Microstructure and Oxidation Behavior of Low Pressure Plasma Sprayed Iron Aluminides

Naoya MASAHASHI, Sadao WATANABE and Shuji HANADA

Institute for Materials Research, Tohoku University, Katahira, Aoba, Sendai 980-8577 Japan.
E-mail: masahasi@imr.tohoku.ac.jp

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Microstructure and oxidation behavior of plasma sprayed iron aluminide have been investigated focusing on the spraying conditions of atmosphere and pressure. Iron aluminide powder for spraying was prepared by ball milling of turnings fabricated from an Fe–40at%Al ingot. Microstructure of laminated layers including cavities was observed in all samples and particles with a size of about 100 μm were observed only in the sample sprayed in 50 Torr Ar atmosphere. Chemical analysis revealed an amount of aluminium loss and oxygen pick-up in samples sprayed in air, while X-ray diffraction analysis exhibited only the iron aluminide spectra without the second phase. The intensity of superlattice spectra of aluminide was strong in the samples sprayed in Ar compared with in air. Change of mass gain in oxidation testing was small in the sample sprayed in 50 Torr Ar, which is equivalent to as-cast bulk sample, while large in other samples. SEM observation revealed the evolution of iron oxides in the samples sprayed in air, which was not observed in the sample sprayed in Ar. The mechanism for superior resistance to oxidation in the sample sprayed in 50 Torr Ar is attributed to infusible particles deposition, which inherited the intrinsic oxidation resistant property of iron aluminides.

KEY WORDS: intermetallic compound; iron aluminide; microstructure; plasma spray; oxidation; surface modification.

1. Introduction
Iron aluminides based on DO2 type Fe3Al and B2 type FeAl have been expected for structural material due to its superior performances in mechanical and chemical properties at high temperatures.1–3) Strength and ductility of iron aluminides are well understood in relation to the phase transformation between order and disorder phase,4) which depends on temperature and alloy composition. In spite of the outstanding properties, the iron aluminides have a drawback of poor workability for applications. On the other hand, good oxidation and corrosion resistance due to the formation of the stable and protective α-alumina layer is attractive feature for applications. On the other hand, good oxidation and corrosion resistance due to the formation of the stable and protective α-alumina layer is attractive feature for application. This α-alumina layer is formed homogeneously on the iron aluminides5) at low oxygen partial pressure when aluminum content in aluminides exceeds 15 at%.6) Murata et al. revealed that homogeneous α-alumina in the inner layer together with iron oxides in the outer layer was formed in the early stage of oxidation by X-ray photoelectron spectroscopy (XPS).7) This protective α-alumina layer plays a beneficial role to corrosion till the break-away due to the difference of thermal expansion coefficient between iron aluminide (16.5×10^-6 K^-1)8) and α-alumina (8.0×10^-6 K^-1)9) at elevated temperatures up to 1 473 K9) and the “pest” oxidation.10)

This paper aims at investigating the possibility of application of iron aluminide as surface coating by using thermal plasma spraying. In thermal plasma spraying, raw powder is deposited on substrate through melting, quenching, consolidation and self-annealing in a single operation, producing a thick and dense layer. High cooling rate of up to 10^7 K·s^-1 is attainable to induce microstructure refinement improving mechanical properties.11) Low-pressure plasma spraying (LPPS) is one of thermal plasma spraying technique, in which the chamber atmosphere is controlled to suppress the oxidation. Also, the flight length of plasma jet is relatively long and melting efficiency is high due to the long duration of powders in plasma jet. In this paper, the dependence of microstructure and oxidation behavior on process condition is investigated. Finally, the possibility of iron aluminide fabrication by LPPS will be discussed.

2. Experimental Procedure
An iron aluminide (Fe–40at%Al) ingot was produced by high frequency induction melting in an alumina crucible under an argon atmosphere, followed by machining the surface of a few millimeter thickness to avoid the inclusion of oxidation layer. From this ingot rod, thin turnings were produced by a lathe and put into a tungsten carbide container with tungsten carbide balls, followed by ball milling in air. The ball milled powders were sieved to obtain fine powders less than 90 μm, see Fig. 1, and supplied for plasma spraying. LPPS experiments were conducted using Miller
Thermal Plasma Systems under conditions of a power of 750 A in air with 200 Torr or 500 Torr atmosphere and in Ar with 50 Torr or 500 Torr atmosphere. The distance from gun to substrate was set to a constant of 250 mm. Cold rolled and grit-blasted iron plate of 3 mm thickness was used as the substrate.

