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Improvement of adhesive strength of Ti–Al plasma sprayed coating

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Abstract

In order to improve the adhesive strength of plasma sprayed titanium coating, titanium–aluminum mixed powder was used as a material for plasma spraying. Adhesive strength of the plasma sprayed Ti–Al coatings was examined by changing the Al powder ratio in the Ti–Al mixed powder and input electrical power to the plasma torch. And then, they were discussed from the points of microstructure, hardness and oxygen and nitrogen contents of the coating. The plasma sprayed Ti–Al coating was found to be composed of Al and Ti compounds of $TiN_{0.3}$, Ti(N,O) and Ti_3Al, which were synthesized during the powder particles flight in plasma jet. The adhesive strength of the coating was improved by filling cracks and pores of the Ti compounds layers with the Al phase to form a dense microstructure, and also by hardening the Ti compounds and Al phase with the oxygen and nitrogen contained in the coating.

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1. Introduction

Thermal spray coating of titanium (Ti) by plasma spraying in the air is predominantly comprised of Ti oxide and nitride, as Ti is an active metal to react easily with ambient gases containing oxygen and nitrogen while spraying [1,2]. The sprayed Ti coating has high hardness of about 1000 HV, and the Ti compounds of the coating have excellent corrosion resistance [3]. So, the coating has a possibility to be applied as an undercoating to a thermal spray ceramic coating on a steel substrate, which might achieve highly adhesive and corrosion resistant properties. However, the sprayed Ti coating contains so many cracks and pores internally, which cause to decrease the adhesive strength and the corrosion protection properties [1].

Therefore, we tried to produce a dense sprayed coating to improve the properties by using Ti powder mixed with aluminum (Al) powder as a material for thermal spraying. The objectives of the present study were to investigate the process of the coating formation and to discuss the effect of spray materials and spraying conditions on the adhesive strength of the coating. The coating depositions were performed with various Al powder ratios in the Ti–Al mixed powder and the input electrical power to the plasma torch. Adhesive strength, hardness, phase composition of the coating and oxygen and nitrogen contents in the coating were evaluated.

2. Experimental procedure

Ti powder with powder size distributions of 60–80 μm from Sumitomo Titanium Corporation, and Al powder with powder size distributions of 40–60 μm from Hikari Sozai Corporation were used as starting materials. The Ti powder was mixed uniformly with the Al powder in advance, and then applied for the spraying.

The plasma spraying was performed using an Aeroplasma Limited Company APS7050 system in the air atmosphere. Argon gas and compressed air were used as plasma gas. The coatings with thickness of 150–200 μm were made on blasted mild steel substrates under the various conditions of spraying. The spray parameters for the main sample coatings, material content, input electrical power to the plasma torch and plasma gas mass flow, are shown in Table 1. The spray distance was kept constant to be 0.1 m.

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Table 1
Spray parameters for main sample coatings

Sample	Contents of spraying material (mass%)		Input electrical power (kW)	Plasma gas mass flow (10^{-5} m^3/s)	
	Ti	Al		Ar	Air
(a)	100	0	27	8.3	16.7
(b)	0	100	27	8.3	16.7
(c)	50	50	20	8.3	16.7
(d)	50	50	27	8.3	16.7
(e)	50	50	32	8.3	16.7
(f)	50	50	20	6.7	13.4
(g)	50	50	27	25	0

X-ray diffraction measurements were performed to identify the synthesized phases in the coatings from the surface of as-sprayed coatings. Cross-sections of the coatings were polished and observed by scanning electron microscopy (SEM). Elements distributions were measured by electron probe micro-analyzer (EPMA). Porosity of the coatings was measured with the image analysis of the SEM cross-section micrographs.

Vickers hardness measurements of the synthesized phases in the coatings were carried out on the cross-section of the coatings with an indenting load of 0.5 N.

Tensile adhesive strength measurements of the coatings were carried out with an Instron type testing machine. Test specimens were made of mild steel bars of 25 mm in diameter. Each sample was sprayed on the end face, and its face was bonded to the same diameter bar end by an epoxy resin adhesive. Self-aligning device was used for applying the tensile load to the assembly of the coating and fixtures.

The oxygen and nitrogen contents of the coatings were measured by the method of the inert gas melting–infrared (IR) and thermal conductivity (TC) detection.

3. Results and discussion

3.1. Microstructure and synthesized phase

The X-ray diffraction pattern for the sprayed Ti coating, sample (a), indicated the presence of $TiN_{0.3}$ and Ti(N,O) (TiN–TiO solid solution), and for the sprayed Al coating, sample (b), the presence of only Al. While, for the Ti–50 mass% Al mixed powder sprayed coatings, sample (c)–(g), were detected Al, $TiN_{0.3}$, Ti(N,O) and small peaks of synthesized phase of Ti_3Al.

