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Functionally Graded Zirconia Composite Coatings Formed by Gas Tunnel Type Plasma Spraying†

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Abstract

The zirconia-alumina (ZrO_2-Al_2O_3) composite coating formed by gas tunnel type plasma spraying at short spraying distances, also has a high hardness layer at the surface side of the coating. The Vickers hardness (Hv=1300) of the ZrO_2 composite coating is much higher than a zirconia (ZrO_2) coating, and the graded functionality becomes large. In this paper, the graded functionality of such high hardness ZrO_2 and its composite coating in the case of different spraying conditions is investigated. The enhancement of the graded functionality of such composite coatings is discussed. For these composite coatings, the Vickers hardness of the high hardness layer near the coating surface becomes higher with an increase in the traverse number of plasma spraying. In the case of large traverse numbers, the hardness distribution is much smoother, and the graded functionality is improved. The microstructure of this composite coating has a distribution of embedded thin ZrO_2 splats in a Al_2O_3 matrix, with parallel alignment of the splats relative to the substrate surface.

Keywords: Graded functionality, Zirconia-alumina composite coating, High hardness, Gas tunnel type plasma spraying, Traverse number. Microstructure, Vickers hardness, Thermal barrier coating

1. Introduction

Ceramic coatings generally have excellent characteristics such as corrosion resistance, thermal resistance wear resistance, and so on. In particular, the zirconia (ZrO_2) coating has a superior property as a thermal barrier coating (TBC), and has been used in high-temperature turbine blade applications etc. This occurs because ZrO_2 has high temperature resistance, low thermal conductivity, and thermal shock resistance [1]. The porosity in plasma sprayed ZrO_2 coating also has an advantage for thermal insulation, although, it causes the problem that there is substrate corrosion at high temperatures because of high porosity in the coating. Therefore in order to use ZrO_2 coating as a TBC for high temperature operation, such as engine parts, a much denser coating has been demanded to prevent such corrosion. One of the keys to this solution will be the graded functionality of the TBC.

Recently, high functionally graded coatings (FGC) of ceramics are applied in many fields such as electronics and so on. However, the development of FGC for corrosion protection at high temperatures using plasma spray techniques is still in an embryonic stage and will require significant R&D effort [2].

In these circumstances, the study of ceramic sprayed coatings using the newly developed gas tunnel type plasma spraying has been started by the authors [3]. The fundamental properties of ceramic coatings formed by gas tunnel type plasma spraying have been investigated in detail in the previous studies [4,5,6]. The Vickers hardness of this sprayed coating became 20-30 % higher than that of conventional plasma spraying. For example, In the case of alumina (Al_2O_3) coatings, high hardness of Hv =1500 was obtained at a spraying distance L=30mm when the power input P=30 kW [7].

In ZrO_2 coatings by means of the gas tunnel type plasma spraying, the Vickers hardness of the cross section was also increased with decreasing spraying distance L, and a higher Vickers hardness Hv could be obtained at a shorter spraying distance. For example, Vickers hardness of ZrO_2 coating was Hv=1050 at L=30 mm, when P=20 kW. And at L=30 mm when P=33 kW, the Vickers hardness of ZrO_2 coating was about Hv=1200 [8]. Thus, a ZrO_2 coating formed by the gas tunnel type plasma spraying at a short spraying distance has a high hardness layer at the surface side of the coating, which shows the graded functionality of hardness [9].

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In this paper, the graded functionality of such high hardness ZrO_2 and its composite coating in the case of different spraying condition was investigated. The Vickers hardness of the high hardness layer near the coating surface was investigated briefly, by changing the number of traverses of plasma spraying. The influences on the microstructure of the coating and the coating density were also discussed.

2. Experimental Procedure

The gas tunnel type plasma spraying apparatus used in this study is shown in **Fig.1**. The experimental method to form the high hardness ceramic coatings by means of the gas tunnel type plasma spraying have been described in the previous papers [4,5,6]. In this case, the gas divertor nozzle diameter was d=20 mm. The power input to the pilot plasma torch (gun), which was supplied by the power supply, PS-1 was zero during spraying. The gun is a hollow cathode type, which allows the injection of powders along the centerline of the gun. All spraying experiments were conducted inside a spraying chamber, however, the chamber was not evacuated and no shroud or filler gas was used.

