Liquid Mn Penetration and Reaction Treatment of Plasma-sprayed Al_2O_3 Coating

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The penetration phenomena of liquid Mn to porous Al_2O_3 coating plasma-sprayed on SS400 steel substrate was studied by heating at 1573 K in vacuum atmosphere. Moreover, the possibility of improving the Al_2O_3 coating properties was examined. The formation of MnAl_2O_4 was clearly recognized in the connected porosity of Al_2O_3 coating penetrated with liquid Mn. It was revealed that the hardness and the fracture stress of the composite coating consisted of Al_2O_3 and MnAl_2O_4 without porosities after heat-treatment with Mn increased greatly compared with as-sprayed Al_2O_3 coating.

KEY WORDS: Al_2O_3 coating; MnAl_2O_4 ; liquid manganese; penetration; plasma-spraying; heat-treatment; SS400 steel.

1. Introduction

Plasma-sprayed ceramic coatings have been widely applied in many industrial fields because of an excellent wear, erosion, heat resistance, and corrosion resistance which ceramics possess themselves. Al_2O_3 coatings plasma-sprayed are well known as wear and insulation coatings.¹⁾ However, because of existence of the connected porosity in ceramics coatings, the properties of ceramic coatings, such as their resistance to wear, corrosion, erosion, high temperature oxidation *etc.* are reduced. In order to improve the properties of coatings, various methods have been reported,^{1–3)} such as sealing with resin and chromium trioxide, electro-plating of metal *etc.* In order to make greater use of Al_2O_3 coatings at high temperature, it is necessary to develop more effective post-treatment methods.

In this study, the penetration of liquid Mn into connected porosity in Al_2O_3 coatings was utilized to form a dense and composite coating in order to improve the properties of the coatings. The penetration behavior of liquid Mn, and the improving the mechanical properties of Al_2O_3 coatings were examined.

2. Materials and Experimental Procedures

2.1. Materials

The substrate was a SS400 mild steel plate with 15 mm × 15 mm × 3 mm. The surface was grit blasted before spraying. Commercially available Al_2O_3 powder was used as the plasma spray powder. The mean particle size of the powder was 10–44 μm . Plasma spraying was carried out in the air and Al_2O_3 coating with a thickness of 150–200 μm was produced by employing the spraying

conditions shown in Table 1. Metals for the penetration treatment were of purity 99.99 wt% Mn, Ni and Cu plate, of about 3–5 g. Sintered alumina plate of purity 99.7 wt% in 15 mm diameter and 3 mm thickness for the reaction with liquid Mn was used. These assembly were degreased

Table 1. Plasma spraying condition for Al_2O_3 coating.

Spray apparatus		Plasmadyne (Mach 1)
Plasma gas (Ar)	Pressure	7 kg·cm ⁻²
	Flow rate	47 l·min ⁻¹
Auxiliary gas (He)	Pressure	4.2 kg·cm ⁻²
	Flow rate	5.7 l·min ⁻¹
Powder carrier gas (Ar)	Pressure	5.6 kg·cm ⁻²
	Flow rate	38 l·min ⁻¹
Plasma power		27.2 kW
Spray current		800 A
Plasma distance		100 mm
Hopper setting		6.3 M·min ⁻¹
Cooling air pressure		2.0 kg·cm ⁻²

Fig. 1. Schematic diagram of the experimental apparatus for liquid Mn penetration treatment.

Fig. 2. (a) Typical SEM microstructure of a copper-electroplated Al_2O_3 coating. White strings are copper and represent vertical cracks in individual lamella and non-bonded interfaces between flattened particles, and (b) schematic illustration of cross section of ceramic coating.

in acetone with an ultrasonic bath, before the heat-treatment.

2.2. Method of Liquid Mn Penetration Treatment

Figure 1 shows a schematic diagram of the experimental apparatus of liquid metal penetration treatment. The metals of the definite quantity were contacted with the surface of Al_2O_3 coatings and was heated under vacuum of 1.33×10^{-1} or 1.33×10^{-3} Pa at 1573 K at the heating rate of 50 K/min. After keeping at the appointed temperature, the assembly was cooled in the furnace at the cooling rate of 1.5 K/min. Alumina crucible with 13 mm inside diameter and Mn was set on the surface of Al_2O_3 coating.

