work by the development of In-Flight Combustion Synthesis which allows the use of simple metal powders instead of pre-alloyed powders.

1.2. Nickel Aluminide Coatings

Nickel-aluminide coatings [8] have attracted significant attention because of their technological and scientific applicability. Due to its relatively low density and high melting point, good thermal conductivity and excellent oxidation resistance, NiAl has long been used as a coating material on industrial and structural elements, where its function is mainly to minimize the thermo-mechanical stresses at the substrate-coating interface and to promote coating adhesion. Its role, however, has mostly been restricted as a bond coat between the core component and a ceramic top coat. Its use as a top coat material has not been reported so far for industrial applications. Such NiAl intermediate coatings are used in applications when wear resistance combined with oxidation or hot corrosion resistance is required. The high temperature oxidation behavior of NiAl coatings has been reported as 750–850 °C in flowing air [9,10]. In general, nickel-aluminium alloys and their derivatives [8] have demand in the aerospace industry and other high performance applications as the yield strength of these alloys increases with increasing temperature.

The other important nickel aluminide [8,10], Ni_3Al, has also drawn attention since, technologically, Ni_3Al is an important strengthening constituent of NiAl, and this combination is used extensively as high temperature structural material for jet engine and aerospace applications. It is responsible for the strength and creep resistance of the super alloys at elevated temperatures. Ni_3Al containing about 25 wt% Al has the ability to form protective aluminium oxide scales, resulting in excellent oxidation resistance. Industrial interest in NiAl and Ni_3Al-based coatings has increased lately and this interest arises because the alloys possess a unique combination of properties including high strength and good oxidation and corrosion resistance at elevated temperatures and relatively low density compared with many Nickel-based, high temperatures super alloys [11–13]. A brief summary of these advantages is given in Table 2.

Table 2. Properties and applications of nickel-aluminide coatings [8].

Properties	Applications
Generally low cost	Turbo charger rotors in diesel engine trucks
Good high temperature oxidation resistance, excellent strength at high strain rates	Die materials for isothermal forging; Moulding material for glass processing
Resistance to carburizing and oxidizing atmospheres	Fixture material for heat treatment of auto parts in high temperature furnaces

Table 2. *Cont.*

Properties	Applications
High temperature strength, good oxidation & corrosion resistance	Rollers for steel slab heating furnaces
Excellent vibration and cavitation resistance in water	Hydro turbine rotors
Low & high temperature strength for cutting tools	Cutting tools
Superior strength & creep resistance	Turbine blades vanes for jet engines.

1.3. Combustion Synthesis (CS)

Combustion synthesis (CS) (a special case of which is the self-propagating high temperature synthesis of solids, SHS), is a low-cost method for the production of various industrially useful materials, especially alloys, oxides, nitrides, carbides *etc.* Today CS has become a very popular approach for preparation of powdered materials, including nanostructured materials and is used in as many as 65 countries [14]. Both solid combustion synthesis (SHS) and solution combustion synthesis (SCS) have been developed.

Combustion synthesis relies on systems able to react exothermally when ignited and to sustain the exothermic reaction to form a combustion wave. The temperature of the combustion can be very high (as high as 4000 °C for some metal carbide systems) and the rate of reaction wave propagation can be very rapid (25 cm/s is not unusual). Hence this process offers the opportunity to investigate reactions in conditions of extreme thermal gradients (as high as 10^5 °C/cm). Under typical SHS conditions the reactants are usually fine powders, mixed and compacted into a pellet to increase the intimate contact between these. The reactant mixture is placed in a refractory container and ignited in air, vacuum or inert atmosphere at a pre-heating temperature rarely higher than 900 °C [15]. Combustion is initiated (sometimes with the aid of a spark) and the combustion zone propagates from one end of the compact to the other until all material has reacted [16,17]. The heat energy released heats up the remaining reagent mixture in front of the combustion zone thus the reaction is self-propagating and continues till the total consumption of the reactants. The final product is obtained rapidly as the whole synthesis process is completed in seconds or minutes. The products of the reaction are often very porous, typically 50% of theoretical density [18] and so pressure is sometimes applied at the time of combustion to increase the final density. In general, a large range of high temperature materials, catalysts, alloys, oxides, nitrides, carbides *etc.* are now produced by CS.

Because of the very high heating and cooling rates during Combustion synthesis, the atomic structure of the materials produced is highly distorted, something which is useful for many catalytic applications. In addition, the low pre-heating temperature of SHS allows for the processing of many sensitive materials than is possible in traditional processes. Another type of CS, Solution Combustion Synthesis (SCS) has recently been shown to be capable of synthesizing nanostructured materials of many types and compositions [19].

In addition to solid combustion or combustion in solution, it is also possible for combustion synthesis to take place between powders in a flame. This fact has been developed in the present work as "Combustion-Assisted Flame Spraying" (CAFSY) method, which is the core innovation of this project. It is a special manifestation of CS and allows for very fast, in-flight reactions between component metal

powders to produce the required coating alloys when they reach the surface of the substrate, instead of relying on expensive pre-alloyed powders.

1.4. SHS of Nickel Aluminides

Nickel aluminides can be produced by self-propagating high-temperature synthesis [20]. The reagents, Ni and Al powders in a compact experience high heating rates, typically hundreds of degrees per second, and the method can produce Ni_3Al, NiAl as well as other phases, depending on the starting mixtures and conditions (e.g., [21–23]). SHS alloy powders are now routinely supplied commercially by various producers since they tend to be very pure and well crystallized but they are very expensive and available in limited compositions.

Reactive plasma spraying of alloys has been reported before and there are a few works devoted to reactive plasma spraying of elemental powders. In those works (e.g., [24–27]), initial powders react during spraying in the SHS regime. Plasma spraying method has the disadvantages discussed earlier and that is why in this work we concentrated on developing NiAl coatings by In-Flight Combustion Synthesis (CAFSY) in oxy-acetylene flame. We have studied the mechanism of synthesis of protective coatings of composite nickel aluminides using only non-agglomerated mixtures of metallic Ni and Al powders, as well as NiO in some cases. Various mixtures of Ni and Al powders are sprayed together in the flow of an oxyacetylene flame and react in-flight ultra-rapidly exothermically and form nickel aluminides.

2. Experimental

The Ni, NiO and Al powders used were obtained from Sulzer Metco 56C-NS (Ni), Shreenivas Chemicals Pvt. Ltd (NiO), and Aluminium Powder Company APOCO Ltd (Al) and had particle sizes of were 45–75 μm, 50–90 μm and 45–90 μm, respectively. In total, five powder mixtures were made by hand in the proportions shown in Table 3.

Table 3. The five samples made by mixing the powders.

Sample #	wt% NiO	wt% Ni	wt% Al
1	58.14	–	41.86
2	–	42.1	57.9
3	–	59.3	40.7
4	–	65.1	34.9
5	–	86.8	13.2

The powder mixtures were then sprayed on stainless steel 304 substrate coupons of dimensions approximately 50 mm × 40 mm × 5 mm using oxy-acetylene flame spraying. Prior to spraying, all samples were sand-blasted to get a rough surface using 0.5–1 mm sand and the roughness of the substrate was measured to be R_a = 2 ± 0.5 μm. Flame spraying was carried out by a Sulzer's Metco Thermospray Gun at various spraying distances and with various substrate temperatures. During spraying, the Ni-Al powder mixtures are ignited by the combustion flame and react producing nickel aluminide compounds on the surface of the coupon. A schematic of the CAFSY process is shown in Figure 1a.

The morphology and microstructure of the composite coatings were examined by scanning electron spectroscopy (SEM) with EDX elemental analysis, optical metallography and X-ray diffraction (XRD). The development of the various intermetallics was monitored by calculating the peak ratio of intensities of particular peaks. The peaks we used were: for Aluminium metal, *hkl*: 111, for NiAl, *hkl*: 220, for Ni_3Al, *hkl*: 311 and for $NiAl_3$, *hkl*: 112. The peaks used were selected so that they were not mixed with any other peaks in the XRD spectra. The various phases were also characterized using microhardness measurements. Physical and mechanical properties of the coatings, such as porosity, surface roughness, erosion wear resistance and coating adhesion strength were also determined. Porosity was determined by image analysis on polished cross section samples (10 measurements per sample). The Leica image analysis method is used extensively for the measurement of porosity and coating thickness. Images are normalized by adjusting the magnification, light intensity and source type and polarization and standardized so that the images examined were comparable on all thin sections sampled. Pores were identified by a process of color segmentation. By placing the cursor on a pore, that pore color, and all pores of that color were electronically identified and tallied. This procedure was repeated until all pores had been accurately identified [28].