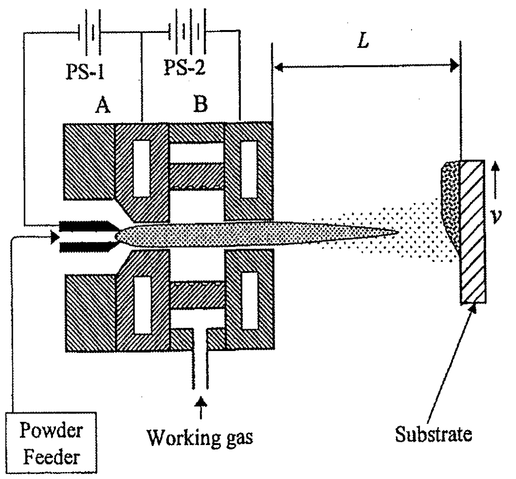

Fig.1 Gas tunnel type plasma spraying apparatus used in this study; L: spraying distance. Gas divertor nozzle was 20 mm.

Table 1 Experimental conditions.

Power input:	P = 23-26 kW
Working gas (Ar) flow rate:	Q = 180 l/min
Powder feed gas (Ar)	Q_{feed} =10 l/min
Spraying distance:	L = 40 mm
Traverse speed:	v = 25-1000 cm/min
Powder feed rate:	w = 30g/min

Table 2 Chemical composition and size of zirconia powder used.

	Composition (wt%)					Size (μm)
ZrO_2	ZrO2	Y2O3	Al2O3	SiO2	Fe2O3	
	90.78	8.15	0.38	0.20	0.11	10-44
Al_2O_3	Al2O3	Na2O	SiO2	Fe2O3		
	99.80	0.146	0.01	0.01		10-35

The experimental conditions for this plasma spraying are shown in **Table 1**. The power input to the plasma torch was about P=25 kW, and the spraying distance was a short distance of L=40 mm. The working gas flow rate for gas tunnel type plasma spraying torch was Q=180 l/min of Ar gas, the gas flow rate of carrier gas was 10 l/min, and the powder feed rate of zirconia/alumina mixed powder was w=30 g/min. The traverse speed of the substrate was changed from the low value of v=25 cm/min to v=250 cm/min.

Table 2 shows the chemical composition and the size of zirconia (ZrO_2) and alumina (Al_2O_3) powder used in this study. The ZrO_2 powder was a commercially prepared type of K-90: 8% yttria-stabilized ZrO_2, and Al_2O_3 powder was the type of K-16T. The mixing ratio of Al_2O_3 to ZrO_2 powder was 50- 70 wt % in this study. The substrate was SUS304 stainless steel (50x50x3t), which was sand blasted before using.

The zirconia-alumina (ZrO_2-Al_2O_3) composite coatings produced in 30-140 μm thicknesses on the substrate by plasma spraying at L=40 mm, at the traverse speed of 25 cm/min, when the traverse number was changed 1-4 times. On the other hand, in order to obtain the same coating thickness, the ZrO_2 composite coating was formed by changing both the traverse speed and traverse number under the condition of the same spraying time of 12 s.

The measurement of distribution of the Vickers hardness in the cross section of the ZrO_2 coating was carried out at each distance from the coating surface in the thickness direction. The Vickers hardness of the sprayed coatings was measured at the non-pore region in those cross sections under the condition that the load weight was 50 or 100 g and its load time was 15 s. The Vickers hardness was calculated as a mean value of 10 points measurements.

The cross section of these ZrO_2 composite coatings was observed with an optical microscope, at magnifications of 200 or 400. The X-ray diffraction (XRD) method was conducted on the surface of the coating. The X-ray source was Co, and the tube voltage was 30 kV and the tube current was 14 mA.

3. Results and Discussion

3.1 Distributions of Vickers hardness on the cross section of zirconia composite coating

Figure 2 shows the distributions of Vickers hardness on the cross section of ZrO_2 composite coatings produced by the gas tunnel type plasma spraying at the same traverse speed of v = 25 cm/min. In this case, the Ar gas flow rate was Q=180 l/min, the power input: P=25 kW and the spraying distance: L=40 mm. The powder feed rate was w=30 g/min. These coating were formed by one time traverse, two times traverse, and 3 times traverse (3 pass sprayed). The coating thickness was approximately proportional to the traverse number, and was 60, 90, 140 μm for 1, 2, 3 times traverse, respectively. The coating thickness per one traverse was about 50 μm for each coating in these results.

