# Spray deposition of an iron aluminide

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High velocity oxyfuel (HVOF) spray forming of an iron aluminide [Fe–12.5 Al–2.93 Ni–0.02 B (wt %), containing 300 p.p.m. oxygen], followed by heat treatment for 24 h at 500 °C, 18 h at 600 °C and 20 min at 800 °C, and multipass hot rolling at 800 °C has been studied. Three different thicknesses (0.43, 0.93 and 1.33 mm) of sprayed deposit were produced by spraying for different times (approximately 10, 20 and 30 min). The spray-deposited layers exhibited some oxide and some porosity. This porosity was reduced by heat treatment. The as-deposited layer had a high degree of B2 order, and a B2 antiphase domain size of 4.5 nm. On hot rolling this material to a reduction of 38%, it was found to be more susceptible to edge cracking than similar material processed by an ingot–extrusion–hot rolling route. In heat treatment, the aluminide-sprayed layer formed a non-protective $Fe_2O_3$ oxide, rather than the usual $Al_2O_3$ that forms on the binary alloy. This is attributable to the Ni content of the iron aluminide powder employed. © *1998 Kluwer Academic Publishers*

## 1. Introduction

Iron aluminides based on $Fe_3Al$ are being developed for high temperature structural applications because of their good oxidation and hot corrosion resistance. They exhibit, however, limited room temperature ductility, which has restricted their use. The ductility of these alloys may be improved by processing and compositional control. A number of processing methods have recently been subject to investigation at the University of Sheffield. This programme has comprised several different processing techniques: co-rolling of elemental foils followed by heat treatment to form the intermetallic [1], strip casting [2], and extrusion followed by hot rolling, cold rolling and heat treatment [3, 4].

Hitherto, the production of aluminides based on $Fe_3Al$ by thermal spray deposition has not been widely reported. In general terms, thermal spraying [5–7] involves the formation of a relatively thick ( > 250 μm) coating on a solid substrate from a stream of molten or partially molten droplets. The droplets normally impact on the substrate at speeds in excess of 150 m s$^{-1}$, depending on the spray process employed, spread out to form splats, and rapidly solidify at cooling rates of about $10^6$ K s$^{-1}$. The bulk coating develops through the formation of successive layers of splats.

The nature of the bond formed between the coating and substrate and between individual splats has been a matter of controversy for many years [8,9]. However, factors such as intersplat oxide and porosity formation, initial substrate roughness and coefficient of thermal expansion mismatch are known to be of significance. Hence, it is recognized that, to produce well bonded, sprayed layers, high particle impact velocities must be achieved without excessive overheating of the droplets (to minimize oxidation and other undesirable reactions).

In recent years high velocity oxyfuel (HVOF) thermal spraying [7,10], in which a fuel gas such as hydrogen is burned with oxygen to produce a hot gas jet, has emerged as a technique well suited to the spraying of metallic alloys because it allows, under optimum processing conditions [11], high particle velocities to be attained without excessive particle heating and oxidation. The purpose of the present paper is to report results on the production of iron aluminides, in the form of thick (up to 1.3 mm) coatings using the HVOF process, and their subsequent processing.

## 2. Experimental procedure

Powder of composition Fe–12.5 Al–2.93 Ni–0.02 B (wt %), containing oxygen 300 p.p.m. as oxide, and of a particle size range of approximately 20 – 65 μm was HVOF spray deposited using hydrogen as a fuel gas on to steel sheet substrates of dimensions 25 × 55 mm and of approximately 0.7 mm thickness. The substrates were attached vertically to the cylindrical periphery of a horizontal table rotating at 80 r.p.m., to provide a horizontal traverse rate relative to the spray jet of approximately 1 m s$^{-1}$. The powder was fed through the Miller Thermal–UTP HVOF gun, which directed the resulting spray horizontally. The gun was scanned up and down at a vertical speed of approximately 5 mm s$^{-1}$ to achieve uniform coverage of the

substrate. Three different thicknesses (0.43, 0.93 and 1.33 mm) of sprayed deposit were produced by spraying for different times (approximately 10, 20 and 30 min). Heat treatments of sections of the as-deposited material were carried out, in air, for 24 h at 500 °C, 18 h at 600 °C and 20 min at 800 °C.