The surface roughness (10 measurements per sample) was measured using the portable Time TR200 Roughness Tester (TIME High Technology Ltd, Beijing, China), conforming to ISO standard, the adhesion (3 measurements per sample) was measured using a portable elcometer (110 P.A.T.T.I., Elcometer, Zevenhuizen, The Netherlands) according to ASTM C633-01, the erosion wear was determined by air-born quartz 100–1000 μm with a mass flow of 240 g/min using air pressure in the gun 2.5 bar in the apparatus shown in Figure 1b. Each erosion wear test was carried out for 30 s (4 measurements per sample). The substrate temperature was measured using an industrial IR thermometer UEI INF151.

All results are displayed with error bars estimated in each case taking account of the number of measurements and the trend shown is the best fit to the points calculated by regression analysis.

The effect of processing conditions such as the starting temperature of the flame and of substrate, gas speed, sample composition and particle size of the metal powders, and their feed rate *etc.* were all studied with respect to the composition and morphology of the coatings produced.

Figure 1. (**a**) Schematic diagram of "Combustion-Assisted Flame Spraying" (CAFSY) method; (**b**) Photo of the erosion wear tester developed in our lab and used in this work.
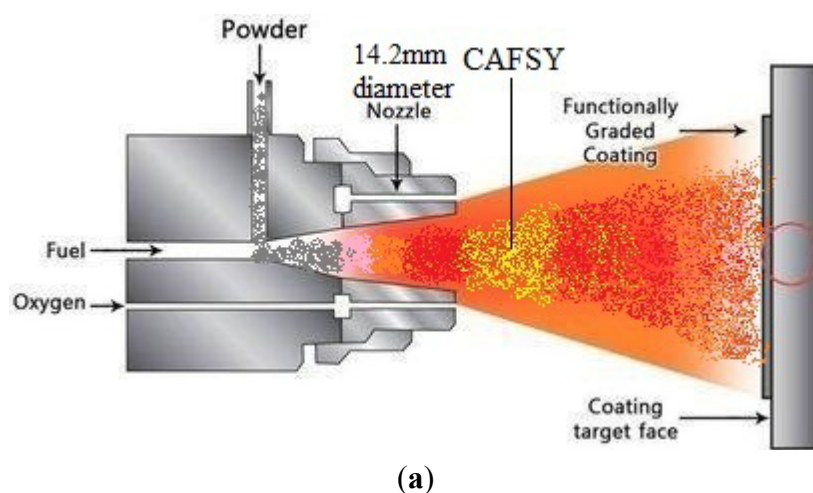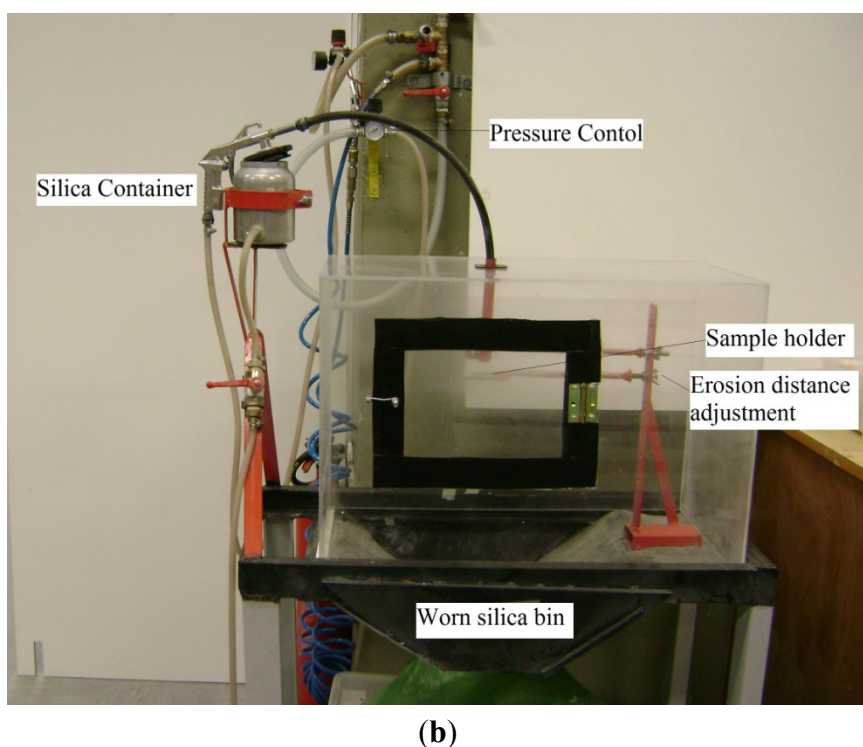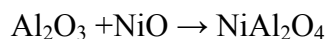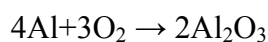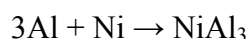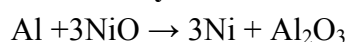

(**a**)

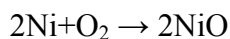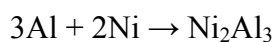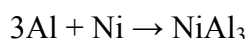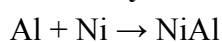**Figure 1.** *Cont.*

(b)

3. Results and Discussion

3.1. Reactions and Formation of Intermetallic Phases by CAFSY Flame Spraying

The XRD results show that the composite coatings consist of various fractions of Ni, Al, Al_3Ni, Ni_3Al, NiAl and small amounts of NiO and spinel $NiAl_2O_4$. The compounds are formed by the following reactions which take place by SHS in-flight in the flame over times of milliseconds:

NiO + Al system	**Ni + Al system**
$Al + 3NiO \rightarrow 3Ni + Al_2O_3$	$Al + Ni \rightarrow NiAl$
$3Al + Ni \rightarrow NiAl_3$	$3Al + Ni \rightarrow NiAl_3$
$4Al + 3O_2 \rightarrow 2Al_2O_3$	$3Al + 2Ni \rightarrow Ni_2Al_3$
$Al_2O_3 + NiO \rightarrow NiAl_2O_4$	$2Ni + O_2 \rightarrow 2NiO$
	$4Al + 3O_2 \rightarrow 2Al_2O_3$
	$Al_2O_3 + NiO \rightarrow NiAl_2O_4$
	$Al + 3Ni \rightarrow Ni_3Al$

Nickel, has a melting point of 1440 °C, aluminium reaches its melting point of 660 °C. As shown in Table 4, the Gibbs free energy of formation of aluminides is negative, *i.e.*, the intermetallic reactions are exothermic. As the aluminium melts in the flame and comes in contact with the heated (probably partially melted) nickel, NiAl (stoichiometric melting point of 1640 °C) is formed by an exothermic reaction, releasing large amounts of heat, aiding the spray coating and encouraging further reactions. The molten aluminium can also react exothermically to form $NiAl_3$ and Ni_3Al. The regime under which these combustion reactions take place depends on a number of parameters. Under some processing conditions the Ni and Al powders do not react completely but coat the intermetallic phases. In addition,

because of the oxygen in the air, the presence of oxides on many areas of the coating is expected and is due to partial oxidation in the combustion flame and immediately after deposition.

Table 4. Gibbs free energy of formation of some nickel aluminides [29].

Reaction	Gibbs free energy of formation ΔG_f° (kJ·mol^{-1})
$Ni + Al \rightarrow NiAl$	−133.0
$Ni + NiAl_3 \rightarrow Ni_2Al_3$	−144.1
$2Ni + 3Al \rightarrow Ni_2Al_3$	−311.0
$Ni + 3Al \rightarrow NiAl_3$	−166.8

The SEM photos in Figure 2 show the surface microstructure and morphology of two coatings together with their XRD spectra. It was found that the coatings made with NiO-Al powder mixtures consist of Al_3Ni, Al_2O_3, Ni, Al and NiO, which indicates that NiO and Al do not react completely by a two-phase chemical reaction. The small amount of $NiAl_2O_4$ spinel phase comes from the chemical reaction $Al_2O_3 + NiO \rightarrow NiAl_2O_4$. The intermetallic Al_3Ni phase arose when contiguous Al and Ni melted eutectically. The Ni-Al coating on the other hand consists of Al, Ni, Al-Ni, Al_3Ni and small amounts of NiO, Al_2O_3 and spinel $NiAl_2O_4$.