The distribution of Vickers hardness on the cross section of ZrO_2 composite coating for 1 time traverse shows one parabolic curve as shown in Fig. 2. The hardness near the coating surface was highest value of Hv=1140, much higher than that of near the coating substrate.

On the other hand, the distribution of Vickers hardness of ZrO_2 composite coating for 2 times traverse consists of two parabolic curves as shown in the same figure. From this distribution, it was found that the Vickers hardness of the coating surface layer (corresponding to the second pass) was more than 1200. The highest value of this high hardness layer was about Hv = 1210 at the distance from the coating surface of l=20-30 μm.

For 3 times traverse, the hardness distribution was that combined by 3 parabolic curves as shown in Fig.2. The Vickers hardness of the coating surface layer (the third pass) was highest value of about Hv = 1240. The hardness near the substrate was a lower value of Hv=1000. In this case, the hardness difference between the surface side and substrate side was much larger than in the case of less time traverse. Thus, as the traverse number increased, the graded functionality of hardness became greater in the thickness direction.

These results were similar to the case of ZrO_2 coatings obtained in the previous study. For an increase in the traverse number, the surface temperature of the coating during spraying became higher. Therefore it would be expected that coating density would be increased when the traverse number increases.

3.2 Dependence of Vickers hardness of zirconia composite coating on the traverse number

Figure 3 shows the relation between the traverse number and the Vickers hardness on the surface layer of ZrO_2 composite coating. In this case, those coatings for 1-3 times traverse were the same coating used in Fig. 2.

The value of Vickers hardness for each coating increased as the traverse number was increased. The maximum hardness was increased from Hv = 1120 to Hv = 1240. This would also correspond to an increase in the thickness of the coating. (60-140μm) For ZrO_2 coatings, the dependence of Vickers hardness was the same as the ZrO_2 composite coatings.

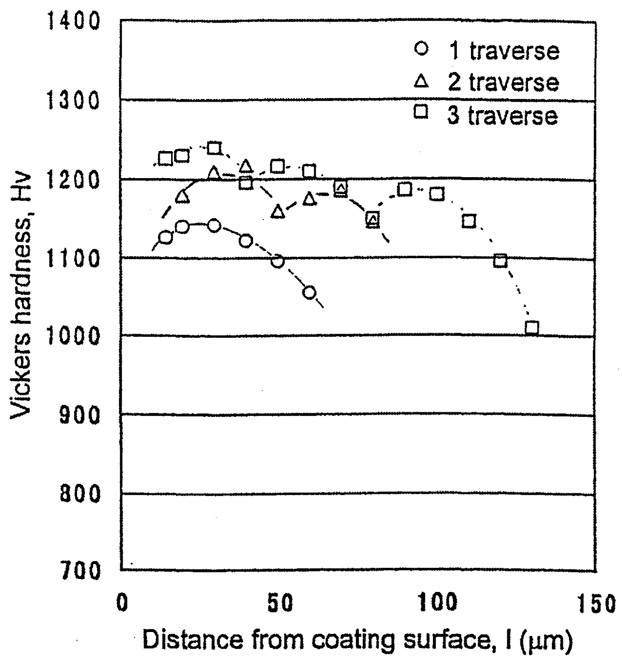

Fig.2 Distributions of Vickers hardness on cross section of zirconia composite coatings sprayed at L=40mm when P=25 kW.
Data plots: 1 time, 2 times and 3 times traverse.

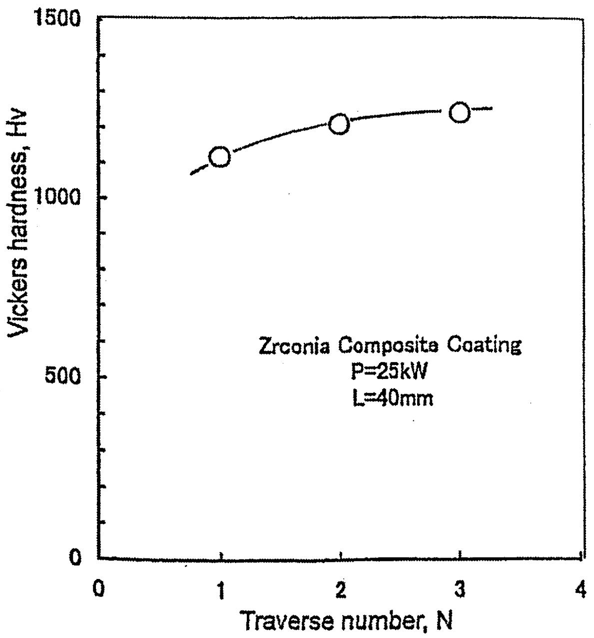

Fig.3 Dependences of Vickers hardness on the zirconia composite coatings on the traverse number at L=40mm when P=25 kW.