For hot rolling, two coupons of spray-deposited material still attached to their substrates were placed sprayed sides together, and retained inside a steel sheet holder. The total thickness of the resulting package was approximately 5.5 mm. The package was preheated at 800 °C for 20 min for hot rolling, which was carried out on a Hille 50 rolling mill at a roll speed of $0.3 \, \text{m s}^{-1}$. Five passes, with the mill gap set at 5.0, 4.5, 4.0, 3.5 and 3.0 mm, (each pass was of 10–15% reduction, corresponding to a total reduction of approximately 40%) were made with the material being re-heated back to 800 °C for 5 min between passes.

Sections from the various treatments were prepared by standard metallographic procedures and etched in Kalling's reagent. Further imaging and analysis were carried out on a Jeol 6400 scanning electron microscope (SEM) and X-ray diffraction (XRD) was performed on a Philips 1710 diffractometer using $CoK\alpha$ radiation.

## 3. Results

XRD indicated that the as-received powder had a B2 structure, and SEM showed a dendrite cell size of approximately 2–3 μm (Fig. 1). Chemical analysis of the as-deposited layer indicated the composition to be Fe–12.2 Al–2.94 Ni–0.74 (wt%) oxygen. The microstructure of the as-deposited layer, for all the samples observed, appeared to be uniform (Fig. 2a): the majority of the deposit was iron aluminide with layers of oxide (approximately 1 μm in thickness) at intersplat boundaries. The presence of thin oxide layers is expected since oxidation takes place at the surface of particles in flight [12] and, on impact with the substrate, droplet flattening and spreading occurs, giving splats covered with thin oxide sheets. Some near-spherical particles are also visible in Fig. 2a and these probably result from incomplete melting of larger particles during spraying. In addition there is
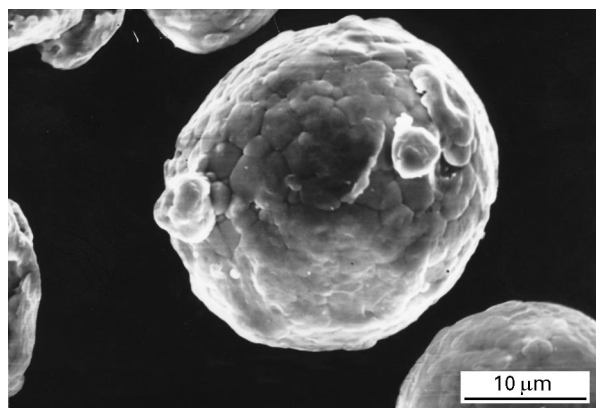






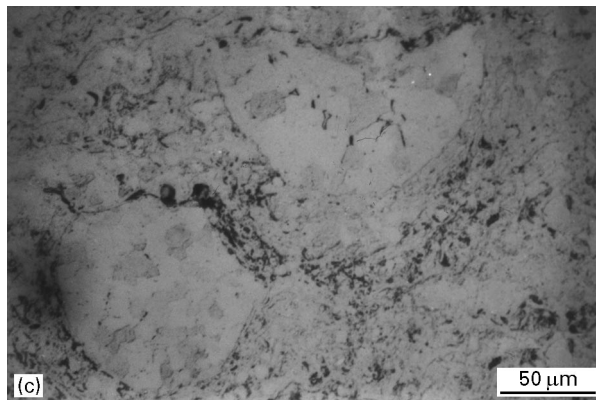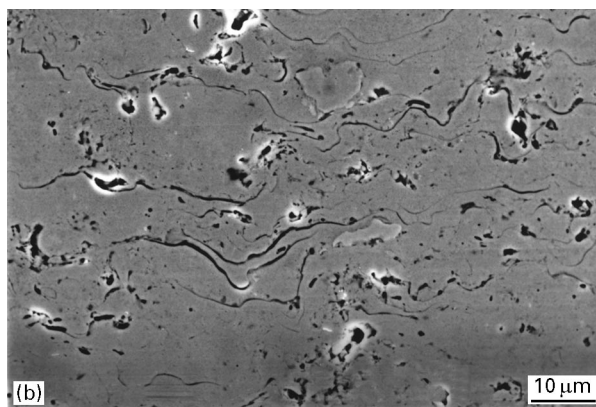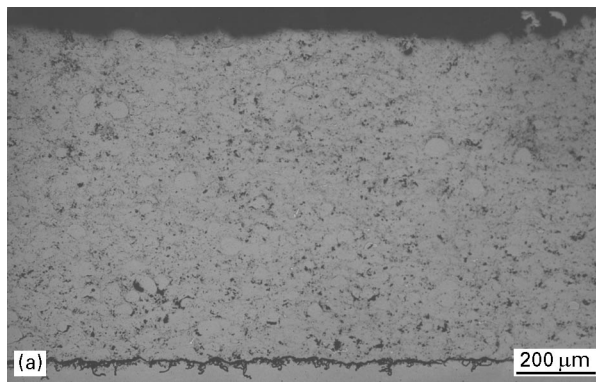*Figure 2* Micrographs of as-spray deposited layer: (a) as-polished, (b) SEM to show porosity and oxide layers, and (c) etched in Kalling's reagent.