The SEM/EDAX microstructural examinations of the composite coatings (Figure 3) presented a multiphase situation. The splat grey phases visible can be assigned to a Ni-rich, Al-rich or intermetallic phases (Al_3Ni, NiAl). The light grey zones are identified with the oxides Al_2O_3 and NiO. The $NiAl_2O_4$ phase could not be found on the surface. Thus, it can be concluded that the microstructure of the composite coating is built of three main phases with different morphologies (Metallic/Intermetallic phase, Oxide phase and Spinel phase).

Because best spraying results were received using specific Ni-Al powder mixtures further studies were based on this system, a good example of which is shown in the SEM microstructure analysis of the cross section shown in Figure 3.

Figure 2. Scanning electron spectroscopy (SEM) photos of (**a**) NiO-Al and (**b**) Ni-Al coatings and (**c**,**d**) corresponding X-ray diffraction (XRD) spectra.
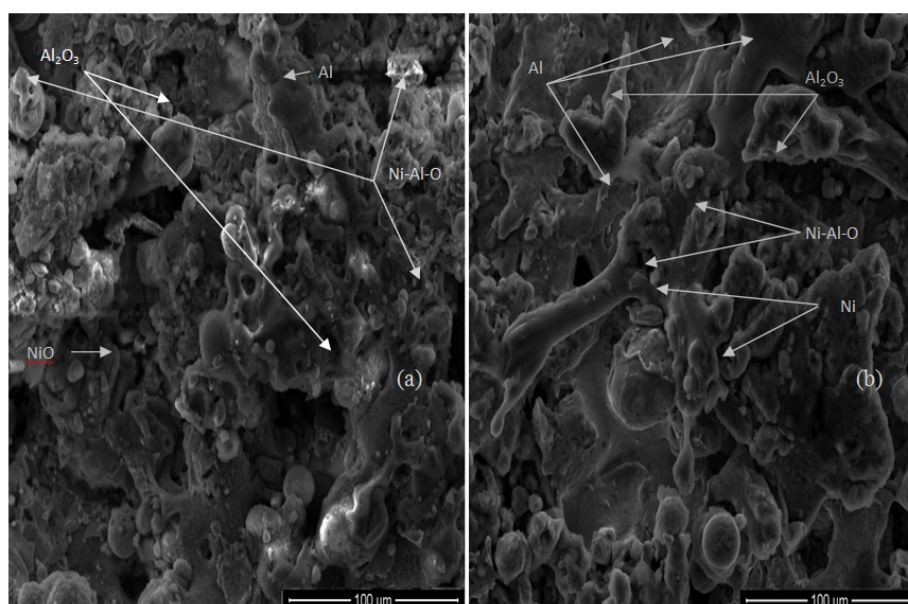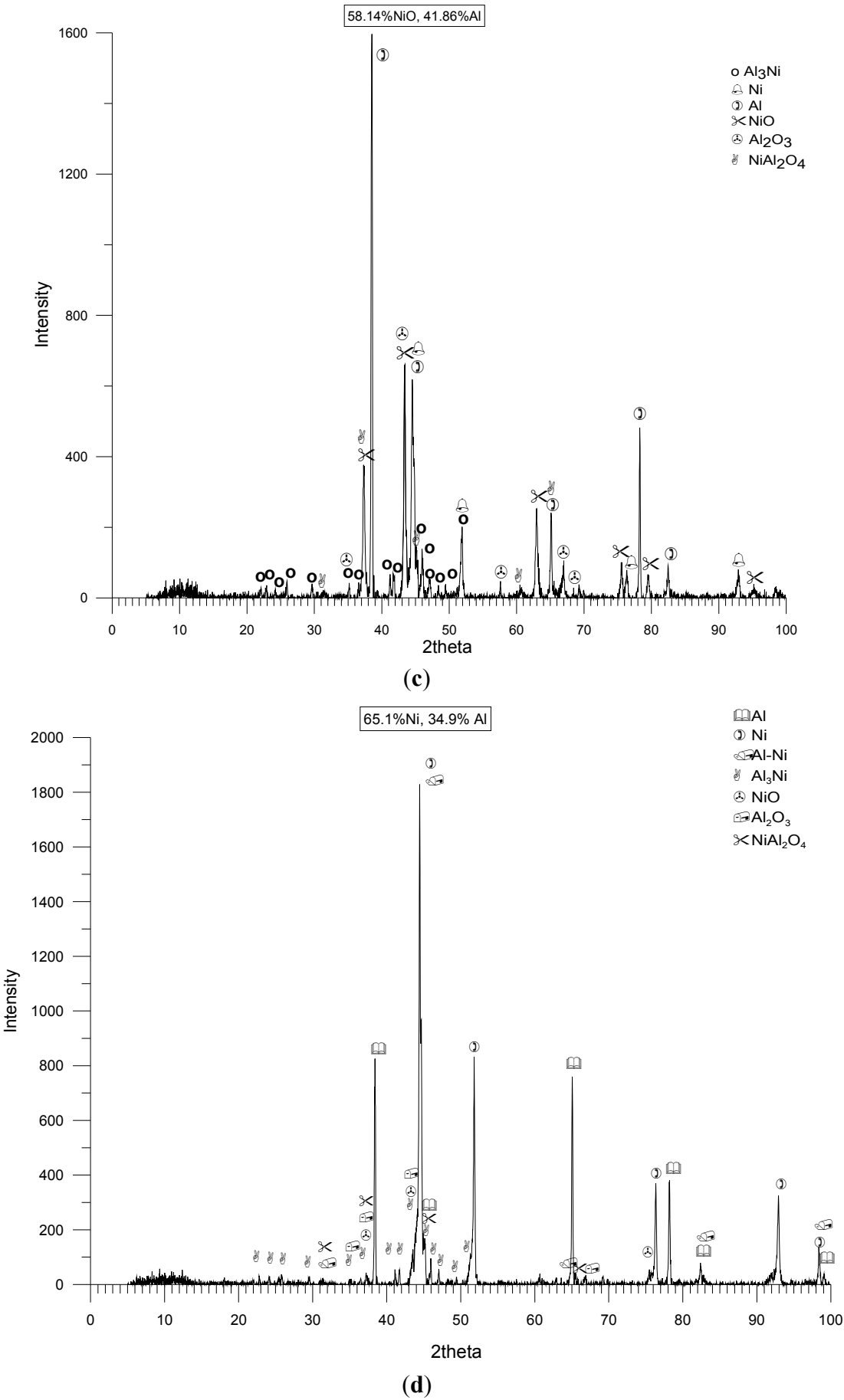
Figure 2. *Cont.*

(c)

(d)

Figure 3. (**a**) SEM/EDAX microstructure analysis of cross section and (**b**) a typical XRD spectrum of the system Ni-Al.