Fig. 1 shows SEM micrographs of cross-sections of those sprayed coatings. The sprayed Ti coating, sample (a), had a porous structure and included cracks and pores in high density. The sprayed Al coating, sample (b), had a dense microstructure. And the sprayed Ti–50 mass% Al coatings, sample (c)–(g), had a dense laminated structure composed of Ti compounds phase and Al phase.

The elemental mapping of the cross-section of sample (d) by determined EPMA showed that Ti and Al elements were detected overlapping each other at a small portion of the interior of the Ti compound layer. The synthesized phase at the position would be Ti_3Al, as detected by X-ray diffraction analysis.

The formula of Ti_3Al formation is given by

$$3\mathrm{Ti} + \mathrm{Al} = \mathrm{Ti_3Al}$$

$$\Delta G^{\mathrm{f}} = -29633.6 + 6.70801T/\mathrm{K}$$

ΔG^{f} : the Gibbs energy of Ti_3Al formation $(\mathrm{Jmol^{-1}})$ [4]

That is, from the view of the thermodynamics, Ti_3Al can be easily formed from Ti with Al. The pressures of O_2 and N_2 in the atmosphere are much higher than the equilibrium pressure O_2 and N_2 to form Ti_3Al from TiO with Al and TiN with Al

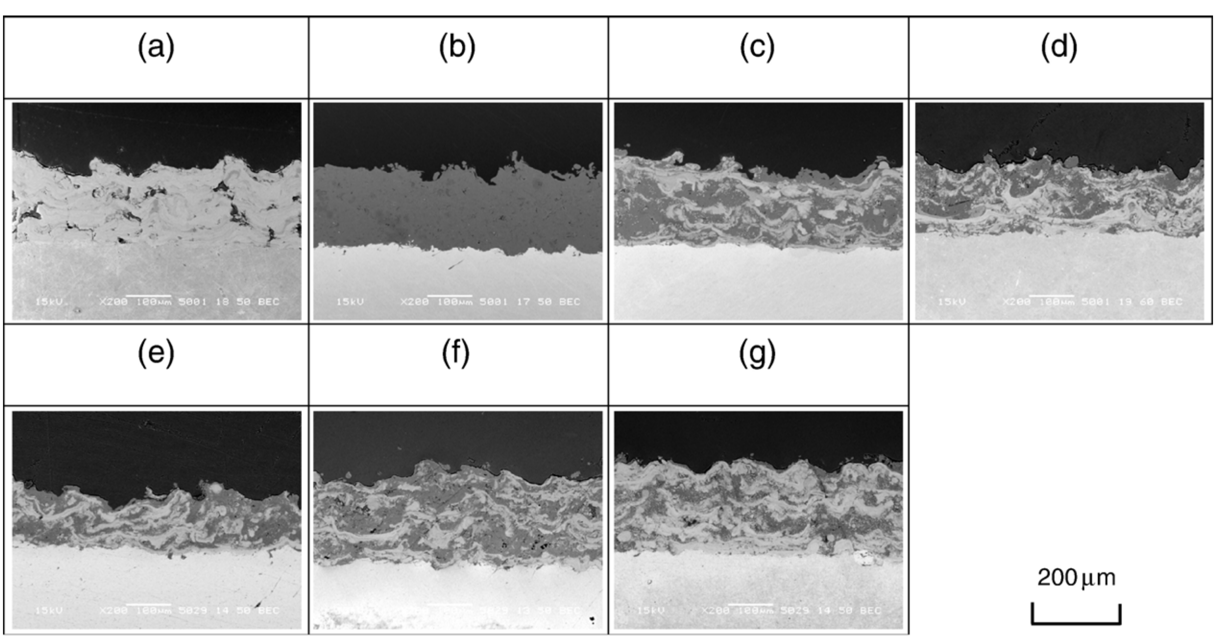

Fig. 1. SEM micrographs of cross-sections of sprayed coatings.

[4,5]. So, Ti_3Al cannot be formed thermodynamically from TiO with Al or TiN with Al under the condition of spraying in the air atmosphere. And also, Ti_3Al was detected always at the interior of the Ti compound layer, not at the interface of the Ti compound and Al layers. This phenomenon indicates that Ti_3Al would be synthesized from Ti and Al particles dynamically during flight, and not from Ti(N,O) or $TiN_{0.3}$ with Al on the substrate. The reaction would proceed at the interface of the Ti particle contacted with the Al particle.

