Study of Flame Spray Coated Fe-Al Using N₂ as a Gas Carrier

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Abstract. We studied the effect of using N₂ as a gas carrier on the structural and mechanical properties of Fe-Al coating. Typically, using air as the gas carrier in flame spray coating method was prone to the formation of intrinsic Fe-oxide(s), thus reducing its further resistance against oxidation at elevated temperature. The use of N₂ to replace air as the gas carrier was conducted in this research to minimize the possible Fe-oxide(s) formation. We found that there were still Fe-oxide (wuestite) formed even after the replacement, indicating the contribution of O₂ gas used in the fuel mixture (Acetylene/O₂) and/or oxygen from the environment on the oxidation. Further optimization was then conducted by tuning the Acetylene/O₂ gas ratio under N₂ gas carrier and cooling down the sprayed samples under N₂ gas exposure. Samples free of Fe-oxide(s) species thus have been successfully obtained. The effect of spraying distance was also studied to improve the intermetallic formation. Higher hardness of the shorter distance samples gives early indication of the improvement of mechanical properties induced by the intermetallic formation.

1. Introduction
In the coating technology for high temperature applications, Fe-Al aluminide intermetallic coating is one of the most interesting systems. Due to its ability to produce a protective Al₂O₃ scale when exposed to high temperature conditions [1, 2], it has beneficiary properties such as high melting point, relatively low density, and remarkable resistance against corrosion and oxidation at high temperatures [3]. Furthermore, it has a relatively lower production cost compared to that of other similar aluminide intermetallic, good wear resistance, and is relatively easy to fabricate [2, 3].

Methods to synthesis aluminide intermetallic coatings include mechanical alloying[2, 3], cold spraying [4], thermal spraying [5–9], and hot dipping [10]. Thermal spray techniques, such as detonation gun [7, 9], flame spraying [5, 6], high velocity oxygen fuel (HVOF) [5, 8], and atmospheric plasma spraying [5], have been widely used in the past decade to deposit aluminide coatings. These thermal spray techniques produce excellent coating properties due to the high energy generated by fuel combustion was transferred to the coating powder to make it in the molten or semi-molten state. It was then strongly attached to the substrate when it was collided on substrate’s surface. Due to the exposure with oxygen during the spraying process, oxide(s), especially Fe-based ones, is prone to be intrinsically formed in the sprayed coating. This is detrimental since it will provide intrinsic oxygen source which eventually hamper oxidation resistance during exposure at high temperatures. In order to reduce and further eliminate the possibility for Fe-oxide formation, the exposure of molten or semi molten powders to the oxygen need to be reduced. In the flame spray technique, the main sources of oxygen exposure, besides the environment, are from the use of O₂ gas in the fuel mixture (acetylene/O₂) and pressurized air used as gas carrier. Since the O₂ gas is needed for combustion, the
most feasible method to reduce the exposure is to change the gas carrier, from air to other inert gas. Here, we use N₂ gas as the carrier, and examine the structural and mechanical properties of the coatings prepared with different gas carriers. Subsequent optimizations were then performed under the usage of N₂ as a gas carrier.

We found that the Fe-oxide species were formed on both sprayed samples using air and N₂ as gas carriers. This evidence indicates that the O₂ content in the fuel mixture and/or in the environment plays a role in the oxide formation. Further efforts to minimize the oxide species formation was then performed involving reducing O₂ in the fuel mixture, as well as cooling down the sprayed samples under N₂ gas exposure. Samples that are free of Fe-oxide(s) species were then successfully obtained. We also found that the Fe-Al intermetallic phase was not clearly observed on the as-sprayed samples. Further annealing process was needed for the intermetallic formation. To increase the possibility of the intermetallic formation, the spraying distance was then shortened as this leads to the increase of the substrate temperature. The more detailed discussion of the optimization will be presented in this paper.

2. Experimental Methods

The substrate used was 2 mm thick Stainless Steel 430 (Nilaco) with the area of 1.5 × 1.5 cm². It was ultrasonically cleaned in methanol and sand-blasted prior to coating deposition. Spray powder used was a 50:50 (at%) mixture of Fe (> 99%, Aldrich) and Al (99.9%, MIT Korea). Spray flame equipment (Metallisation MK 47 Flamespray System, UK) was used with Acetylene (C₂H₂, Ultra High Purity (UHP) grade) and Oxygen (O₂, UHP grade) as the fuel. The default pressures of acetylene and oxygen were 1.15 and 2.3 bar, respectively, which were then further varied for optimization. For typical spraying process, 10 g of the spray powder was used to coat 5 samples at one time by moving the spray nozzle in scanning fashion left and right on the substrates. For optimization process, only 1 substrate that was sprayed at one time using 2 g of the powder each, and the spray nozzle was kept at a fixed position (not scanned). Pressurized air or N₂ gas with pressure of 4 bar was used as the carrier. Unless mention otherwise, the spraying distance was at ± 30 cm. For heat treated samples, it was conducted in vacuum furnace at 800°C for 2 h.