Surface and cross section microstructures were observed by scanning electron microscopy (SEM, Hitachi S-3100) with energy dispersive X-ray analysis (EDX) and by optical microscopy (OM). Phase assignment and texture evolution were examined by X-ray diffraction (XRD, Philips XPERT MPD) with Mo-Kα radiation. XRD experiments were conducted by $\theta-2\theta$ method with a scan speed of 0.01 degree per second and time per step of 1.0 s. Vickers hardness measurements were carried out for both the surfaces and cross sections using a load of 0.98 N. The chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP) as summarized in Table 1, showing a loss of aluminium and pick up of oxygen after spraying. In the samples sprayed in the high-pressure atmosphere, the amount of aluminium loss is large in air compared with in Ar. The amount of oxygen is also large in air compared with in Ar, while the dependence of Ar pressure on oxygen content in coatings is small.

Coupon type specimens ($5 \times 5 \times 0.3 \text{ mm}^3$) of sprayed layer for oxidation experiments were prepared by sectioning the sprayed plate, abrading the cut surface to remove the substrate with SiC paper down to #1 500, and buffing with 1 and 0.3 μm alumina particles. Oxidation tests were conducted at temperatures of 973 K, 1 073 K, 1 173 K and 1 273 K in air. Oxidized surface was analyzed by XRD and SEM-EDX to investigate the phase and composition of oxidation layer.

### 3. Results

#### 3.1. Microstructure Observation and EDX Analysis

Figures 2 and 3 exhibit surface and cross section microstructures of as-sprayed samples, respectively, revealing the typical sprayed microstructure of isolated cavities in plan-view (Fig. 2) and successively laminated morphology in cross section view (Fig. 3). In the sample sprayed in 50 Torr Ar, particles with a size of 100 μm were observed. Figure 4 shows SEM images of sprayed samples with the results of EDX analysis. Microstructures are almost similar in all samples except for the particles in the sample sprayed in 50 Torr Ar. Oxygen spectra in the profile were detected in samples sprayed in air, while not in Ar, which is consistent with the chemical analysis result as shown in Table 1. The values of Vickers hardness of surface and cross section are summarized in Table 2, showing high value in samples sprayed in Ar and low value in air.

#### 3.2. X-ray Diffraction Analysis

Figure 5 summarizes X-ray diffraction spectra of raw powder for spraying and as-sprayed samples, revealing that the detected spectra are assigned to the B2 phase without additional peaks like oxides. Both intensities of (100) and (111) superlattice spectra are strong in the samples sprayed in Ar compared with in air. Figure 6 shows (110) textures of samples, revealing that there is no evolution of preferential orientation specific crystal orientation in all samples other than a slight accumulation of (110) in samples sprayed in Ar.

#### 3.3. Oxidation Behavior

Figure 7 shows the change in the mass gain in oxidation testing for 345.6 ks of plasma sprayed samples with as-cast bulk sample as reference, showing high resistance to oxidation of samples sprayed in 50 Torr Ar, which is almost equivalent with that of as-cast sample. In the sample sprayed in 50 Torr Ar and as-cast, the mass gain at 973 K was negligibly small to measure and became detectable at 1 073 K and 1 173 K. On the other hand, the other three samples exhibited the increase of mass gain with temperature; the sample sprayed in 500 Torr air shows the largest. Figures 8, 9 and 10 exhibit SEM images with the results of
Fig. 2. Plan view of optical microstructures for samples sprayed in; (a) 50 Torr Ar, (b) 500 Torr Ar, (c) 200 Torr air and (d) 500 Torr air.