2.3. Method of Analysis and Evaluation of Coating

Cross-sections of sprayed test pieces and heat-treatment test pieces were examined by scanning electron microscopy (SEM), and changes in elemental composition of the cross-section of coating and in crystal structure of the coating were studied by mean of an electron probe micro analyzer (EPMA) and X-ray diffraction analyzer (XRD) respectively. The micropores of coating, the distribution and existence of porosity in coating were appreciated by mean of observing copper deposited in the coating by electroplating.³⁾ Fracture stress of the coating and sintered alumina were the maximum tensile stress at inflection point from the relation between applied load and friction force for coating or sintered alumina through scratch test.⁴⁾

3. Experimental Results and Discussions

3.1. Micropores of Al_2O_3 Coating

Plasma-sprayed ceramics coatings have a layer structure formed by the deposition of flattened, rapidly solidified particles. The connected porosities which were composed of micropores, a non-bonded area between ceramic lamellae and microcracks in individual flattened particles exist in the coating. Figure 2(a) shows typical SEM microstructure of a cross-section of a copper-electroplated Al_2O_3 coating. The distribution of the connected porosities, non-bonded area between flattened particles and the vertical crack in individual flattened particles in the coating are observed clearly by the deposited copper of white area. It has been reported that the width of these vertical direction and horizontal

Fig. 3. Shape of various metals on Al_2O_3 coating surface after heat-treatment.

direction of porosities are about $0.16\text{--}0.19\text{ }\mu\text{m}$ and $0.25\text{--}0.38\text{ }\mu\text{m}$.⁵⁾ Schematic diagram of the distribution of the connected porosities from coating surface to the interface between coating and substrate is shown like network in Figure 2(b).

3.2. Penetration Behavior of Liquid Mn into Connected Porosities in Al_2O_3 Coating

In order to certify the penetration of liquid Mn into

Fig. 4. SEM microstructures of Al_2O_3 coatings heat-treated with Mn at 1573 K in 1.33×10^{-3} Pa: (a) for 0.9 ks; (b) for 3.6 ks.

Al_2O_3 coating, metals such as Cu, Ni, Mn was set on Al_2O_3 coating and heated for 0.3 ks at temperature of 50 K over melting point of each metal in vacuum. Figure 3 shows the shape of various metals on Al_2O_3 coating after heat-treatment. The apparent contact angle of Cu, Ni and Mn were about 140° , 115° and 0° , respectively. It was recognized that the penetration of liquid metal into Al_2O_3 coating occurred with Mn on Al_2O_3 coating. However, Cu and Ni were not penetrated into Al_2O_3 coating. Figure 4 shows the SEM microstructure of cross-section of Al_2O_3 coating after heat-treatment with Mn for 0.9 and 3.6 ks at 1573 K in 1.33×10^{-3} Pa, respectively. In the case of 0.9 ks, it was recognized that the thin dense layer of about $2\text{--}5\text{ }\mu\text{m}$ was formed on the surface of coating, but in the inside of coating the densification did not occur and the microstructure is like that of as-sprayed Al_2O_3 coating. In the case of 3.6 ks compared with that of 0.9 ks, a thick dense layers were formed on the surface of coating and at interface between coating and SS400 steel substrate. The defects of porosity *etc.* also disappeared in middle area of coating. Figure 5 shows XRD results of surface layer and inside of the Al_2O_3 coatings shown in Figs. 4(a) and 4(b). Existence of a little amount of MnAl_2O_4 was recognized on the surface of coating in the case of 0.9 ks and $\alpha\text{-Al}_2\text{O}_3$ is main phase. In inside of same coating, existence of a little amount of $\alpha\text{-Mn}$ was recognized and intensity ratio of $\text{MnAl}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ is smaller than that of the surface.

(a)

(b)

Fig. 5. XRD results of surface and inside of Al_2O_3 coatings heat-treated with Mn: (a) for 0.9 ks; (b) for 3.6 ks.

Compare with that of 0.9 ks, the MnAl_2O_4 on the new dense surface layer of the coating heat-treated with Mn for 3.6 ks was markedly increased and became composite phase composed of MnAl_2O_4 as main phase and Al_2O_3 . The inside of the coating, where the MnAl_2O_4 phase was increased with disappearance of $\alpha\text{-Mn}$ compare with that of inside of coating heat-treated for 0.9 ks, was composed of Al_2O_3 phase as main phase and MnAl_2O_4 spinel. It may be considered that MnAl_2O_4 was formed by reaction

Fig. 6. SEM image and EPMA line analysis results of cross-section of Al_2O_3 coating heat-treated with Mn for 3.6 ks at 1573 K in 1.33×10^{-3} Pa.

of liquid Mn dissolved oxygen in vacuum atmosphere and Al_2O_3 . **Figure 6** shows the microstructure and EPMA line analysis results of cross-section of Al_2O_3 coating shown in Fig. 4(b). From this EPMA analysis, Mn concentration in dense layers on the surface and at the interface of the coating is higher than that of the inside of coating, and the intensity ratio between Mn and Al in both layers is almost same. Therefore, it may be considered that the dense layer of the interface is also composite phase composed of MnAl_2O_4 as main phase and Al_2O_3 phase such as that of dense layer of the surface.