Conclusively, the formulas of compounds formation can be described as follows:

$$Ti + 1/2N_2 + 1/2O_2 \rightarrow Ti(N, O)$$

$$Ti + N_2 \rightarrow TiN_{0.3}$$

$$3Ti + Al \rightarrow Ti_3Al$$

And the formation of the Ti–Al sprayed coating on the substrate would proceed as follows. At first, the compounds of Ti oxide and nitride in the fused particles would be solidified almost as soon as adhering to the substrate, as the melting points of TiO and TiN are 2023 K and 3223 K, respectively, which are much higher than that of Al, 933 K. Then, cracks and pores between the Ti compound layers would be filled with the melting Al particles, and the coating finally became solidified as a whole.

3.2. Effect of Al powder ratio of Ti–Al mixed powder and input electrical power to the plasma torch on adhesive strength of sprayed Ti–Al coating

The adhesive strength of the sprayed Ti–Al coatings varied with Al powder content of the sprayed Ti–Al mixed powder under the input electrical power to the plasma torch of 20 kW. The maximum strength was 45 MPa at the Al content of 50 mass%.

Fig. 2 shows adhesive strength of the sprayed Ti coatings, the sprayed Al coatings and the sprayed Ti–50 mass% Al coatings with various input electrical power to the plasma torch at plasma gas flow rates of argon (Ar) of 8.3×10^{-5} m^3/s and compressed air of 16.7×10^{-5} m^3/s. The sprayed Ti–50 mass% Al coatings had higher adhesive strength than the other coatings sprayed with the same power, and had the maximum value of 60 MPa at the input electrical power to the plasma torch of 27 kW. While the adhesive strength of the other coatings increased with an increase in the input electrical power to the plasma torch. In the adhesive tests all the specimens were fractured at the inside of the coating, and the fracture was referred to as cohesive failure. The fracture surface changed depending on the Al content of mixed sprayed powder. Irregular contours of the splats were observed on the fracture surface of the sprayed Al coating, sample (b). This indicated the sprayed Al coating fractured at the interfaces of laminated splats. In contrast, in the sprayed Ti coating, sample (a), was observed a mirror-like fracture surface, which generally caused by brittle fracture at inside of the splat. While, the fracture surface of the sprayed Ti–50 mass% Al coating, sample (d), presented a mixed failure of the separated Al splats and the brittle fracture of the Ti compound phase.

It is known that brittle fracture strength of a thermal spray coating is related to the mechanical properties by Griffith equation [6].

$$\sigma = \sqrt{\frac{2E\gamma_s}{\pi c}}$$

E: Young's modulus
γ_s: energy required to break bonds associated with unit area of surface
c: half length of the crack in the coating

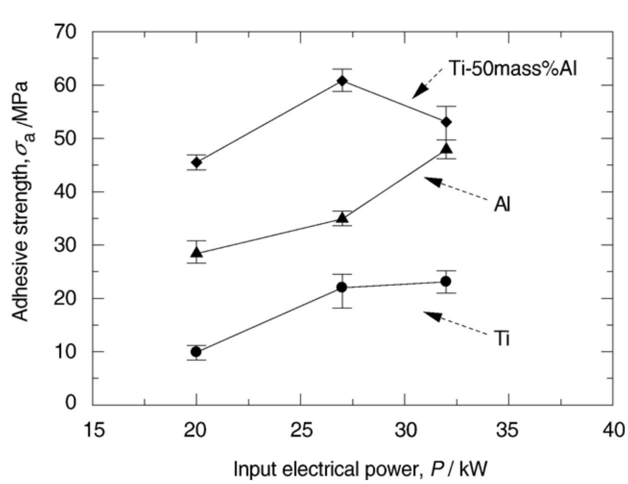

Fig. 2. Effect of input electrical power to the plasma torch on adhesive strength of Ti, Al and Ti–50 mass% Al coatings.

Table 2
Oxygen and nitrogen contents, hardness and porosity of the coatings

Sample	O or N contents of the coating (mass%)		Hardness of the coating (HV 0.5)		Porosity (%)
	Oxygen	Nitrogen	Ti compound phase	Al phase	
(a)	4.2	5.3	1050		6.8
(b)	0.88	0.33		42	0.3
(c)	2.5	2.6	817	46	1.0
(d)	3.0	3.0	848	56	0.8
(e)	3.2	3.3	845	63	0.6
(f)	3.1	3.4	923	66	1.0
(g)	2.4	2.3	691	42	0.8

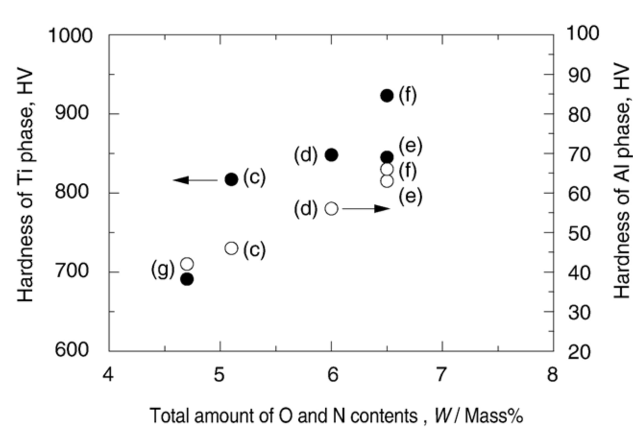

Fig. 3. Effect of total amount of the oxygen and nitrogen contents on hardness of Ti compound phase (●) and of Al phase (○) in the Ti–50 mass% Al coatings.