(a)

Figure 3. *Cont.*

(**b**)
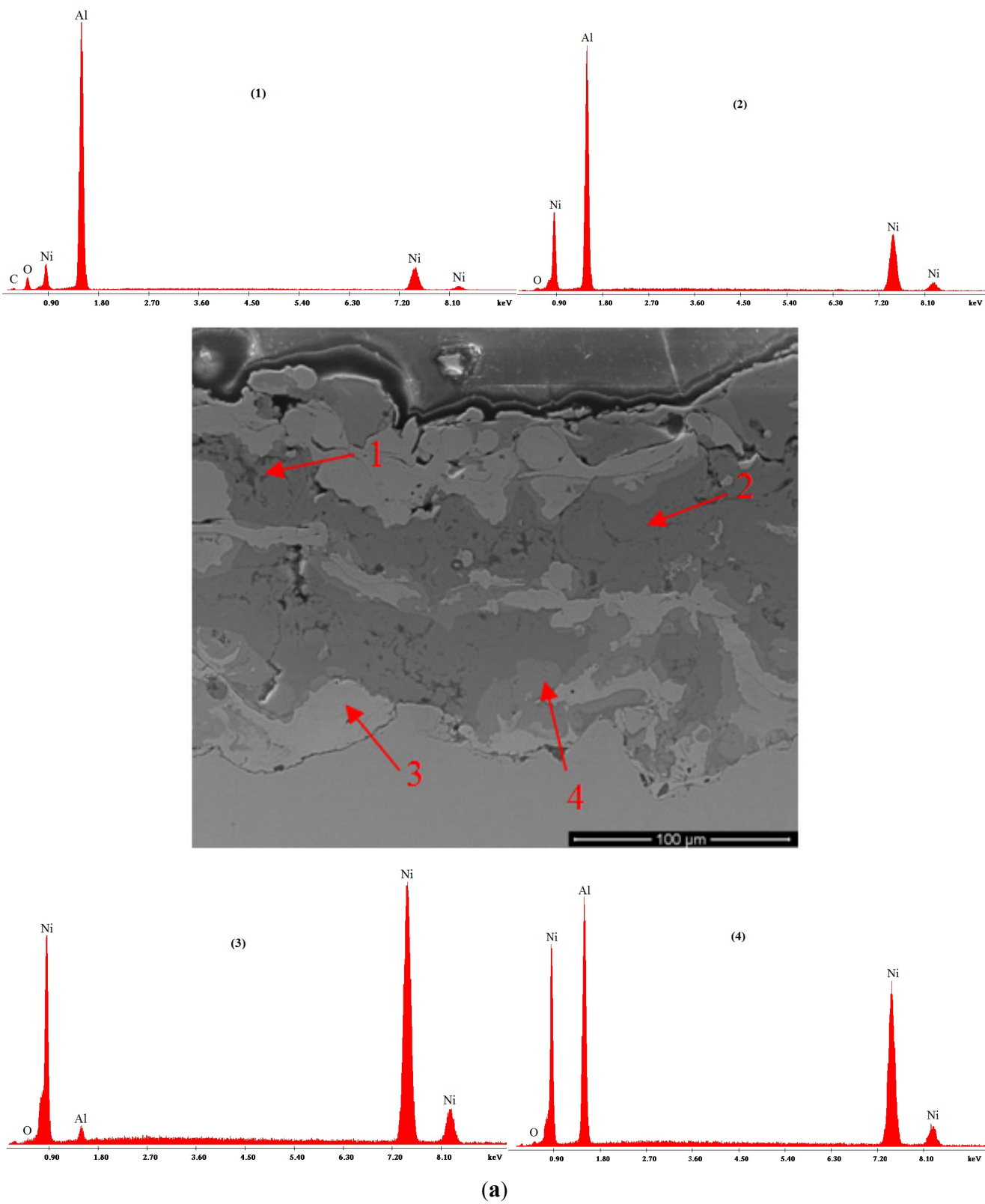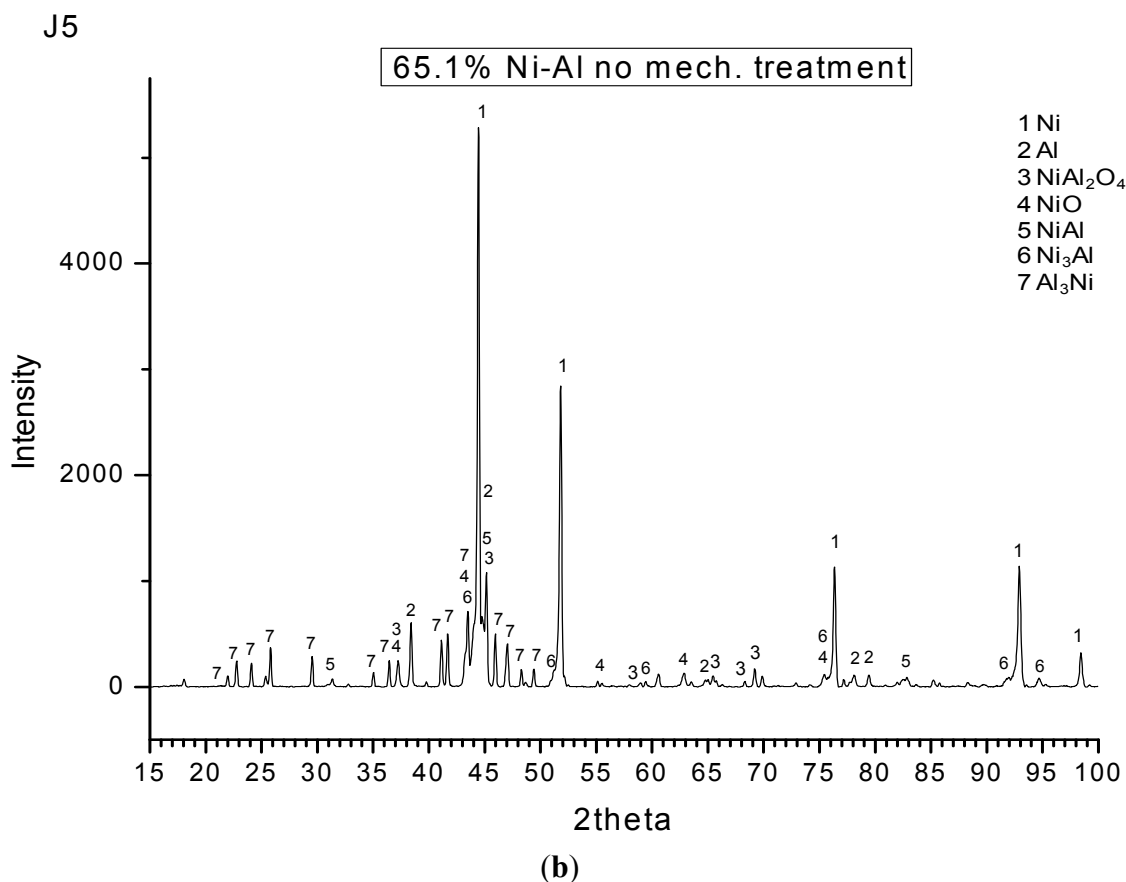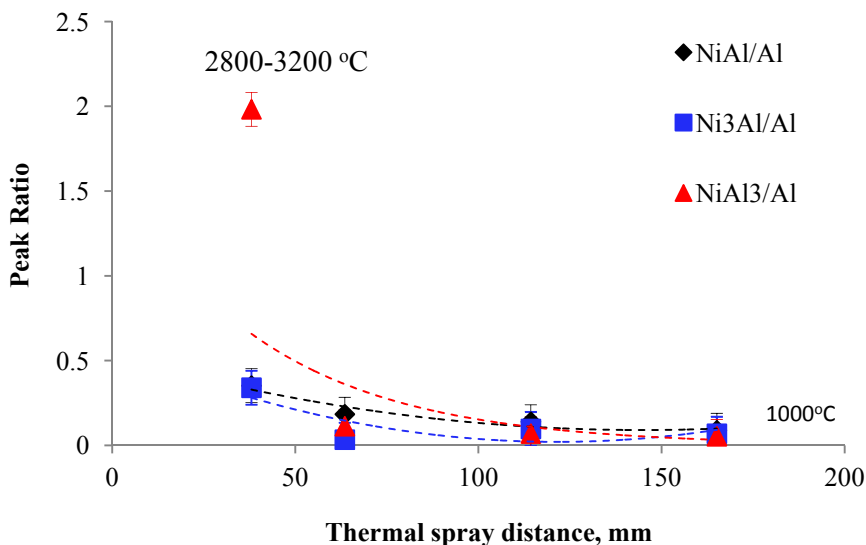
By a series of experiments, it was found that thermal spray flame temperature, which depends on the distance to coating plate and substrate temperature affects the concentration of the intermetallic phases in the coatings. Figure 4 shows the effect of thermal spray distance on the composition of the coatings in NiAl, Ni_3Al and $NiAl_3$ in relation to the remaining unreacted aluminium. The position of the substrate with respect to the flame is particularly important as the flame heats it up as well. Additionally, under certain conditions, the substrate may be in zones where different products of acetylene combustion are present—the substrate may be in a reduction zone (where hydrogen and CO are produced) or an oxidizing zone. In general, we found that the yield of intermetallic compounds increases with increasing flame zone temperature. A minimum concentration of oxides and spinels was produced in reducing atmosphere ($CO + H_2$) in a high temperature zone.
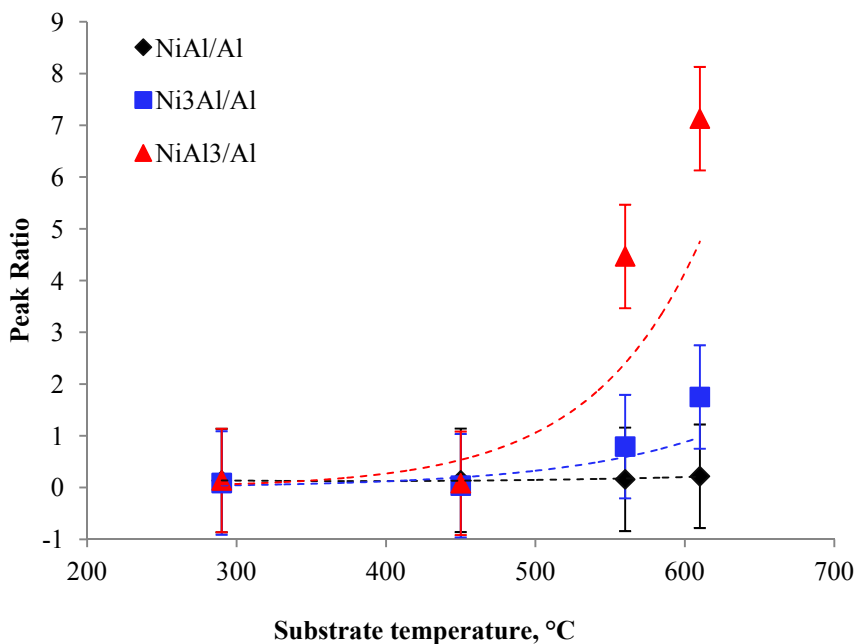
The substrate temperature also affects the production of intermetallics on the surface. As shown in Figure 5a, the higher the substrate temperature the more intermetallic compounds are produced, especially $NiAl_3$. There is some evidence to suggest that this occurs because of the reaction of molten Al in the spray with molten Ni or intermediate intermetallics on the surface. Increasing substrate temperature leads to increasing combustion temperature on the substrate during continuing exothermic reactions. Melted Al reacts with NiAl on the substrate surface with the appearance of $NiAl_3$. Ni_3Al, and $NiAl_3$ which have low adiabatic temperatures and therefore need higher preheating temperatures of substrate for their reactions to initiate.