In the inside of the coating, almost uniform alternate change of concentration of Mn and Al are recognized and narrow peaks of Mn existed between broad peaks of Al which shows the deposited Al_2O_3 particle part. From the result, it is considered that MnAl_2O_4 spinel exists among the Al_2O_3 particles deposited. Moreover, the constant Mn concentration gradient from the coating side to SS400 steel substrate is recognized and Mn-Fe alloy layer with about $70 \mu\text{m}$ was seen in the substrate side.

From these results, the liquid Mn could penetrate easily into inside of Al_2O_3 coating until the interface between the coating and substrate through the connected porosities of coating in short time. The formation of MnAl_2O_4 by the reaction of $\text{Mn}(\text{O})$ and Al_2O_3 particle in the connected porosities increased with increase of heat time. The porosities in Al_2O_3 coating were filled with MnAl_2O_4 spinel formed around Al_2O_3 deposited particles in the inside of Al_2O_3 coating. On the other

Fig. 7. SEM micrographs of cross-section of copper-electroplated Al_2O_3 coatings heat-treated for 3.6 ks at 1573 K in 1.33×10^{-3} Pa: (a) Al_2O_3 coating heat-treated without Mn; (b) Al_2O_3 coating heat-treated with Mn.

hand, thick layer composed of MnAl_2O_4 as main phase was formed on the surface of Al_2O_3 coating due to supply of a large amount of liquid $\text{Mn}(\text{O})$. **Figure 7** shows SEM images of cross-section of copper-electroplated Al_2O_3 coatings heat-treated with and without Mn for 3.6 ks at 1573 K in vacuum. As shown in this figure, the deposited copper was not found without the connected porosities in the inside of Al_2O_3 coating heat-treated with Mn.

3.3. Reaction of Al_2O_3 Particle and Liquid Mn

Figure 8 shows SEM image and EPMA line analysis results of cross-section of sintered Al_2O_3 plate heat-treated with Mn for 3.6 ks at 1573 K in 1.33×10^{-3} Pa. **Figure 9** shows XRD analysis result of the surface of sintered Al_2O_3 heat-treated with Mn on the same conditions as shown in Fig. 8. From these results, the formation reaction of MnAl_2O_4 between sintered Al_2O_3 and liquid Mn occurred as shown in the case of Al_2O_3 coating. A dense reaction layer formed newly on the surface of sintered Al_2O_3 plate.

As mentioned above, Mn reacted with Al_2O_3 particle to give MnAl_2O_4 during Mn penetration in Al_2O_3 coating. Therefore, it must be useful to consider a reaction between Mn and Al_2O_3 during heat-treatment with Mn at 1573 K in vacuum atmosphere. On the reaction.

Fig. 8. SEM image and EPMA line analysis results of cross-section of sintered alumina plate heat-treated with Mn for 3.6 ks at 1573 K in 1.33×10^{-3} Pa.

Fig. 9. XRD result of surface of sintered alumina heat-treated with Mn.

$$\Delta G^\circ = 92458.8 - 22.275T \quad \text{J mol}^{-1} \quad \text{.....(2)}$$

The direct reaction between Mn and Al_2O_3 at 1573 K could not occur in thermodynamics, since the Gibbs free energy is positive ($\Delta G^\circ = +57420 \text{ J/mol}$). However, in this study the formation of MnAl_2O_4 was seen. It may be considered that oxygen (O_2) contained in vacuum atmosphere dissolved into liquid Mn and participated in the formation reaction of MnAl_2O_4 between liquid Mn and Al_2O_3 .

For the reaction and Gibbs energy of the formation of MnAl_2O_4 .

$$\Delta G^\circ = -439970 + 90.93T \quad \text{J mol}^{-1} \quad \text{.....(4)}$$

In the case, it is possible that the formation reaction of MnAl_2O_4 occurs because ΔG° is -296973 J/mol at 1573 K.

Effect of pressure for heat-treatment on Mn penetration into Al_2O_3 coatings was examined. Figure 10 shows SEM images and image analyses of Mn, Al and O for Al_2O_3 coatings heat-treated with Mn for 3.6 ks at 1573 K in pressures of 1.33×10^{-1} and 1.33×10^{-3} Pa, respectively. In the case of heat-treatment in a highly evacuated condition, Mn is distributed like network over inside of Al_2O_3 coatings. Moreover, thick Mn rich layer is seen on the surface of Al_2O_3 coating and at the interface between Al_2O_3 coating and SS400 substrate. However, in a low evacuated condition, a remarkable existence of Mn in the inside of Al_2O_3 coating is scarcely seen, although thin Mn rich layer exists on the surface of coating and at the interface. It may be considered that oxygen amount dissolved in liquid Mn in a low evacuated condition is greater than that in a highly evacuated condition. So that liquid Mn contained a greater amount of oxygen reacts more easily and quickly with Al_2O_3 particle to give much MnAl_2O_4 on the surface of Al_2O_3 coating. Because of formation of a great amount of MnAl_2O_4 on the surface of coating, the penetration of liquid Mn into the inside of coating may be suppressed during heat-treatment with Mn in the low evacuated condition.