*Figure 1* SEM micrograph of powder before HVOF deposition, of composition: Fe–12.5 Al–2.93 Ni–0.02 B (wt%), and 300 p.p.m. oxygen content.

approximately 1% porosity (Fig. 2b). The solidified splats were polycrystalline and had a grain size of 4–8 μm (Fig. 2c). XRD of the as-sprayed deposit showed B2 ordering (Fig. 3). Evidence for this is the presence of B2 superlattice peaks at approximately 36° 2θ. Measurement of lattice parameter, using the high angle 3 1 0 reflection (B2 indices), gave a value of $0.28942 \pm 0.0003$ nm.

XRD line breadths were measured for the 1 0 0 (B2 superlattice) and 1 1 0 (fundamental) diffractions. The antiphase domain (APD) size, $d$, for the B2 structure was determined using the Scherrer relationship ($d = 0.9\lambda/\beta \cos\theta$). The line breadth, $\beta$, for the 1 0 0 peak was corrected for instrumental broadening using Warren's method, with the fundamental 1 1 0 line being used for reference. The B2 APD size for the
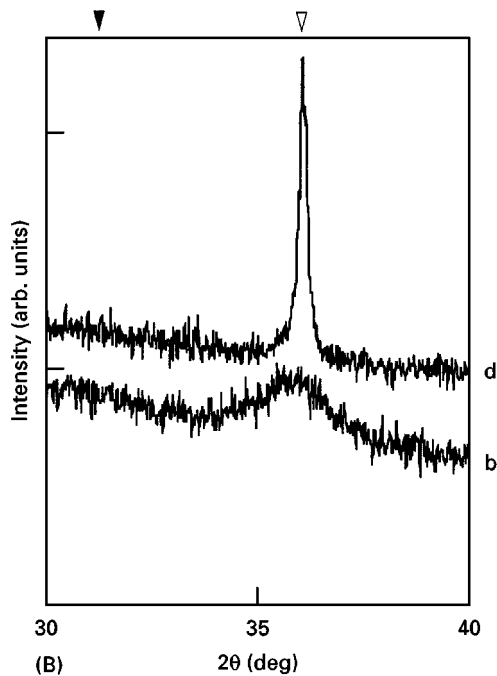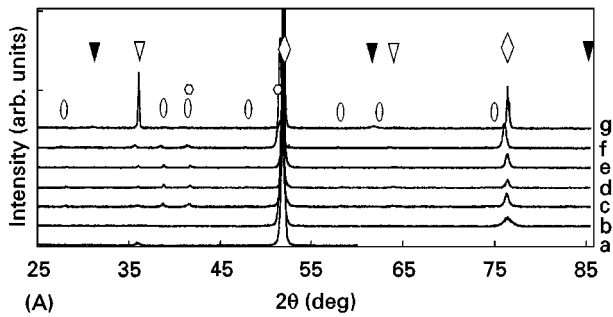
*Figure 4* Micrograph of spray-deposited layer heat treated for 18 h at 600 °C, as-polished. Note reduction in porosity, cf. as-deposited layer in Fig. 2a.
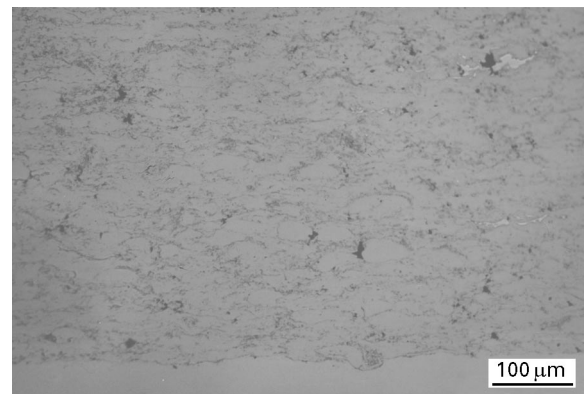