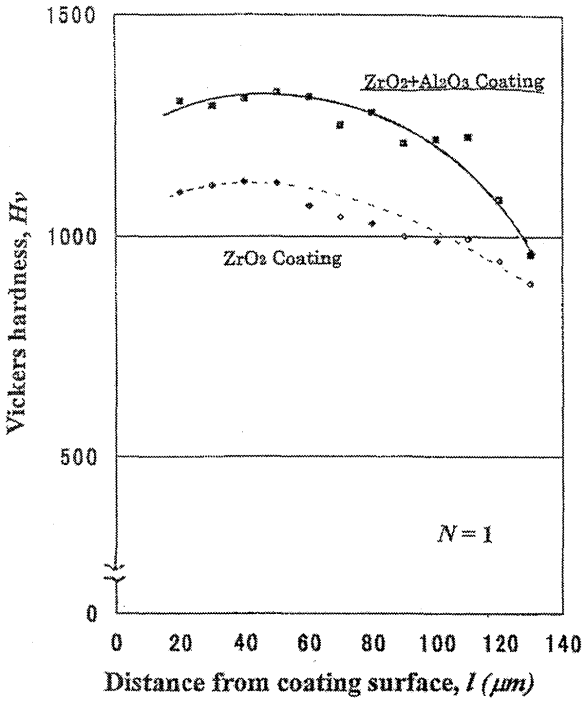

Fig.4 Distributions of Vickers hardness on cross section of zirconia composite coatings sprayed by 1 time traverse at L=30mm when P=20 kW.

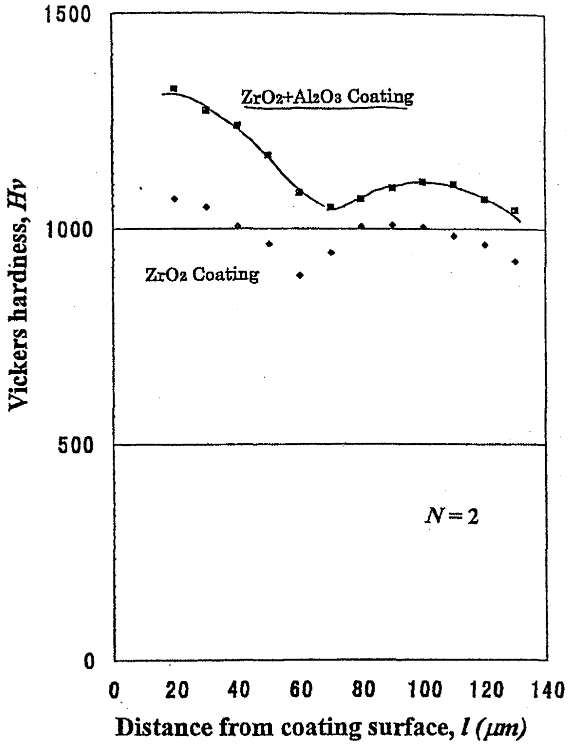

Fig.5 Distributions of Vickers hardness on cross section of zirconia composite coatings sprayed by 2 times traverse at L=30mm when P=25 kW.

In order to examine the effect of traverse number on the Vickers hardness without thickness influence, the ZrO_2 composite coatings with the same thickness, was 25 cm/min for 1 time traverse, 50 cm/min for 2 times traverse, 100 cm/min for 4 times traverse and so on, under the condition: L=40 mm, when P=25 kW. The spraying time was about 10 seconds, and the thickness of each coating was about 140 μm for each traverse number. In this case the mixing ratio of Al_2O_3 to ZrO_2 was about 70 %.

Figure 4 shows the distributions of Vickers hardness on the cross section of ZrO_2-Al_2O_3 composite coating for 1 time traverse. In Fig.4 the coating thickness was 140μm for 1 time traverse, and the hardness distribution was a parabolic curve. The highest value of about Hv = 1300 at the distance from the coating surface of l=40 μm. This maximum hardness became much higher than that of 1 time traverse as shown in Fig.3. This would be caused by an increase in the coating thickness.