Fig. 3. Cross section view of optical microstructure for samples sprayed in; (a) 50 Torr Ar, (b) 500 Torr Ar, (c) 200 Torr air and (d) 500 Torr air.
EDX analysis for samples oxidized at 973 K, 1073 K and 1173 K for 345.6 ks, respectively. It should be noted in Fig. 8 that electron charge-up at a layer with low electron conductivity, which was verified to be iron oxides by both XRD and EDX analysis, occurred frequently in the samples sprayed in air. On the other hand, the amount of oxygen is relatively small in the surface layer of the samples sprayed in Ar. At 1173 K, surfaces of samples sprayed in air exhibited needle-like microstructures of iron oxides, while those in Ar were not changed and similar to the microstructure observed at 973 K. At 1273 K, the contents of oxygen in surface increased up to 50 at% for all the samples. Figure 11 summarizes XRD spectra of surface layer oxidized at 1273 K, revealing the FeO evolution in samples sprayed in air, while no spectra other than iron aluminides were detected in samples sprayed in Ar and as-cast bulk sample.

4. Discussion

Oxidation resistance of the sample sprayed in 50 Torr Ar atmosphere is superior to that of the others, and is equivalent to that of the as-cast bulk sample. The microstructure of sample sprayed in 50 Torr Ar is characterized by particles with an average size close to that of raw powder, about 100 μm. This suggests that the observed particles are originated from the infusible powder in spraying. Other coating layers exhibited homogeneous microstructure free of particles, indicating that sprayed powder deposited on substrate through melt and solidification process. The outstanding oxidation resistance in the sample sprayed in 50 Torr Ar is related to the particles, which are speculated to originate in the raw iron aluminate powder. Oxidation property and microstructure evolutions associated with oxidation are similar to those of as-cast bulk sample, implying that the oxidation resistance is due to the infusible particles. According to the XRD profiles, the sample sprayed in 50 Torr Ar shows strong superlattice spectra compared with the others, suggesting that the ordered structure as the bulk sample is inherited. This is supported by the Vickers hardness test.

| Table 2. Vickers hardness of coatings measured in the surface and cross section. |
|---|---|---|---|---|---|
| Atmosphere | Surface | FeAl | Fe |
| | | Center | Interface | Center | Interface |
| 50 Ar | 288 | 276 | 260 | 115 | 123 |
| 500 Ar | 101 | 150 | 133 | 112 | 99 |
| 200 Air | 248 | 233 | 254 | 116 | 93 |
| 500 Air | 111 | 234 | 159 | 126 | 113 |

Fig. 5. X-ray diffraction spectra of raw powder for spraying and coatings.

EDX analysis for samples oxidized at 973 K, 1073 K and 1173 K for 345.6 ks, respectively. It should be noted in Fig. 8 that electron charge-up at a layer with low electron conductivity, which was verified to be iron oxides by both XRD and EDX analysis, occurred frequently in the samples sprayed in air. On the other hand, the amount of oxygen is relatively small in the surface layer of the samples sprayed in Ar. At 1173 K, surfaces of samples sprayed in air exhibited needle-like microstructures of iron oxides, while those in Ar were not changed and similar to the microstructure observed at 973 K. At 1273 K, the contents of oxygen in surface increased up to 50 at% for all the samples. Figure 11 summarizes XRD spectra of surface layer oxidized at 1273 K, revealing the FeO evolution in samples sprayed in air, while no spectra other than iron aluminides were detected in samples sprayed in Ar and as-cast bulk sample.

Fig. 4. SEM microphotos inserting the SEM-EDX results of samples sprayed in; (a) 50 Torr Ar, (b) 500 Torr Ar, (c) 200 Torr air and (d) 500 Torr air.

Fig. 5. X-ray diffraction spectra of raw powder for spraying and coatings.
showing the highest value in the sample sprayed in 50 Torr Ar (Table 2). Moreover, Figs. 8, 9 and 10 showing the microstructure evolution with oxidation support the above speculation. Needle-like microstructure observed in the samples sprayed in air or high pressure Ar is assigned to be FeO by the EDX analysis, while similar microstructure is not observed in the sample sprayed in 50 Torr Ar and as-cast bulk sample. The evolution of FeO is responsible for immense mass gain, because the chemical reaction to FeO is enormously fast due to the metal vacancy (p-type semiconductor) of FeO crystal lattice,\(^{12}\) causing thick scale development. To explain the FeO formation in these coating layers, isolated iron or weak bonding between iron and aluminium should be considered.\(^{13}\) Iron aluminate powder is exposed to high temperature to melt in the combustion process and the momentarily melted powders solidify on the substrate. In the present experiments, it is speculated that the conversion of iron aluminate occurred in the samples sprayed in air or high pressure Ar. As for the conversion, chemical composition shift by aluminium volatilization, decrease of ordering by rapid quenching, picking up of oxygen from atmosphere, and chemical reaction with atmosphere are dominated, which lower the phase stability of iron aluminate to cause dissociation or decomposition. Although the reason why the microstructure depends on spray condition severely has not been elucidated, these experimental results suggest that the microstructure involving infusible particles is closely related to high oxidation resistance.