*Figure 5* Micrograph of spray-deposited layer hot rolled at 800 °C to give a 38% reduction, as-polished, showing mainly sound layer, but with some cracking–decohesion around the ends of the particles (dark areas).

*Figure 3* (A) XRD traces from spray-deposited iron aluminide, and heat treated ingot material, and (B) enlarged intensity scale to show B2 1 0 0 peak for as-sprayed and for sprayed plus heat treated material. (a) Powder before spraying; (b) as-sprayed; (c–e) sprayed plus heat treated for 24 h at 500 °C, 18 h at 600 °C or, 20 min at 800 °C, respectively; (f) sprayed and hot rolled by 38%; (g) iron–14 wt % Al(Fe$_3$Al), heat treated 12 h at 800 °C. (▼) D0$_3$, (▽) B2/D0$_3$, (◇) α-Fe/B2/D0$_3$, (■) Fe$_2$O$_3$, (■) Al$_2$O$_3$.

spray-deposited material determined by this method was 4.5 ± 0.5 nm.

Heat treated deposits appeared microstructurally similar to the as-sprayed deposits, but with a reduction in porosity (compare Fig. 4 with Fig. 2b). No significant interdiffusion between the sprayed deposit and the substrate was evident. XRD of all heat treated specimens indicated an increase in the extent of order, compared with the as-deposited layer: 24 h at 500 °C showed D0$_3$ and B2 order, while 18 h at 600 °C and 20 min at 800 °C both showed B2 order (Fig. 3). All heat treated specimens also showed a series of reflections that correspond to Fe$_2$O$_3$ (Fig. 3). Measurement of lattice parameter, using the high angle 3 1 0 reflection, gave a value of 0.28 9 71 ± 0.0003 nm, for all heat treatments.

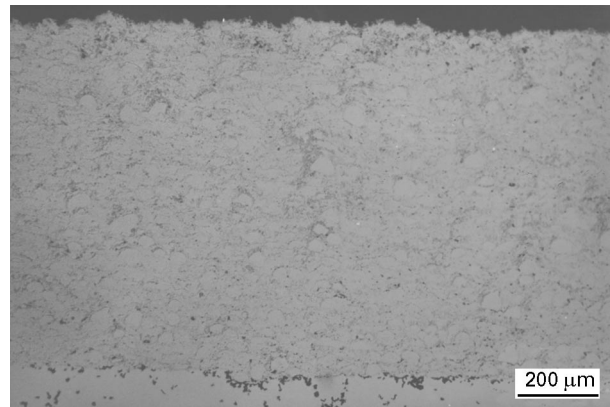Hot rolling of two coupons of spray-deposited material at 800 °C resulted in some cracking, which appeared to have started from the edge of the coupons and had propagated for approximately 5–8 mm. The final thicknesses of the sprayed layers of the specimens after hot rolling were 0.29 and 0.58 mm (from initial thicknesses of 0.46 and 0.93 mm), which corresponds to a reduction of 38%. Metallographic examination of the sound parts of the hot-rolled deposit indicated it to be free of porosity, and mostly crack free, a limited degree of cracking being observed around the ends of some of the larger splatted particles principally around the unmelted or partially melted feedstock powder particles referred to earlier (Fig. 5). Again, no significant interdiffusion between the sprayed deposit and the substrate was evident. XRD indicated a B2 structure (Fig. 3).