3.4. Mechanical Properties of Al_2O_3 Coating after Heat-treatment with Mn

Figure 11 shows the Vickers hardness distribution of cross-section of Al_2O_3 coatings heat-treated with Mn at 1573 K in 1.33×10^{-3} Pa, as-sprayed Al_2O_3 coating and sintered Al_2O_3 . From the results, the hardness of Al_2O_3 - MnAl_2O_4 composite coating after heat-treatment with Mn was increased remarkably, compared with about 700–800 Hv, of as-sprayed Al_2O_3 coating. Hardness of cross-section of Al_2O_3 composite coating in the case of heat-treatment with Mn for 10.8 ks reached 1600 Hv, it is greater than about 1450 Hv of sintered Al_2O_3 .

These results can be considered that as-sprayed Al_2O_3 coating with connected porosities became dense and the bond among deposited Al_2O_3 particles strengthened. Because the connected porosities in coating were penetrated with liquid Mn(O) and were filled up with MnAl_2O_4 formed by the reaction of Al_2O_3 particle and liquid Mn(O).

The fracture stress of the Al_2O_3 coatings *etc.* calculated as follows. The relation between applied load and friction force was obtained from scratch test for surface of the test pieces polished, and the applied loads of Al_2O_3 coating heat-treated with Mn for 3.6 ks at 1573 K, as-sprayed Al_2O_3 coating and sintered Al_2O_3 were 3.1, 1.2 and 2.2 N as the inflection point respectively as shown in Fig. 12. The maximum tensile stress can be obtained as follows:

$$\sigma = \sigma_o \left(\frac{1-2\nu}{2} \right) (1 + A \cdot f) \quad \text{.....(5)}$$

Fig. 10.
EPMA image for Al_2O_3 coating heat-treated with Mn for 3.6 ks at 1573 K (a) in 1.33×10^{-1} Pa; (b) in 1.33×10^{-3} Pa.

Fig. 11. Vickers hardness distribution of cross-section of Al_2O_3 coatings as-sprayed, heat-treated with Mn and sintered alumina.

Fig. 12. Relation between applied load and friction force for Al_2O_3 coatings and sintered Al_2O_3 .

Fig. 13. Fracture stress for Al₂O₃ coatings as-sprayed, heat-treated with Mn and sintered alumina.

where

$$\sigma_o = \frac{F}{\pi a^2} \quad \dots\dots\dots(6)$$

$$A = \frac{3\pi(4 + \nu)}{8(1 - 2\nu)} \quad \dots\dots\dots(7)$$

σ : maximum tensile stress; σ_o : average stress over contact area; F : applied load; a : contact radius; f : friction coefficient; ν : Poisson's ratio.

Figure 13 shows results of fracture stress calculated for Al₂O₃ coating heat-treated with Mn for 3.6 ks at 1 573 K, as-sprayed Al₂O₃ coating and sintered Al₂O₃. From the figure, it is recognized that the fracture stress of Al₂O₃ coating changes from 6 to 16 GPa after heat-treatment with Mn.

4. Conclusion

Liquid Mn penetration treatment for plasma-sprayed Al₂O₃ coating was studied by heating in vacuum atmosphere. Mn penetration behavior into connected porosities in coating was examined in order to improve the mechanical properties of Al₂O₃ coating. The main results obtained are as follows.

(1) The penetration of liquid Mn into plasma-sprayed Al₂O₃ coating was recognized by heating at 1 573 K in pressure of 1.33×10^{-3} Pa. The penetration of Mn occurred through connected porosities which are composed of micropores, a non-bonded area between Al₂O₃ particles deposited, and microcracks in individual flattened particles in Al₂O₃ coating. During Mn penetration, liquid Mn(O) reacted with Al₂O₃ particles to form MnAl₂O₄. MnAl₂O₄ filled up the connected porosities in Al₂O₃ coating.

(2) After heat-treatment with Mn, Al₂O₃ coating became dense and the bond among flattened particles in Al₂O₃ coating strengthened. The microhardness of Al₂O₃ coatings reached about 1 600 Hv after heat-treatment with Mn.

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