The structures of the as-sprayed and after heat treated samples were examined by XRD (Rigaku Smartlab). The samples were then dipped in Resin solution and hardened overnight, then cut half to reveal the inner morphology. The rough-cut surfaces were then polished until it became mirror-like before being used for morphology and hardness measurement. The morphology was observed using optical microscope (Bestcope BS-6000AT). The hardness was measured using Microhardness Tester (LM100AT Leco) with 0.3 kgf load for 13s.

3. Results and Discussion

Figure 1 shows the appearance of substrate before and after coated with Fe-Al powder. Before spray coating, the SS 430 substrate (figure 1(a)) was ultrasonically cleaned and then sand-blasted to roughen the surface (figure 1(b)). It was expected that the spray powders thus became easier to attach on it. The spray coated samples using air and N₂ gas carriers are shown in figures 1 (c) and (d), respectively.

![Figure 1](image_url)

**Figure 1.** (a) SS 430 substrate, (b) the substrate after ultrasonically cleaned and sand-blasted. The samples after spray coated by Fe-Al powder using (c) air and (d) N₂ as gas carriers.
It can be seen that the coating powder was sprayed evenly on the substrate. The visual appearance of the coatings has pattern like those of bright dot spreading evenly on darker base. The bright dot was probably Al powder. This indicates that mostly Al powder was still at its original phase after the deposition, very likely not forming the Fe-Al intermetallic yet. From XRD patterns as shown in figure 2 (a) and 2 (b), the intermetallic phase was indeed not clearly detected. Instead, the Fe and Al peaks [11, 12] were sharply observed. There was also Fe-oxide species i.e. FeO-wuestite [13] observed for both sprayed samples. This suggests that the use of N2 to replace air as the gas carrier was still not enough to eliminate oxide formation. This also indicates that there was a contribution of oxygen in the fuel mixture and/or from environment on the oxide formation.

Figure 3 shows the cross-section pictures of the coated samples prepared using air and N2 as gas carriers. The thickness of the coating was approximately 291 ± 50 and 223 ± 46 µm for air and N2 gas carriers, respectively. The morphology of the coatings was like lamellar stacks of molten materials which is typical of spray coating microstructure. This indicates that the sprayed powder was at molten or semi-molten state when it was collided on the substrate. For the samples sprayed using N2 as the gas carrier, a gap was observed at some parts between the coating layer and the substrate interface (See red circle in figure 3 (b). This shows that further study is still needed to optimize the spray coating process. For optimization, the contribution of oxygen on the intrinsic oxide formation, either in the fuel mixture or environment, need to be reduced. For this purpose, in the first step, the oxygen pressure was reduced while the acetylene pressure was kept constant.

![Figure 2. XRD patterns of spray coated Fe-Al using (a), (c) air and (b), (d) N2 as gas carriers. (a) and (b) as sprayed samples and (c) and (d) after heat-treatment](image)

![Figure 3. Cross-sectional optical microscopy (OM) images of flame sprayed Fe-Al coating prepared using (a) air and (b) N2 as gas carriers.](image)
To further prevent possible contribution of oxygen in atmosphere to oxidation, the coated sample was subsequently cooled down to room temperature under N₂ gas exposure after spray deposition was finished and the flame was then extinguished. The different fuel ratio that was used was affecting the combustion process and the flame temperature. Figure 4 shows the appearance of the flame produced at different fuel ratio. The O₂ pressure of 2.3, 1.5 and 1.0 bar results in the flame colour of blue, greenish-blue, and orange, respectively, indicating different temperatures of the flames. The temperature of the flames as a function of fuel gas ratio and spray distance was measured using thermocouple. The aforesaid results are presented in Table 1. The trend shows that the decrease in oxygen pressure leads to the increase of the flame temperature.

Figure 5 shows the cross-section picture of the samples prepared with O₂ pressure of 2.3 and 1.0 bar. The thicknesses were 413 ± 69 and 368 ± 35 µm for 2.3 and 1.0 bar samples, respectively, which are thicker than those of the non-optimized samples. This is probably because in the optimized experiment, the spray gun was kept at stationary position during deposition, rather than scanned as in the previous one. Thus, the loss of the sprayed powder was lesser, leading to a thicker film. It is important to note that the gap between coating and substrate which was observed previously in the sample deposited using N₂ as a gas carrier is no longer observed in these samples. In addition, the cross-section pictures as shown in figure 5 also show good attachment profile between substrate and coating materials, similar to those observed for the air-based sample.

Figure 6 shows the XRD patterns of samples prepared using O₂ pressure of 2.3, 1.5 and 1.0 bar. Al and Fe peaks are clearly observed for these samples, while the FeO-wuestite peak is no longer observed. This shows that the optimization procedure successfully suppressed the intrinsic oxide formation. From the XRD result, we can also infer that since the disappearance of the oxide also happen even at the 2.3 bar sample, the contribution of oxygen in the fuel mixture on the oxide formation was very likely insignificant. The oxygen in the environment was very likely the one that contributes most to the oxide formation. Our procedure was to keep the N₂ flow after deposition was finished until the samples cooled down to room temperature. It was the key to suppress the formation of intrinsic oxide on the coating. Evidently, the intensity of Al peak at 20 of about 38.4° tends to decrease when the O₂ pressure is decreased. However, we couldn’t clearly observe the presence of the intermetallic phase from the XRD, probably because the fraction was quite small to be clearly distinguished from the background noise. Further study is needed to answer this issue.