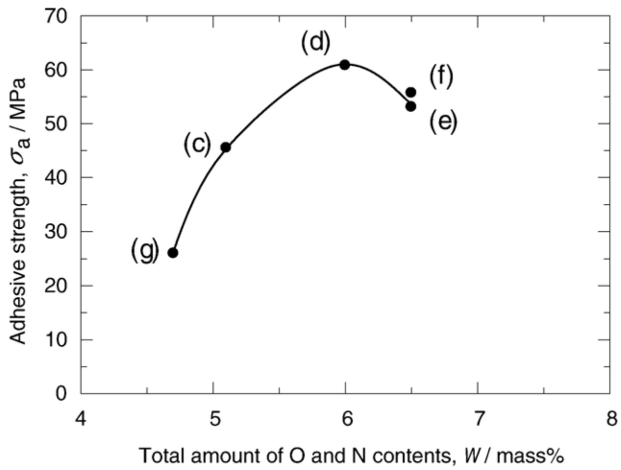

Fig. 4. Effect of total amount of the oxygen and nitrogen contents on adhesive strength of the Ti–50 mass% Al coatings.

According to this equation, the fracture strength is proportional to the inverse of the square root of the crack length in the coating. The low adhesive strength of sprayed Ti coating would be attributed to the fact that the coating had a porous structure including large cracks and pores as shown in Fig. 1. On the contrary, the dense microstructure of the sprayed Ti–Al coating would provide the high adhesive strength.

3.3. Effects of oxygen and nitrogen contents on hardness and adhesive strength of the coatings

Table 2 shows the oxygen and nitrogen contents of the various sprayed coatings fabricated under the condition of Table 1. Those contents increased with an increase in the input electrical power to the plasma torch except for the coating of sample (g) sprayed with Ar of plasma gas. The hardness of Ti compound and Al phases in the coatings are also given in Table 2.

Fig. 3 shows hardness of the Ti compound and Al phases of the sprayed Ti–50 mass% Al coatings plotted against a total amount of the oxygen and nitrogen contents of the coatings. The hardness values of the both phases, particularly in the Ti compound phase, increased with an increase in the total amount of the oxygen and nitrogen contents. This was because the amount of the synthesized Ti oxide and nitride in the coating increased with an increase in the total amount of the oxygen and nitrogen. As for the Al phase, hard particles of synthesized Ti compounds dispersed in the Al phase would lead to precipitation hardening.

Fig. 4 shows the adhesive strength of the sprayed Ti–50 mass % Al coatings plotted against a total amount of the oxygen and nitrogen contents of the coatings. The adhesive strength increased up to 60 MPa with an increase up to 6 mass% in the total amount of the oxygen and nitrogen contents, and then decreased slightly with further increase in them.

As shown in Table 2, the porosity of Ti–50 mass% Al coatings was low and not affected by spray parameters, whereas the adhesive strength of them was affected evidently. So, the coating porosity would not be correlated with the adhesive strength in this work. And also, the phase distribution of Ti compounds and Al in the coatings varied slightly with the spray parameters as shown in Fig. 1. The changes in adhesive strength of the coatings shown in Fig. 4 should be attributed to the strength of the synthesized phases in the coatings.

The coatings of sample (e) and sample (f) contained almost the same amount of oxygen and nitrogen contents, leading to have the same adhesive strength despite the differences in spray parameter, and the hardness of the both coatings was harder than that of sample (d). However adhesive strength of the both coatings was slightly lower than that of sample (d). The excess oxygen and nitrogen retained in both coatings would cause the brittle fracture within the Ti compound phase, resulting in the decrease in the adhesive strength.

4. Conclusion

The plasma sprayed Ti–Al coating using Ti powder mixed with Al powder was composed of Al and compounds of $TiN_{0.3}$, Ti(N,O) and Ti_3Al, which were synthesized during the particle flight. The adhesive strength of the coating was improved by filling cracks and pores of the Ti compound layers with the Al phase to form a dense microstructure, and highest strength was obtained with the Ti–Al mixed powder of 50 mass% Al content. The adhesive strength was correlated with the hardness of the coating, particularly of the synthesized Ti phase, and also was affected by the total amount of the oxygen and nitrogen contents of the coating.

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