On the other hand, the ZrO_2 coating of the same thickness had a flat distribution of the Vickers hardness, whose maximum value was about Hv=1100, lower than that of the ZrO_2 composite coating.

Figure 5 shows the distributions of Vickers hardness of ZrO_2-Al_2O_3 composite coating for 2- times traverse. The coating thickness was about 140μm, and the distribution consisted of two parabolic curves. The maximum hardness was about Hv = 1300 near the coating surface of l=20 μm. The Vickers hardness of this coating was similar value in the case of three times traverse as shown in Fig.3. Also, this maximum value of Hv = 1300 was almost the same as in those cases for 1, 4, and 10 times traverse, when the coating thickness of about 140μm.

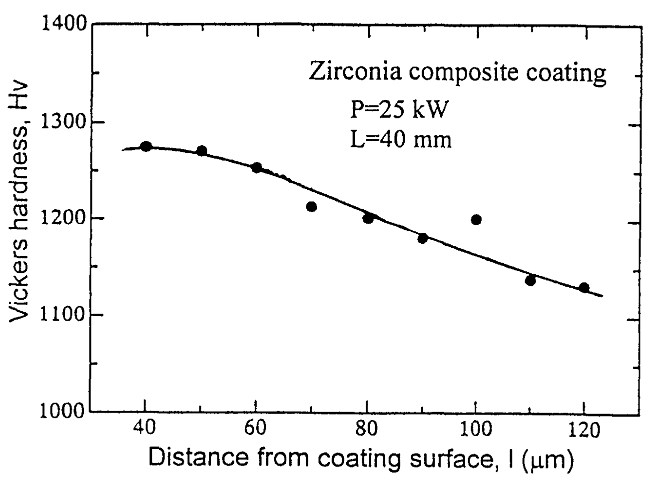

Fig.6 Distributions of Vickers hardness on cross section of zirconia composite coatings sprayed by 30 times traverse at L=30mm when P=25 kW.

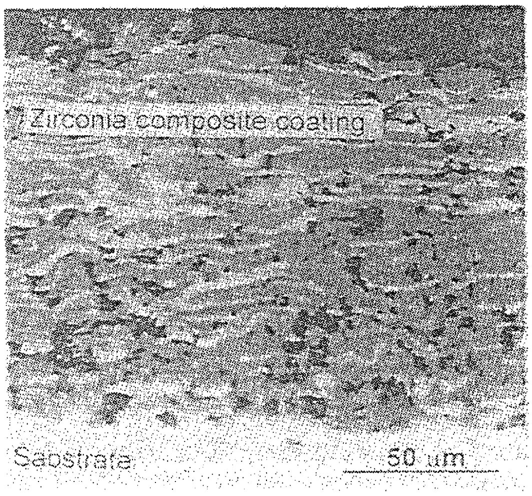

Fig.7 Microphotograph of cross section of zirconia composite coating. Sprayed by 30 times traverse at L=30mm when P=25 kW.

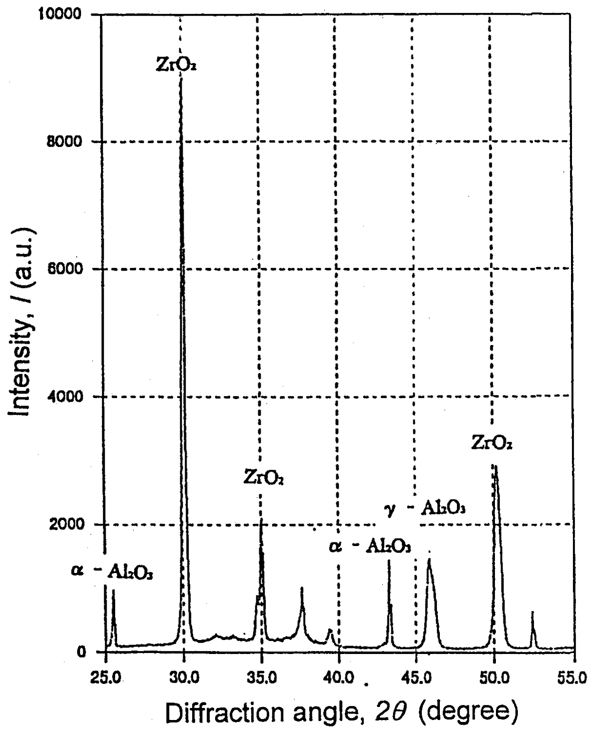

Fig.8 X-ray diffraction patterns of zirconia composite coating for 2-times traverse in Fig.6.