![Figure 4](image.png)

**Figure 4.** Pictures of flames produced from different fuel pressure. C₃H₂ was fixed at 1.15 bar and O₂ was varied: (a) 2.3, (b) 1.5 and (c) 1.0 bar

| Spraying Distance (cm) | O₂ = 2.3 bar | O₂ = 1.5 bar | O₂ = 1.0 bar |
|------------------------|--------------|--------------|--------------|
| 40                     | 170          | 180          | 195          |
| 30                     | 250          | 310          | 325          |
| 20                     | 450          | 550          | 610          |
| 10                     | 1150         | 1275         | 1345         |
Figure 5. Cross-sectional optical microscopy (OM) images of flame sprayed Fe-Al coating prepared using N$_2$ as a gas carrier and O$_2$ pressure in the fuel mixture at (a) 2.3 and (b) 1.0 bar.

Figure 6. XRD patterns of flame sprayed Fe-Al coating prepared using N$_2$ as gas carriers and O$_2$ pressure in the fuel mixture at (a) 2.3, (b) 1.5 and (c) 1.0 bar.

From XRD in figure 1, we can see that the as-sprayed samples have not clearly formed the Fe-Al intermetallic phase yet. After heat treatment (figure 1 (c) and (d)), the intermetallic phase (Fe$_2$Al$_5$ [3]) is detected. Meanwhile, the Al peak’s intensity is greatly diminished after heat treatment indicating its expense to form the intermetallic. The intermetallic formation after heat treatment means that extra energy is required to form the intermetallic phase. This was rather redundant since the flame spray was operated at very high temperature at the tip of the nozzle. However, since the spray was typically done at a certain distance, the temperature then greatly diminished as the distance was further away. The flame temperature measurement shown in table 1 clearly shows the effect of the distance on the flame temperature. The typical spray distance was about 30 cm, and this was the distance used in the experiments explained in the previous parts of this paper. If this abundant high energy can be utilized, we can perform in-situ annealing which will reduce the extra process needed to form the intermetallic. Hence, it is interesting to observe the effect of reducing the spraying distance. Here we reduce the distance from ± 30 cm to 20 and 10 cm. At 20 cm, a rather uniform coating layer can still be observed with the thickness of 818 ± 59 µm (figure 7 (a)). However, for 10 cm one, the coating layer is no longer uniform. At the centre of the substrate, very dense layer is formed, in the range of millimetres.
Figure 7. Cross-sectional optical microscopy (OM) images of sample deposited at a distance of (a) 20 and (b) 10 cm. Bar length is 100 µm.

Figure 8. Picture of Vicker hardness indentation mark of the Fe-Al coating; (a) typical sample deposited at a distance of about 30 cm, (b) sample deposited at a distance of 10 cm.

While at the edge, much thinner layer is formed, probably at the range of tens to hundreds of micrometres. For both samples though, the attachment was still rather good in which no gap can be observed. In figure 7 (b), the cross view of 10 cm sample (at the coating near the substrate) is shown, and we can observe that the coating morphology seems to be more compact and no observable lamellar stack of the molten material typically found in the thermal spray coating.

The hardness measurement was conducted and a much higher values were observed for samples with shorter spraying distances. As can be seen in figure 8, the hardness of sample deposited at 10 cm distance is 798.49 HV, much larger than those of typically deposited at distance of ±30 cm (241.44 HV). This higher hardness is very likely due to the formation of the intermetallic phase which strengthens the mechanical properties of the coating. Further study is still needed for these samples deposited at shorter spraying distance to confirm the structural properties and its effect on the enhanced mechanical properties, as well as to perform optimization to improve the uniformity of the coating layer. These will be the subjects of our future research.

4. Conclusions
We have studied the use of N₂ to replace air as the gas carrier in flame spray coating to reduce or eliminate intrinsic Fe-oxide formation which was the drawback in typical spray coating method. The use of N₂ to replace air solely was not enough to prevent the oxidation. Optimizing the coating procedures by changing the fuel gas ratio and preventing oxygen from the environment into the sample right after the deposition resulted in the successful prevention of the oxide formation. The prevention of the oxygen contact from environment right after the deposition was very likely the key
to the prevention of the oxide formation. The as-sprayed samples did not have an obvious intermetallic phase which requires heat treatment as an extra step to form the desired Fe-Al intermetallic. Shortening the spray distance to increase the possibility of in-situ intermetallic phase formation thus performed. The sample deposited at shorter distance show increase of hardness value which was very likely indicated the effect of the intermetallic formation which strengthen the mechanical properties.

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