## 4. Discussion

The appearance of the microstructure of the layer is typical for this type of sprayed material [5]. The B2 1 0 0 superlattice reflection is broadened and only just resolvable for the as-sprayed material, which suggests that either the degree of order is low, or that it has a small B2 domain size. A further measure of the order can be obtained from lattice parameter values. For Fe$_3$Al, the lattice parameter increases with increasing disorder. For slow cooled fully B2 ordered binary

Fe$_3$Al a lattice parameter of 0.289 68 ± 0.0003 nm has been measured [13], compared with a value of 0.290 75 ± 0.0003 nm when mechanically disordered (by cold rolling 80%). The lattice parameter value obtained from the as-sprayed material was 0.289 42 ± 0.0003 nm, and from the sprayed and heat treated (20 min at 800 °C) material was 0.289 71 ± 0.0003 nm. It is estimated that the effect of approximately 3% Ni on the lattice parameter of Fe$_3$Al will be negligible, from lattice parameters of FeAl and NiAl, and Ni in solid solution in α-Fe [14]. A comparison of lattice parameter values from the sprayed material with that of fully ordered material show them to be the same, within experimental error. This indicates that the as-sprayed material has a high degree of B2 order, together with an anti-phase domain size of 4.5 ± 0.5 nm. The latter has resulted from the relatively high cooling rate in spray deposition (cf. conventional casting). It is worth noting that Prakash et al. [15] showed that chill-block melt-spinning of Fe$_3$Al gives insuffiently rapid cooling, in the critical temperature range, to prevent substantial B2 order from being established. Both techniques, however, provide cooling that is sufficiently rapid to inhibit the formation of D0$_3$ order.

The porosity, which was present in the as-sprayed material, was reduced by heat treatment. In practice, this would be beneficial if the layer was to be used at elevated temperatures as the defects in the as-sprayed material would heal on heat treatment at such temperatures. A possible mechanism of pore closure is by sintering. Calculations of the rate of closure of a spherical hole by lattice diffusion at 800 °C show that a time of $6 \times 10^6$ s is required to close a hole of 2 μm radius (typical of the largest pores observed in the as-sprayed deposit). If pore closure by grain boundary or surface diffusion is considered the time to close the hole reduces to $1 \times 10^6$ s, which is still too long to account for the disappearance of the hole in 1200 s at a temperature of 800 °C. It is, however, possible that a differently shaped pore may speed up sintering.

Hot rolling of the as-sprayed material has been shown to be feasible, but it is more susceptible to edge cracking than Fe–14 wt % Al (Fe$_3$Al) processed by an ingot–extrusion route [3]. Cracking is probably more prevalent in the spray-deposited material because of the amount of oxide and porosity contained within the material. This is illustrated by the micrograph of the spray-formed material in the as-hot rolled state, which shows the presence of cracks around splatted particles, which would have been surrounded by oxide (Fig. 5). The oxides present in the coating are regions of mechanical weakness. This is clear from the fact that these regions crack during rolling. However, the coating remained on the substrate, which suggests that the cracking does not seriously affect the mechanical integrity of the layer. The oxide layers are uniformly distributed, which possibly results in many weak points in the coating such that during deformation many cracks can form. It seems preferable that many small cracks form rather than one or two severe ones.

The formation of an iron oxide (Fe$_2$O$_3$) on the surface of the spray-deposited material exposed to air at elevated temperatures is unusual, as iron with > 8 wt % (15 at %) Al forms a protective alumina scale [16]. The addition of Ni, however, increases the amount of Al required to form an alumina layer [17]. A further experiment was carried out, which confirmed that oxidation of binary Fe–14 wt % Al (Fe$_3$Al) processed by an ingot–extrusion route showed the formation of Al$_2$O$_3$ (possibly with some Fe$_2$O$_3$) after exposure for 12 h at 800 °C in air (no oxide peaks were found by XRD after exposure for 20 min at 800 °C, cf. the spray formed material; Fig. 3).

## 5. Conclusions

1. HVOF deposition of an iron aluminide has been carried out successfully. The spray-deposited layer exhibited some oxide layers and some porosity. This porosity was reduced by heat treatment. The as-deposited layer has a high degree of B2 order, and a small B2 APD size of 4.5 ± 0.5 nm.

2. Hot rolling of the as-sprayed material has been shown to be feasible, though it is more prone to cracking than similar material processed by an ingot–extrusion–hot rolling route.

3. The aluminide-sprayed layer formed a non-protective Fe$_2$O$_3$ oxide, rather than the usual Al$_2$O$_3$, which forms on the binary alloy. This is attributable to the Ni content of the iron aluminide powder employed.

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