The ratio of O_2/C_2H_2 determines the temperature of the flame during spraying and, as mentioned above, the flame temperature influences the reaction between Ni and Al (Figure 5b) in the flame, but it displays a complicated effect on the actual NiAl surface concentration. Although surface NiAl increases with increasing flame temperature, the surface concentration of Ni_3Al and $NiAl_3$ depends on the flame temperature, the time spent in the cooling zone and the amount of excess oxygen in the flame as it increases the possibility of oxidation of Al and Ni.

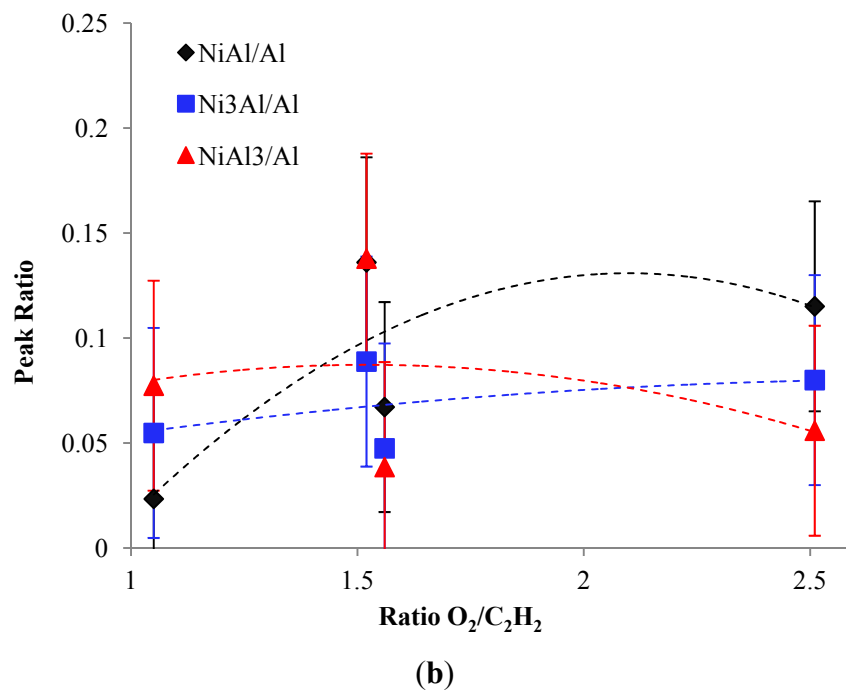**Figure 4.** Influence of thermal spray distance on the composition of the coating.

Figure 5. Influence of (**a**) substrate temperature and (**b**) ratio O_2/C_2H_2 on the final composition of the coating.
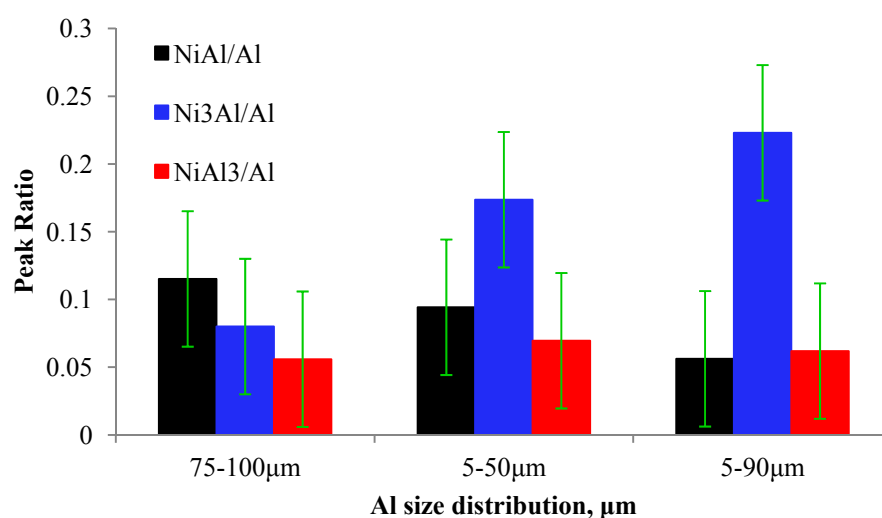

(**a**)

Figure 5. *Cont.*

(b)

Particle Size Effect

The Aluminium particle size has a significant effect on the composition of the coatings, as shown in Figure 6. The formation of NiAl phase is favored when the Al size distribution is 75–100 μm, but Ni_3Al is favored when small particles are included in the mixture. In agreement with previous work [30], a particle size about 20 μm seems to give an intermediate composition where all intermetallics are present.