The \(\alpha\)-alumina formation in the oxidized coatings is not identified clearly by the XRD profiles as shown in Fig. 11, probably due to the thickness of alumina layer. Assuming that the mass gain at 1273 K is due to only pure \(\alpha\)-alumina (3.98 g cm\(^{-3}\))\(^{14}\) without pore, its thickness of layer is calculated to be about 1.5 \(\mu\)m, which is too small to detect by usual XRD measurement. According to the reference, the alumina exists under iron oxides (Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\) from the surface) and its thickness is so small.\(^{7}\) Hence, specific surface analysis such as secondary ion mass spectroscopy (SIMS) or X-ray photoelectron microscopy (XPS) should be employed to elucidate alumina formation. On the other hand, the verification of \(\alpha\)-alumina formation will be possible by evaluating whether the growth rate is controlled by parabolic or linear rate constants from the \textit{in-situ} mea-
Fig. 8. SEM microphotos with EDX analysis results oxidized at 973K for samples sprayed in; (a) 50 Torr Ar, (b) 500 Torr Ar, (c) 200 Torr air and (d) 500 Torr air.

Fig. 9. SEM microphotos with EDX analysis results oxidized at 1073K for samples sprayed in; (a) 50 Torr Ar, (b) 500 Torr Ar, (c) 200 Torr air and (d) 500 Torr air.
surement of mass gain with time. Hagel reported α-alumina formation below 1 173 K and α-alumina above 1 173 K for Fe–22at%Al alloy. Tortorelli also assigned the oxide as α-alumina from the kinetics curve of mass gain. Additional experiment like isothermal oxidation tests should be conducted to assign the oxide.

Generally, infusible particle deposition is attainable in high velocity oxygen-fuel flame spray process (HVOF), in which combustion-driven high-speed gas jet produces dense coatings with less oxide formation. This process makes it possible to suppress the volatilization and oxidation of fine particles. In the present work, the loss of aluminium as shown in Table 1 is explicit, causing the deterioration of chemical properties of iron aluminide. In order to obtain highly qualified iron aluminide coating, HVOF experiments should be tried as future work. It is expected that the optimum process condition in plasma spraying enable the iron-aluminides for oxidation resistant layer. The additional function of anti-oxidation and probably sulfidation in conventional commercial steel could be imposed by this surface modification.

5. Conclusions

Microstructure and oxidation behavior of low-pressure plasma sprayed iron aluminide Fe–40at%Al have been investigated focusing on the spray conditions of atmosphere and pressure. The principle conclusions are summarized as follows.

(1) Microstructure of laminated layers including cavities is observed in all samples and particles with a size of 100 μm are observed only in the sample sprayed in 50 Torr Ar atmosphere.

(2) Chemical analysis revealed a loss of aluminium and
oxygen pick-up in samples sprayed in air. XRD analysis exhibited only iron aluminide spectra without the second phase. The intensity of superlattice spectra of aluminide is strong in the samples sprayed in Ar compared with in air.

(3) Mass gain in the oxidation test with temperatures is small and insensitive to temperature in the sample sprayed in 50 Torr Ar, which is equivalent to as-cast bulk sample, while it increases significantly with temperature in other samples.

(4) SEM observation revealed the evolution of iron oxides in the samples sprayed in air, while not in the sample sprayed in Ar. The mechanism for good resistance to oxidation in the sample sprayed in 50 Torr Ar is attributed to infusible particle deposition responsible for protective α-alumina formation, which inherited the intrinsic oxidation resistance of iron aluminides.

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