It was found that the graded functionality of the Vickers hardness of this ZrO_2-Al_2O_3 composite coating was much clearer than that of 1 time traverse in Fig. 4. But, the ZrO_2 coating of the same thickness had a more flat distribution of the Vickers hardness. The maximum value was as the same of about Hv=1100 as in Fig.4.

Figure 6 shows the hardness distribution for 30 traverses at v=1000 cm/min, when P=25 kW, L=40 mm. Here the coating thickness was 150μm, and the distribution was a very smooth line, without a boundary to each traverse. The maximum hardness was near to Hv = 1300 as Fig.5. The highest value was at the distance from the coating surface of l=40 μm.

Thus, the maximum hardness was almost the same when the coating thickness was the same, but the graded functionality became much better, and the distribution of Vickers hardness was much smoother as the traverse number was increased. The part near the substrate did not change so much, but the Vickers hardness near the coating surface became much higher than that of a less traversed coating. Therefore the graded functionality can be enhanced by an increase in the traverse number, and this leads to the development of thermally sprayed FGC.

3.3 Structure of functionally graded zirconia composite coating

Figure 7 shows the microphotograph of the cross section of ZrO_2 composite coating. This was produced by 33 time traverse at P=25 kW and L=40 mm and the thickness was 140 μm. The traverse speed was about 1000 cm/min. In the coating, black parts were the pores and the microstructure was consisted of two areas; one is gray area, and another was white area. It was found from EPMA analysis, that the white area was ZrO_2, while gray area was Al_2O_3. Some large pores existed near the substrate, but the size and number decreased close to the coating surface, and the coating density was much higher.

Thus, the microstructure of ZrO_2 composite coating shows that the dense ceramic matrix composite coating with thin ZrO_2 splats embedded inside a dense Al_2O_3 matrix. The ZrO_2 is in the form of flat stripes. This anisotropic composite coating combined with the large difference in thermal conductivity between ZrO_2 and Al_2O_3 will alter the thermal behavior of the coating. The coating structure might suppress the pores as compared to the ZrO_2 coating as described in the previous paper.

The X-ray diffraction pattern of the surface of the composite coating is shown in **Fig.8**. This was the same coating as that in Fig. 5. There were several strong peaks of ZrO_2 and a few Al_2O_3 peaks. The peak at the degree of 30 was the maximum peak of ZrO_2. Other peaks appeared near the degrees of 35, 50, and 60, respectively. The crystal form of ZrO_2 in the powder was thought to be the cubic phase containing small amounts of tetragonal ZrO_2 [10].

Regarding the phase of alumina in the pattern, intensity of the α-Al_2O_3 peak was strong as shown in Fig.8. This indicates that the γ-Al_2O_3 of Al_2O_3 powder was transformed to α-Al_2O_3 by the high energy plasma spraying process.

4. Conclusion

Functionally graded high hardness ZrO_2-Al_2O_3 composite coatings were formed by the gas tunnel type plasma spraying, and the coating properties were investigated, and the following results were obtained.

(1) The distribution of Vickers hardness on the cross section of those coatings depends on the traverse number and appears as parabolic curves in the thickness direction for 1-3 times traverse spraying. Higher value of Vickers hardness was obtained as compared pure ZrO_2 coating.

(2) With an increase in the traverse number, Vickers hardness of the high hardness layer became higher, and changed from Hv=1120 to Hv=1240, under the spraying condition: P=25 kW, L=40 mm. This was caused by an increase in the coating thickness from 60 to 140 μm.

(3) The graded functionality was enhanced by the increase in the traverse number. Also, the hardness distribution became smoother as the number increased. Enhancement of graded functionality should be achieved by controlling the traverse number and the coating thickness.

(4) The microstructure of the ZrO_2 composite coating showed a dense ceramic matrix composite with ZrO_2 splats embedded inside a dense Al_2O_3 matrix. The crystal form of the cubic ZrO_2 and tetragonal phase, α-Al_2O_3, and γ-Al_2O_3 composed this composite coating.

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