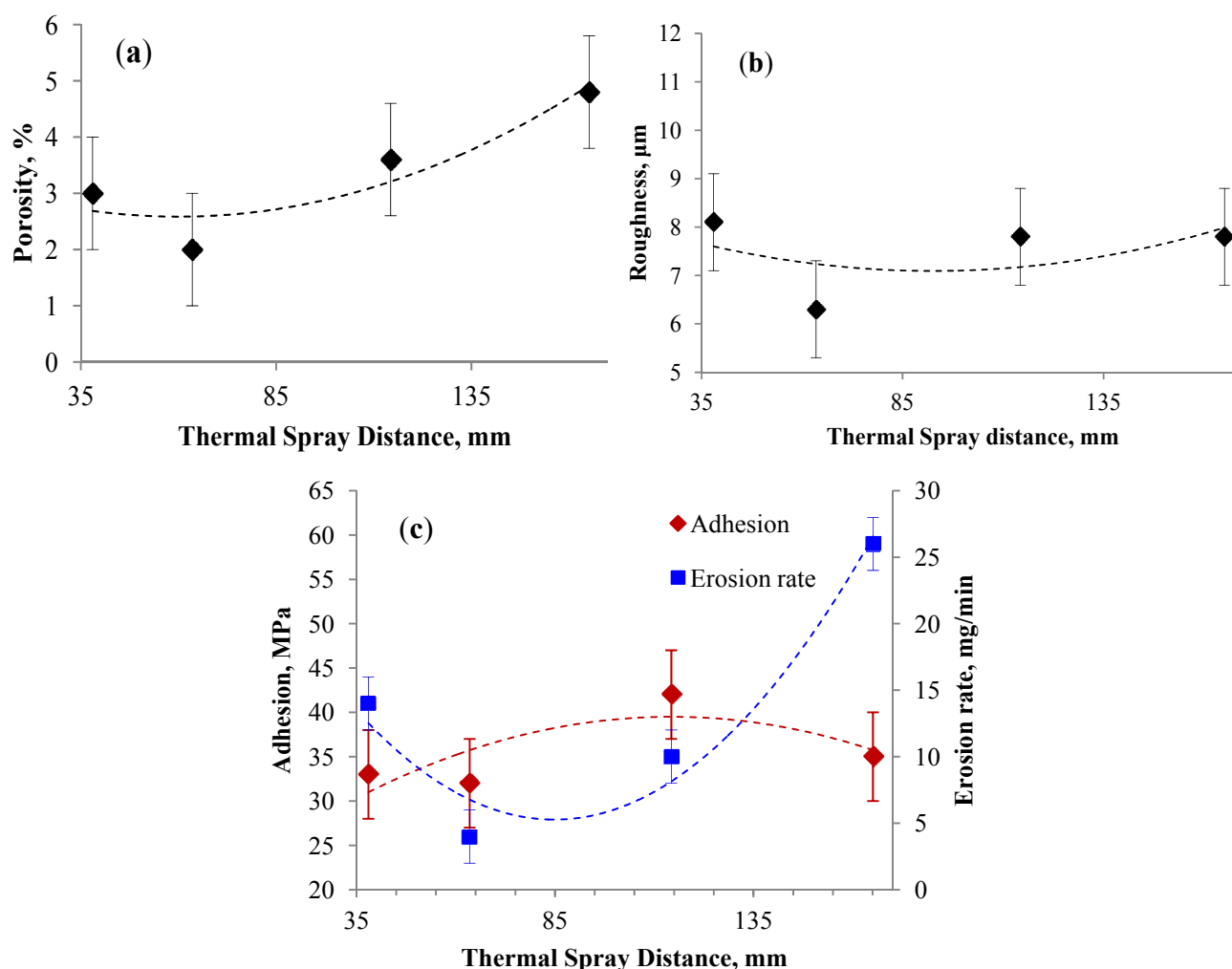**Figure 6.** Influence of particle size on the yield of Ni-Al aluminides.

3.2. Properties of the Ni-Al Coatings as Functions of the Spraying Conditions

3.2.1. Effect of Spray Distance

The net porosity of the coatings produced depended on the processing conditions and the characteristics of the powders used and could be decreased to manageable levels by adjustment of the flame conditions and substrate temperature. At short distances the flame temperature is highest and as a consequence more melted products and lowest porosity were found (Figure 7a) with a shallow minimum at intermediate distance. The surface roughness is connected with the porosity and the trend observed is approximately similar with thermal spraying distance, as expected (Figure 7b). At a very short distance (approximately 38 mm), where the temperature is highest, both porosity and roughness are highest probably because of splashing of fully melted particles on the surface. In this regard, it is important to emphasise that the spray distance also affects the temperature of the substrate which in turn also influences the properties of the coatings obtained.

Reflecting the above results, the adhesion strength and erosion resistance also show a shallow minimum with spraying distance (Figure 7c) since both these properties are directly influenced by the porosity.

Figure 7. Dependence of the properties of Ni-Al coatings on thermal spray distance: (**a**) Porosity; (**b**) Roughness and (**c**) Adhesion strength and erosion rate.

3.2.2. Effect of O_2/C_2H_2 Ratio

The stoichiometric ratio of O_2/C_2H_2, is expected to give the maximum flame temperature (close to 3000 °C), resulting in minimum porosity (Figure 8a). Porosity appears to be lowest at a ratio of $O_2/C_2H_2 = 1.56$ probably due to the observed presence of semi-melted particles and substantial overlaps of the splats. For constant spraying distance, there appears to be limited splashing if the substrate is in the zone of combustion, which gave the most promising coatings. Porosity is high at the stoichiometric ratio of $O_2/C_2H_2 = 2.5$ because the flame temperature is highest and the particles are fully melted leading to splashing when they impact on the substrate. The increased roughness at maximum flame temperatures (Figure 8b) was probably due to the splashing of the particles as well as the observed presence of oxide phases, which generally have high temperature melting points The erosion rate did not appear to be influenced by the flame temperature (Figure 8c).On the other hand, decreasing the porosity increases the adhesion strength up to 40 MPa (Figure 8c).

Figure 8. Dependence of the properties of Ni-Al coatings on O_2/C_2H_2 ratio: (**a**) porosity; (**b**) roughness and (**c**) adhesion strength and erosion rate. Flame temperatures shown are approximate.
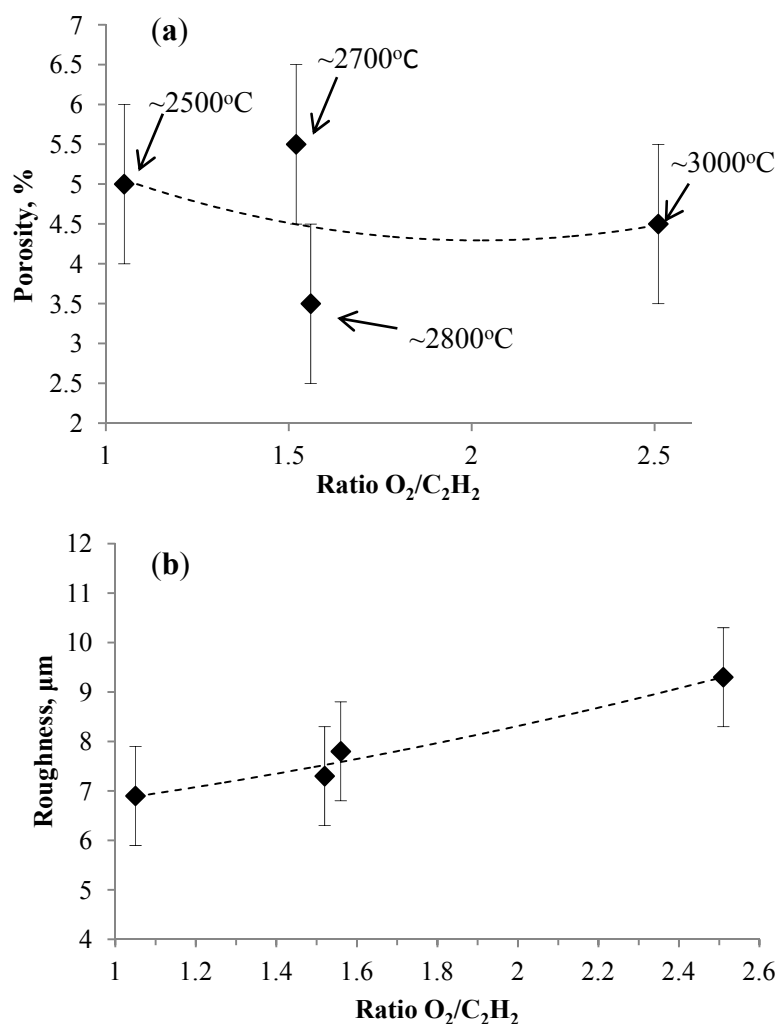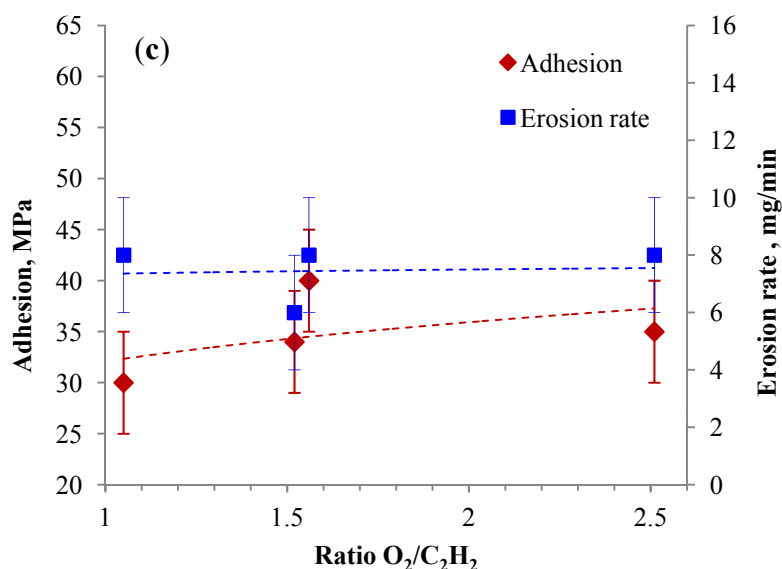
Figure 8. *Cont.*

3.2.3. Influence of Substrate Temperature during Thermal Spraying

Our results show that increasing substrate temperature enhances the formation of low melting point phases. The mechanism appears to be influenced by the increased time of reaction, because those intermetallic compounds which were not formed in-flight can still be formed on the surface. This results in lower porosity and roughness (Figure 9a,b) and stronger adhesion up to 450 °C, but adhesion decreased beyond 450 °C, probably due to the enhanced formation of oxides, as indicated in Figure 9c.

Figure 9. Influence of substrate temperature during thermal spraying on (**a**) porosity; (**b**) roughness and (**c**) adhesion strength and erosion rate.
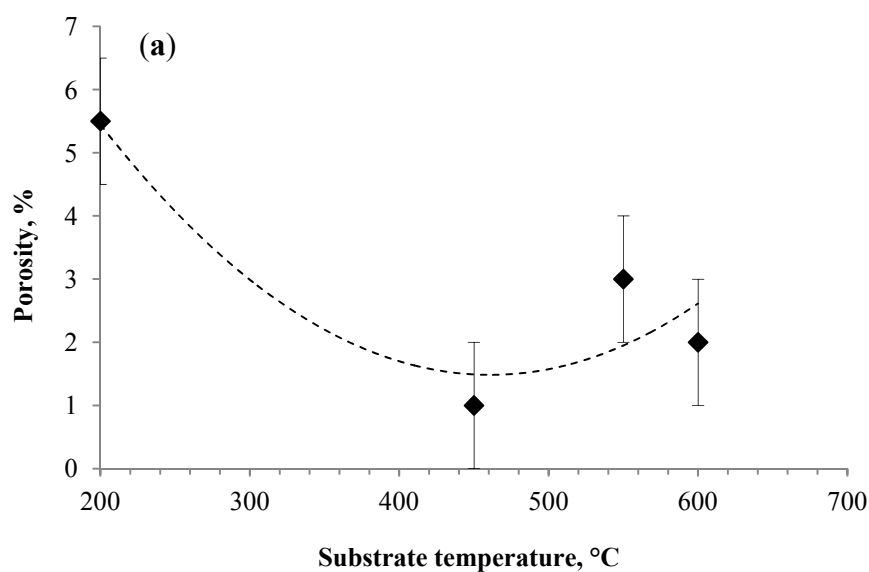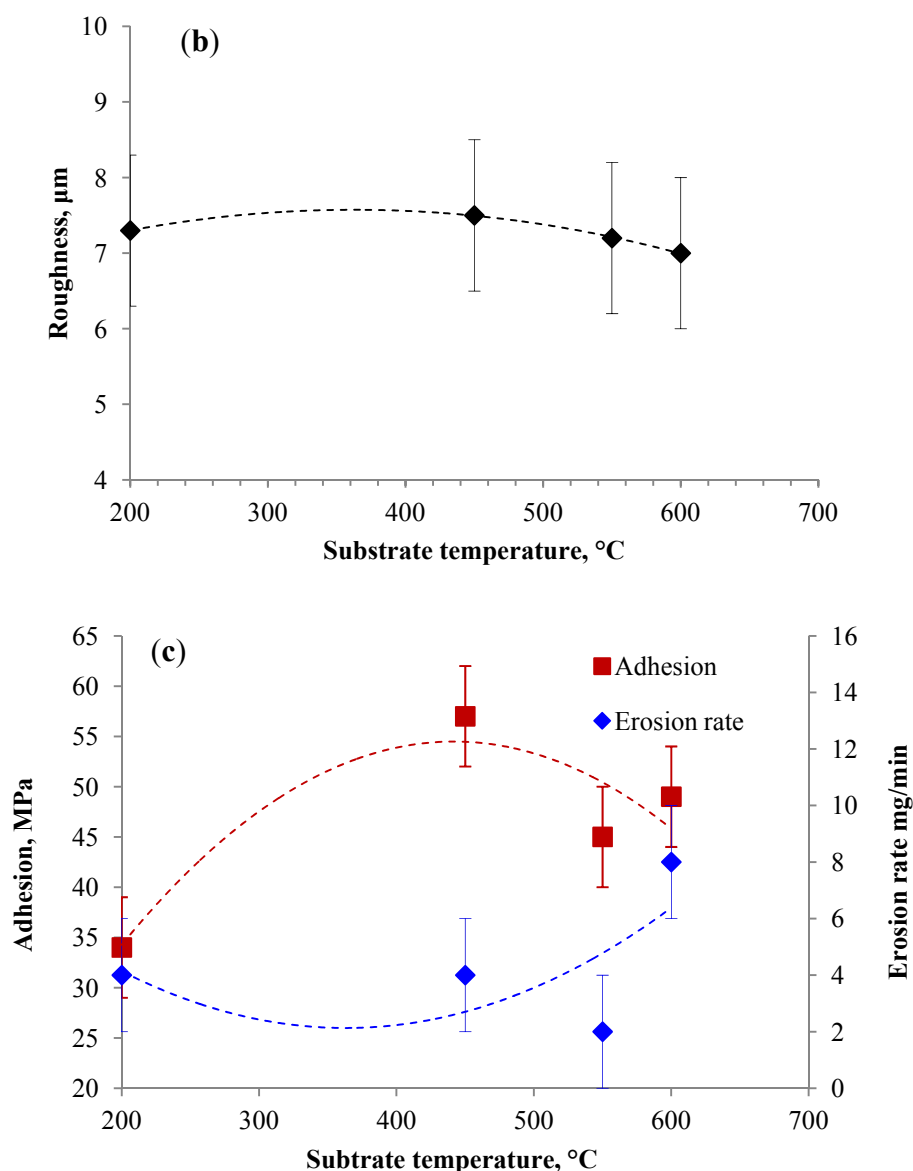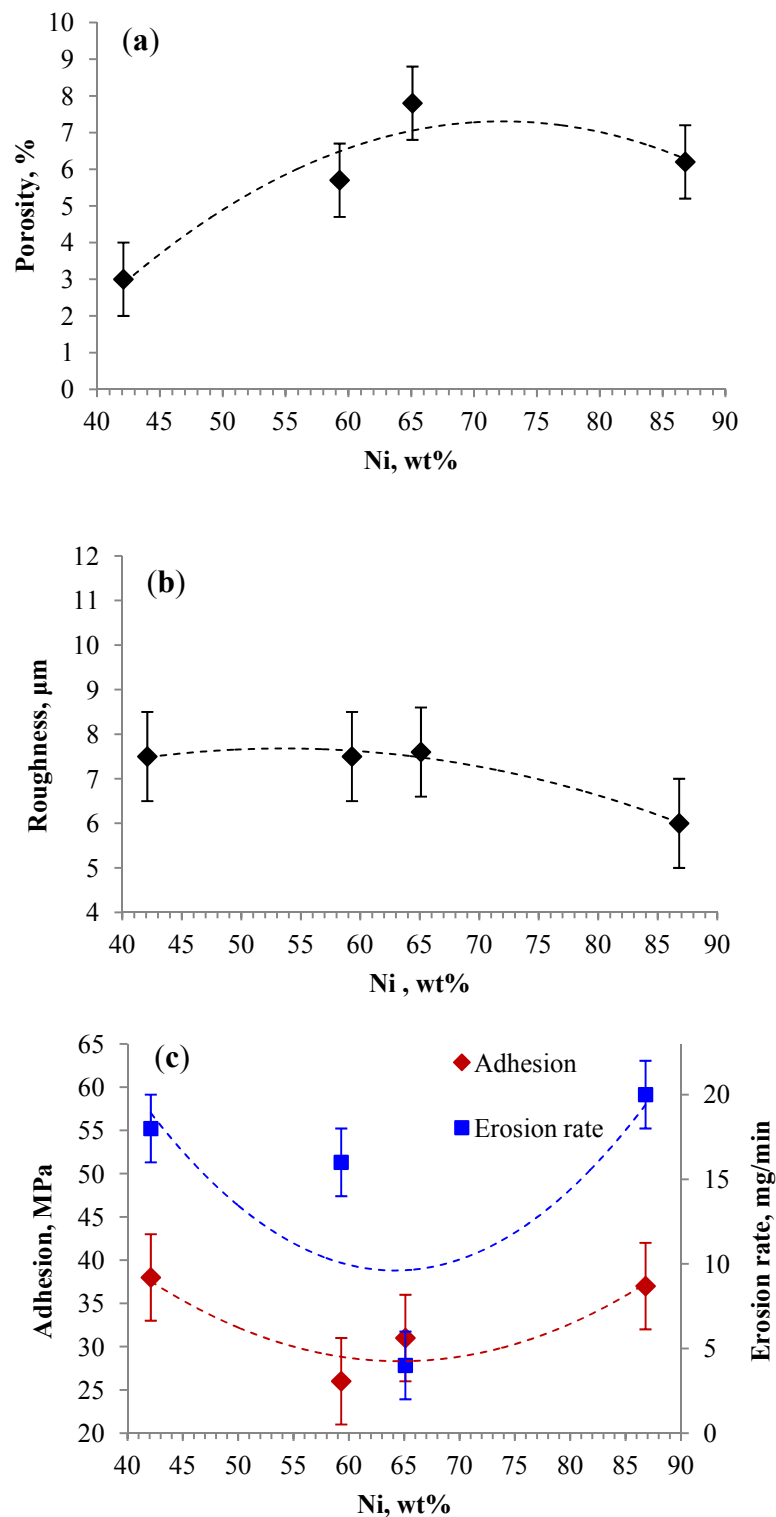
Figure 9. *Cont.*

3.2.4. Initial Powder Mixture Composition

As it was mentioned above (Figure 5), increasing Ni concentration in the initial mixture increases the total amount of intermetallics in the products. However, the curves in Figure 10 show maxima and minima, which may be explained by considering the two competing mechanisms: on the one hand, porosity decreases due to enhanced melting and on the other, the formation of high temperature intermetallic compounds results in reduced adhesion strength and a maximum in porosity. For example a powder mixture containing 42.1% Ni and 57.9% Al (stoichiometric amounts for $NiAl_3$ with a melting point of 1127 °C), whereas at 65.1% Ni, NiAl forms preferentially (melting temperature 1911 °C) and with 86.8%Ni, Ni_3Al forms preferentially (melting temperature 1668 °C). Since the highest melting point intermetallic is NiAl at 65% Ni, this is probably the reason that the porosity (Figure 10a) displays a maximum at this Ni concentration but the erosion rate displays a minimum at the same Ni concentration (Figure 10c).

Figure 10. Influence of the initial charge composition treatment of the powder on the (**a**) porosity; (**b**) roughness and (**c**) adhesion strength and erosion rate.

SEM observations (Figure 11) corroborate these findings. They show that with increasing Ni concentration, Al reacts readily and increases the intermetallic phases. The percentage fractional area of intermetallic phase quantified by image analysis and for the four different compositions 46.1%, 59.3%, 65.1% and 86.8% Ni was measured approximately to be 10%, 15%, 20% and 35% respectively. At

86.8% Ni there is a maximum amount of intermetallic products (*cf.* Figure 5) but there is still a large amount of pure Ni in the coating. To avoid this, we have now concentrated our work on mixtures with 65.1% Ni, which allows us to increase the NiAl phase while at the same time reducing the porosity.

Figure 11. SEM photos of the produced coatings with initial mixture composition (**a**) 42.1% Ni; (**b**) 59.3% Ni; (**c**) 65.1% Ni and (**d**) 86.8% Ni.

3.3. Summary of Most Promising Coatings

Table 5 summarises the physical and mechanical properties of the most promising Ni-Al coatings we produced using CAFSY, compared with coatings produced using a commercial powder alloy (Sulzer Metco 450P, Sulzer Metco, Westbury, NY, USA) under industrial conditions. Even though a purely intermetallic coating was not produced, the CAFSY coatings display clearly superior adhesion strength, porosity and erosion wear resistance, while the roughness is similar to the commercial alloy coating.

Table 5. Comparison between Sulzer Metco pre-alloyed powder coating and two different coatings produced by CAFSY method.

Sample	Porosity, %	Roughness, μm	Adhesion Strength, MPa	Erosion rate, mg/min
Commercial Ni-Al Coating	4.5 ± 1.0	6.4 ± 0.5	41.0 ± 1.0	6
CAFSY Coating J5	3.0 ± 0.5	7.2 ± 0.5	45.5 ± 1.0	2
CAFSY Coating J6	2.0 ± 0.8	7.0 ± 0.6	49.5 ± 1.0	8

From the results obtained in this work, the basic mechanisms of the "CAFSY" method can be illustrated as follows, at least in the case of the Ni-Al system: when prepared mixtures of Ni and Al powders are sprayed together in the flow of an oxy-acetylene flame they react in-flight ultra-rapidly exothermically and form nickel aluminides with good density when they impact the incident surface. This very fast reactivity is possible because the actual temperature of the flame is increased beyond what is usually achievable by oxygen and acetylene mixtures due to the added heat liberated during the exothermic combustion reactions. This has a positive thermal feedback effect: increasing the temperature, increases the reaction kinetics, which further increases the amount of heat liberated per unit time. The final result is the production of intermetallic phases in extremely short times, probably nucleating even before the powders hit the surface. Because of the specifics of the reaction, very useful combinations of intermetallic phases mixed with protective oxides are possible [21]. The higher spraying temperature also appears to improve the coating-to-substrate adhesion as well. The creation of the intermetallic phases depends on a number of variables, such as the starting powder size and distribution, thermal spray distance, flame and substrate temperature. It is the first time that in-flight SHS has been demonstrated using oxy-acetylene flame thermal spraying with good quality hard coatings.

From the industrial point of view, the potential for customizing the final composition and therefore the properties of the coatings, and the non-reliance on expensive pre-alloyed powders for spraying, is a major advantage. The overall potential cost benefits of such a flexible method are estimated at over 50% and the use of an ordinary, hand-held flame thermal spray gun means the method is cheap, mobile and can be used for on-site repairs as well as for new coatings.

Generally in industry, intermetallic coatings are deposited on metallic substrates by thermal spraying of alloy powders. Since pre-alloyed intermetallic alloy powders are very expensive, the costs for coating the plant components are relatively high but the range of available alloy powders is limited, which restricts the possibilities to optimize and customize coating properties by source powder selection. In addition, the equipment needed for thermal spray deposition of high quality coatings is generally stationary and not mobile, so that on-site deposition of coatings, e.g., for repairs or refurbishment, is generally difficult or impossible for large parts. CAFSY offers a viable and very promising, low-cost solution to these disadvantages.

The work presented here is continuing with the aim of improving CAFSY to produce even higher amounts of intermetallic phases, with adjustments of the processing and spraying parameters.

4. Conclusions

Combustion-assisted flame spraying (CAFSY) has been shown to be able to successfully coat metallic substrates with hard, strong and wear resistant coatings in the Ni-Al system using only Ni and Al base-metal powders and a simple hand-held type flame oxy-acetylene flame spray gun. This new, low-cost adaptation eliminates the need for expensive pre-alloyed powders and allows tailoring of the properties of the coatings according to the needs of the ultimate application. The work presented here shows that it is possible to initiate and control combustion reactions between base metal powder mixtures in-flight during flame spraying and, it is expected that, with appropriate process optimisation, the method will produce satisfactory composite coatings on stainless steel, with physical and mechanical

properties at least as good as those obtained with pre-alloyed commercial powders, even with lower total amounts of intermetallic phases.

Conflicts of Interest

The authors declare no conflict of interest.

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